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Title	Developing a Highly Efficient Multimetallic Catalyst for CO ₂ -assisted Oxidative Dehydrogenation and Dry Reforming of Propane
Author(s)	XING, Feilong
Degree Grantor	北海道大学
Degree Name	博士(工学)
Dissertation Number	甲第15417号
Issue Date	2023-03-23
DOI	https://doi.org/10.14943/doctoral.k15417
Doc URL	https://hdl.handle.net/2115/89661
Type	doctoral thesis
File Information	Feilong_XING.pdf



Developing a Highly Efficient Multimetallic Catalyst for CO₂-assisted oxidative dehydrogenation and dry reforming of propane

(CO₂によるプロパンの酸化脱水素および改質反応に有効な多元素合金
触媒の開発)

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2023

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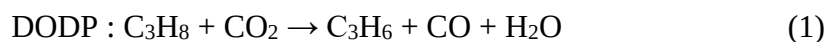
Chapter One

General Introduction

1. General Introduction

1.1 The status of oxidative dehydrogenation of propane using CO₂

The global demand for propylene, a raw material for petrochemicals, has resulted in a significant supply–demand gap as the feedstock has shifted from naphtha to shale gas production.^[1–3] Increasing propylene supply from shale gas is highly desired in highly efficient technologies.^[3] Unlike the conventional process that would produce 6–10 tons of CO₂ per ton of olefin via Fischer–Tropsch to olefins (FTO) and methanol to olefins approaches,^[4–6] a greener process is becoming more attractive. Although the on-purpose propylene production via the direct dehydrogenation of propane (DDP) has been developed and industrialized using Pt-based and CrO_x-based catalysts in recent years, the harsh temperature condition (usually between 550°C–750°C) and the rapid deactivation owing to coke formation remain problems that require solutions.^[7–9] In contrast, the oxidative dehydrogenation of propane (ODP) can be an excellent solution to these problems. O₂-ODP as a promising alternative process is widely studied, as it suppresses the coke formation and is not limited by thermodynamic equilibrium. Most O₂-ODP reaction catalysts suffered from the overoxidation that produced carbon oxides (CO_x) as the main by-product.^[10,11] Different soft oxidants, such as H₂O, CO₂, N₂O, and S-containing compounds, are considered a choice to address this issue.^[12–14] However, to compare the higher raw material prices and hazardous properties of these gases (N₂O and S-containing compounds), CO₂-ODP has been mostly studied from the environmental and economic aspects. Among these studies, two reaction schemes are generally considered: direct ODP (DODP: eq. 1) and non-ODP (DDP: eq. 2) followed by reverse water-gas-shift (RWGS: eq. 3) reaction.



Other side reactions, such as dry-reforming of propane, reverse Boudouard reaction, and propane cracking, are also involved under an actual reaction environment. The contribution of these reactions strongly depends on the catalyst and the reaction conditions.^[13] Therefore, clarifying the reaction mechanism is crucial for catalyst design and selection. The complexity

of the entire catalytic environment and the variability of the reactants make targeted catalyst design challenging. CO₂ requires adsorption and activation at a basic site. In contrast, propane requires an acidic site, indicating that two different functional sites capable of activating C–O and C–H bonds while inhibiting undesired over-dehydrogenation and C–C scission are needed.

In recent years, CO₂-ODP reactions have increasingly attracted much attention (Figure 1a) owing to their great potential for effective CO₂ utilization in industrial dehydrogenation processes. In addition, CO₂-ODP provides a possibility of making the current DDP process carbon neutral, which is highly beneficial to realizing “net-zero emission” in the chemical industry. Notably, previous studies have focused more attention only on CO₂ utilization to improve propane conversion, and only a few studies have reported the efficient use of both gases. Some did not even mention CO₂ conversion. Moreover, catalyst materials have been mostly focused on metal oxides, such as CrO_x or VO_x. Furthermore, the development of metal-catalyzed CO₂-ODP is just in its infancy. Although several review papers have summarized CO₂-ODP reactions in recent years, they have mainly focused on the role of CO₂^[12,15] and the mechanistic differences among various metal oxides^[13,16–20] but rarely on the catalytic performance and design concept of metallic catalysts. Therefore, we summarized and compared the trends in the catalytic performance of the reported metal oxide- and metal-based catalysts in terms of CO₂ versus C₃H₈ conversion (Figure 1b). Most metal oxide-based catalysts, such as CrO_x, GaO_x, and VO_x, showed very low CO₂ conversion; however, some exhibited outstandingly high propane conversion because of the low CO₂ activating ability or use of excess CO₂ in these systems. By contrast, metallic catalysts showed much higher CO₂ conversion without lowering the ability of propane activation. Considering the recent global demand for net-zero emission, achieving high CO₂ conversion with 1:1 stoichiometry is highly desired. Therefore, focusing on the catalyst design strategy based on metallic materials is timely and highly beneficial for researchers in the relevant fields. Here, I first summarize some recent advances in metal oxide-based catalysts in the last decades (Section 1.2) and explain the general catalyst design concept of metallic materials for CO₂-ODP (Section 1.3) and their catalysis in detail (Section 1.4). Finally, the conclusion and outlook are presented to summarize and provide perspective comments for future development (Section 1.5).

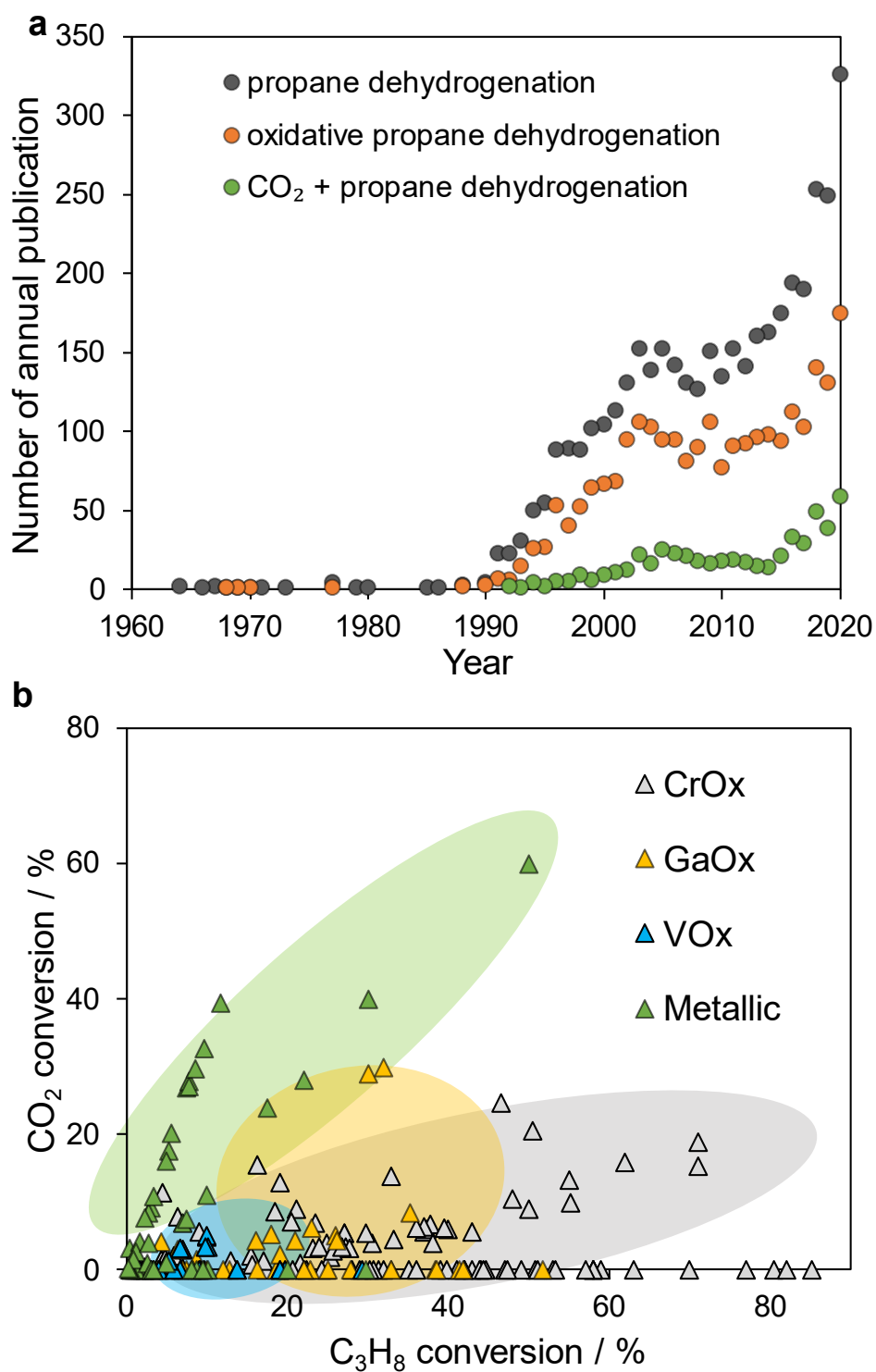


Figure 1.1. a. Annual increases in the number of publications in which titles include “propane dehydrogenation,” “oxidative propane dehydrogenation,” or “CO₂ propane dehydrogenation.” Certain data included here are derived from the Clarivate Web of Science. ©Copyright Clarivate 2022. All rights reserved. **b.** C₃H₈ and CO₂ conversion plot for CrO_x, GaO_x, VO_x, and metallic catalysts in CO₂-ODP reaction.

1.2 Development of metal oxides in CO₂-ODP

Metal oxides have been the earlier and most widely studied catalysts for CO₂-ODP in the last two decades. Chromium-based catalysts have attracted the most attention among these catalysts since the study was first reported by Takahara *et al.*^[21] They studied the effect of CO₂ on the catalytic performance in CO₂-ODP using Cr₂O₃ supported on Al₂O₃, activated carbon, and SiO₂.^[21–23] Interestingly, propane conversion was increased by adding CO₂ when using SiO₂ as a support, whereas decreased when using Al₂O₃. Similar results were also reported by Michorczyk *et al.*,^[24] demonstrating that acid–base property of the support significantly influences the CO₂-ODP activity.

Shishido *et al.*^[31,37,38] revealed that (1) ODP over the Cr⁶⁺ site ($\text{Cr}^{6+} + \text{C}_3\text{H}_8 \rightarrow \text{Cr}^{3+} + \text{C}_3\text{H}_6 + \text{H}_2\text{O}$) was faster than DDP over the Cr³⁺ site; therefore, the addition of CO₂ continuously provided a faster ODP path by reoxidizing the Cr³⁺ site. However, (2) the strong adsorption of CO₂ on Al₂O₃ inhibited the adsorption of propane, thereby resulting in the negative effect on the overall reaction rate. In the past two decades, extensive research has been conducted using various acidic and neutral supports, such as SiO₂,^[24–33] well-structured porous SiO₂ (SBA-1,^[34,35] SBA-15,^[36] MCM-41,^[37–39] MSS-x,^[40] MSU-x,^[41] and TUD-1^[42]), zeolites (ZSM-5,^[43,44] b-zeolite,^[45] silicalite-1,^[46,47] and H[B]MFI^[46]), and other supports (ZrO₂,^[48–50] active carbon,^[51] and diamond^[52]). Although much progress has been made through (Figure 1.2a), the lack of catalyst stability (typically deactivated within a few hours) and low selectivity (~80%) in the high conversion region (Figure 1.2b) are challenges for chromium-based catalysts.

Similarly, VO_x has been well studied in CO₂-ODP, and more widely in O₂-ODP,^[10,53] due to the redox property (V³⁺ to V⁵⁺). Zhaorigeru *et al.*^[54,55] reported the use of vanadium oxide-based catalysts (LnVO_x, Ln = rare earth metal) in the O₂-ODP reaction using CO₂ as a co-feed gas for the first time. They revealed that CO₂ adsorption blocked the reaction site causing the overoxidation of C₃H₆, resulting in an improvement of C₃H₆ selectivity. Following this discovery, Nakagawa *et al.*^[52] conducted an inspiring study using oxidized diamond-supported V₂O₅ catalysts. In the dehydrogenation of lower alkanes, the catalytic activity was increased twofold with CO₂ addition. The UV-Vis analysis showed that CO₂ addition may have retained the higher oxidation state of vanadium species. Further investigations were conducted from different catalyst design, such as surface doped vanadia catalysts (7V7W, 7V5Mo, and 7V4Cr),^[56] mixed oxides (WO_x-VO_x/SiO₂^[57] and CeVO_x^[58]), modified supports (VO_x/La₂O₃-g-Al₂O₃,^[59] nV-MSNSs,^[60] and nV-MCM-41^[61]), and the specific preparation method using 3D printing.^[44,62–64] However, designing an efficient vanadium-based catalyst remains

challenging due to the controversy over the active site (oxidized vanadium, oligomeric vanadium, and V_2O_5 crystallite) in various complex systems. From the reported data, I find that most vanadium-based catalysts show very low activity after 2 hours of reaction and low CO_2 conversion ($\sim$ below 5%, [Figure 1.2c](#)). Although the vanadium-based catalysts have excellent renderability and potential suitability for O_2 -ODP, the low CO_2 utilization efficiency will limit their application in CO_2 -ODP.

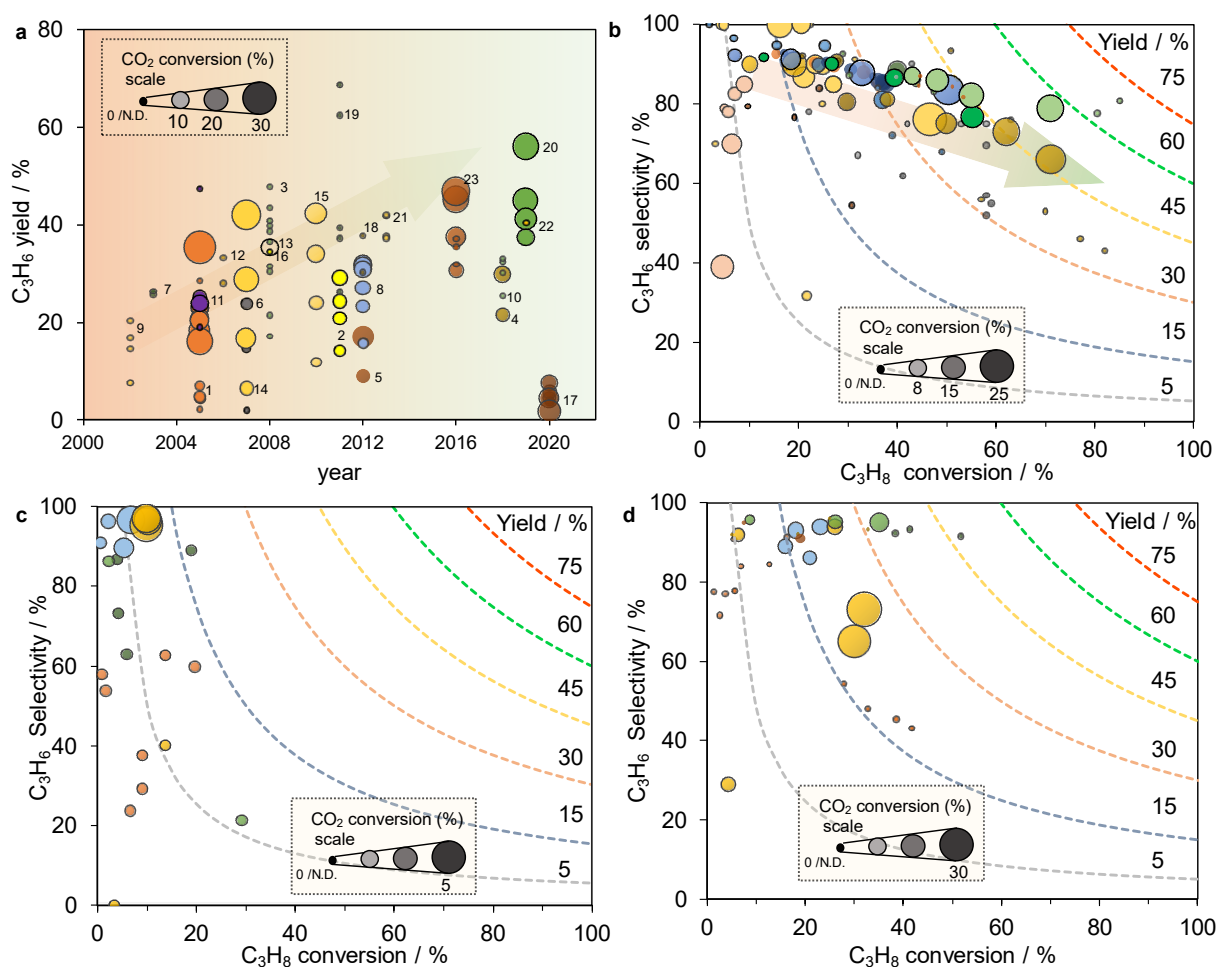


Figure 1.2. **a.** Timeline of the development for CrO_x -based catalyst, Selectivity–conversion plot for propylene and propane in CO_2 -ODP reaction. **b.** CrO_x -based catalyst, **c.** VO_x based catalyst, and **d.** GaO_x based catalyst. The color of the point refers to the difference in literature. The size of the point refers to the difference in CO_2 conversion. The data collected from the ref.^[18,65]

Other than the early transition metal oxide catalysts, extensive studies have also focused on main group metal oxide catalysts, such as Ga-based catalysts. For example, Ga-based catalysts were discovered as efficient catalysts for CO₂-ODP reactions.^[66,67] However, the negative effects of CO₂ addition and rapid deactivation have prevented Ga₂O₃ catalysts from receiving more attention in the same group. Following this hint, various studies by Gao *et al.*^[68–73] showed that β -Ga₂O₃ with unsaturated Ga³⁺ cations and abundant strong acid sites on the surface was the main active species. After verifying the active species, support effects were investigated using different supports, including TiO₂, ZrO₂, Al₂O₃, SiO₂, MgO, H-ZSM-x, and SBA-15,^[74] revealing that the dispersion of gallium cations and the strength of the Lewis acid sites significantly affect the activation ability of propane. However, in most cases, CO₂ addition harms the reaction (Figure 1.3).

To further improve the dispersion of tetrahedral Ga ions and produce more medium-strong Lewis acid sites, researchers prepared Ga₂O₃-Al₂O₃ catalysts using different preparation methods.^[75–77] The initial propylene yield was increased from 10% to 35.2%, but a rapid deactivation occurred within 10 h of the reaction. Therefore, gallium oxide-based catalysts having higher coke resistance are still needed for better performance. Although the catalytic performance in the initial stage has significantly improved in the past decades, insufficient on-stream stability has still not been resolved. The intrinsic low efficiency of Ga-based catalysts for CO₂ utilization has posed a challenge (Figure 1.2d). Recently, GaN supported on porous SiO₂ or NaZSM-5^[78,79] showed the highest catalytic performance among the reported Ga-based systems. GaN can not only activate the C–H bond, but also block the acid sites of SiO₂ by forming Si–O–GaN–H species. This unique site can capture CO₂ to form a COOH intermediate and facilitate the dissociation to CO and Si–O–GaN species. This contrasts with other gallium oxide-based catalyst systems, in which CO₂ has a negative effect on activity. It will stimulate further research on Ga-based catalysts and potential industrial applications.

There have also been reported other early transition metal-oxide/carbide- (Mo₂C,^[80,81] MoO_x,^[82,83] Zn_xZr_{1-x}O_{2-x},^[84] and ZrTiO_x^[85]) and typical metal oxide-based catalysts (In₂O₃-Al₂O₃,^[86,87] In-HZSM-5,^[88] and ZnO-HZSM-5^[89]). Although there have been many attempts at marginal elements, extensive research is lacking because their lower selectivity and poor stability cannot be compared with those of gallium and chromium catalysts.

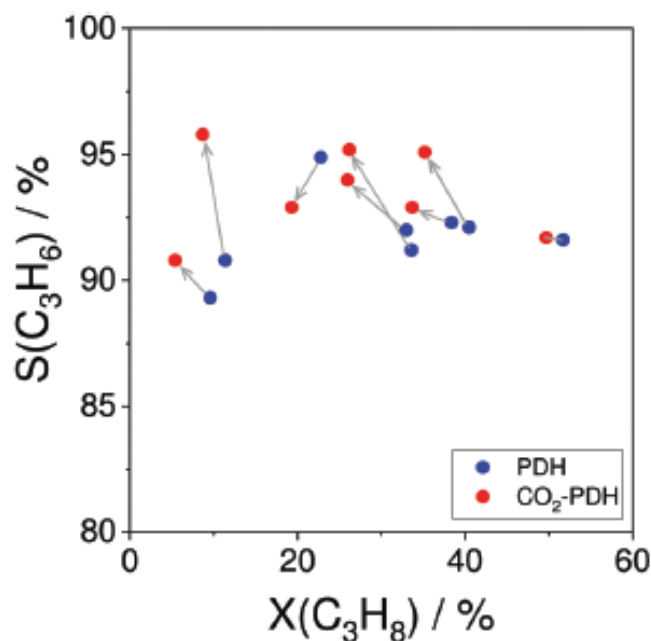


Figure 1.3. Conversion–selectivity plot in DDP (PDH in the figure) and CO₂-ODP (CO₂-PDH in the figure) over GaO_x/Al₂O₃ and GaAlO_x. Reproduced from ref.^[20] with permission. Copyright© 2020 The Royal Society of Chemistry.

1.3. Design concept of metallic catalysts

As summarized in Section 1.2, the CO₂-ODP reaction with oxide-based catalysts generally proceeds on redox-active metal centers. The high oxidation state is reduced to a low oxidation state by reacting with propane to form propylene; then the reduced active center is reoxidized to the original state by CO₂. Catalyst deactivation is often triggered due to the following reasons: (1) shortage in the high oxidation site, (2) strong adsorption of CO₂ on basic or active sites, (3) low ability of CO₂ activation, and (4) difficulty in coke removal. These drawbacks suggest the need for alternative materials that are nonoxide and redox-free but sufficiently capable of C–H scission, CO₂ capture/activation, and coke removal. As shown in Figure 1.1b, metallic catalysts are potentially suitable, particularly for CO₂ activation ability. In this section, I introduce some promising catalyst design strategies of multifunctional catalysis for efficient CO₂-ODP.

1.3.1 Use of transition metals capable of CO₂ activation

The intrinsic low ability of oxide-based materials for CO₂ activation may be improved when a transition metal capable of activating CO₂, such as Co, Ni, Ru, or Pd, is added as a promoter

to the oxide catalysts. This can not only increase CO₂ conversion but also enhance catalyst stability by promoting coke combustion via the reverse Boudouard reaction. Loading such a transition metal on a mixed metal oxide support (e.g., Pd/CeZrAlO_x and Ni/CrO_x-SBA-15) is also effective in constructing the dual active sites for propane and CO₂. This is a common strategy employed for the oxidative dehydrogenation of ethane by CO₂. Here, chemical interactions between the metal and support play key roles in the enhanced catalysis for CO₂-ODP, which is discussed in detail in Section 1.4.1.

1.3.2 Bimetallic systems

Bimetallic catalysts, such as PtSn, have been well established in the industrial processes for DDP. The catalytic property of the main active metal can be modified by alloying it with a certain second metal that changes the geometric and electronic environments of the active site. Using this strategy for metallic catalysts capable of CO₂ activation may be a promising technique for efficient CO₂-ODP. The combination of two transition metals suitable for selective activation of the C–H bond and CO₂ is also an effective strategy. Recently, several bimetallic catalysts have been developed by different researchers. I will introduce the outline of this chemistry in Section 1.4.2.

1.3.3 Multimetallic catalyst system

Given the complexity of the CO₂-ODP reaction mechanism and various demands from the catalyst design for efficiency, two metals alone may be insufficient to meet high catalytic performance, i.e., high propane conversion, propylene selectivity, catalyst stability, and CO₂ utilization efficiency. To meet these criteria, one should satisfy the following demands in the catalyst design for CO₂-ODP: (1) high ability for C–H activation, (2) facile CO₂ conversion, (3) minimum C–C cracking, and (4) decoking ability. (1) and (2) can be achieved when appropriate metals are selected. Alloying with some inactive metals, such as typical metals, seems to be promising for (3), similar to DDP. Using some metals or supports that facilitate (4) further improves the long-term stability of a catalyst. Such a multifunctional reaction environment may be constructed using multimetallic alloys having three or more metals. In Section 1.4.3, I will introduce state-of-the-art multimetallic catalysts that meet all these demands and show significantly high catalytic performance.

1.4 CO₂-ODP over metallic catalysts

Based on the aforementioned strategies for metallic catalysts, I will explain the detailed catalytic performance, reaction mechanism, and role of each metallic species. Furthermore, I will classify various metallic materials into three categories, monometallic, bimetallic, and multimetallic materials, to correspond to each section in Section 1.3.

1.4.1 Monometallic catalysts

Solymosi *et al.*^[90] compared the catalytic performance of metallic Rh catalysts deposited on different supports (Al_2O_3 , SiO_2 , TiO_2 , and MgO) in DDP and CO_2 -ODP reactions. In the DDP reaction, propylene selectivity was 50%–60%, along with the by-products ethylene and methane. However, for the CO_2 -ODP reaction, the main products were CO and H_2 , indicating that the reaction pathway shifted from DDP to dry-reforming of propane. This is confirmed by the reaction using propylene and CO_2 , which proceeded at a high rate, producing CO and H_2 . Thus, metallic catalysts are more favorable for the dry-reforming of propane than dehydrogenation due to the strong C–C bond cleavage ability, which highlights the difficulty in developing an efficient catalyst using metallic catalysts. Mixed oxide or doped metal oxide supports may be more selective and stable due to their electron transfer capability^[91] and oxygen storage/release capacity (OSC).^[92] From this viewpoint, Sivaram *et al.*^[91] investigated the effect of support and oxygen transfer capacity in the CO_2 -ODP reaction by comparing the activity of Ru/ CeO_2 and Ru/ ZrO_2 . Although 5% Ru/ CeO_2 has higher oxygen mobility and stronger reduction ability than Ru/ ZrO_2 , the two catalysts have the same performance below 450°C and are comparable above that temperature. More disappointingly, for the Ru-doped catalysts, only C–C cracking and dry-reforming activities were enhanced compared with the unmodified host oxides. Although Ru-based catalysts have been reported to favor dry-reforming reactions, Ru has also been widely used for CO_2 methanation.^[94,95] Unlike Ru-based catalysts, Cr-based catalysts usually exhibit limited CO_2 conversion, as mentioned in Section 1.2. Combining these, Jin *et al.*^[93] proposed that adding Ru to SiO_2 -supported chromium oxide catalysts could convert the reaction pathway from a dry-reforming to the CO_2 -ODP reaction. The reaction was conducted at 496°C over the $\text{Cr}_{10}\text{O}_x/\text{SiO}_2$ catalysts having different Ru loadings (0–3 wt%). The Ru-free catalyst showed 4.9% C_3H_8 conversion, whereas the CO_2 conversion was much lower (1.1%). The reaction pathway occurred mainly via the DDP pathway, which was verified by nearly the same H_2 ($6.5 \text{ mmol g}_{\text{catal}}^{-1} \text{ h}^{-1}$) and C_3H_6 ($6.8 \text{ mmol g}_{\text{catal}}^{-1} \text{ h}^{-1}$) productivities. C_3H_8 conversion showed a volcano-like trend with Ru loading, with a maximum conversion of 9% for C_3H_8 at a Ru loading of 1 wt%, whereas CO_2 conversion

linearly increased. The formation rate of C_3H_6 ($13.6 \text{ mmol g}_{\text{catal}}^{-1} \text{ h}^{-1}$) was increased twofold compared to that of the catalyst without Ru.

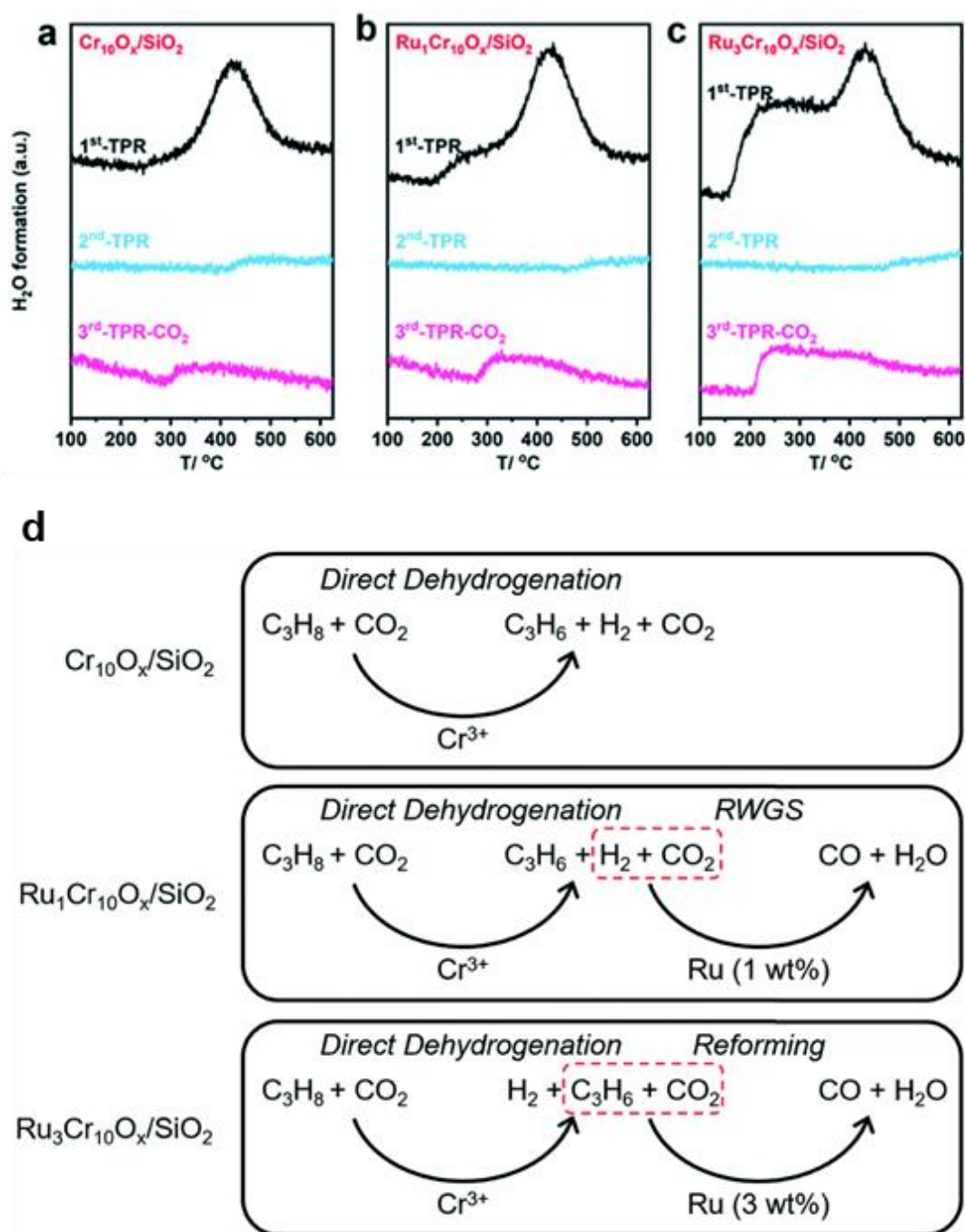


Figure 1.4. Three-step H_2 -TPR results of as-prepared catalysts: a) $Cr_{10}O_x/SiO_2$, b) $Ru_1Cr_{10}O_x/SiO_2$, and c) $Ru_3Cr_{10}O_x/SiO_2$. d) Proposed catalytic pathways over different catalysts for the ODP reaction. Reproduced with permission from ref.^[93] Copyright © 2020 The Royal Society of Chemistry.

Meanwhile, H₂ productivity (9.5 mmol g_{catal}⁻¹ h⁻¹) was much lower, indicating that C₃H₆ was produced by the DDP and ODP reactions. With a further increase in Ru loading, C₃H₈ conversion and C₃H₆ selectivity decreased significantly, but CO₂ conversion and CO/H₂ production rates kept increasing. To gain more insight into the role of Ru, a "three-step" H₂-TPR analysis was performed to verify the effect of catalyst reducibility (Figures 1.4a-c). In the 1st-TPR results, a broad peak assigned to reducing Cr⁶⁺ to lower oxidation Cr³⁺ and Cr²⁺ was observed in the high-temperature region. In contrast, smaller peaks appeared at a lower temperature when Ru was added. In the 2nd-TPR results of all three samples, H₂ consumption was negligible, which indicates that Cr⁶⁺ and Ru species were fully reduced in the 1st-TPR. Then, the 3rd-TPR was performed after the 2h-CO₂ treatment. Very small peaks were observed in Cr₁₀O_x/SiO₂, whereas the peak increased by increasing the doping amount of Ru. This suggests that CO₂ oxidation cannot recover the highly oxidized state of Cr⁶⁺. Next, CO₂ hydrogenation (RWGS) was performed to determine the two-step facilitation pathway over the Ru catalyst (Figure 1.4d middle). The CO₂ activity was significantly improved by the Ru-modification, whereas Cr₁₀O_x/SiO₂ showed poor activity even in higher temperature regions, indicating that CO₂ activity was increased mainly due to Ru addition. In contrast, CO₂ conversion could be further improved by modifying 3 wt% Ru, but C₃H₈ conversion and C₃H₆ selectivity were decreased due to the reforming reaction. A possible reaction mechanism derived from these results is shown in Figure 1.4d. The low oxidation state of chromium played a key role in propane dehydrogenation, whereas Ru addition increased its activity via RWGS and reforming reactions.

Nowicka *et al.*^[92] reported a Pd/CeZrAlO_x catalyst that exhibited long-term stability and selectivity for C₃H₆ (during 140 h of continuous operation) with a strategy to prepare highly active OSC supports. Although Sivaram *et al.*^[91] reported that CeO₂ and ZrO₂ supported catalysts only enhanced the dry-reforming activity, the use of mixed oxides may have a promotional effect. The 5 wt% Pd/CeZrAlO_x catalyst was tested in the presence or absence of CO₂. The catalytic activity decreased rapidly after the first 1.5 h, resulting in active oxygen consumption in the support. Meanwhile, CO₂ treatment restored activity and improved selectivity. They also performed a regeneration study on this catalyst and found that CO₂ treatment fully recovered the original catalytic performance, whereas helium treatment did not. They also performed various characterization studies using the fresh, spent, and reoxidized catalysts to verify the relationship between structure and catalytic performance. For the fresh catalysts, PdO and Ce⁴⁺ were mainly present on the catalyst surface. PdO was converted to the metallic Pd for the spent catalysts, while cerium was partially reduced. Note that Pd and cerium

were reconverted to PdO and Ce^{4+} after re-oxidation by CO_2 . In addition, temporal analysis of the products and diffuse reflectance infrared Fourier transform spectroscopy were used to elucidate the role of CO_2 in this study. Unlike the mechanism proposed in previous studies, CO_2 undergoes the RWGS reaction by consuming H_2 generated by the DRP reaction, where the lattice oxygen extracts H_2 from C_3H_8 to form C_3H_6 , and CO_2 is dissociated to CO by Pd. Combined with the aforementioned catalytic performance results and structural characterization, it was shown that the redox of Pd and Ce species were involved in the catalytic cycle, whereas Pd mediated the oxygen transfer from CO_2 to CeO_2 (Figure 1.5).

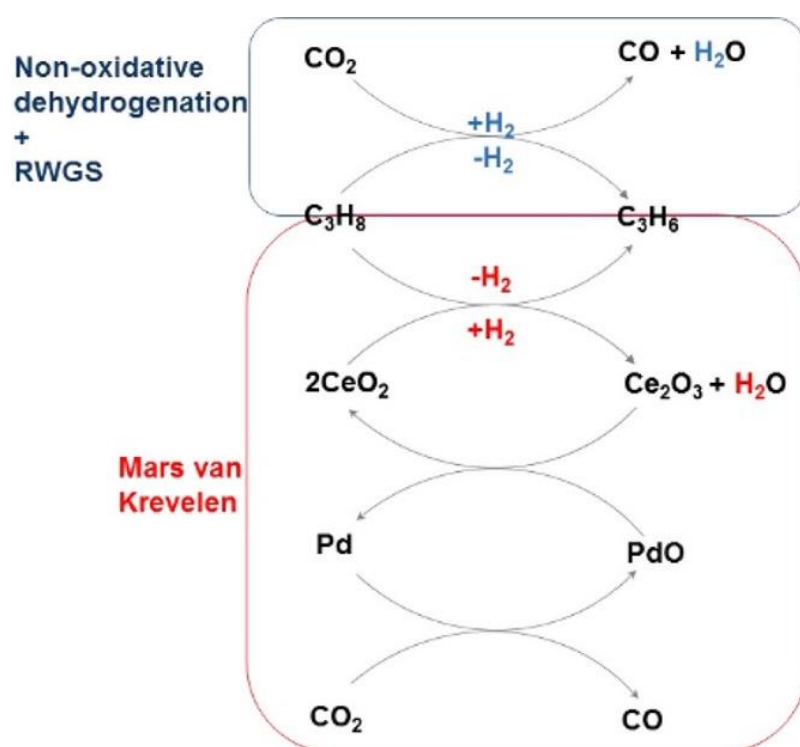


Figure 1.5. Representative scheme of the reactions involved in the overall ODP process. Reproduced with permission from ref.^[92] Copyright © 2020 American Chemical Society.

Although most of the studies are based on noble metal systems, some studies still investigate the catalytic performance of non-precious metals in CO_2 -ODP. Michorczyk *et al.*^[96] investigated different Fe-containing catalysts supported on different supports (Al_2O_3 , AC, MgO-10 , and MgO-30). TPR analysis was used to investigate the reducing ability of Fe, showing that pure Fe_2O_3 and $\text{Fe}_2\text{O}_3/\text{AC}$ were reduced to Fe in three steps, followed by Fe_3O_4 and FeO. However, by increasing the reduction temperature, $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalysts formed spinel phase FeAl_2O_4 , whereas $\text{Fe}_2\text{O}_3/\text{MgO}$ catalysts formed MgFeO_x due to the strong

stabilization of reduction of Fe^{3+} species. Next, the catalytic activity showed that the conversion and selectivity of Fe_2O_3 and $\text{Fe}_2\text{O}_3/\text{AC}$ were improved by changing the DDP reaction to the CO_2 -ODP reaction. In contrast, an opposite result was obtained for the other catalysts. One hypothesis is that propane is oxidized to propylene by lattice oxygen from the iron oxide (Fe_2O_3 or Fe_3O_4) phase, and CO_2 subsequently reoxidizes the reduced catalyst. However, a further detailed study is necessary. From the pioneering work of JG Chen *et al.*^[97] and incorporating the OSC characterization strategy, Wang *et al.*^[98] investigated the performance of different Fe-doped CeO_2 (Fe 1wt%–15wt%) catalysts in the CO_2 -ODP reaction recently. All the Fe-containing catalysts had well dispersed Fe species in the ceria lattice, and XRD detected no crystalline hematite ($\alpha\text{-Fe}_2\text{O}_3$) phase. The conversion of propane and CO_2 increased with increasing iron content, reaching a maximum between 10FeCeO_2 and 15FeCeO_2 . In addition, C_3H_6 selectivity increased linearly, with a slight decrease in 15FeCeO_2 . The increase in activity and selectivity could be attributed to the increase in the surface area and iron-rich oxygen sites of the catalyst with high iron loading. Stability experiments were performed for both low and high Fe content catalysts. Propane conversion gradually decreased for all catalysts, but the selectivity of ethylene and methane increased for the low-iron-containing catalysts. In contrast, no significant change was observed for the high-iron-containing catalysts. Further studies revealed that carbon deposition and coke formation necessitated the deactivation of the low-iron-containing catalysts, whereas cerium crystal sintering and iron migration to form large-size particles necessitated the deactivation of the high-iron-containing catalysts.

1.4.2 Bimetallic catalysts

Alloying the main active metal with a certain second metal has also been used to alter the electronic or geometric structure and the resulting catalytic performance.^[99–101] The active metal–metal ensembles can be diluted by a catalytically inert second metal, thus suppressing undesired side reactions, such as C–C bond scission (so-called ensemble effects^[7,9]). The application of platinum-based alloy catalysts in the DDP reaction was well investigated using this design concept to improve activity and selectivity. Various monometallic (Ni, Fe, and Pt) and bimetallic transition metals (FeNi , NiPt , and FePt) were also tested to study their intrinsic activity in CO_2 -ODP and DRP reactions^[97]. Fe_3Ni exhibited the highest C_3H_6 selectivity, corresponding to 58.2%, whereas the monometallic Ni catalyst showed only 12% C_3H_6 selectivity and the monometallic Fe showed no activity. Notably, the bimetallic Fe_3Ni catalyst has a synergistic effect on Ni and Fe. By changing Ni to precious metal Pt (Fe_3Pt), C_3H_6

selectivity was decreased to 32%, and C_3H_6 selectivity was further reduced to 2.8% for the Ni_3Pt catalyst. In other words, the non-precious bimetallic catalyst preferred dehydrogenation reaction, whereas the Pt-containing alloys enhanced dry-reforming activity. Kinetic studies have shown that Fe_3Ni and Ni_3Pt catalysts differ in their competitive adsorption of reactants and/or surface intermediates. For Fe_3Ni catalysts, the propane reaction rate decreased when the CO_2 partial pressure was increased. In contrast, the propane reaction rate first increased with the CO_2 partial pressure and then dropped at a higher-pressure region for Ni_3Pt catalysts. A similar trend was also observed for the propane partial pressure. These results indicate that the intermediates block the active sites on the catalyst surface, leading to decreased propane/ CO_2 reaction rate at high CO_2 /propane partial pressures.

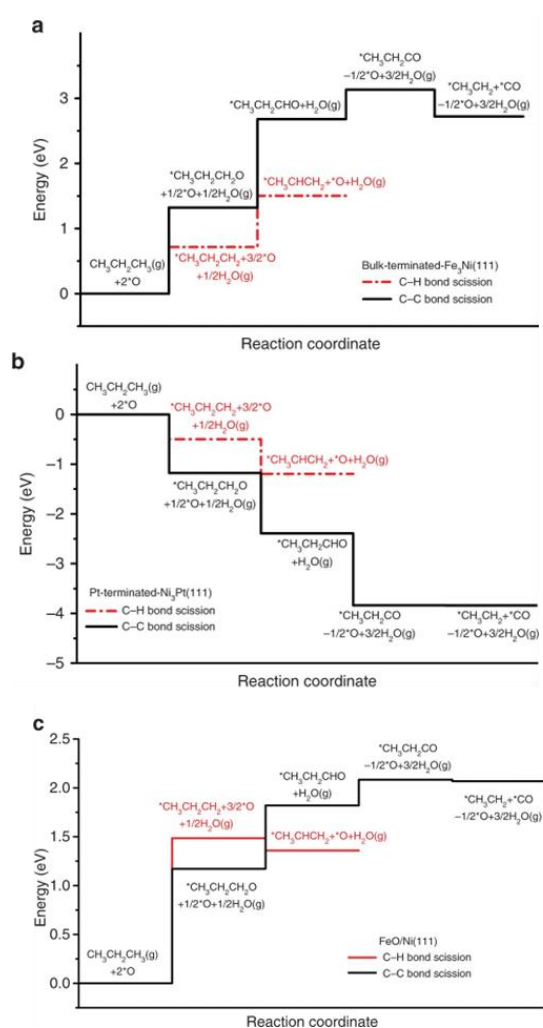


Figure 1.6. DFT calculated energy profiles for the oxidative C-H and C-C bond scission pathways. a) Bulk Fe_3Ni (111) surface, b) Pt-terminated Ni_3Pt (111) surface, and c) $FeO/Ni(111)$ interface. Reproduced with permission from ref.^[97] Copyright © 2018 Springer Nature.

DFT calculations are consistent with the experimental studies (Figure 1.6), where the C–H activation energy on Fe₃Ni (111) was lower than that of the C–C bond. In contrast, an opposite trend was observed for the Pt (111) and Ni₃Pt (111). To better understand the reaction pathway of the Ni₃Fe catalyst, the FeO–Ni interfacial active site structure was further investigated because iron oxide was observed by an *in situ* characterization of the Fe₃Ni catalyst. Although the C–H activation energy was downhill at the Fe–O–Ni interfacial active site, the C–C activation energy was uphill, revealing that Fe₃Ni is more favorable for propylene production than lower hydrocarbons. JG Chens' group further developed a library of metal-based catalysts by studying the reactivity of other transition metals, such as Pd, Co, and their combined bimetallic catalysts.^[102] These experiments revealed that Pt-based bimetallic catalysts showed better conversion and TOF than Pd-based bimetallic catalysts. The Co_xNi_y catalysts favor dry-reforming compared with the Fe_xCo_y and Fe_xNi_y systems. There are currently no candidates for acceptable propylene yields and persistent catalysts; however, these previous studies are imperative, as they build a bimetallic library and investigate its inherent activity, which may help in future catalyst discovery in CO₂-ODP reaction.

Recently, the FeNi system was further investigated by controlling the defect concentration of the cerium supports.^[103] Two cerium supports with different defect properties were prepared using the precipitation method by controlling the amount of ammonia and Ce³⁺ concentration. Fe₃Ni supported on these cerium oxides showed a significant difference in the catalytic performance. The defect-rich cerium oxide showed 49% selectivity for propylene, which was much higher than the defect-deficient cerium oxide catalyst (0.7% selectivity). This difference is not due to the mobility of the oxygen atoms on the cerium oxide support but rather to the strong interaction between the iron and cerium oxide. As mentioned in the work of Gomez *et al.*,^[97] iron oxide plays a key role in this system. Defect-rich cerium can immobilize FeNi species to avoid aggregation. In contrast, FeNi species in defective cerium tend to be reduced to FeNi alloys, which are more prone to cleave C–C bonds (Figure 1.7a). However, further studies are needed to elucidate the deeper reasons why the alloy or oxide state affects catalytic performance.

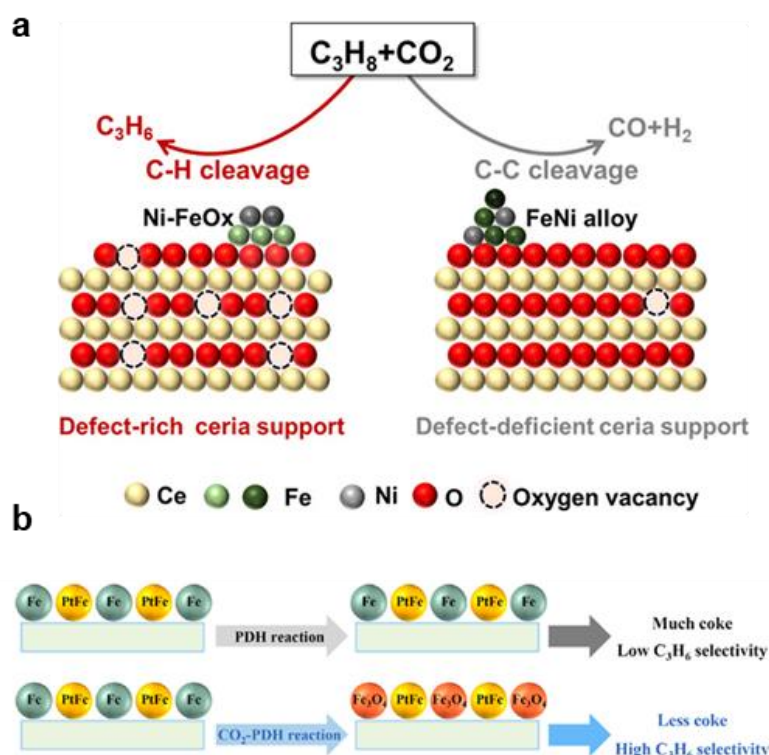


Figure 1.7. a. Defect-induced selective C–H/C–C bond cleavage of propane in the presence of CO_2 over ceria-supported FeNi catalysts. Reproduced with permission from ref.^[103] Copyright © 2021 American Chemical Society. **b.** A conjecture of Structural Evolution over the PtFe Bimetallic Catalyst under Different Reactive Atmospheres. Reproduced with permission from ref.^[104] Copyright © 2021 Elsevier Inc.

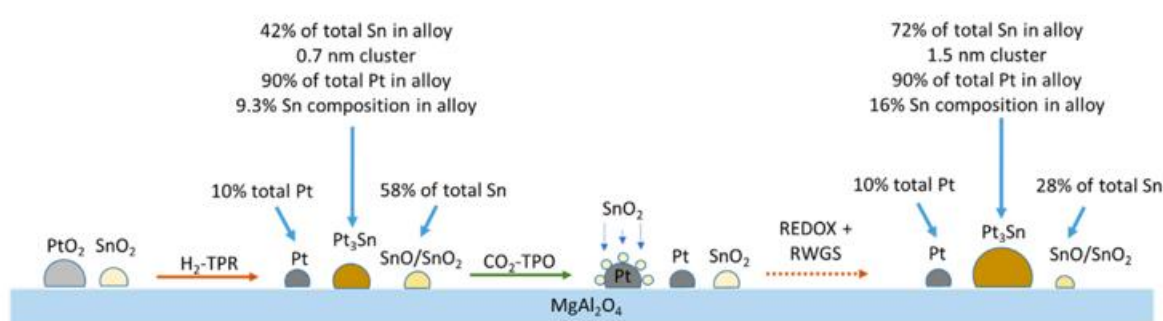


Figure 1.8. Scheme depicting the evolution of the calcined Pt:Sn/HSA sample over different treatments based on the XAS data. Reproduced with permission from ref.^[104] Copyright © 2021 Elsevier Inc.

Similar results were obtained by Bian *et al.*^[105] where the metallic iron lowered C₃H₆ selectivity but increased coke formation. They prepared different PtFe bimetallic catalysts and tested them in the PDH reaction. Although Pt₁Fe₇/S-1 (S-1: silicalite-1) was the most stable in all the catalysts, the amount of coke was also the highest. Interestingly, the amount of coke was significantly reduced after introducing CO₂ into the PDH reaction. In general, coke can be removed by the reverse Boudouard reaction^[65,106,107] when the co-fed CO₂ is used as a reactant. They concluded that the oxidation of Fe (0) to Fe₃O₄ during the reaction necessitates anti-coking ability based on the reverse Boudouard reaction. The XPS and XAS analyses confirmed this hypothesis, showing that the spent catalyst of Pt₁Fe₇/S-1 after the CO₂-ODP reaction comprised PtFe alloy and unalloyed Fe species (~95% Fe₃O₄ and ~5% Fe(0)) with 1:1 ratio (Figure 1.7b). Notably, CO₂ introduction improves the anti-coking ability and changes the inherent activity of the catalyst by adjusting its structure.

PtSn-based catalysts have also recently been investigated as established commercial catalysts for industrial PDH processes.^[8,108,109] Unlike monometallic Pt-based catalysts with a strong ability to cleave C–C bonds, alloying with Sn will be transformed into a more favorable C–H bond cleavage ability by improving Pt dispersion and changing the electrical properties of Pt. Srinath *et al.*^[104] investigated the structural and electronic properties of PtSn/MgAl₂O₄ catalysts in the CO₂-ODP reaction. Due to the specific structure and properties of MgAl₂O₄ with basicity and acidity, it is an ideal support for the adsorption of propane and carbon dioxide.^[13,19,110] To investigate the alloy formation mechanism, an *in situ* XAFS experiment was conducted under an H₂-TPR, CO₂-TPO, and RWGS reaction conditions (Figure 1.8). The Sn atoms in the PtSn alloy on MgAl₂O₄ was oxidized stepwise to SnO and SnO₂ by the addition of CO₂, and then reduced to Sn by the subsequent H₂ treatment. However, the Sn species was oxidized and migrated to the surface of the alloy when increasing the CO₂:H₂ ratio in the RWGS condition. This is further demonstrated by applying CO₂-ODP reaction. The reaction is performed by using different CO₂:C₃H₈ ratios, and the results indicated that a low ratio of 0.25:1 is more favorable for this reaction (C₃H₆ selectivity ~95%). On the other hand, for the high CO₂:C₃H₈ ratio condition (0.5:1 and 1:1), Sn oxidizes more rapidly to SnO₂ and cannot be reduced to Sn in time, which then leads to separation into Pt and SnO_x. The CO₂+C₃H₈ regeneration reaction was then performed by flowing CO₂ to further check the role of CO₂. After the introduction of CO₂, the activity was only partially recovered. This may be due to the insufficient decoking capacity of CO₂ or gradual oxidation of the catalyst. Overall, the rapid deactivation and the lack of active sites for CO₂ remains a key issue for this catalyst. To better address this challenge, Wang *et al.*^[111] reported PtSn/SiO₂ catalysts with the addition of CeO₂

as a promoter, which could improve the catalytic activity and selectivity. As in previous studies,^[15,112] CeO₂ with high oxygen storage capacity and abundant oxygen defects was chosen to activate CO₂. However, in this study, the order of the catalytic activity (PtSn/SiO₂ < PtCe/SiO₂ < PtSnCe/SiO₂) could be explained simply by the grain size and metal dispersion. Therefore, the chemical effect of Ce on the catalysis of CO₂-ODP remains unclear in this study.

1.5 Aim of this thesis

In addition to the metal oxide catalysts that have been widely studied in the past, I summarized the metallic catalysts that have been gradually and widely explored in recent years, exploring the concept of catalyst design, identifying the active sites, and different reaction mechanisms. Although the CO₂-ODP reaction has made some progress in recent years, whether metal oxide-based, metallic, or other types of catalysts, it certainly shows the great importance of designing a bifunctional or even multifunctional catalyst. Due to current environmental issues and international policies, this reaction has become more demanding and challenging. It is not only necessary to use CO₂ to increase the conversion rate of propane but also to improve the efficiency of CO₂ utilization while considering the comparable propylene yield. While CO₂ reutilization and capture technology are maturing, it is also important to develop to involve CO₂ in large-scale industrial manufacturing. With further development of the research, this design concept can be applied to the production of high value-added products, not only for the dehydrogenation of low-chain alkanes, such as propane and ethane, but also for the one-step process of oxidative coupling of carbon dioxide with olefins to produce acrylic acid and acrylates, as well as for the CO₂-assisted aromatization of light alkanes.

By collating past research, I can identify future research challenges that need to simultaneously address (1) propane activation, (2) CO₂ activation, (3) cracking suppression, and (4) coking suppression. Additionally, catalyst sintering and phase separation are still crucial challenges. To meet these requirements and solve current problems, I propose the following directions on how to design and develop more efficient CO₂-ODP catalysts.

1.5.1 Fine-tuning metallic catalysts

To solve these problems well, it is important to design the catalyst in detail. Considering the multiple requirements on catalysts for CO₂-ODP, multifunctional active sites are highly desirable for CO₂ adsorption/activation, C–H cleavage, and minimum C–C scission. New

materials such as multimetallic or high-entropy alloys (HEAs), which may be suitable for such complicated reaction systems, should be further studied. Particularly, HEI catalysts,^[115–117] which have recently attracted significant attention, have unique characteristics as efficient catalysts. Unlike the conventional random alloy systems, such as HEA, HEI partly retains the ordered atomic arrangement originating from the parent intermetallic structure due to the largely negative formation enthalpy, thereby allowing greater thermal stability of the alloy phase and site isolation of the active metals for highly selective conversion. However, as the number of elements increases, so does the difficulty of synthesizing multimetallic alloy nanoparticles with high homogeneity and phase purity. To precisely control the bulk and surface structures of a catalyst, sophisticated synthetic methods need to be applied, such as precision-regulated hydrothermal methods^[77], 3D printing techniques^[64], atomic layer deposition,^[118] microwave heating,^[119] non-equilibrium flow-synthesis,^[120] and fast-moving-bed pyrolysis method.^[121]

Dual activation and inhibiting undesired side reactions are important factors for better efficiency. Site isolation is a promising approach for highly selective C–H activation. In this context, “single atom catalyst” (SAC) might be another possible strategy to design an effective reaction environment for CO₂-ODP. However, for the aforementioned multifunctionalization, the SAC system should also be multifunctionalized by adding a second element with an isolated state, namely, a “dual SAC” system.

Another unavoidable problem is catalyst sintering and coke accumulation. Controlling the morphology of nanoparticles with supports by applying strong metal-support interactions (SMSI) may be a good approach. The spatial separation of the active species using “nanocages,” such as zeolite, MOF, and COF, may be another approach. Coke-removing ability should also be enhanced by modifying the oxygen-releasing ability of the catalyst support. Using mixed metal oxides that are highly reducible and have high oxygen release/storage capability would be beneficial not only for facile coke combustion but also for greater SMSI. Therefore, when designing a suitable metallic nanoparticle, it is crucial to select and develop an appropriate and effective support to facilitate coke combustion and inhibit metal sintering. Using machine learning may accelerate the design and discovery of new promising catalyst materials for CO₂-ODP.

1.5.2 Accelerate the reaction mechanism study of metallic catalysts

The reaction path of CO₂-ODP differs depending on the catalytic system, undergoing direct ODP (DODP: eq. 1) or non-ODP (DDP: eq. 2) followed by RWGS (eq. 3) reaction. Therefore, for a more proper design of metallic systems, one should correctly identify the true picture of the active sites and reaction mechanism using multiple approaches, such as kinetic studies, *in situ* characterizations (IR, XAFS, and temperature-programmed analyses), and DFT calculations. Particularly, understanding the RDS of CO₂-ODP is essential to improve overall catalytic activity. Microkinetic modeling based on experimental kinetic data and calculated energy landscapes would be helpful to understand the RDS of such complicated systems. The CO₂-ODP reaction has a long way to go from academic research to effective industrial applications because there remains room for improvement in catalytic performance and clarifying the reaction mechanism. I hope that this introduction provides readers with inspiration, guides to newer directions, and opportunities for further development in the catalysis of CO₂-ODP.

1.6 Outline of thesis

In this regard, two approaches have been used (i) pseudo-binary alloy: is the ternary alloy of composition A_m(B_{1-x}C_x)_n, where one metal site of the intermetallic A_mB_n is partially replaced by third metal C. (ii) High-entropy intermetallics (HEIs): are multi-metallic alloys with five or more elements whose specific crystal structure is derived from the parent binary intermetallic. Chapter 2, Chapter 4 are introduced the pseudo-binary alloy used for CO₂-ODP and DRP reactions. Chapter 3 exhibited that the HEIs could further enhancement of the performance of CO₂-ODP.

Chapter 2 showed that Pt–Co–In ternary alloy on CeO₂ exhibited a highly efficient catalyst for CO₂-ODP. Both the C₃H₈ dehydrogenation and CO₂ reduction smoothly proceed on the Pt–Co active site to form 2H and O, as well as the main products: C₃H₆ and CO. Alloying with In enhances the C₃H₆ selectivity due to the ensemble effect and decreases the amount of coke that accumulates on the catalyst surface. The doped Co improves the adsorption strengths of the C and H species, which promotes the activation of C₃H₈ and CO₂. The O atoms oxidize the eliminated H to form H₂O or combust coke on the alloy surface or neighboring CeO₂ sites. Coke can be combusted also by the lattice oxygen of CeO₂, where CeO₂ is partially reduced to form an oxygen vacancy. This oxygen vacancy is refilled by an O atom derived from CO₂ activation, enabling continuous coke combustion through the redox of CeO₂. Thus, CeO₂ can facilitate coke combustion via a Mars-van Krevelen-type mechanism, which significantly

enhances the coke resistance and catalyst stability. Pt–Co–In/CeO₂ exhibits outstanding catalytic activity, C₃H₆ selectivity, long-term stability, and CO₂ utilization efficiency, all of which are greater than typical values ever reported.

Pt–Co–In/CeO₂ catalyst exhibited remarkably high performance for CO₂-ODP, however, irreversible catalyst deactivation still occurred, which was likely caused by the accumulation of incombustible coke and nanoparticle sintering. In **Chapter 3**, we further designed and prepared a PtSn-based HEIs catalyst as a highly coke resistant and thermally stable catalyst. The Pt and Sn sites of intermetallic PtSn were partially substituted with Ni/Co and In/Ga, resulting in nanoparticles with a HEI structure of (PtCoNi)(SnInGa). The multi-metallization sufficiently isolates Pt atoms, preventing propylene decomposition and coke formation. The incorporation of Ni and Co significantly enhanced the ability to activate CO₂. Doping In(Ga) into the Sn site improved catalyst stability, probably due to the enhanced entropy effect. The combination of these abilities significantly enhances coke resistance and catalyst lifetime. Furthermore, because of the increased thermal stability, multi-metallization also prevents nanoparticle sintering. The HEI/CeO₂ catalyst shows 2- and 1.5-times higher catalyst life and specific activity than those of the best catalyst ever reported.

Considering the recent global demand for net-zero emissions, converting CO₂ into a value-added chemical is an appealing approach. We further applied our Pt–Co–In ternary alloy system to the CO₂-assisted dry-reforming of propane (DRP) reaction (**Chapter 4**), which has attracted much attention as a syngas production technology for liquid fuels and oxygenated chemicals with a low H₂/CO ratio. Compared to the dry-reforming of methane, the use of propane can consume more carbon dioxide than methane, and in particular, propane can be activated more easily than methane at lower reaction temperatures. The PtCo₂In₃/CeO₂ ternary catalyst for the DRP reaction with high selectivity and stability even over 100 h. The results show that the catalytic behavior of these catalysts is highly sensitive to the amount of cobalt doping. By controlling the amount of cobalt doping, the catalytic activity of PtCo₂In₃/CeO₂ catalysts can be improved, and the C-H/C-C bond of propane can be selectively cleaved in the presence of CO₂.

1.7 Conclusion Remark

In conclusion, our work not only demonstrates excellent catalytic performance, but also opens a new window for the design of multi-metallic catalysts. The results obtained in this study can promote the carbon-neutralization of industrial processes for light alkane conversion.

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Chapter Two

Platinum–cobalt–indium nanoalloy on ceria as a highly efficient catalyst for the oxidative dehydrogenation of propane using CO₂

2.1 Introduction

Propylene is a very important raw materials for the production of a variety of petrochemicals in several industries.^[1] The recent shift in the feedstock for steam crackers from oil-based naphtha to shale-based ethane has resulted in a significant gap between the limited supply of propylene and its increasing demand globally.^[2] Therefore, the development of highly efficient technologies to meet the rising global demand for propylene is greatly desired.^[3] Although the direct dehydrogenation of propane (DDP) has been studied and industrialized for this purpose, high reaction temperatures (typically ≥ 650 °C) are required to obtain a sufficiently high propylene yield due to the process's endothermicity.^[4] Furthermore, the harsh conditions inevitably induce severe catalyst deactivation and the thermal decomposition of propylene, limiting the applicability of the approach. The oxidative dehydrogenation of propane using CO₂ as a mild oxidant (CO₂-ODP: $\text{C}_3\text{H}_8 + \text{CO}_2 \rightarrow \text{C}_3\text{H}_6 + \text{CO} + \text{H}_2\text{O}$) is a promising strategy for solving such issues.^{[5], [6]} The equilibrium conversion of propane increases when dry reforming of C₃H₈ proceeds in parallel ($\text{C}_3\text{H}_8 + 3\text{CO}_2 \rightarrow 6\text{CO} + 4\text{H}_2$),^{[7],[8],[9]} which can decrease the reaction temperature required to achieve a high propane conversion.^[7] Moreover, CO₂ can remove the coke deposited on the catalyst surface via the Boudouard reaction ($\text{CO}_2 + \text{C} \rightarrow 2\text{CO}$).^[10] Unlike strong oxidants such as O₂, CO₂ suppresses the over-oxidation of propylene and the catalyst itself, thus potentially providing an efficient catalytic system for propylene production. Moreover, the catalytic conversion of CO₂ into a value-added chemical is beneficial for carbon recycling and greenhouse gas reduction.^{[11], [12]}

The previous studies on the CO₂-ODP focused predominantly on early transition or typical metal oxides (Cr₂O₃, V₂O₅, Ga₂O₃, and In₂O₃)^{[5], [13], [14], [15], [16]} and late transition metals (Pd, and Fe₃Ni)^{[7], [17]} as the main active species. Among these materials, chromium oxide species dispersed on mesoporous silica^[18,19] showed the highest specific activity and good propylene selectivity (ca. 80%) at high propane conversion regions. However, these catalysts showed very low CO₂ conversion and rapid deactivation within a few hours. Although the transition metal catalysts exhibited much longer catalyst life, the conversions of propane and CO₂ were quite low (typically, <12%). In this context, to date, no catalyst has been reported that exhibits at the same time a high catalytic activity, selectivity, stability, and CO₂ utilization efficiency. The

challenge is that the catalyst should simultaneously activate both propane and CO₂ without undesired side reactions and catalyst deactivation. Therefore, a multifunctional active material that successfully meets these requirements should be developed as an innovative catalyst for the CO₂-ODP. Possible candidates are multimetallic alloys.^{[20], [21], [22]} A highly efficient CO₂-ODP may be realized based on an appropriate combination of elements that can facilitate C–H scission and CO₂ capture/activation, as well as the inhibition of undesired over-dehydrogenation and C–C scission.

Motivated by this concept, we designed a ternary alloy catalyst consisting of three different classes of metals for the aforementioned functions in catalysis. First, Pt was chosen as the main active metal for the C–H scission because it is known to be highly active for C–H scission,^{[23], [24]} while it is minimally active for the C–C scission compared to other transition metals.^[25] Further, the late 3d transition metals such as Co, Ni, and Cu,^{[26], [27]} which are efficient catalysts for CO₂ reduction, were chosen to accelerate CO₂ capture and activation. Finally, inert typical elements such as Ga, In, and Sn were considered to enhance the dehydrogenation selectivity, owing to an ensemble effect on alloying.^[28] CeO₂ was also applied as the catalyst support to promote CO₂ capture and coke combustion, owing to its basicity and oxygen-releasing ability, respectively.^{[7], [29]} In particular, we show that the combination of Pt, Co, In, and CeO₂ can afford the multiple functions required to achieve a highly efficient CO₂-ODP, i.e., a remarkably active, selective, and stable catalysis is achieved using a Pt–Co–In/CeO₂ nanoalloy.

2.2 Experimental

2.2.1 Catalyst preparation

Pt/CeO₂, Pt–Co/CeO₂, Pt–In/CeO₂, Pt–Sn/CeO₂, and Pt–Co–In/CeO₂ (Pt: 3 wt%) were prepared by a conventional impregnation method using H₂PtCl₆ (aqueous solution, Kojima Chemicals, Pt 8.77 wt%), In(NO₃)₃·3H₂O, Co(NO₃)₂·6H₂O, and SnCl₂ as metal precursors. The CeO₂ support (JRC-CEO-2, S_{BET} = 123.1 m²g^{−1}) was added to a vigorously stirred aqueous solution (50 mL H₂O per gram of CeO₂) containing Pt and the corresponding second and/or third metal precursor(s) (Pt:Co = 1:1, Pt:In = 1:1, Pt:Sn = 1:1, and Pt:Co:In = 1:1:2), followed by stirring for 3 h at room temperature. The mixture was dried under a reduced pressure at

50 °C using a rotary evaporator, followed by calcination under flowing air at 500°C for 1 h and reduction under flowing H₂ (50 mL/min) at 600 °C for 1 h. Co/CeO₂ and In/CeO₂ were prepared by a similar method, where the amounts of Co and In were adjusted to be equal to those included in Pt–Co–In/CeO₂. A series of Pt–Co–In catalysts supported on various oxides other than CeO₂ (Pt–Co–In/MO_x, where MO_x = Al₂O₃ (prepared by calcination of boehmite [γ -AlOOH, supplied by SASOL chemicals] at 900 °C for 3 h, γ -phase), TiO₂ (P25, S_{BET} = 35-65 m²g⁻¹, anatase+rutile), ZrO₂ (JRC-ZRO-6, S_{BET} = 279.3 m²g⁻¹); Pt:Co:In = 1:1:2, Pt: 3 wt%) was also prepared by the same method mentioned above. Pt–In+Co /CeO₂ was prepared as a control catalyst having a Pt–In alloy phase and cationic Co, by impregnating the reduced Pt–In/CeO₂ with an aqueous solution of Co(NO₃)₂·6H₂O so that the final Pt:Co:In ratio became 1:1:2. Comparing the catalytic performances of Pt–Co–In/CeO₂ and Pt–In/CeO₂+Co allows to understand whether Co should be included in the alloy phase or not for enhanced catalysis.

2.2.2 Characterization

The crystal structure of the prepared catalyst was examined by powder X-ray diffraction (XRD) using a Rigaku MiniFlex II/AP diffractometer with Cu Ka radiation. High-angle annular dark field scanning transmission electron microscopy (HAADFSTEM) was carried out using a JEOL JEM-ARM200 M microscope equipped with an energy dispersive X-ray (EDX) analyzer (EX24221M1G5T). STEM analysis was performed at an accelerating voltage of 200 kV. To prepare the TEM specimen, all samples were sonicated in ethanol and then dispersed on a Mo grid supported by an ultrathin carbon film. For the particle size distribution, we counted 126 particles with ten high-resolution STEM images.

TPO experiment was performed using BELCAT II (MicrotracBEL) to quantify the amount of coke deposited on the spent catalysts after 20 h of CO₂-ODP at 550 °C (0.1g of the catalyst with 0.9g quartz sand). The spent catalyst placed in a quartz tube reactor was treated under flowing He (30 mL/min) at 150 °C for 30 min, followed by cooling to room temperature. Then, the catalyst bed temperature was increased (40–900 °C, ramping rate: 5 °C min⁻¹) under flowing O₂/He (50%, 40 mL/min). The amount of CO₂ in the outlet gas was quantified by an online mass spectrometer. CO₂- and He-TPSR experiments were performed for coked catalysts

in a similar fashion using the flow of CO₂/He (10%, 30 mL/min) and pure He (30 mL/min). The dispersion of Pt and Co in the catalysts (percentage of exposed Pt+Co to the total amount of Pt+Co) was measured by chemisorption of CO at room temperature. Prior to chemisorption, the catalyst (40 mg) was treated by 5% H₂/Ar (30 mL/min) at 550 °C for 0.5 h, followed by cooling to ca -110 °C by liquid nitrogen with an He purge (30 mL/min). Then, introduced a pulse of 10% CO/He into the reactor and quantified the CO passed through the catalyst bed using a TCD detector. This pulse measurement was repeated until no more CO was adsorbed. The dispersion was estimated assuming a 1:1 stoichiometry of CO adsorption on Pt and/or Co.

Laser Raman spectroscopy experiments were carried out using a JEOL NRS-5100 spectrometer at room temperature to investigate the carbonaceous deposits over the spent catalysts, with 2 cm⁻¹ resolution of the apparatus and a 532 nm excitation source.

X-ray absorption fine structure (XAFS) spectra of the prepared catalysts were collected at the BL01B14 beamline of SPring-8, Japan Synchrotron Radiation Research Institute (JASRI) using Si(111) (for Co K- and Pt L_{III}-edges) and Si(311) (for In K-edge) double-crystals as monochromators. Prior to the measurement, the catalyst was pelletized (ca. 150 mg with a diameter of 10 mm) and pretreated by H₂/N₂ (20%, 40 mL/min) at 550 °C for 0.5 h in an in-situ quartz cell, followed by cooling to room temperature with N₂ purge (32 mL/min). The XAFS spectra were recorded in a transmission (In K-edge) and a fluorescence (Pt L_{III}-, and Co K-edge: using a 19-element Ge solid-state detector) modes at room temperature. Athena and Artemis softwares ver. 0.9.25 implemented in the Demeter package were used for the analysis of the obtained XAFS spectra. FEFF8 was used for the calculation of the back-scattering amplitude and phase shift functions.^[30] We defined the R-factor (R^2) for curve-fitting as follows: $R^2 = \sum_i \{k^3 \chi_i^{exp}(k) - k^3 \chi_i^{fit}(k)\}^2 / \sum_i \{k^3 \chi_i^{exp}(k)\}^2$.

XPS X-ray photoelectron spectroscopy (XPS) analysis for the catalysts was carried out using a JEOL JPS-9010MC (Mg-K α irradiation) spectrometer. The catalysts were reduced in a quartz tube reactor under following H₂ (0.1 MPa, 20 mL min⁻¹) at 550°C for 30 min, then transferred into the spectrometer using a sealed vessel and an Ar globe box without exposing to air. Binding energies were calibrated with the O 1s emission of CeO₂ as 529.9 eV.

2.2.3 Catalytic test

CO₂-ODP was performed in a quartz fixed-bed reactor with 6 mm of internal diameter under an atmospheric pressure. The catalyst (0.10 g) diluted with sea sand (0.90 g, Miyazaki Chemical, 99.9%) was treated under flowing hydrogen (10 mL/min) at 550°C for 0.5 h prior to the catalytic reactions. Then, the catalysts were evaluated by feeding reactant gas mixture (C₃H₈: CO₂: He = 1:1:2, a total flow rate of 20 mL/min). The gas phase was analyzed and quantified using an online thermal conductivity detection gas chromatograph (Shimadzu GC-8A, column: Gaskuropack 54) equipped downstream. For all the catalysts, C₃H₆, C₂H₄, C₂H₆, CH₄, CO, CO₂, H₂O, and H₂ were detected as reaction products in outlet gas. The C₃H₈ and CO₂ conversions were defined as follows:

$$\text{C}_3\text{H}_8 \text{ conversion: } X_{\text{C}_3\text{H}_8} (\%) = \frac{F_{\text{C}_3\text{H}_8}^{\text{in}} - F_{\text{C}_3\text{H}_8}^{\text{out}}}{F_{\text{C}_3\text{H}_8}^{\text{in}}} \times 100 \quad (1)$$

$$\text{CO}_2 \text{ conversion: } X_{\text{CO}_2} (\%) = \frac{F_{\text{CO}_2}^{\text{in}} - F_{\text{CO}_2}^{\text{out}}}{F_{\text{CO}_2}^{\text{in}}} \times 100 \quad (2)$$

where, F_x^{in} and F_x^{out} indicate the inlet and outlet flow rates of x (mL · min⁻¹), respectively.

In this reaction, CO can be formed from C_xH_y by dry reforming as well as from CO₂ via reverse water gas shift reaction, which were distinguished as follows:

$$\text{CO formed from CO}_2: F_{\text{CO}}^{\text{CO}_2} = F_{\text{CO}_2}^{\text{in}} - F_{\text{CO}_2}^{\text{out}} \quad (\text{mL} \cdot \text{min}^{-1}) \quad (3)$$

$$\text{CO formed from C}_x\text{H}_y: F_{\text{CO}}^{\text{C}_x\text{H}_y} = F_{\text{CO}}^{\text{out}} - F_{\text{CO}}^{\text{CO}_2} \quad (\text{mL} \cdot \text{min}^{-1}) \quad (4)$$

Then, two different expressions of C₃H₆ selectivity and yield were defined to compare with those reported in literature.

$$\text{C}_3\text{H}_6 \text{ sel. in C}_x\text{H}_y: S_{\text{C}_3\text{H}_6}^{\text{C}_x\text{H}_y} (\%) = \frac{F_{\text{C}_3\text{H}_6}^{\text{out}}}{F_{\text{C}_3\text{H}_6}^{\text{out}} + \frac{2}{3}F_{\text{C}_2\text{H}_6}^{\text{out}} + \frac{2}{3}F_{\text{C}_2\text{H}_4}^{\text{out}} + \frac{1}{3}F_{\text{CH}_4}^{\text{out}}} \times 100 \quad (5)$$

$$\text{net C}_3\text{H}_6 \text{ sel.: } S_{\text{C}_3\text{H}_6} (\%) = \frac{F_{\text{C}_3\text{H}_6}^{\text{out}}}{F_{\text{C}_3\text{H}_6}^{\text{out}} + \frac{2}{3}F_{\text{C}_2\text{H}_6}^{\text{out}} + \frac{2}{3}F_{\text{C}_2\text{H}_4}^{\text{out}} + \frac{1}{3}F_{\text{CH}_4}^{\text{out}} + \frac{1}{3}F_{\text{CO}}^{\text{C}_x\text{H}_y}} \times 100 \quad (6)$$

$$C_3H_6 \text{ yield in } C_xH_y: Y_{C_3H_6}^{C_xH_y} (\%) = \frac{X_{C_3H_8} \cdot S_{C_3H_6}^{C_xH_y}}{100} \quad (7)$$

$$\text{net } C_3H_6 \text{ yield: } Y_{C_3H_6} (\%) = \frac{X_{C_3H_8} \cdot S_{C_3H_6}}{100} \quad (8)$$

H₂ yield was defined as follows:

$$H_2 \text{ yield: } Y_{H_2} (\%) = \frac{F_{H_2}^{out}}{F_{C_3H_8}^{in}} \times 100 \quad (9)$$

Material balance was considered using the following scales:

$$\text{carbon balance in } C_xH_y = \frac{F_{C_3H_8}^{out} + F_{C_3H_6}^{out} + \frac{2}{3}F_{C_2H_6}^{out} + \frac{2}{3}F_{C_2H_4}^{out} + \frac{1}{3}F_{CH_4}^{out}}{F_{C_3H_8}^{in}} \times 100 \quad (10)$$

$$\text{carbon balance in } CO_x = \frac{F_{CO_2}^{out} + F_{CO}^{out}}{F_{CO_2}^{in}} \times 100 \quad (11)$$

$$\begin{aligned} \text{total carbon balance} = \\ \frac{F_{C_3H_8}^{out} + F_{C_3H_6}^{out} + \frac{2}{3}F_{C_2H_6}^{out} + \frac{2}{3}F_{C_2H_4}^{out} + \frac{1}{3}F_{CH_4}^{out} + F_{CO_2}^{out} + \frac{1}{3}F_{CO}^{C_xH_y} + F_{CO}^{CO_2}}{F_{C_3H_8}^{in} + F_{CO_2}^{in}} \times 100 \end{aligned} \quad (12)$$

$$\text{oxygen balance} = \frac{2F_{CO_2}^{out} + F_{CO}^{out} + F_{H_2O}^{out}}{2F_{CO_2}^{in}} \times 100 \quad (13)$$

Deactivation constant, mean catalyst life, CO₂ utilization efficiency, turnover frequency (TOF), average coke selectivity, and turnover number of coke were defined as follows.

$$\text{Deactivation constant: } k_d = \left\{ \ln \left(\frac{1 - X_{C_3H_8}^f}{X_{C_3H_8}^f} \right) - \ln \left(\frac{1 - X_{C_3H_8}^i}{X_{C_3H_8}^i} \right) \right\} (t^f - t^i)^{-1} \quad (14)$$

$$\text{Mean catalyst life: } \tau = \frac{1}{k_d} \quad (15)$$

$$CO_2 \text{ utilization efficiency } (\%) = X_{CO_2} \left(1 - \frac{|X_{CO_2} - Y_{C_3H_6}|}{X_{CO_2} + Y_{C_3H_6}} \right) \quad (16)$$

$$TOF_{C_3H_8/CO_2} (\text{site}^{-1} \text{min}^{-1}) = \frac{M_{C_3H_8/CO_2}^{in} \times X_{C_3H_8/CO_2}^i}{n_{Pt+Co} \times D} \quad (17)$$

$$\text{average coke selectivity: } S_C (\%) = \frac{\frac{1}{3} n_C^t}{\int_0^t (F_{C_3H_8}^{in} - F_{C_3H_8}^{out}) dt} \times 100 \quad (18)$$

$$\text{TON}_{\text{coke}} (\text{site}^{-1}) = \frac{n_C^t}{n_{\text{Pt+Co}} \times D} \quad (19)$$

where, $X_{C_3H_8}^i$ and $X_{C_3H_8}^f$ indicate the initial (t^i : 0.5 h) and final (t^f : 20 h) $X_{C_3H_8}$, respectively. $M_{C_3H_8/CO_2}^{in}$ and $M_{C_3H_8/CO_2}^{out}$ are the inlet and outlet molar flow rates (mol/min) of C_3H_8 or CO_2 , respectively. $n_{\text{Pt+Co}}$ and D correspond to the mole of active metal in the catalyst and its dispersion estimated by CO chemisorption, respectively. n_C^t indicates mole of coke accumulated at time on stream of t ($x = C$). The second term in the parenthesis of eq (16) represents the degree of deviation between X_{CO_2} and $Y_{C_3H_6}$. We also used a flame ionization detection gas chromatograph (FID-GC: Shimadzu GC-14B, column: Porapak-Q) equipped with a methanizer (Shimadzu MTN-1) to detect oxygenated products. All the catalytic tests for kinetic analysis were performed under differential conditions by adjusting the catalyst amount, where the reactant conversion was lower than 15% (typically 5~10%).

2.2.4 Computational details

Periodic DFT calculations were performed using the CASTEP code^[31] with Vanderbilt-type ultrasoft pseudopotentials and the revised version of Perdew–Burke–Ernzerhof exchange–correlation functional based on the generalized gradient approximation.^[32] The plane-wave basis set was truncated at a kinetic energy of 360 eV. A Fermi smearing of 0.1 eV was utilized. Dispersion correlations were considered using the Tkatchenko–Scheffler method with a scaling coefficient of $s_R = 0.94$ and a damping parameter of $d = 20$.^[33] The reciprocal space was sampled using a k -point mesh with a spacing of typically $0.04 \text{ \AA}^{-1}$, as generated by the Monkhorst–Pack scheme.^[34] Geometry optimizations and transition state (TS) searches were performed on supercell structures using periodic boundary conditions. The surfaces were modeled using metallic slabs with a thickness of four atomic layers with 13 Å of vacuum spacing. We chose $\text{Pt}_2\text{In}_3(012)$ as the most stable surface, which has the highest surface atom density and diffraction intensity.^{[35],[36]} $\text{Pt}_2\text{In}_3(012)\text{--Co}$ was constructed as a model of the surface $(\text{Pt}_{1-x}\text{Co}_x)_2\text{In}_3$ pseudo binary alloy by replacing one of the surface Pt atoms of

Pt₂In₃(012). The unit cells were (2 × 2) for Pt(111), (1 × 1) for C₃H₈ dehydrogenation and H₂ formation on Pt₂In₃(012)(–Co), and (2 × 1) for CO₂ reduction and H₂O formation on Pt₂In₃(012)(–Co). Geometry optimizations were performed using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm.^[37] The unit cell size of the bulk material (Pt and Pt₂In₃) was firstly optimized, followed by modeling the slab structure and surface relaxation with the size of the supercell fixed. The convergence criteria for structure optimization and energy calculation were set to (a) an SCF tolerance of 1.0 × 10^{−6} eV per atom, (b) an energy tolerance of 1.0 × 10^{−5} eV per atom, (c) a maximum force tolerance of 0.05 eV Å^{−1}, and (d) a maximum displacement tolerance of 1.0 × 10^{−3} Å.

The adsorption energy was defined as follows: $E_{\text{ad}} = E_{\text{A-S}} - (E_{\text{S}} + E_{\text{A}})$, where $E_{\text{A-S}}$ is the energy of the slab together with the adsorbate, E_{A} is the total energy of the free adsorbate, and E_{S} is the total energy of the bare slab. The adsorption energy for an oxygen-preadsorbed slab was calculated using E_{SH} , which is the total energy of the oxygen-adsorbed slab, instead of using E_{S} . The d band center (ε_{d}) was defined as the average energy of the occupied d band relative to the Fermi level as follows:

$$\varepsilon_{\text{d}} = \int_{-\infty}^0 E \rho_{\text{d}}(E) \, dE / \int_{-\infty}^0 \rho_{\text{d}}(E) \, dE \quad (20)$$

where ρ_{d} is the density of states projected to d orbitals.

The transition state (TS) search was performed using the complete linear synchronous transit/quadratic synchronous transit (LST/QST) method.^{[38],[39]} Linear synchronous transit maximization was performed, followed by energy minimization in the directions conjugating to the reaction pathway. The approximated TS was used to perform QST maximization with conjugate gradient minimization refinements. This cycle was repeated until a stationary point was found. Convergence criterion for the TS calculations were set to root-mean-square forces on an atom tolerance of 0.05 eV Å^{−1}.

The activation energy (E_{A}) was determined as the largest energy barrier among all the focused steps: for CO₂ conversion; CO₂ activation, for C₃H₈ conversion, the 1st or 2nd C–H activation. We also consider theoretical apparent activation energy, E_{A}^* , for the comparison

with the experimental values. This is identical to E_A except when the initial state for E_A is a weakly adsorbed state, like physisorption, where the apparent activation energy should be expressed as $E_A^* = E_A + E_{ad}$ as often considered in literature.^[31] In this study, the 1st C–H activation on Pt_2In_3 falls into this case: $E_A^* = E_A (153.3) + E_{ad} (-13.2) = 140.1$ kJ/mol.

Vibrational frequencies of the adsorbates were computed by phonon calculation based on harmonic approximation using the finite displacement method in CASTEP. Fractional positions of all the metal atoms were fixed so that only C, H, and O atoms were considered for phonon calculation. The contribution of solid surface to the vibrational terms, which is typically much lower than that of adsorbates, was ignored. The threshold for energy convergence for each iteration was set to 10^{-10} eV per atom. The entropy (S), Gibbs free energy (G), and partition function (q) of each species were estimated at 550 °C using the calculated vibrational frequencies (ν_n) as follows:^[40]

$$G(T, P) = E_e + E_{trans} + E_{rot} + E_{vib} + PV - T(S_{trans} + S_{rot} + S_{vib}) \quad (21)$$

where, E_e is the electronic energy,

$$E_{trans} = \frac{3}{2}RT \quad (22), \quad E_{rot} = RT \quad (23) \text{ (for linear molecule),}$$

$$E_{rot} = \frac{3}{2}RT \quad (24) \text{ (for nonlinear molecule), } E_{vib} = R \sum_n \frac{h\nu_n}{k_B} \left(\frac{1}{2} + \frac{1}{e^{h\nu_n/k_B T} - 1} \right) \quad (25)$$

$$S_{trans} = R \left(\ln q_{trans} + \frac{5}{2} \right) \quad (26), \quad \text{where } q_{trans} = \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \frac{k_B T}{P} \quad (27)$$

$$S_{rot} = R(\ln q_{rot} + 1) \quad (28) \text{ (for linear molecule), where } q_{rot} = \frac{1}{\sigma} \left(\frac{8\pi^2 k_B T}{h^2} \right) \times I \quad (29)$$

$$S_{rot} = R \left(\ln q_{rot} + \frac{3}{2} \right) \quad (30) \text{ (for nonlinear molecule),}$$

$$\text{where } q_{rot} = \frac{\sqrt{\pi}}{\sigma} \left(\frac{8\pi^2 k_B T}{h^2} \right)^{3/2} \times \sqrt{I_x I_y I_z} \quad (31)$$

$$S_{vib} = R \sum_n \left(\frac{h\nu_n/k_B}{e^{h\nu_n/k_B T} - 1} - \ln(1 - e^{-h\nu_n/k_B T}) \right) \quad (32)$$

where, I is the moment of inertia, σ is the rotational symmetry number, and m is the mass of the molecule. For surface species, the rotational and translational contributions were converted into vibrational modes and the PV term was approximated to be negligible compared with the energetic terms; therefore, the Gibbs free energy for surface species was considered as follows: $G(T, P) = E_e + E_{vib} - TS_{vib}$. Neglecting the spurious frequencies contributes to the enthalpy

and entropy; hence, spurious frequencies lower than 100 cm^{-1} were replaced with 50 cm^{-1} for all the structures to provide consistent results as reported in literature.^[41] The properties of the reactant (C_3H_8 and CO_2) and product (C_3H_6 , CO , and H_2O) molecules in gas phase were calculated using an ideal gas approximation at $550\text{ }^\circ\text{C}$ and their translational and rotational contributions were evaluated at relative pressures (P/P^0) of 0.24 and 0.01, respectively.

2.3 Results

2.3.1 Characterization of the catalysts structure

The Pt–Co–In/CeO₂ (Pt: 3wt%, Pt:Co:In = 1:1:2) catalyst was prepared by a conventional impregnation method using CeO₂ as the support. Figure 2.1a and 2.1b show the high-resolution high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images of Pt–Co–In/CeO₂. Small nanoparticles with diameters in the range of 2–3 nm were mainly observed on the CeO₂ support. The mean diameter (3.9 nm, Figure 2.1c) was slightly higher than the size of major species because of the presence of a small amount of relatively large particles (10–16 nm). Since recent studies have demonstrated that reverse water-gas shift reaction^[42] and propane dehydrogenation^[43,44] are structure sensitive (smaller particles afford higher activity), large particles (>10 nm) may have little contribution to the overall reaction rate in CO₂-ODP. The elemental map acquired by energy-dispersive X-ray (EDX) analysis showed that the nanoparticles consisted of Pt, Co, and In, and some Co species were also present outside of the nanoparticles (Figures 2.1d–2.1h). The Pt:Co:In atomic ratios of the nanoparticles (regions 1–4, designated by dashed yellow squares in Figures 2.1a and 2.1b) were approximately 1:0.5:2 (Figure 2.1i), where the Co content was lower than that supplied in the catalyst preparation (Pt:Co:In = 1:1:2). Therefore, some of the Co species appear to not be included in the nanoparticles and are highly dispersed on the CeO₂ support. Figure 2.1j shows the STEM image of a single Pt–Co–In nanoparticle, where a crystal structure with interplanar distances of 2.28 and 2.29 Å was observed. These values were close to those of the (110) and (102) planes of intermetallic Pt₂In₃ (Figures 2.1j and 2.1k).^[45] Considering that the atomic ratio of (Pt+Co):In is close to 2:3 (2:2.7), the nanoparticles likely have a (Pt_{1-x}Co_x)₂In₃ pseudo-binary alloy structure, where some Pt atoms in Pt₂In₃ are substituted by Co (Figure 2.1l).

Further, we performed an X-ray diffraction (XRD) analysis of Pt–Co–In/CeO₂, from which a diffraction pattern similar to that of Pt₂In₃ was obtained, although the diffraction angles were slightly lower than those of pure Pt₂In₃ (Figure 2.2). This indicates the lattice expansion of Pt₂In₃ by Co doping and supports the formation of the (Pt_{1-x}Co_x)₂In₃ pseudo-binary alloy structure. To obtain further structural information, X-ray absorption fine structure (XAFS) analysis was subsequently performed. The Pt–Co–In/CeO₂ sample was reduced in-situ by a flow of H₂ at 550°C for 0.5 h. The Pt L_{III}-, Co K-, and In K-edge X-ray absorption near edge spectra (XANES) of the pretreated Pt–Co–In/CeO₂ were similar to those of the corresponding foils, indicating that these metals are reduced mostly to a zero-valent state (Figure 2.3). A small contribution of In₂O₃ was observed in the In K-edge XANES (Figure 2.3) and extended XAFS (EXAFS) spectra (Figure 2.4, the Fourier transform of EXAFS is shown in Figure 2.4). This suggests that the residual In species, which did not participate in the alloy formation, is present as an oxide on CeO₂. EXAFS curve-fitting (Figure 2.4 and Table 2.1) suggested the presence of Pt–In (In–Pt) and Co–In (In–Co) scatterings. This result agrees with the formation of the (Pt_{1-x}Co_x)₂In₃ pseudo-binary alloy structure and supports that Co was doped at the Pt sites of Pt₂In₃. For Co K-edge fitting, Co–Co scattering with an interatomic distance (*R*: 2.44) close to that of Co foil (2.49 Å) was also suggested. This indicates the presence of monometallic Co nanoparticles on CeO₂ and is consistent with the result of the HAADF-STEM-EDX analysis. In–O scattering was also derived for In K-edge fitting, indicating the presence of In₂O₃ as observed for the XANES. Thus, the XAFS analysis demonstrated the formation of (Pt_{1-x}Co_x)₂In₃ pseudo-binary alloy nanoparticles on CeO₂. The residual Co and In species, which did not participate in alloy formation, remained as monometallic Co and In₂O₃ nanoparticles. Besides, we conducted an X-ray photoelectron spectroscopy (XPS) analysis on the catalysts. Pt/CeO₂ and Pt–Co–In/CeO₂ showed similar Pt 4f_{7/2} emissions at 71.6 and 71.4 eV, respectively, which are assigned to metallic Pt (Figure 2.5a).^[46] The small negative shift indicates that Pt was slightly electron-enriched upon alloying with In and Co. The In 3d XPS spectrum showed that the surface In species was mainly metallic. A small part of In was

oxidized (Figure 2.5b, $\text{In}^{(0)}$: 443.5 eV and In^{3+} : 444.5 eV),^[46] which can be attributed to the ternary alloy phase and residual In_2O_3 , respectively, as suggested by the XAFS study.

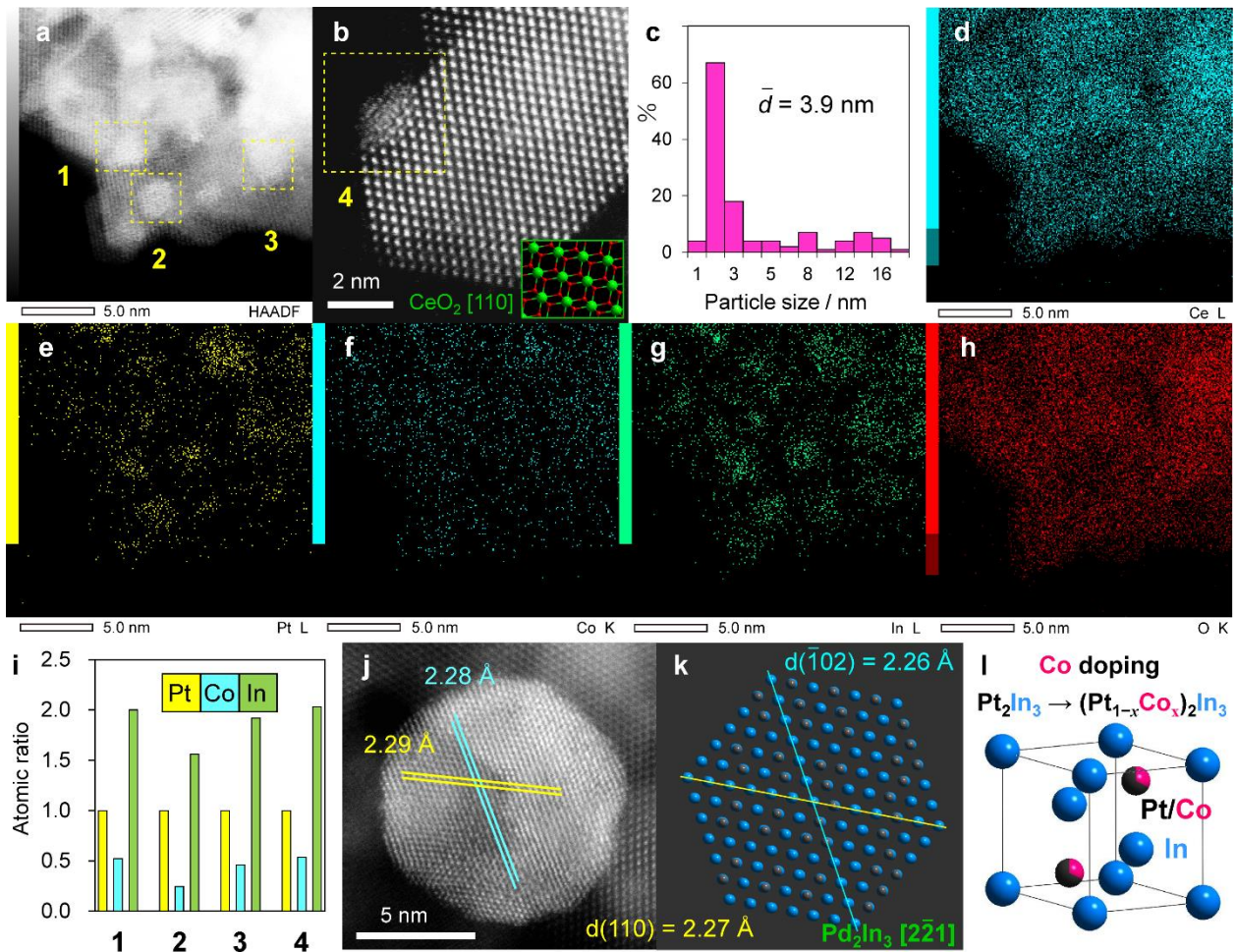


Figure 2.1. : Characterization of Pt–Co–In/CeO₂. **a, b** HAADF-STEM image of Pt–Co–In/CeO₂ (Pt:Co:In =1:1:2). **c** Particle-size distribution. **d–h**, Elemental maps of **(d)** Ce, **(e)** Pt, **(f)** Co, **(g)** In, and **(h)** O in **a**, acquired by EDX. **i** Atomic ratios of Pt, Co, and, In present in the regions 1–4, designated by dotted yellow squares in **a** and **b**. **j** HAADF-STEM image of a single nanoparticle on Pt–Co–In/CeO₂. **k** Crystal structure of the intermetallic Pt_2In_3 viewed along the $[2\bar{2}1]$ direction. **l** Model of the $(\text{Pt}_{1-x}\text{Co}_x)_2\text{In}_3$ pseudo-binary alloy structure with the crystal structure unit.

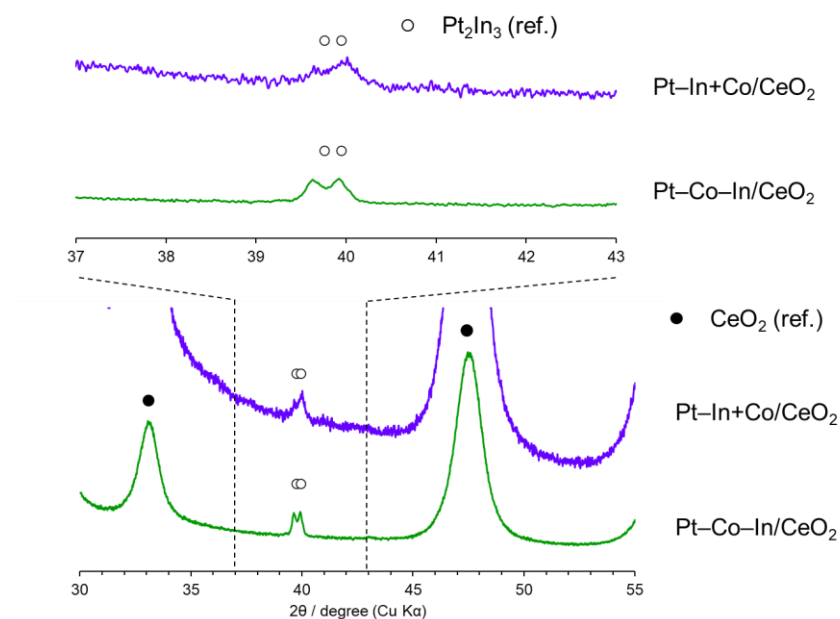


Figure 2.2. XRD patterns of for Pt–Co–In/CeO₂ and Pt–In+Co/CeO₂ catalysts. Pt–In+Co/CeO₂ showed the diffraction pattern assignable to that of intermetallic Pt₂In₃, indicating that the additional Co species was not included in the intermetallic phase. In contrast, the corresponding diffraction pattern of Pt–Co–In/CeO₂ was shifted to lower angles, which suggests that the lattice constant of Pt₂In₃ was changed by doping of Co into Pt₂In₃.

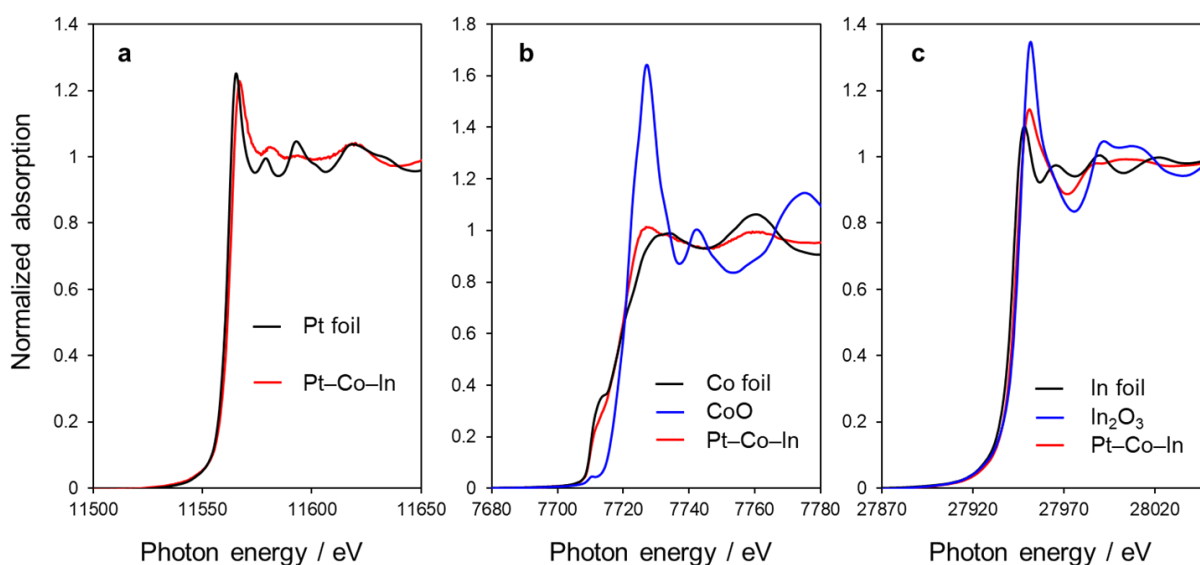


Figure 2.3. **a** Pt L_{III}, **b** Co K and **c** In K-edge X-ray absorption near edge structure (XANES) spectra of the in-situ reduced catalysts and reference compounds.

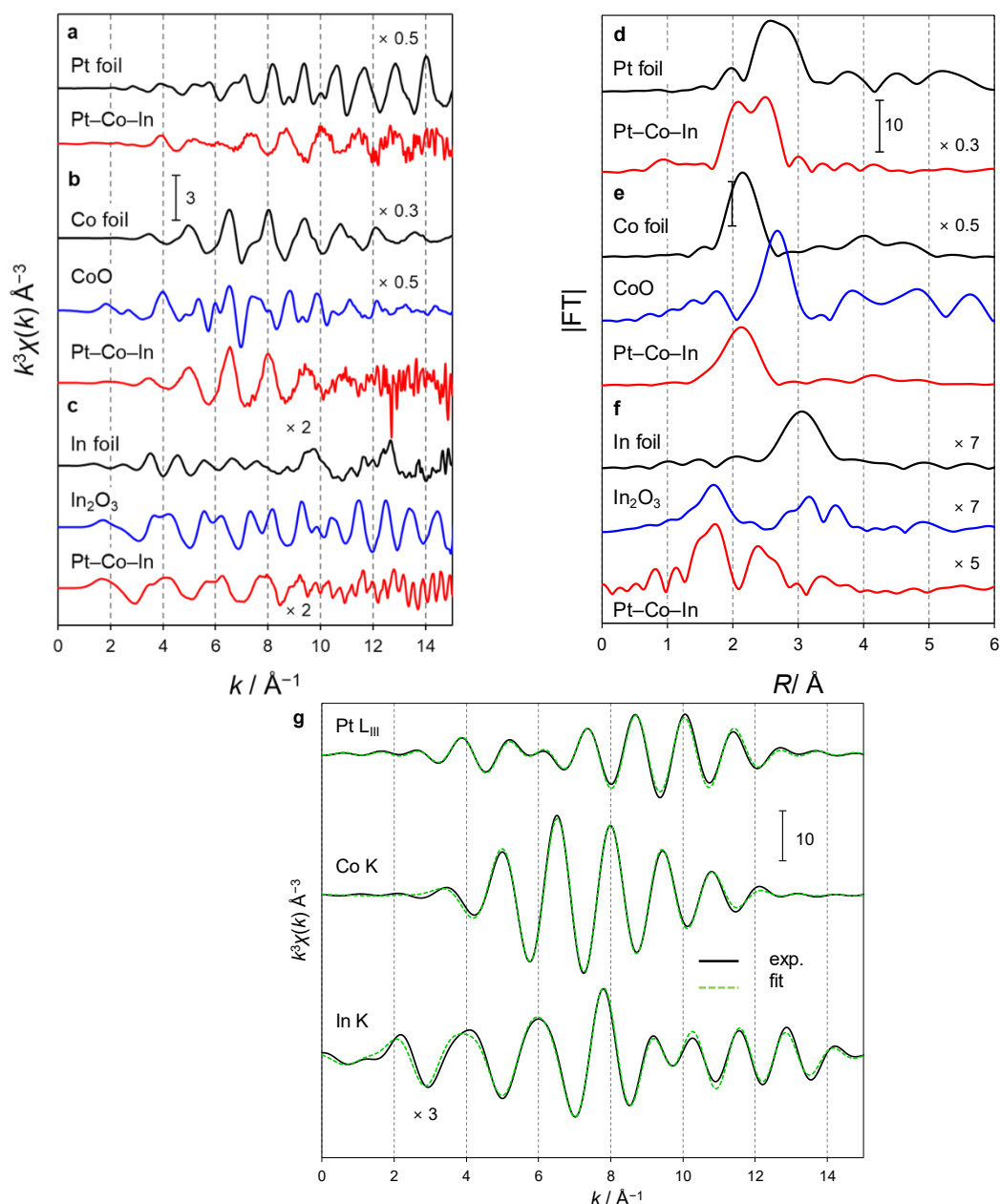


Figure 2.4. **a** Pt L_{III}, **b** Co K and **c** In K-edge Fourier transform of EXAFS of the in-situ reduced catalysts and reference compounds. **d.** Pt L_{III}, **e** Co K and **f** In K-edge extended X-ray absorption near edge structure (EXAFS) spectra of the in-situ reduced catalysts and reference compounds. **g** Curve-fitting for the Pt L_{III}-, Co K-, and In K-edge k^3 -weighted EXAFS oscillations of Pt-Co-In/CeO₂. The k^3 -weighted EXAFS oscillation was Fourier-transformed in the k range of 3–12 $\text{\AA}^{-1}$, 3–12 $\text{\AA}^{-1}$, and 3–14 $\text{\AA}^{-1}$ for Pt L_{III}-, Co K-, and In K-edges, respectively. Curve-fitting was performed using the back Fourier-transforms of the coordination peaks ranging between 1.0–3.0 $\text{\AA}$, 1.0–3.0 $\text{\AA}$, and 1.3–3.2 $\text{\AA}$ for Pt L_{III}-, Co K-, and In K-edges, respectively.

Table 2.1. Results of EXAFS curve-fitting for Pt–Co–In/CeO₂ and the reference foils.

Sample	Edge	Shell	S_0^{-2} ^a	CN ^b	R (Å) ^c	ΔE_0 (eV) ^d	σ^2 (Å ²) ^e	R-factor
Co foil	Co K	Co–Co	0.74	12 (fix)	2.49 ± 0.00	2.6 ± 0.4	0.006 ± 0.000	0.001
Pt foil	Pt L _{III}	Pt–Pt	0.82	12 (fix)	2.77 ± 0.00	9.0 ± 0.6	0.005 ± 0.000	0.002
In foil	In K	In–In	0.86	8 (fix)	3.18 ± 0.01	2.9 ± 0.7	0.024 ± 0.003	0.009
		In–In		4 (fix)	3.33 ± 0.04			
Pt–Co–In/CeO ₂	Co K	Co–Co	0.74	7.4 ± 2.4	2.44 ± 0.02	-4.8 ± 2.9	0.012 ± 0.003	0.003
		Co–In	(fix)	1.3 ± 1.0	2.61 ± 0.03		0.007 ± 0.004	
	Pt L _{III}	Pt–In	0.82	3.0 ± 0.5	2.64 ± 0.01	4.9 ± 1.3	0.006 ± 0.001	0.008
		Pt–Pt	(fix)	4.0 ± 2.2	2.69 ± 0.02		0.011 ± 0.005	
		In–O		3.8 ± 0.9	2.11 ± 0.02		0.011 ± 0.002	
	In K	In–Pt	0.86	2.3 ± 0.7	2.64 ± 0.01	-1.0 ± 2.9	0.008 ± 0.001	0.017
		In–Co	(fix)	1.2 ± 0.7	2.70 ± 0.07		0.025 ± 0.009	

^a Amplitude factor. ^b Coordination number. ^c Distance between absorber and backscatterer atoms. ^d Correction term in the absorption edge. ^e Debye–Waller factor.

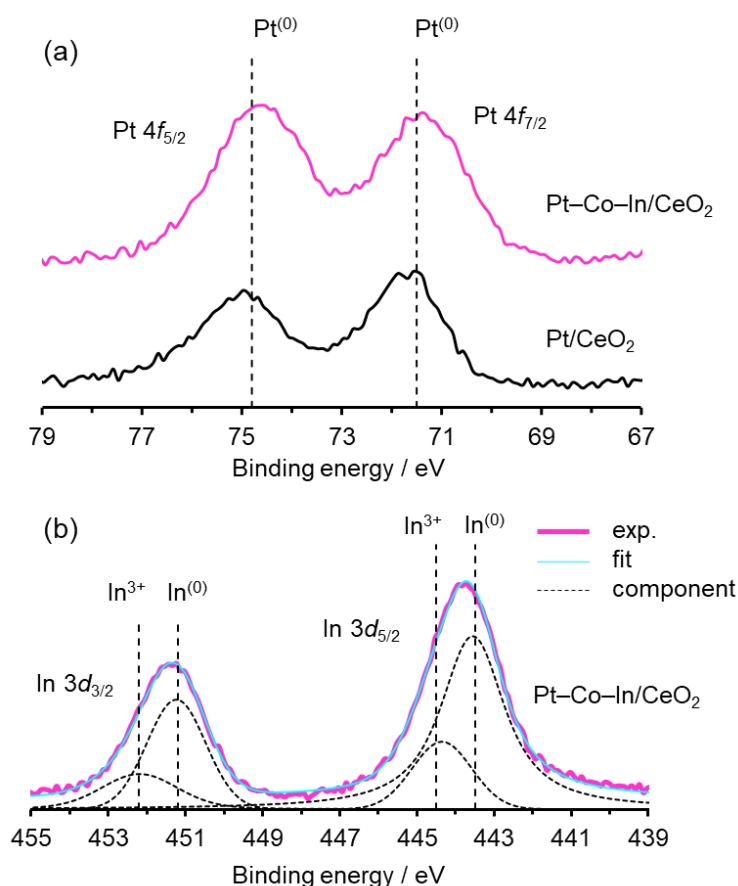
**Figure 2.5.** (a) Pt 4f and (b) In 3d XPS spectra of Pt/CeO₂ and Pt–Co–In/CeO₂.

Table 2.2. Metal dispersions of CeO₂-supported Pt-based catalysts.^a

Catalyst	Active metal (Pt and Co) dispersion (%) estimated by CO chemisorption
Pt/CeO ₂	25.4
Pt-Co/CeO ₂	27.2
Pt-In/CeO ₂	26.5
Pt-Co-In/CeO ₂	29.6

^a The loading amount of Pt was fixed at 3 wt% for all the catalysts.

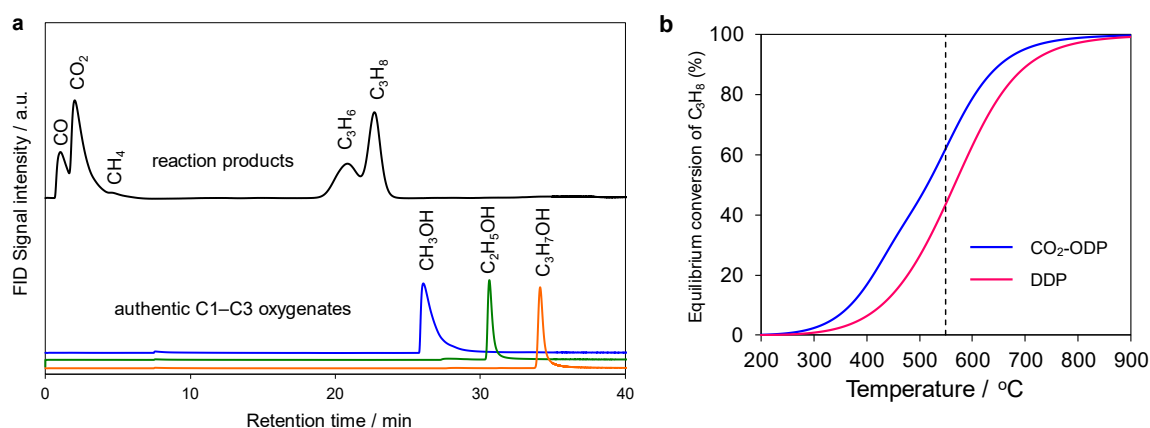


Figure 2.6. a. FID-GC chart of the outlet gas from CO₂-OPD on Pt-Co-In/CeO₂ at 550°C. The retention times of authentic C1–C3 alcohols as possible oxygenated products are also shown. No products other than CO and hydrocarbons were detected in the outlet gas. CO and CO₂ were detected using a methanizer. **b.** Calculated equilibrium conversion of C₃H₈ in DDP (C₃H₈:He = 5:10) and CO₂-ODP (C₃H₈:CO₂:He = 5:5:10) as a function of temperature. Calculation was done by a Gibbs free energy minimization algorithm implemented in HSC Chemistry 8.

The equilibrium C₃H₈ conversion in DDP and CO₂-ODP at 550°C were 43% and 62%, respectively. This increase is originated from a large contribution of dry reforming^{[7],[9],[8]} and the reduced partial pressure of C₃H₈ (0.33 atm to 0.25 atm) by adding CO₂. The C₃H₈ conversion obtained in CO₂-ODP over Pt-Co-In/CeO₂ was approximately 50%, which was slightly higher than 43% and much lower than 62%. Considering that the contribution of dry reforming in CO₂-ODP over Pt-Co-In/CeO₂ was minor, this conversion increase can be attributed mainly to the reduced partial pressure of C₃H₈ and partly to dry reforming.

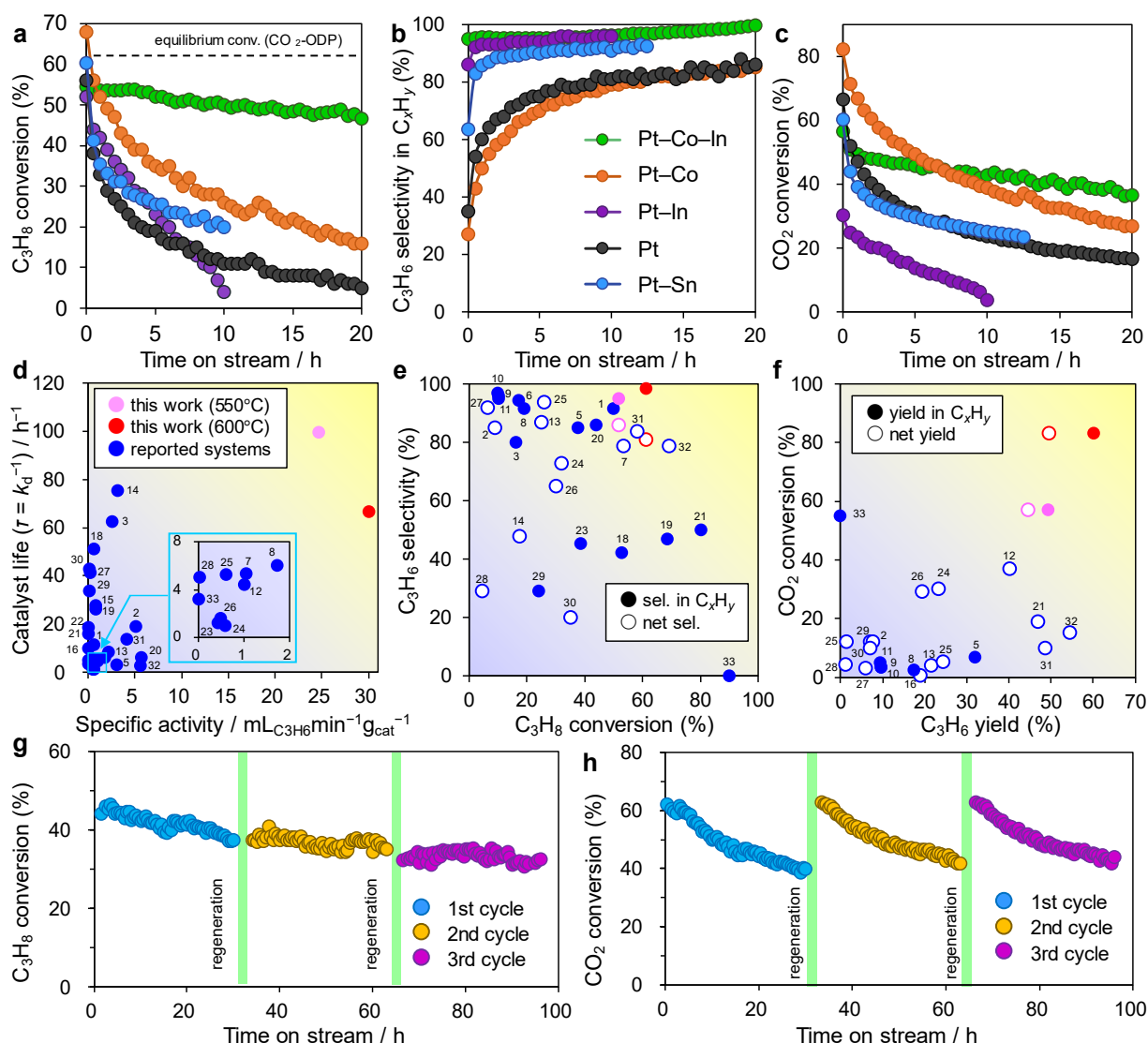


Figure 2.7: Catalytic performance of Pt–Co–In/CeO₂ in the CO₂-ODP. Reaction conditions: catalyst amount, 100 mg; gas feed, C₃H₈:CO₂:He = 5:5:10 mL·min⁻¹; temperature, 550 °C. **a, b, c** Time course of (a) C₃H₈ conversion, (b) C₃H₆ selectivity, and (c) CO₂ conversion. **d, e, f** Comparison of the catalytic performances with those of reported systems: (d) specific activity vs. expected catalyst life, (e) C₃H₈ conversion vs. C₃H₆ selectivity, and (f) C₃H₆ yield vs. CO₂ conversion. Numbers correspond to the entries in Tables 2.4 and 2.5. Dashed curves indicate the iso-yield curves of C₃H₆. **g, h** Long-term stability test with catalyst regeneration: C₃H₈:CO₂:He = 5:5:20 mL·min⁻¹. Time course of (g) C₃H₈ and (h) CO₂ conversions. Regeneration conditions: CO₂:He = 5:20 mL·min⁻¹ for 5 h, followed by H₂:He = 10:20 mL·min⁻¹ for 0.5 h at 550 °C.

2.3.2 Catalytic Reactions

Afterward, the Pt–Co–In/CeO₂ catalyst was tested for the CO₂-ODP at 550°C. Some Pt-based binary alloy catalysts (Pt–M/CeO₂ : M = Co, In, and Sn), of which the Pt dispersion is similar to that of Pt–Co–In/CeO₂ (Table 2.2), and monometallic Pt/CeO₂ were examined to understand the individual effect of each second metal. For all the catalysts, the products were CO, C₃H₆, C₂H₄, C₂H₆, CH₄, H₂O, and H₂. No other byproducts such as oxygenates were detected in the outlet gas (Figure 2.6a). Figures 2.7a–2.7c show the time course of C₃H₈ conversion, C₃H₆ selectivity in hydrocarbons (C_xH_y), and CO₂ conversion, respectively (see Figure 2.6b for details of equilibrium conversion). Although the Pt/CeO₂ and Pt–M/CeO₂ catalysts showed a high initial C₃H₈ conversion (52–68%), rapid deactivation occurred within 5–10 h. Pt–Sn, which is known to be selective and stable for DDP,^[28] was not effective for CO₂-ODP. In contrast, Pt–Co–In/CeO₂ retained a high C₃H₈ conversion (ca. 50%) for 20 h. Predictably, catalysts containing a typical metal (In or Sn) exhibited a high C₃H₆ selectivity (82–95%), attributed to the ensemble effect by alloying, where the highest selectivity was obtained with Pt–Co–In (95%). Pt and Pt–Co showed very low C₃H₆ selectivities (35 and 27%, respectively) at the beginning of the reaction, owing to undesired side reactions to generate C1 and C2 hydrocarbons (hydrogenolysis, Figure 2.8). Pt and Pt–Co catalysts also showed a significant deviation of material balance from unity (e.g., for Pt, C_xH_y: 0.71 and CO_x: 1.31, Figure 2.9), which suggests that dry reforming of C₃H₈ to CO also occurred to a large extent. Conversely, the carbon balances in C_xH_y and CO_x were close to unity for Pt–Co–In, indicating a minor contribution of dry reforming on the ternary alloy catalyst (Figure 2.10). The net C₃H₆ selectivity and yield, which consider CO from C₃H₈ as a byproduct, were still high (86–97%, Figure 2.11 and 47–44%, Figure 2.11, respectively). H₂ yield for Pt–Co–In was less than 5% (Figure 2.12), indicating that a large part of hydrogen derived from C₃H₈ was consumed by reverse water-gas shift reaction. This also suggests that the contribution of DDP versus CO₂-ODP to the overall C₃H₆ production, which is reflected roughly by the H₂ yield/C₃H₆ yield ratio,^[47] was considerably low (~10%). Considering that H₂ can also be formed by dry reforming to a small extent, the actual contribution of DDP should be much lower than 10%. For the CO₂ conversion stability (Figure 2.7c), a similar trend to that of C₃H₈ was observed: only Pt–Co–In showed good stability, while other mono- and bimetallic catalysts were

deactivated within 10 h. Interestingly, the initial conversion of CO₂ differed depending on the metal component in the following order: Pt–Co > Pt, Pt–Sn, Pt–Co–In >> Pt–In. This result implies that Co promotes CO₂ capture and activation as expected, and that alloying with In alone significantly reduces this ability. Therefore, alloying Pt with both Co and In may neutralize the negative effect of In, thereby promoting the CO₂ conversion, comparable to the level of monometallic Pt. Thereafter, monometallic Co/CeO₂ and In/CeO₂ catalysts were also tested for the CO₂-ODP as control experiments (Figure 2.13). Although Co/CeO₂ was active for both C₃H₈ and CO₂ conversions at the beginning of the reaction, it rapidly deactivated within only 0.5 h (C₃H₈: 48%→7%, CO₂: 54%→22%). After the deactivation, Co/CeO₂ retained the low CO₂ conversion (22%), which is probably due to the contribution of Co oxide species to CO₂ reduction^[48,49] (Co/SiO₂ was not fully reduced by reduction at 600°C; see H₂-TPR, Figure 2.14). In/CeO₂ was almost inactive for both reactions. Therefore, the residual metallic Co and In oxide species in Pt–Co–In/CeO₂ are unlikely to contribute to the high catalytic performance. We performed further control experiments using physical mixtures of the binary and monometallic catalysts (Pt–Co/CeO₂+In/CeO₂, Pt–In/CeO₂+Co/CeO₂, and Co–In/CeO₂+Pt/CeO₂) and Pt–In+Co/CeO₂, where the Co cation was loaded on Pt–In/CeO₂. Their catalytic activities and stabilities were much lower than those of Pt–Co–In/CeO₂ (Figures 2.15–2.17), demonstrating that the ternary alloy structure with Co doped into Pt–In alloy is essential for a high catalytic performance. A temperature-programmed oxidation (TPO, Figure 2.18) and Raman analysis (Figure 2.19) of the spent catalysts after the 20 h catalytic run showed almost no coke accumulation on Pt–Co–In/CeO₂, unlike the case with other deactivated catalysts. The average coke selectivity was calculated at 10 h by dividing the mole of accumulated coke by the total mole of the converted C₃H₈ and carbon number of C₃H₈, which was lower than 0.1% (Table 2.3).

The obtained high catalytic performance of Pt–Co–In/CeO₂ was compared with a number of reported systems for the CO₂-ODP, considering the activity, selectivity, stability, and CO₂ utilization efficiency (Tables 2.4, 2.5, and Figure 2.20 for details with references). For a better comparison, the catalytic performance of Pt–Co–In/CeO₂ at 600°C (Figure 2.21) was also included. For alkane dehydrogenation, high catalytic activity is often achieved at the expense

of selectivity and stability via the triggering of undesired side reactions.^[50] Therefore, plotting stability or selectivity versus activity can be a good indication of the overall performance. More specifically, the mean catalyst life as a reciprocal deactivation constant ($\tau = k_d^{-1}$) versus specific activity ($\text{mL}_{\text{C}_3\text{H}_6} \cdot \text{min}^{-1} \cdot g_{\text{cat}}^{-1}$) and the conversion–selectivity relationship were considered (Figures 2.7d, e, respectively). The specific activity of our catalyst was approximately five times higher than the typical values ever reported. This outstanding high catalytic activity is attributed to the use of Pt as a main active metal for the selective CO₂-ODP. Moreover, the mean catalyst life of our catalyst at 550°C was also the highest among those ever reported. For the selectivity–conversion plot, we showed the two selectivity descriptions for better comparison with reported systems using each, i.e., that considering by-products other than C_xH_y such as CO (net C₃H₆ selectivity) or not (C₃H₆ selectivity in C_xH_y). Our catalyst exhibited the highest C₃H₆ selectivity (86% and 95% for open and filled circles, respectively) at a high C₃H₈ conversion region (> 50%), indicating its significant ability to suppress undesired side reactions. Figure 2.7f shows the plot of the CO₂ conversion versus the C₃H₆ yield, which reflects the CO₂ utilization efficiency. A high CO₂ conversion with C₃H₆ production in 1:1 stoichiometry (the upper-right direction in Figure 2.7f) is preferred for a high CO₂ utilization efficiency (see Equation 16 for the definition of CO₂ utilization efficiency). In this context, our catalyst exhibited the highest CO₂ conversion and C₃H₆ yield with near 1:1 stoichiometry among the typical systems ever reported, where the CO₂ utilization efficiency was 53% at 550 °C and 70% at 600 °C (Figure 2.20c). We also examined the reusability and long-term stability of Pt–Co–In/CeO₂ by applying a regeneration process. The regeneration of deactivated catalysts typically uses oxygen or air to combust deposited carbon. In this study, CO₂ was used instead as a soft oxidant for the Boudouard reaction and relatively easy handling. To switch the catalytic run to the regeneration process, only the supply of C₃H₈ was cut off to feed CO₂/He for 5 h, followed by H₂ reduction for 0.5 h at the same temperature. By this process, the CO₂ conversion was fully recovered, and it had no negative effect on the C₃H₈ conversion (Figures 2.7g and h, see Figure 2.22 for C₃H₆ selectivity). Although a slight decrease in C₃H₈ conversion was observed, the conversion reached a steady-state after 70 h and retained 33% conversion at 96 h. Thus, the Pt–Co–In/CeO₂ catalyst displayed multiple properties of outstanding catalytic

activity, excellent C_3H_6 selectivity, high CO_2 utilization efficiency, long-term stability, and reusability.

In Figure 2.7g, C_3H_8 conversion was not fully recovered under the regeneration condition, indicating that coke on the active site for C_3H_8 dehydrogenation is relatively not easy to be removed compared with that of CO_2 activation. We also performed a control experiment with a DDP- CO_2 cycle test on Pt-Co-In/ CeO_2 , where the gas feed was switched from C_3H_8 /He (2 h) to CO_2 /He (0.5 h). Although the C_3H_8 conversion decreased to near zero within 2 h in the absence of CO_2 , it was recovered by the CO_2 treatment (Figure 2.23). Thus, the Pt-Co-In/ CeO_2 catalyst is highly capable of coke combustion by CO_2 , which enables continuous coke removal and long-term stability in CO_2 -ODP.

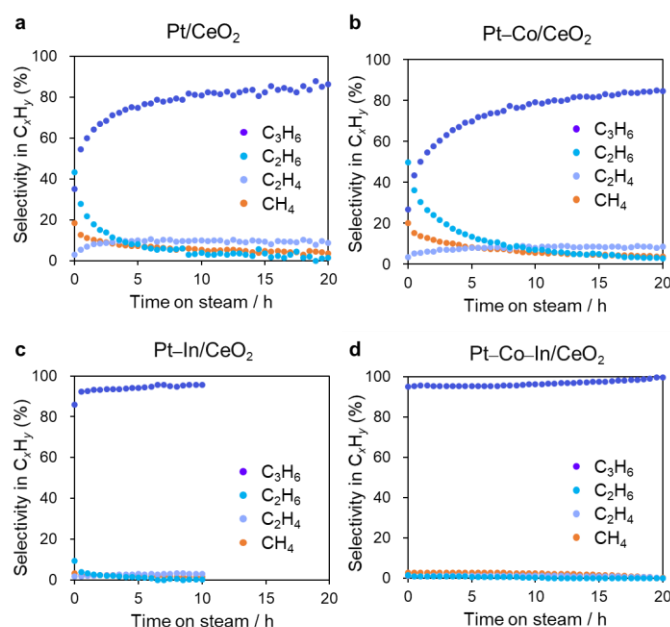


Figure 2.8. Selectivity in C_xH_y in CO_2 -ODP on Pt-based catalysts. **a.** Pt/ CeO_2 **b.** Pt-Co/ CeO_2 **c.** Pt-In/ CeO_2 **d.** Pt-Co-In/ CeO_2 . Reaction condition: catalyst; 100 mg, gas feed; $C_3H_8:CO_2:He = 5:5:10$ mLmin $^{-1}$; temperature; 550 °C.

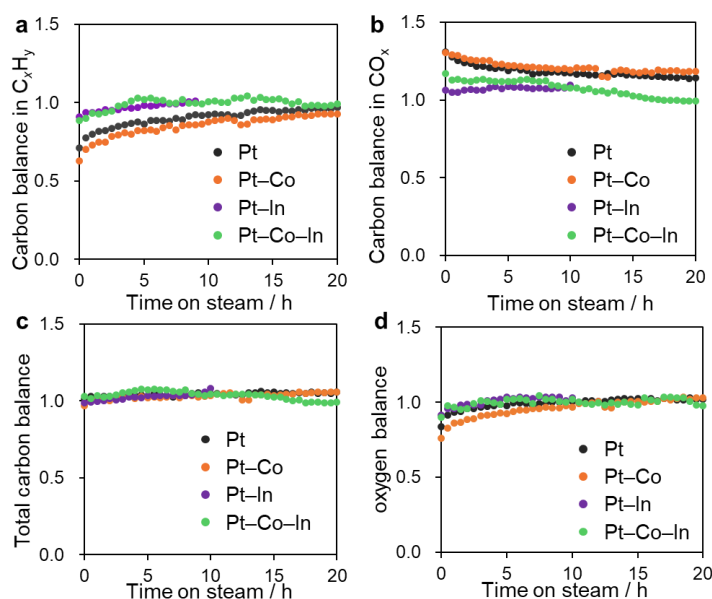


Figure 2.9. Material balance for CO₂-ODP over Pt-based catalysts at 550°C. **a** Carbon balance in C_xH_y, **b** carbon balance in CO_x, **c** total carbon balance, and **d** oxygen balance. The deviations from unity in **a** and **b** reflect the occurrence of dry reforming. The decrease in oxygen balance in **d** at the beginning of reaction is attributed to the filling of oxygen vacancy of CeO₂ because the catalyst was reduced before the reaction.

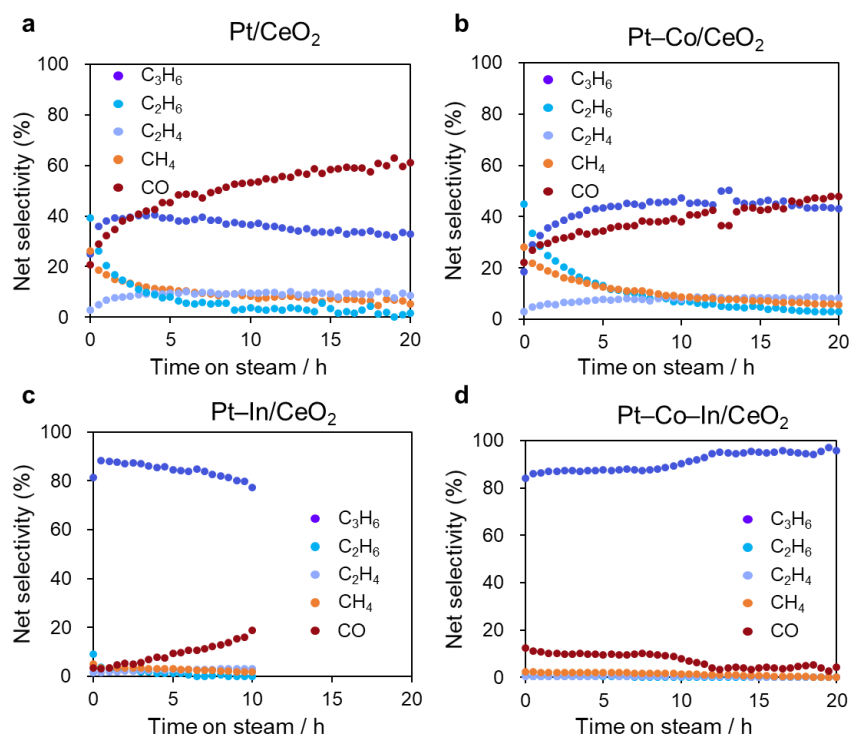


Figure 2.10. Product distribution including CO in CO₂-ODP on Pt-based catalysts. **a.** Pt/CeO₂ **b.** Pt-Co/CeO₂ **c.** Pt-In/CeO₂ **d.** Pt-Co-In/CeO₂. Reaction condition: catalyst; 100 mg, gas feed; C₃H₈:CO₂:He = 5:5:10 mLmin⁻¹; temperature; 550 °C.

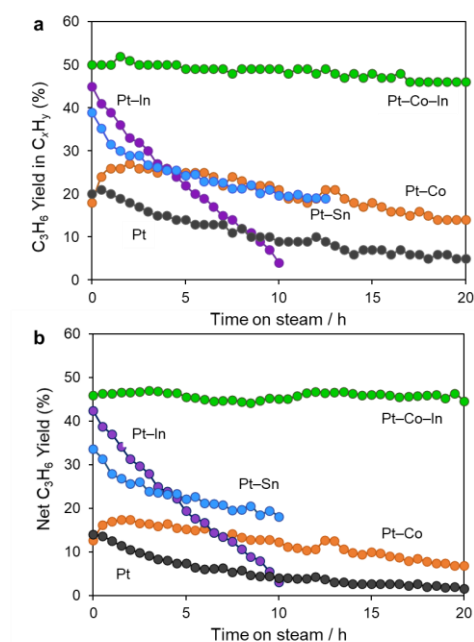


Figure 2.11. Time course of C_3H_6 yield in CO_2 -ODP on Pt-based catalysts. **a** C_3H_6 yield in C_xH_y . **b** net C_3H_6 yield considering CO formed from C_xH_y .

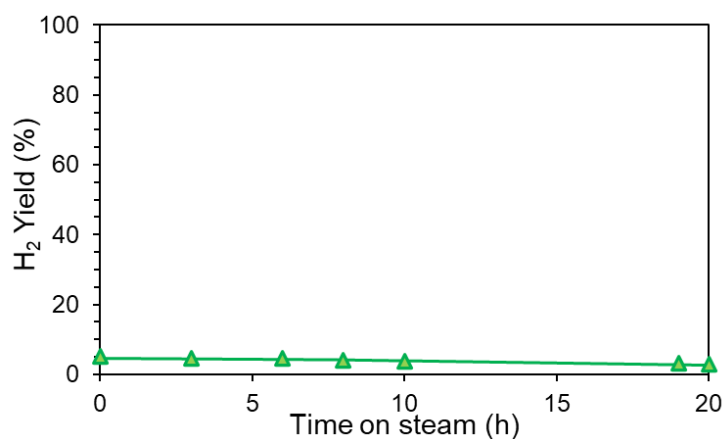


Figure 2.12. H_2 yield in CO_2 -ODP on Pt-Co-In/CeO₂ at 550°C. The definition of H_2 yield is shown in eq (9) in experimental section.

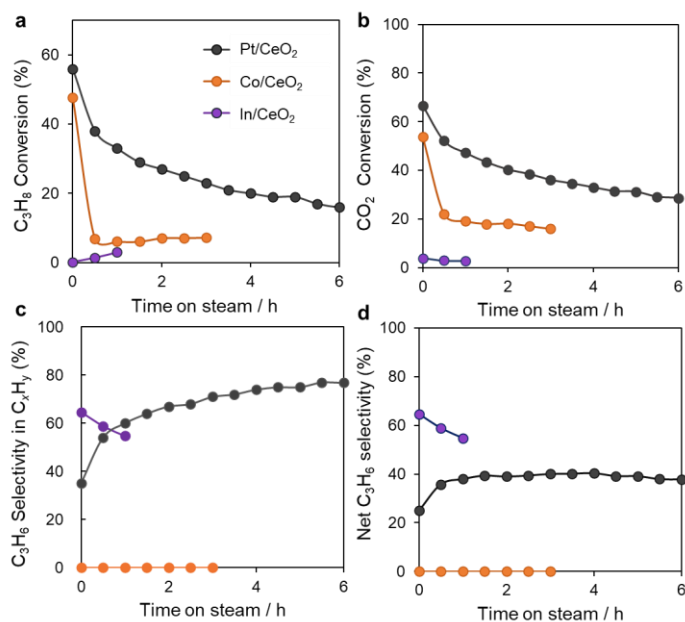


Figure 2.13. Catalytic performance of monometallic Pt/CeO₂, Co/CeO₂, and In/CeO₂ in CO₂-ODP. **a** C₃H₈ conversion, **b** CO₂ conversion, **c** C₃H₆ selectivity in C_xH_y, and **d**.net C₃H₆ selectivity considering CO formed from C_xH_y.

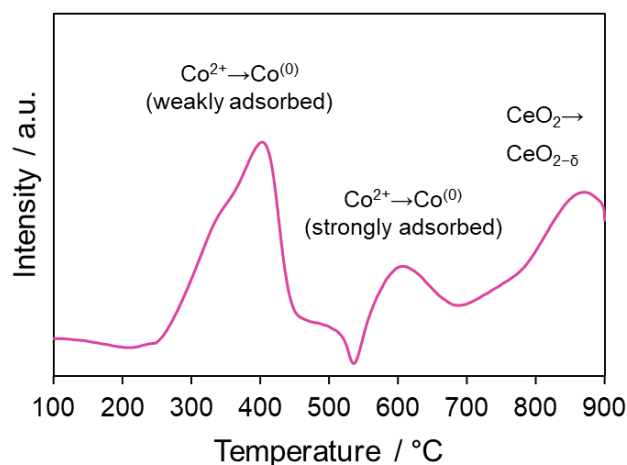


Figure 2.14. H₂-TPR profile of unreduced Co/CeO₂. The reduction peaks appeared at 400 °C and 600 °C are assignable to the reduction of Co²⁺ species that interact weakly and strongly with CeO₂ to metallic Co, respectively,^[49] while that starting from 700 °C can be attributed to the partial reduction of CeO₂ as shown in Figure 2.24e. Thus, the Co/CeO₂ catalyst used in this study (reduced at 600 °C) is not fully reduced and some CoO_x species should remain on CeO₂ surface. CoO_x is also known to be active for CO₂ reduction,^{[51],[48]} while not active for C–H activation. Therefore, it is likely that metallic Co in Co/CeO₂ is immediately deactivated by coke via C–H(C) scission on it, whereas CoO_x has longer life for CO₂ reduction because coke is not directly formed there.

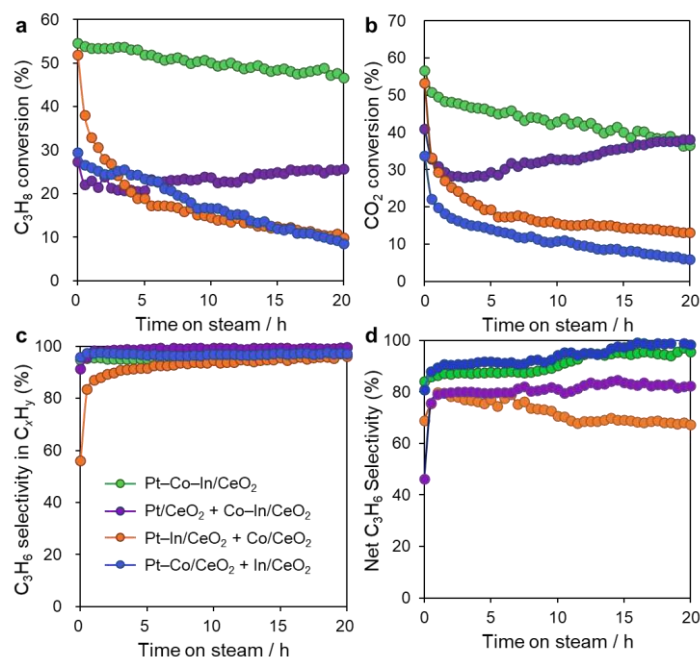


Figure 2.15. Catalytic performance of physical mixtures of Pt/CeO₂ + Co-In/CeO₂, Pt-In/CeO₂ + Co/CeO₂, and Pt-Co/CeO₂ + In/CeO₂ compared with that of Pt-Co+In/CeO₂ and Pt-Co-In/CeO₂ in CO₂-ODP. **a** C₃H₈ conversion, **b**, CO₂ conversion **c**, C₃H₆ selectivity in C_xH_y, and **d** net C₃H₆ selectivity.

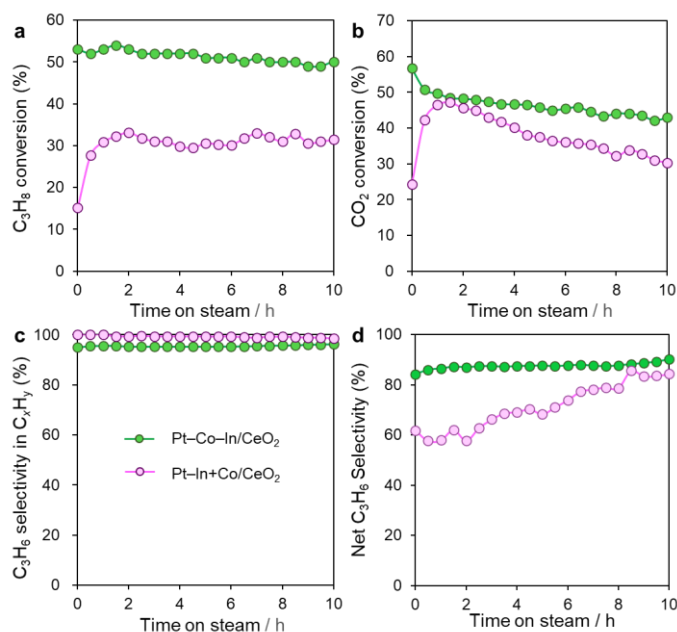


Figure 2.16. Catalytic performance of Pt-In+Co/CeO₂ compared with that of Pt-Co-In/CeO₂ in CO₂-ODP. **a** C₃H₈ conversion, **b**, CO₂ conversion **c**, C₃H₆ selectivity in C_xH_y, and **d** net C₃H₆ selectivity.

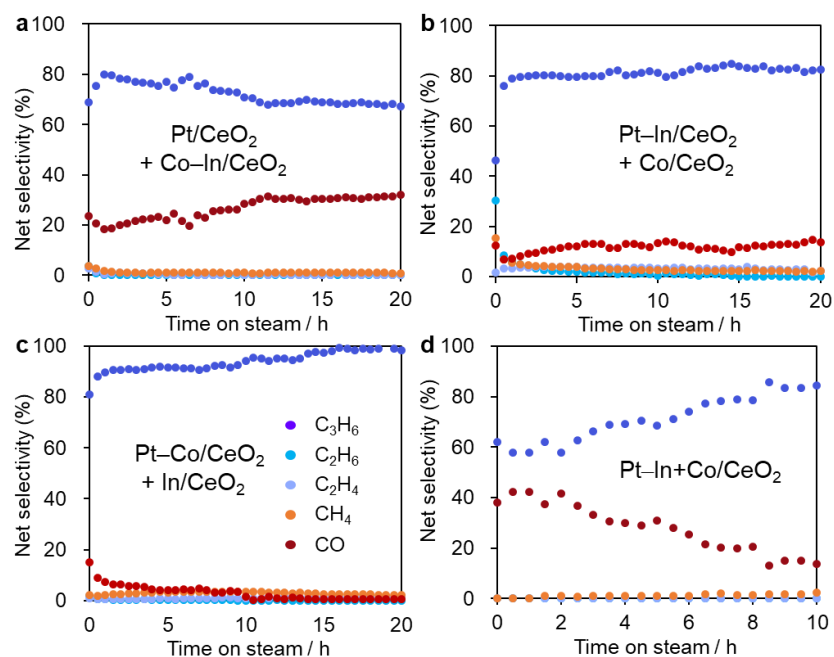


Figure 2.17. Product distribution in CO_2 -ODP using $\text{Pt/CeO}_2 + \text{Co-In/CeO}_2$, $\text{Pt-In/CeO}_2 + \text{Co/CeO}_2$, $\text{Pt-Co/CeO}_2 + \text{In/CeO}_2$, and Pt-Co+In/CeO_2 .

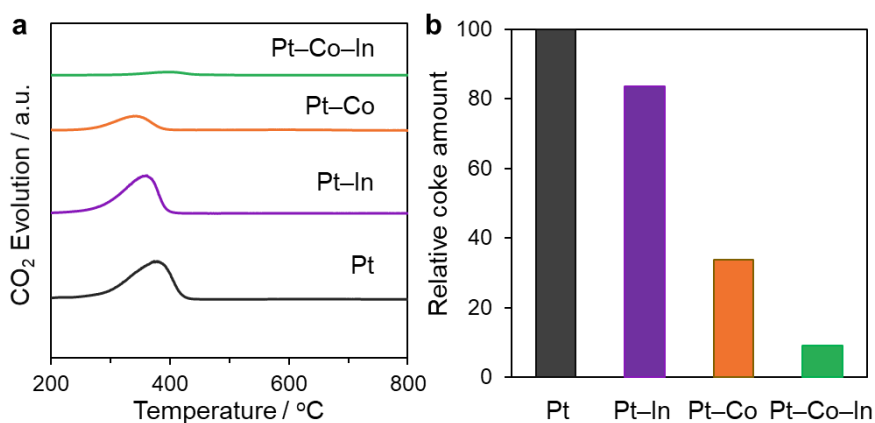


Figure 2.18. a O_2 -TPO profiles of the spent catalysts after 20h of CO_2 -ODP at 550°C . **b** Relative coke amount accumulated on the catalysts estimated from **a**.

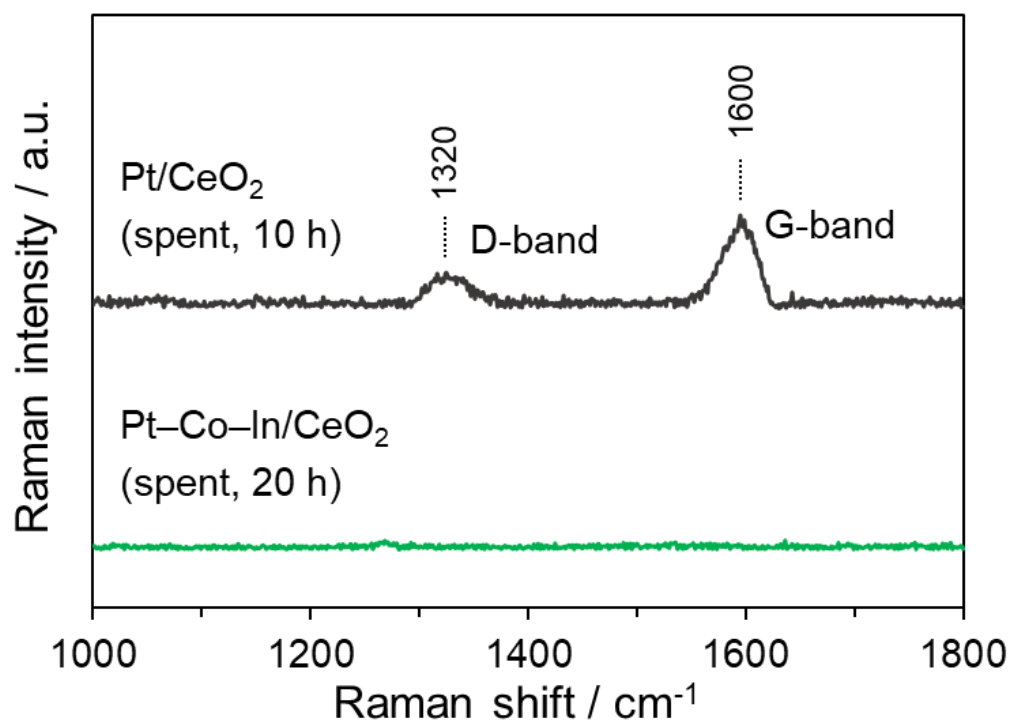


Figure 2.19. Raman spectra of the spent Pt/CeO₂ (10 h) and Pt–Co–In/CeO₂ (20 h). The D and G bands characteristic of graphitic carbon were observed for the spent Pt/CeO₂ (10 h), which demonstrated the accumulation of graphitic coke on the non-selective Pt/CeO₂ catalyst. No band was observed for the spent Pt–Co–In/CeO₂ (20 h), which is consistent with that almost no combustion peak was observed in O₂-TPD.

Table 2.3. Information about coke on the spent catalyst. ^a

catalyst	coke wt% ^b	aver. coke sel. (%) ^c	coke TON ^d
Pt/CeO ₂	2.6	0.068	55
Pt–In/CeO ₂	2.2	0.032	43
Pt–Co/CeO ₂	0.9	0.020	18
Pt–Co–In/CeO ₂	0.3	0.003	5

^a The catalysts after 10 h of catalytic run were used. ^b Gram coke per gram catalyst ×100. ^c Mole of accumulated coke / total mole of converted C₃H₈ × 3. See Supplementary eq. (18) for details. Since the coke selectivity was too low to change the net C₃H₆ selectivity, we ignored coke in the calculation of C₃H₆ selectivity. ^d See Supplementary eq. (19) for details.

Table 2.4. Summary of the catalytic performance of Pt–Co–In/CeO₂ and other reported catalysts for CO₂-ODP.

No	catalyst	Temp. (°C)	Gas feed C ₃ H ₈ :CO ₂ :He	C ₃ H ₈ conc. (%)	C ₃ H ₈ conv. (%)	C ₃ H ₆ sel. (%) (initial-final)	<i>k_d</i> (h ⁻¹)	<i>τ</i> (h)	Ref.
1	Ga ₈ Al ₂ O ₁₅	500	2.5: 5:92.5	2.5	49.7-33.1	91.7-98 ^a	0.089	11.2	[52]
2	Ru ₁ Cr ₁₀ O _x /SiO ₂	500	1:1:1	33.3	9-6.5	85-90 ^b	0.053	18.8	[53]
3	Pd/CeZrAlO _x	500	26:37:37	26	16-2	80-98 ^a	0.016	62.6	[54]
4	Pt–Co–In/CeO ₂	550	1:1:2	25	52-47	95-99 ^a	0.010	99.5	This work
5	7%Cr/SBA-1	550	1:5:9	6.7	37.7-16	85-91 ^a	0.347	2.9	[55]
6	Cr-O/SiO ₂	550	1:5	16.7	17.2	94.4 ^a	-	-	[56]
7	Cr ₂ O ₃ –ZrO ₂ 180	550	2.5:5:92.5	2.5	53.3-27.8	79-90.8 ^b	0.186	5.4	[57]
8	Ga ₂ O ₃ –M	550	1:5:9	6.7	19-11	91.6-95 ^a	0.167	6.0	[58]
9	7V5Mo	550	1:3:4	12.5	10.1	96 ^a	-	-	[59]
10	7V7W	550	1:3:4	12.5	9.9	97 ^a	-	-	[59]
11	7V4Cr	550	1:3:4	12.5	10.0	95 ^a	-	-	[59]
12	7Cr/ZrO ₂	550	1:2:37	2.5	68-38	59-75 ^c	0.226	4.4	[60]
13	Cr2.0SiBeta	550	1:5:9	6.7	24.8-11	87.1-90 ^b	0.123	8.2	[61]
14	FeCeO ₂	550	5:5:90	5	17.5-14	48-53 ^b	0.013	75.2	[62]
15	Fe ₃ Ni/CeO ₂	550	1:1:2	25	4.8-3.4	30-58.2 ^c	0.036	27.5	[7]
16	12% In/HZSM-5	580	1:4:5	10	25.2-17.6	75-70 ^c	0.101	9.9	[63]
17	Pt–Co–In/CeO ₂	600	1:1:2	25	61.3-44	98.3-93.9 ^a	0.020	51.1	This work
18	Ga ₂ O ₃ /HZSM-48	600	2.5:5:92.5	2.5	52.6-48.2	42.2-45.6 ^a	0.020	51.1	[64]
19	ZnO/HZSM-5	600	2.5:5:92.5	2.5	68.3-41.5	46.8-62.1 ^a	0.038	26.1	[65]
20	Cr-MSU-28	600	1:1:8	10	44-36.8	86-90.4 ^a	0.163	6.1	[18]
21	2%Cr/SiO ₂	600	15:30:55	15	80-53	50-90.6 ^a	0.063	15.8	[66]
22	2%Cr ₂ O ₃ /SiO ₂	600	15:30:55	15	71-50	66-90 ^b	0.054	18.7	[14]
23	20%Ga/ZrO ₂	600	2.5:5:92.5	2.5	38.6-6	45.4-77 ^a	0.807	1.2	[67]
24	Ga ₂ O ₃ /TiO ₂	600	2.5:5:92.5	2.5	32-2.5	73 ^b	1.027	1.0	[15]
25	Ga ₂ O ₃ /Al ₂ O ₃	600	2.5:5:92.5	2.5	26-17	94 ^b	0.190	5.2	[15]
26	Ga ₂ O ₃ /ZrO ₂	600	2.5:5:92.5	2.5	30-7	65 ^b	0.614	1.6	[15]
27	Ga ₂ O ₃ /SiO ₂	600	2.5:5:92.5	2.5	6.4-6	92 ^b	0.024	41.2	[15]
28	Ga ₂ O ₃ /MgO	600	2.5:5:92.5	2.5	4.3-2.5	29 ^b	0.198	5.1	[15]
29	10%In ₂ O ₃ /Al ₂ O ₃	600	2.5:10:87.5	2.5	24-20	29-84 ^a	0.030	33.5	[16]
30	In-Al-20	600	2.5:10:87.5	2.5	35-29	20-78 ^b	0.023	42.8	[68]
31	5.2V-MSNS	600	1:4:4	11.1	58-19	84-89 ^b	0.074	13.4	[69]
32	Cr/MSS-2	600	2:8:8	11.1	69-33	79-90 ^b	0.394	2.5	[70]
33	0.5 Ni-Cr/Si	600	1:1:8	10	90-19	0-90 ^a	0.308	3.2	[71]

^a C₃H₆ selectivity in C_xH_y (eq 5). ^b Net C₃H₆ selectivity ($F_{C_3H_6}^{out}/(F_{C_3H_8}^{in} - F_{C_3H_8}^{out}) \times 100$). ^c Net C₃H₆ selectivity (eq 6)

Table 2.5. Summary of the catalytic performance of Pt–Co–In/CeO₂ and other reported catalysts for CO₂-ODP

No	catalyst	Temp. (°C)	CO ₂ conv. (%)	W/F g min mL ⁻¹	CO ₂ util. eff. ^a	TOS (h)	F _(C₃H₆) /W _{cat} (initial)	F _(C₃H₆) /W _{cat} (final)	F _(CO₂) /W _{cat} (initial)	F _(CO₂) /W _{cat} (final)	Ref.
1	Ga ₈ Al ₂ O ₁₅	500	-	0.02	0	8	0.57	0.41	-	-	[52]
2	Ru ₁ Cr ₁₀ O _x /SiO ₂	500	12-9	0.005	9	7.3	5.10	3.90	8.00	0.72	[53]
3	Pd/CeZrAlO _x	500	-	0.0133	0	140	2.50	0.38	-	-	[54]
4	Pt–Co–In/CeO ₂	550	57-37	0.005	53	20	24.70	23.27	28.50	10.55	This work
5	7%Cr/SBA-1	550	6.7	0.007	2	3.5	3.05	1.39	3.19	-	[55]
6	Cr-O/SiO ₂	550	-	0.0167	0	0.2	1.62	0.00	-	-	[56]
7	Cr ₂ O ₃ –ZrO ₂ 180	550	-	0.01	0	6	1.05	0.63	-	-	[57]
8	Ga ₂ O ₃ –M	550	2.4	0.0067	1	4	1.73	1.04	1.19	-	[58]
9	7V5Mo	550	3.34	0.0125	2	2	0.97	0.00	1.00	-	[59]
10	7V7W	550	3.4	0.0125	2	2	0.96	0.00	1.02	-	[59]
11	7V4Cr	550	5.03	0.0125	3	2	0.95	0.00	1.51	-	[59]
12	7Cr/ZrO ₂	550	37-23	0.01	36	6	1.00	0.71	1.85	0.43	[60]
13	Cr ₂ O ₃ /SiBeta	550	4	0.0067	1	8	2.15	0.99	1.99	-	[61]
14	FeCeO ₂	550	-	0.0067	0	20	3.13	2.77	-	-	[62]
15	Fe ₃ Ni/CeO ₂	550	12-5.7	0.005	3	10	0.72	0.99	6.00	0.34	[7]
16	12% In/HZSM-5	580	0.6-3	-	0	5.5	-	-	-	-	[63]
17	Pt–Co–In/CeO ₂	600	83.2-57	0.005	70	36	30.12	25.36	41.58	23.70	This work
18	Ga ₂ O ₃ /HZSM-48	600	-	0.01	0	10	0.55	0.55	-	-	[64]
19	ZnO/HZSM-5	600	-	0.01	0	30	0.80	0.64	-	-	[65]
20	Cr-MSU-28	600	-	0.0067	0	2	5.65	4.97	-	-	[18]
21	2%Cr/SiO ₂	600	-	3.33	0	20	0.02	0.02	-	-	[66]
22	2%Cr ₂ O ₃ /SiO ₂	600	19	3.33	11	16.7	0.02	0.02	0.02	-	[14]
23	20%Ga/ZrO ₂	600	-	0.01	0	3	0.44	0.12	-	-	[67]
24	Ga ₂ O ₃ /TiO ₂	600	30	0.01	26	3	0.58	0.00	1.50	-	[15]
25	Ga ₂ O ₃ /Al ₂ O ₃	600	5.2	0.01	2	3	0.61	0.00	0.26	-	[15]
26	Ga ₂ O ₃ /ZrO ₂	600	29	0.01	23	3	0.49	0.00	1.45	-	[15]
27	Ga ₂ O ₃ /SiO ₂	600	3.1	0.01	2	3	0.15	0.00	0.16	-	[15]
28	Ga ₂ O ₃ /MgO	600	4.2	0.01	2	3	0.03	0.00	0.21	-	[15]
29	10%In ₂ O ₃ /Al ₂ O ₃	600	12-10	0.02	9	8	0.09	0.21	0.60	0.06	[16]
30	In-Al-20	600	10-8	0.02	8	12	0.09	0.28	0.50	0.04	[68]
31	5.2V-MSNS	600	10	0.0133	3	24	4.07	1.41	3.34	-	[69]
32	Cr/MSS-2	600	15-5	0.011	6	4	5.51	3.00	6.06	0.30	[70]
33	0.5 Ni-Cr/Si	600	55-15	0.0067	0	12	0.00	2.55	8.21	1.23	[71]

^a CO₂ utilization efficiency.

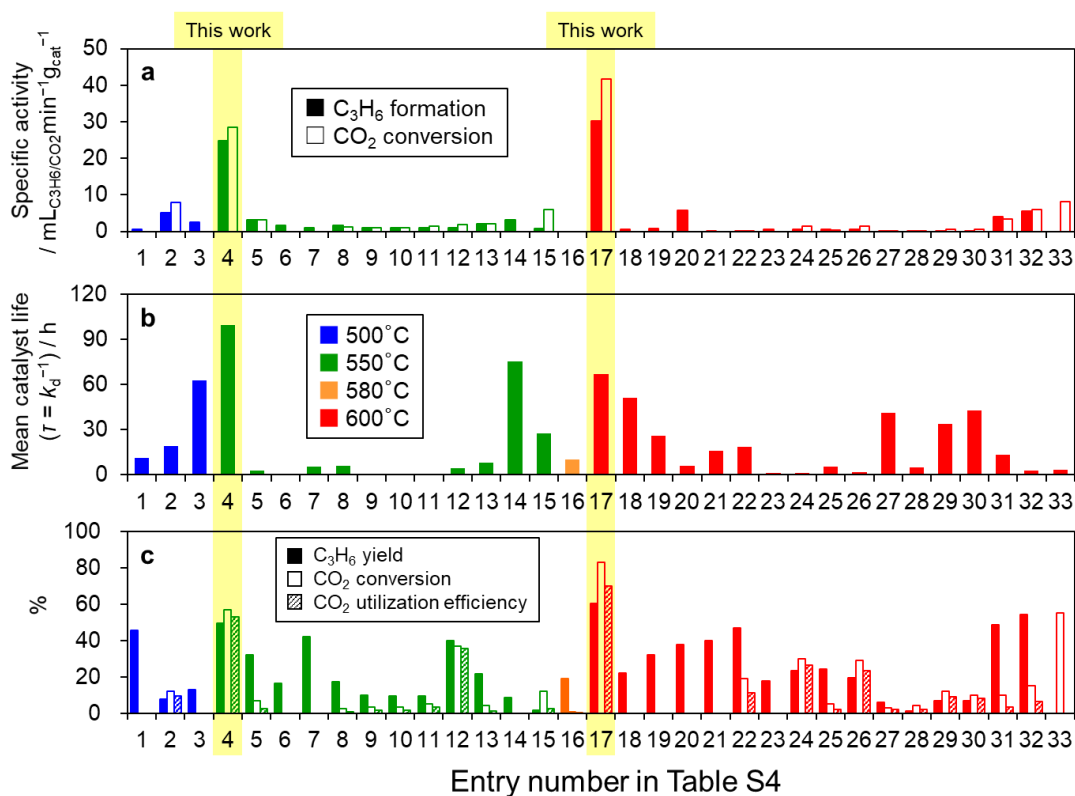


Figure 2.20. Catalytic performance of Pt–Co–In/CeO₂ and reported systems for CO₂-ODP. **a** Specific activity ($\text{mL}_{\text{C}_3\text{H}_6}/\text{CO}_2 \cdot \text{min}^{-1} \cdot g_{\text{cat}}^{-1}$) for C₃H₆ formation and CO₂ conversion. **b** Mean catalyst life ($\tau = k_d^{-1}$). **c**. C₃H₆ yield, CO₂ conversion, and CO₂ utilization efficiency.

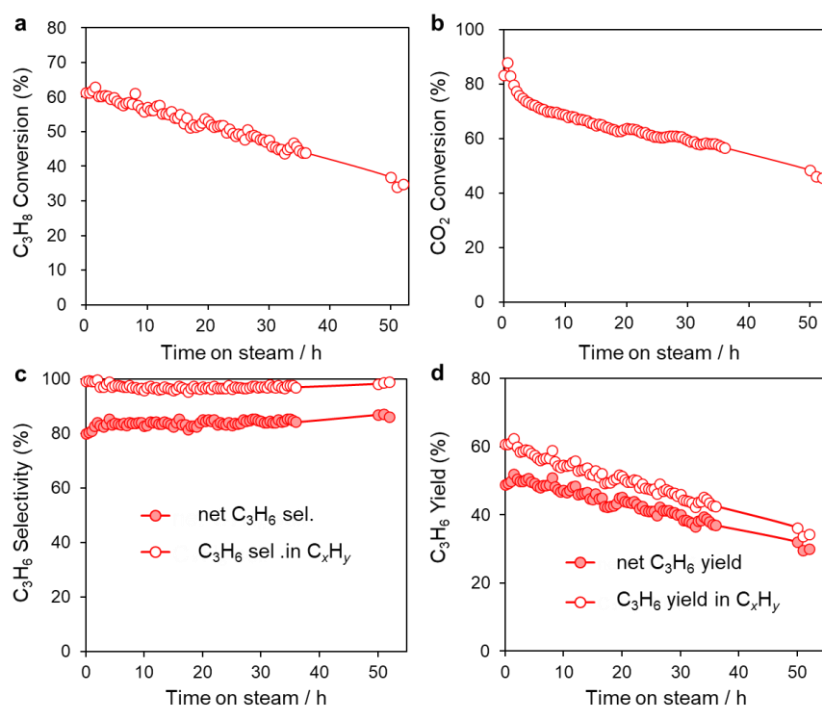


Figure 2.21. Catalytic performance of Pt–Co–In/CeO₂ in CO₂-ODP at 600°C. **a** C₃H₈ conversion, **b** CO₂ conversion, **c** C₃H₆ selectivity, and **d** C₃H₆ yield.

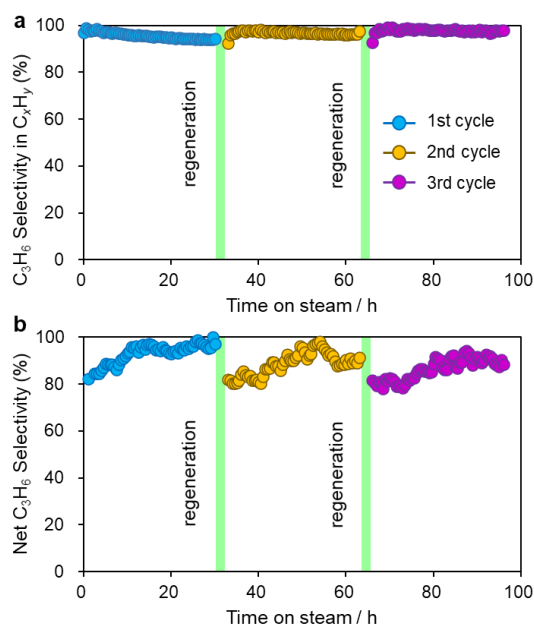
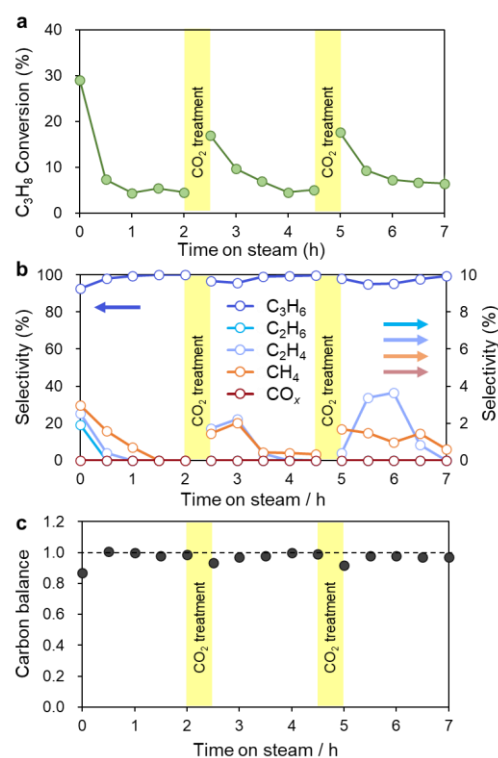


Figure 2.22. Time course of C_3H_6 selectivity in CO_2 -ODP over Pt-Co-In/ CeO_2 with catalyst



regeneration. **a** C_3H_6 selectivity in C_xH_y , **b** net C_3H_6 selectivity.

Figure 2.23. (a) Catalytic performance of Pt-Co-In/ CeO_2 in DDP at 550 °C (C_3H_8 :He = 5:10 mL/min) and the effect of CO_2 treatment (CO_2 :He = 5:10 mL/min, 550 °C, 0.5 h) as regeneration process. The corresponding (b) product distribution and (c) carbon balance. The carbon balance deviated from unity at the beginning of DDP, indicating that a large amount of

coke was formed and left on the catalyst surface. This is consistent with the rapid deactivation at the initial stage.

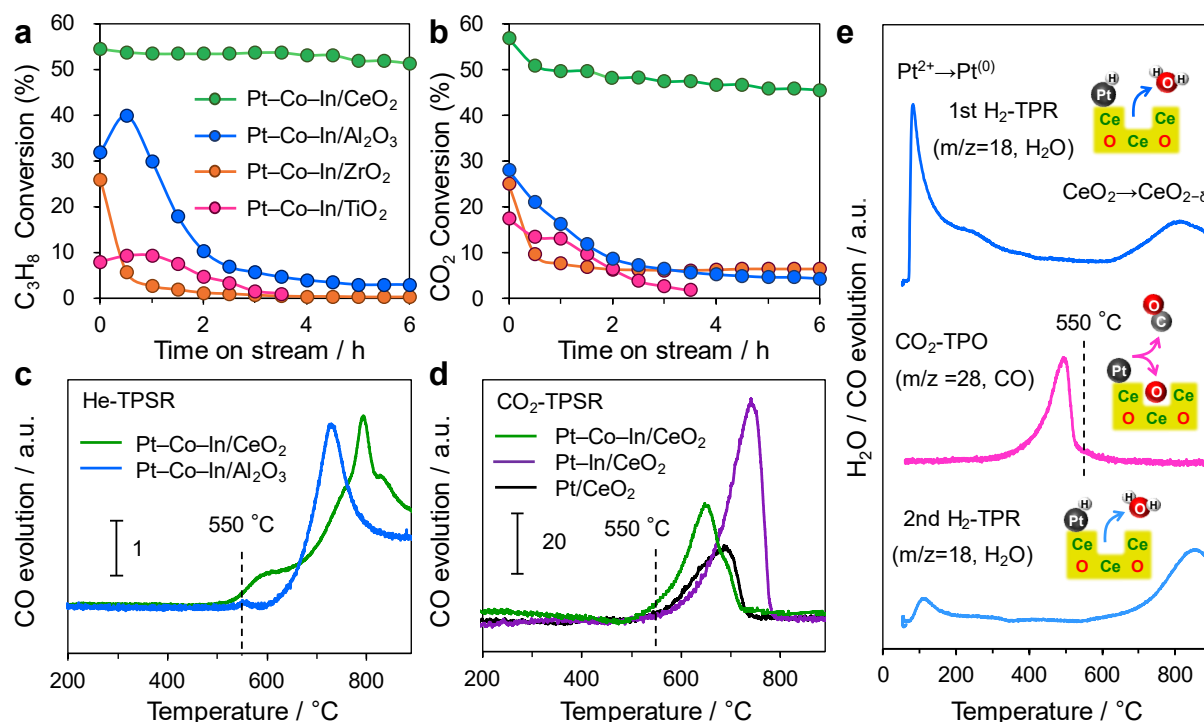


Figure 2.24: Effect of the catalyst support and TPSR on the coked catalysts. **a, b** (a) C_3H_8 and (b) CO_2 conversions in CO_2 -ODP on the Pt–Co–In catalysts using various supports. **c** He-TPSR on the coked Pt–Co–In/ CeO_2 (used in DDP for 2 h) and Pt–Co–In/ Al_2O_3 (used in CO_2 -ODP for 2 h) catalysts. **d** CO_2 -TPSR on the coked Pt/ CeO_2 , Pt–In/ CeO_2 (used in CO_2 -ODP for 2 h), and Pt–Co–In/ CeO_2 (used in DDP for 2 h) catalysts. CO evolution was quantified by the mass intensity of $m/z = 28$. **e** CO_2 -titration (TPO) experiment for the oxygen vacancy of CeO_2 using Pt/ CeO_2 .

2.3.3 Mechanistic study

Next, we performed a mechanistic study to profoundly understand the functions of Co, In, and CeO_2 in the catalysis. First, a kinetic analysis was conducted to understand the rate-determining step (RDS) of the CO_2 -ODP on Pt–Co–In/ CeO_2 . The following reaction rate equation was considered for the CO_2 -ODP: $r_x = kP_{C_3H_8}^\alpha P_{CO_2}^\beta$, where r_x is the consumption rate of x ($x = C_3H_8$ or CO_2), and $P_{C_3H_8}$ and P_{CO_2} are the pressures of C_3H_8 and CO_2 , respectively. The experimental reaction orders were positive and could be higher than unity for $P_{C_3H_8}$, while they were negative for P_{CO_2} (Table 2.6, see Figure 2.25 for details). Here, we considered a

Langmuir–Hinshelwood mechanism involving the two-step dehydrogenation of C_3H_8 to C_3H_6 , CO_2 reduction to CO, and oxidation of the eliminated hydrogen to form water (Table 2.6). We solved the rate equation of each step by applying quasi-stationary approximation and site conservation condition (see Supplementary Note 1 for details). The ranges of predicted reaction orders were fully consistent with the experimental orders only when the CO_2 activation to form CO and O was regarded as the RDS (step 6 in Table 2.6). Besides, we conducted microkinetic modeling based on the transition state theory and steady-state approximation to estimate the forward and reverse reaction rates for each step (Supplementary Note 1 and Table 2.7). For this modeling, some parameters calculated using density functional theory (DFT), such as activation energy (to be described later) and vibrational frequency, were used. As shown in Table 2.6 (calculated reaction rate), step 6 showed the lowest rate. These results showed that the RDS of CO_2 -ODP on Pt–Co–In/CeO₂ was the CO_2 activation. Subsequently, the apparent activation energy (E_A^*) was estimated for Pt–In/CeO₂ and Pt–Co–In/CeO₂ by Arrhenius-type plots. The E_A of CO_2 activation was significantly reduced by the incorporation of Co to Pt–In (168.8→138.3 kJ·mol⁻¹, Table 2.6 and Figure 2.26), which is consistent with the experimental trend of the CO_2 conversion and turnover frequency (TOF), as shown in Figure 2.7c and Figure 2.27, respectively. We also simulated the dependences of the reaction rate on $P_{C_3H_8}$ and temperature using the kinetic modeling, both of which agreed finely with the experimental trends (Figure 2.28; only slight deviations from the experimental values were observed, which may be due to errors in the DFT calculation). This result strongly supports the validity of our kinetic model. Thus, the kinetic analysis revealed that alloying with Co kinetically promoted the CO_2 activation, which is the RDS of the CO_2 -ODP. Compared with reported systems, Pt–Co–In/CeO₂ showed comparable E_A^* : for C_3H_8 dehydrogenation (WO_x–VO_x/SiO₂: 127–145 kJ·mol⁻¹, Fe₃Ni/CeO₂: 115 kJ·mol⁻¹), for CO_2 activation (Fe₃Ni/CeO₂: 135 kJ·mol⁻¹).

We subsequently examined a series of Pt–Co–In catalysts using various supports, such as Al₂O₃, TiO₂, and ZrO₂, so that the role of the CeO₂ support was clarified. Although these catalysts showed moderate initial conversions of C_3H_8 and CO_2 , rapid deactivation occurred within 1–2 h (Figures 2.24a, b). This result strongly indicates that the role of CeO₂ is to significantly enhance the catalyst stability; this is probably attributed to its coke combustion

ability, as mentioned above. To confirm this ability, temperature-programmed surface reactions (TPSRs) were conducted using the coked catalysts under He and CO₂ flows. The coked Pt–Co–In/CeO₂ evolved CO from 500 °C even in the absence of CO₂ (He-TPSR, [Figure 2.24c](#)), whereas the coked Pt–Co–In/Al₂O₃ showed almost no CO evolution up to 600 °C.

The CO evolution from the coked Pt–Co–In/CeO₂ between 500 and 600 °C can be attributed to the coke combustion by the lattice oxygen of CeO₂. Thus, CeO₂ can remove coke at the reaction temperature of CO₂-ODP (550 °C), while Al₂O₃ cannot, which agrees with the stability trend in CO₂-ODP. Interestingly, intense CO evolution was observed from 600 °C for both catalysts, which might be due to the coke combustion by the oxygen atoms of the surface hydroxyl groups. When the TPSR experiment for the coked Pt–Co–In/CeO₂ was performed in the presence of CO₂ (CO₂-TPSR, [Figure 2.24d](#)), a considerably large amount of CO (see the scale bars) was evolved from 500 °C, and the coke was completely combusted at 700 °C. This is clearly due to the continuous oxygen supply from CO₂. The corresponding TPSR for the coked Pt/CeO₂ and Pt–In/CeO₂ showed similar CO evolutions at high temperatures (peak temperature: Pt–Co–In < Pt < Pt–In), although a low evolution was observed at 550 °C. These results are roughly consistent with the deactivation trend (Pt–Co–In < Pt, Pt–In, [Figure 2.7a](#)) and the CO₂ reducing ability (Pt–Co–In, Pt > Pt–In, [Figure 2.7c](#)), which reflects the coke combustion abilities of these catalysts. Based on these results, we concluded that the coke combustion ability depended on the CO₂ reducing ability of the metal nanoparticles, as well as the oxygen-releasing ability of CeO₂. The concert of the ternary alloy and the specific character of the CeO₂ support enabled the continuous self-regeneration function and the remarkably high coke resistance. Furthermore, we verified the filling of oxygen vacancy after the lattice oxygen consumption of CeO₂ using a CO₂-titration (TPO) technique and Pt/CeO₂. As shown in [Figure 2.24e](#), oxygen vacancies of CeO₂ were obtained by H₂-TPR, followed by cooling and subsequent CO₂-TPO. CO evolution was completed by 550 °C, indicating that CO₂ was divided into CO and O. The oxygen atoms were left on the catalyst. H₂-TPR was repeated after CO₂-TPO and cooling, where the reduction peak of CeO₂ appeared again ([Figure 2.24e](#)). These results strongly support that the oxygen atoms derived from CO₂ refill the oxygen vacancies of CeO₂.

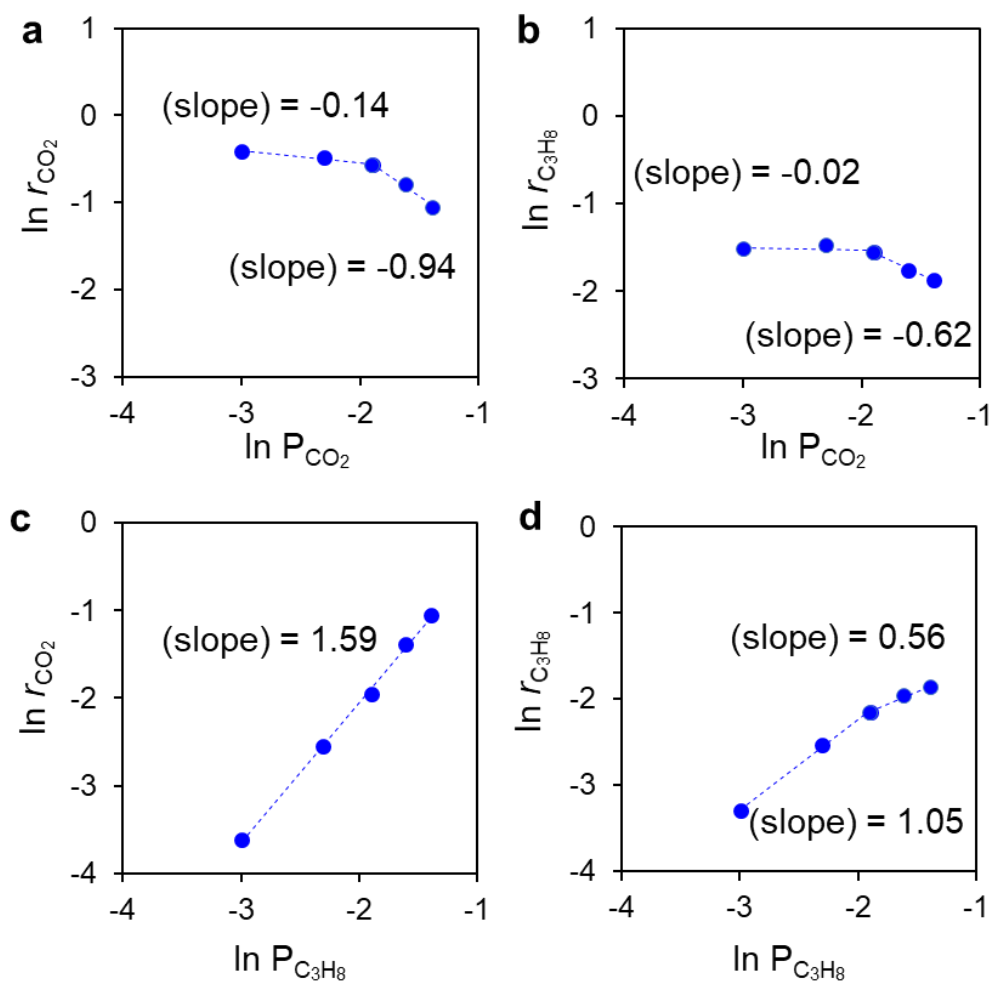


Figure 2.25. Dependence of $\text{C}_3\text{H}_8/\text{CO}_2$ partial pressure ($P_{\text{C}_3\text{H}_8/\text{CO}_2}$) on the reaction rate of $\text{C}_3\text{H}_8/\text{CO}_2$ conversion ($r_{\text{C}_3\text{H}_8/\text{CO}_2}$) in CO_2 -ODP over Pt–Co–In/CeO₂. **a** P_{CO_2} on r_{CO_2} , **b** P_{CO_2} on $r_{\text{C}_3\text{H}_8}$, **c** $P_{\text{C}_3\text{H}_8}$ on r_{CO_2} , and **d** $P_{\text{C}_3\text{H}_8}$ on $r_{\text{C}_3\text{H}_8}$.

Considering that CO_2 activation is the RDS, suppressing the reverse reaction ($\text{CO} + \text{O} \rightarrow \text{CO}_2$) is essential to increase the overall reaction rate. In this context, supplying two H atoms by C_3H_8 dehydrogenation promotes the consumption of O atoms, which suppresses the $\text{CO} + \text{O}$ reaction. The reaction order on $P_{\text{C}_3\text{H}_8}$ higher than unity indicates the O consumption significantly contributes to the overall reaction rate. When $P_{\text{C}_3\text{H}_8}$ increases, this dependency is alleviated to show the lower reaction order. The slightly to largely negative reaction orders on P_{CO_2} indicate that CO_2 adsorption weakly competes with C_3H_8 adsorption when P_{CO_2} is low, whereas strongly competes when P_{CO_2} is high.

Table 2.6. Summary of the kinetic study of CO₂-ODP.

$r_x = kP_{C_3H_8}^\alpha P_{CO_2}^\beta$			apparent activation energy (E_A^*)				
experimental reaction order ^a	α	β	E_A / kJ·mol ⁻¹	experiment		DFT calculation	
				Pt-In	Pt-Co-In	Pt ₂ In ₃	Pt ₂ In ₃ -Co
x = C ₃ H ₈	0.56 ~ 1.05	-0.62 ~ 0.00	C ₃ H ₈	144.4	122.8	140.1	117.5
x = CO ₂	1.59	-0.94 ~ -0.14	CO ₂	168.8	138.3	169.1	135.1
elementary steps in CO ₂ -ODP				possible reaction order ^b		calculated reaction rate ^c	
				α	β	$\vec{r}_i$ / s ⁻¹	$\vec{r}_i$ / s ⁻¹
(1) C ₃ H ₈ + $\sigma \rightleftharpoons$ C ₃ H ₈ · σ		C ₃ H ₈ physisorption	1	-1 ~ 1	3.87×10 ¹²	3.87×10 ¹²	
(2) C ₃ H ₈ · σ + $\sigma \rightleftharpoons$ C ₃ H ₇ · σ + H· σ		1st C-H activation	-1 ~ 1	-2 ~ 1	1.86×10 ⁻¹	1.86×10 ⁻¹	
(3) C ₃ H ₇ · σ + $\sigma \rightleftharpoons$ C ₃ H ₆ · σ + H· σ		2nd C-H activation	-1 ~ 1	-1.5~1.5	1.26×10 ⁻³	1.25×10 ⁻³	
(4) CO ₂ + $\sigma \rightleftharpoons$ CO ₂ · σ		CO ₂ physisorption	-1 ~ 1	1	3.87×10 ¹²	3.87×10 ¹²	
(5) CO ₂ · $\sigma \rightleftharpoons$ CO ₂ [*] · σ		CO ₂ chemisorption	-1 ~ 1	0 ~ 1	2.67×10 ²	2.67×10 ²	
(6) CO ₂ [*] · $\sigma \rightleftharpoons$ CO· σ + O· σ		CO ₂ activation	-2 ~ 2	-1 ~ 1	1.87×10⁻⁵	2.67×10⁻⁶	
(7) H· σ + O· $\sigma \rightleftharpoons$ OH· σ + σ		OH formation	-1.5~1.5	-1 ~ 1	3.46×10 ⁻⁴	3.30×10 ⁻⁴	
(8) OH· σ + O· $\sigma \rightleftharpoons$ H ₂ O· σ + σ		H ₂ O formation	-1 ~ 1	-1 ~ 1	1.02×10 ⁻¹	1.02×10 ⁻¹	
(9) C ₃ H ₆ · $\sigma \rightleftharpoons$ C ₃ H ₆ + σ		C ₃ H ₆ desorption	0 ~ 1	0 ~ 1.5	1.61×10 ¹¹	1.61×10 ¹¹	
(10) CO· $\sigma \rightleftharpoons$ CO + σ		CO desorption	0 ~ 2	0 ~ 1	1.61×10 ¹¹	1.61×10 ¹¹	
(11) H ₂ O· $\sigma \rightleftharpoons$ H ₂ O + σ		H ₂ O desorption	0 ~ 1	0 ~ 1	1.61×10 ¹¹	1.61×10 ¹¹	

^a r_x was determined experimentally by the consumption rate of x . ^b Estimated by quasi-stationary approximation. Order ranges consistent with the experiment are shown in bold. ^c Calculated by microkinetic modeling using DFT-derived parameters: $\vec{r}_i$ and $\vec{r}_i$ indicate the reaction rates per one active site (TOF) for the forward and reverse directions, respectively. The lowest value corresponding to the RDS is shown in bold.

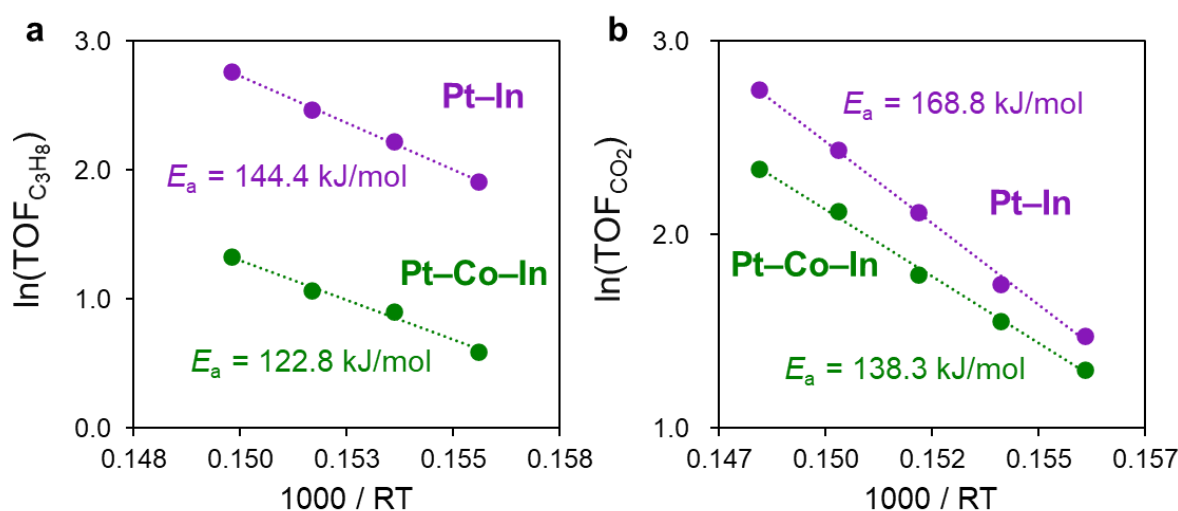


Figure 2.26. Arrhenius-type plots for (a) C_3H_8 and (b) CO_2 conversion rates obtained in CO_2 -ODP on Pt-Co-In/CeO₂ and Pt-In/CeO₂ catalysts. The catalyst amount was set to 20 mg so that the conversion became below 30%.

Table 2.7 Summary of the microkinetic modelling for CO₂-ODP on Pt₂In₃(012)–Co surface. ^a

<i>i</i>	elementary step	rate constant		reaction rate	
		$\vec{k}_i / \text{s}^{-1}$	$\overleftarrow{k}_i / \text{s}^{-1}$	$\vec{r}_i / \text{s}^{-1}$	$\overleftarrow{r}_i / \text{s}^{-1}$
1	C ₃ H ₈ physisorption	1.72×10 ¹³	3.64×10 ¹⁹	3.87×10 ¹²	3.87×10 ¹²
2	1st C–H activation	1.86×10 ⁶	9.67×10 ¹²	1.86×10 ⁻¹	1.86×10 ⁻¹
3	2nd C–H activation	3.42×10 ⁶	5.09×10 ¹⁰	1.26×10 ⁻³	1.25×10 ⁻³
4	CO ₂ physisorption	1.72×10 ¹³	2.26×10 ¹⁸	3.87×10 ¹²	3.87×10 ¹²
5	CO ₂ chemisorption	1.56×10 ⁸	3.31×10 ¹¹	2.67×10 ²	2.67×10 ²
6	CO₂ activation	2.47×10⁴	1.75×10 ¹	1.87×10⁻⁵	2.67×10 ⁻⁶
7	OH formation	2.72×10 ⁵	2.19×10 ⁰	3.46×10 ⁻⁴	3.30×10 ⁻⁴
8	H ₂ O formation	1.30×10 ⁷	3.13×10 ⁷	1.02×10 ⁻¹	1.02×10 ⁻¹
9	C ₃ H ₆ desorption	3.23×10 ²⁰	1.72×10 ¹³	1.61×10 ¹¹	1.61×10 ¹¹
10	CO desorption	2.75×10 ¹²	1.72×10 ¹³	1.61×10 ¹¹	1.61×10 ¹¹
11	H ₂ O desorption	4.67×10 ¹⁹	1.72×10 ¹³	1.61×10 ¹¹	1.61×10 ¹¹

^a Rightward- and leftward pointing arrows indicate the forward and reverse directions of step *i*, respectively. Bold parts indicate the lowest value corresponding to the rate-determining step (RDS). Note that all steps except *i* = 6 (CO₂ activation) show higher reaction rates than *i* = 6 and are in quasi-equilibrium (rates of forward and reverse directions are equal or close to each other).

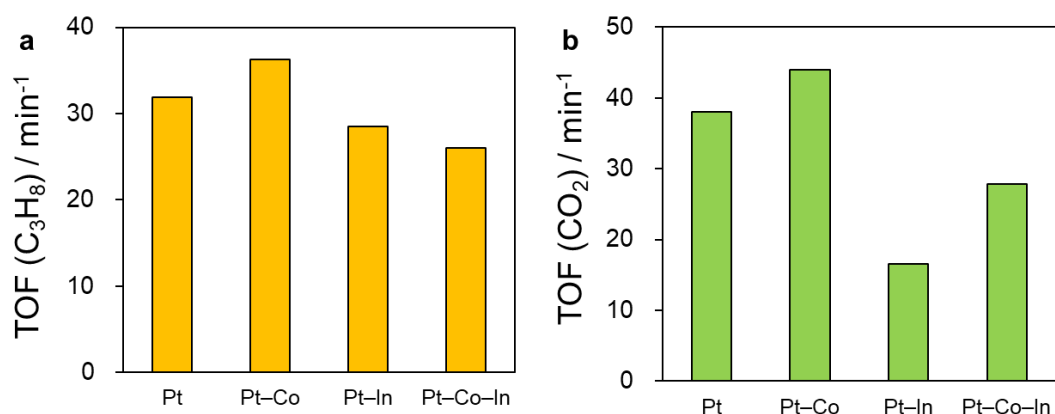


Figure 2.27. TOF of (a) C₃H₈ conversion and (b) CO₂ conversion in CO₂-ODP on Pt/CeO₂, Pt-Co/CeO₂, Pt-In/CeO₂, and Pt-Co-In/CeO₂.

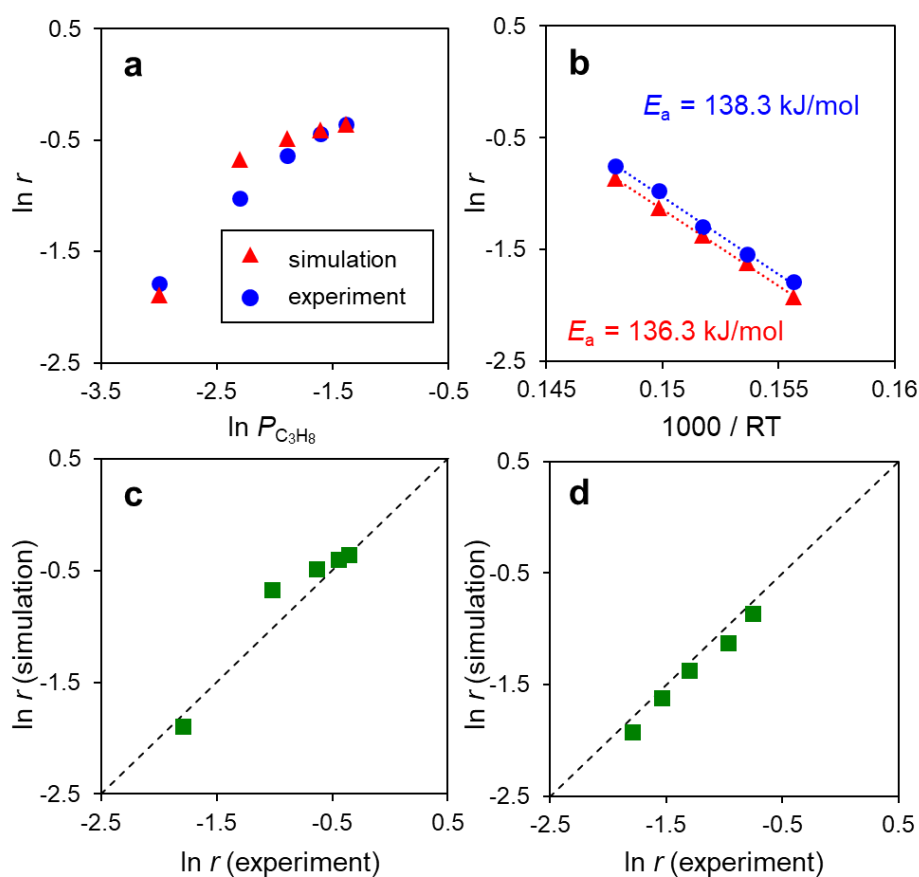


Figure 2.28. Simulated and experimental dependences of the reaction rate (mLmin⁻¹) on (a) partial pressure of C₃H₈ ($P_{C_3H_8}$) and (b) reaction temperature (T). In both cases, the simulation well reproduced the experimental trends and values. For the $P_{C_3H_8}$ dependence, the Langmuir-Hinshelwood-type curve was successfully reproduced. For the temperature dependence in the Arrhenius-type plot, the predicted E_a (136.3 kJ/mol) agreed finely with the experimental value (138.3 kJ/mol). Parity plots for a (c) and b (d) showing the agreement between the experimental reaction rates and the corresponding simulation.

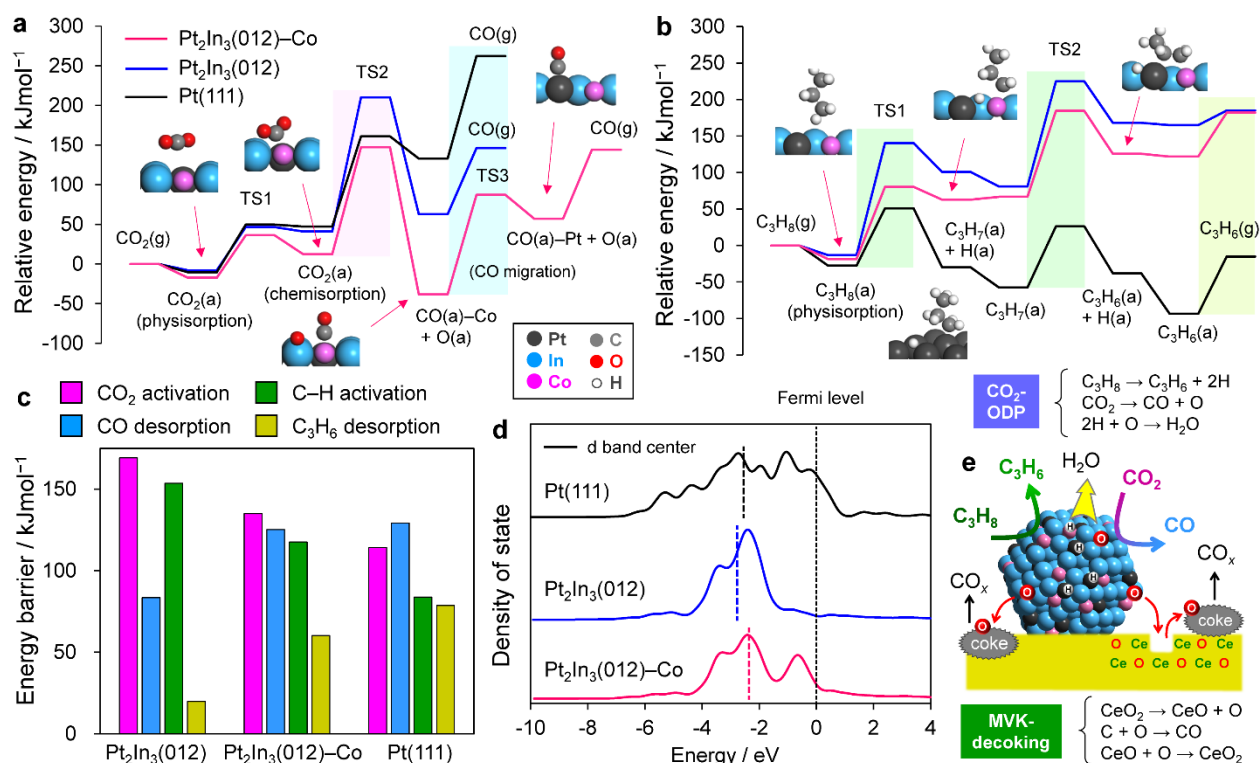


Figure 2.29: DFT calculations and reaction mechanism: a, b Energy diagrams of (a) CO₂ reduction to CO and O and (b) C₃H₈ dehydrogenation to C₃H₆ on Pt(111), Pt₂In₃(012), and Pt₂In₃(012)-Co. **c** Summary of the energy barriers on each surface. For Pt₂In₃(012)-Co, the energy barrier of CO migration was regarded as a desorption barrier. **d** Density of states projected on the d orbitals of the surface atoms of Pt(111), Pt₂In₃(012), and Pt₂In₃(012)-Co slabs. **e** Schematic illustration of the reaction mechanism of CO₂-ODP on Pt-Co-In/CeO₂ with Mars-van Krevelen-type decoking by CeO₂.

2.3.4 DFT calculation

Finally, we conducted DFT calculations to understand the role of the Pt-Co-In ternary alloy in the enhanced catalysis. As a model of the Pt-Co-In alloy surface, the stable (012) surface of intermetallic Pt₂In₃ was considered and one of the surface Pt atoms was replaced with Co, hereafter denoted as Pt₂In₃(012)-Co. Unmodified Pt₂In₃(012) and monometallic Pt(111) surfaces were also considered for comparison. CO₂ reduction to CO, C₃H₈ dehydrogenation to C₃H₆, H₂O formation, and H₂ recombination were considered on these surfaces (see Figures 3.30–3.38 for detailed structures and Figure 39 for Gibbs free energy changes). Figure 2.29a shows the energy diagram of CO₂ reduction, where CO₂ was first physisorbed, then chemisorbed with a bent sp²-like conformation, followed by C–O bond

scission to form CO and O, and lastly, CO desorption. The chemisorption was endothermic and required moderate energy barriers of 55–57 kJ·mol⁻¹. For Pt₂In₃ and Pt₂In₃-Co, the subsequent C–O scission generated CO on a top site of Pt/Co and O at an In–In bridge site, which was more stable than those on Pt(111), probably due to the oxophilicity of In. CO was considerably more stable on Co than on Pt; therefore, the direct desorption of CO from the Co site required a high amount of energy (182.3 kJ·mol⁻¹). Relatively-low energy desorption is still allowed when CO migrates to the neighboring Pt site. However, the microkinetic modeling showed that the constant and reaction rate for the desorption of product molecules were considerably high (Tables 2.6 and Table 2.7) due to the huge contribution of the translational partition function of gas-phase molecules at high temperatures. Thus, the direct desorption of CO from the Co site can smoothly occur even with the large energy barrier. Figure 2.29b represents the energy diagram of C₃H₈ dehydrogenation, where two H atoms of C₃H₈ are subsequently eliminated and moved to infinity (opposite surface of the slab). The two C–H activations were endothermic on the Pt₂In₃-based surfaces, whereas they were slightly exothermic on Pt(111), which may be dependent on whether the eliminated H atoms were located on a less stable Pt–Pt(Co) bridge site or on a highly stable Pt₃ hollow site. The high energy of the unstable H can be released after each C–H scission using the subsequent oxidation reaction (H+O→OH, ΔE = -86 or -115 kJmol⁻¹, Figure 2.39a and Tables 2.8–2.10). Thus, the net energy barriers for the “oxidative dehydrogenation of C₃H₈ (C₃H₈ + O → C₃H₆ + H₂O)” on Pt₂In₃-based surface is not higher than that of C–O scission (Figure 2.40). Figure 2.29c summarizes the major energy barriers on each surface. The Pt(111) surface was more active than the Pt₂In₃-based surfaces for C–H and CO₂ activations, while CO desorption showed the highest energy barrier. For Pt₂In₃(012), CO₂ activation required a high energy barrier of 169.1 kJ·mol⁻¹, which agreed finely with the experimental E_A^{*} (168.8 kJ·mol⁻¹, Table 2.6 and Figure 2.26) and with the low CO₂ conversion and TOF of Pt–In/CeO₂. (Figure 2.7c and Figure 2.27). The E_A of CO₂ activation was significantly decreased to 135.1 kJ·mol⁻¹ on Pt₂In₃(012)–Co, which is also consistent with the experimental E_A^{*} (138.3 kJ·mol⁻¹, Table 2.6) and the significantly improved CO₂ conversion/TOF (Figure 2.7c and Figure 2.27) by Co-substitution. Good agreements were also obtained between the theoretical and experimental E_A^{*} values for

C–H activation (Table 2.6), demonstrating the validity of our calculation. The CO₂ activation still provided the highest energy barrier on Pt₂In₃(012)–Co, which is consistent with the fact that this process is the RDS. The significant decrease in the energy barriers of C–H and CO₂ activations by Co-substitution can be explained by the lowering of the final state energies (Figure 2.29b) in line with the Brønsted–Evans–Polanyi relationship.^[72] The Co atom strongly captures the C and/or H atom of the adsorbate, thus stabilizing the adsorbate state. The stronger adsorption on Co can be rationalized by the d band structure of alloys, as shown in Figure 2.29d. Alloying Pt with In decreased the d band width and the density of states near the Fermi level. This change weakens the metal–adsorbate bonding in accordance with the d band theory.^{[73],[74]} In contrast, Pt₂In₃(012)–Co has a high density of states derived from the Co 3d orbitals near the Fermi level, which recovers the adsorption strengths of C and H, hence promoting the conversion of CO₂ and C₃H₈. Thus, the DFT calculations well supported the experimental results and clarified the role of Co in the enhanced catalysis.

2.4 Discussion

Overall, the reaction mechanism of CO₂-ODP on Pt–Co–In/CeO₂ and the roles of the ternary alloy phase and the CeO₂ support are summarized in Figure 2.29e. Both the C₃H₈ dehydrogenation and CO₂ reduction smoothly proceed on the Pt–Co active site to form 2H and O, as well as the main products: C₃H₆ and CO. Alloying with In enhances the C₃H₆ selectivity due to the ensemble effect and decreases the amount of coke that accumulates on the catalyst surface. The doped Co improves the adsorption strengths of the C and H species, which promotes the activation of C₃H₈ and CO₂. The O atoms oxidize the eliminated H to form H₂O or combust coke on the alloy surface or neighboring CeO₂ sites. Note that coke combustion is allowed when CO₂ conversion is higher than C₃H₈ conversion because of the stoichiometry of the CO₂-ODP. Coke can be combusted also by the lattice oxygen of CeO₂, where CeO₂ is partially reduced to form an oxygen vacancy. This oxygen vacancy is refilled by an O atom derived from CO₂ activation, enabling continuous coke combustion through the redox of CeO₂. Thus, CeO₂ can facilitate coke combustion via a Mars-van Krevelen-type mechanism,^[17] which significantly enhances the coke resistance and catalyst stability. Further information on the

reaction mechanism can be obtained from the results of DDP over Pt–Co–In/CeO₂ shown in [Figure 2.23](#). It is worth noting that no CO_x (CO and CO₂) was formed at all during DDP, indicating that lattice oxygen of CeO₂ does not combust C_xH_y. Thus, only carbonaceous species can be combusted by surface oxygen atom or lattice oxygen of CeO₂. Besides, C₃H₈ conversion in DDP at 550°C was relatively high (30%) and close the equilibrium conversion (43%, [Figure 2.6b](#)) at the beginning of the reaction. This indicates that Pt–Co–In/CeO₂ possesses a high catalytic activity for C–H activation even in the absence of CO₂, although it was immediately deactivated due to the lack of coke combustion. These results suggest that CO₂ does not drastically change the kinetics of the dehydrogenation step, while mainly shifts the equilibrium limitation. Thus, C₃H₈ dehydrogenation and CO₂ conversion are parallel to each other and linked by the hydrogen oxidation processes, which is consistent finely with the mechanism proposed in this study.

In summary, we designed and prepared a Pt–Co–In ternary alloy on CeO₂ as a highly efficient catalyst for the CO₂-ODP. This material comprises small nanoparticles (2–3 nm) with a (Pt_{1-x}Co_x)₂In₃ pseudo-binary alloy structure, where Pt, Co, and In are adjacent to each other on an atomic level. Pt–Co–In/CeO₂ exhibits outstanding catalytic activity, C₃H₆ selectivity, long-term stability, and CO₂ utilization efficiency, all of which are greater than typical values ever reported. Alloying Pt with In and Co significantly enhances the selectivity and activity, respectively, while the CeO₂ support drastically improves the catalyst stability by Mars-van Krevelen-type coke combustion. The results obtained in this study provide not only a highly efficient catalytic system for alkane dehydrogenation and CO₂ reduction, but also significant insights for material design based on multimetallic alloys.

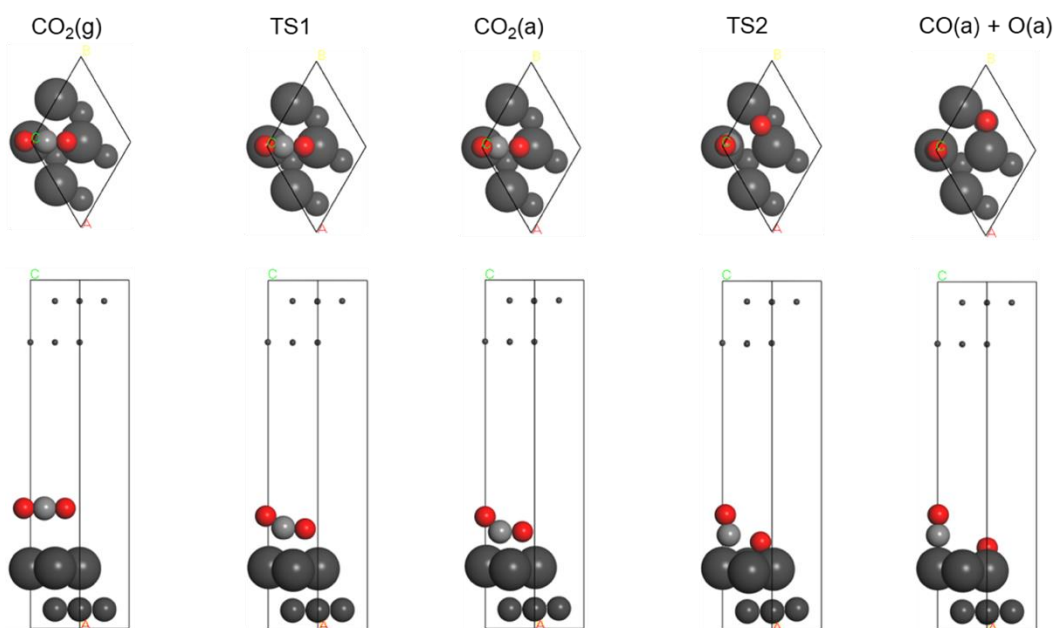


Figure 2.30. Structures of initial (IS), transition (TS), and final states (FS) in CO_2 adsorption and activation on $\text{Pt}(111)$. Atoms in the bulk was shown in smaller sizes for better visibility.

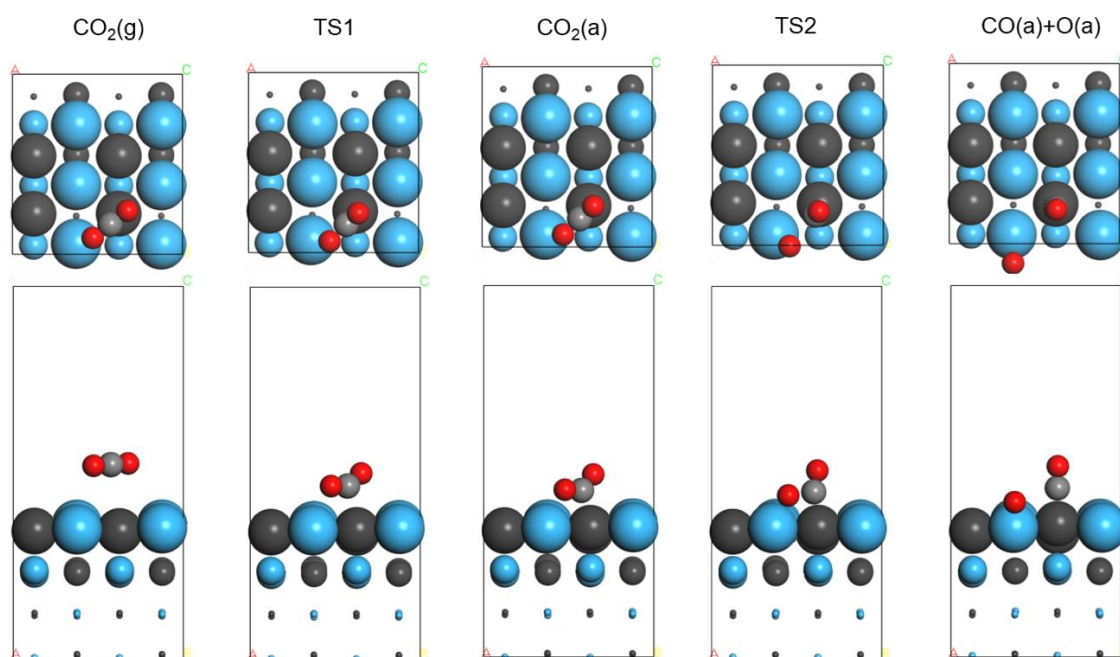


Figure 2.31. Structures of initial (IS), transition (TS), and final states (FS) in CO_2 adsorption and activation on $\text{Pt}_2\text{In}_3(012)$. Atoms in the bulk was shown in smaller sizes for better visibility.

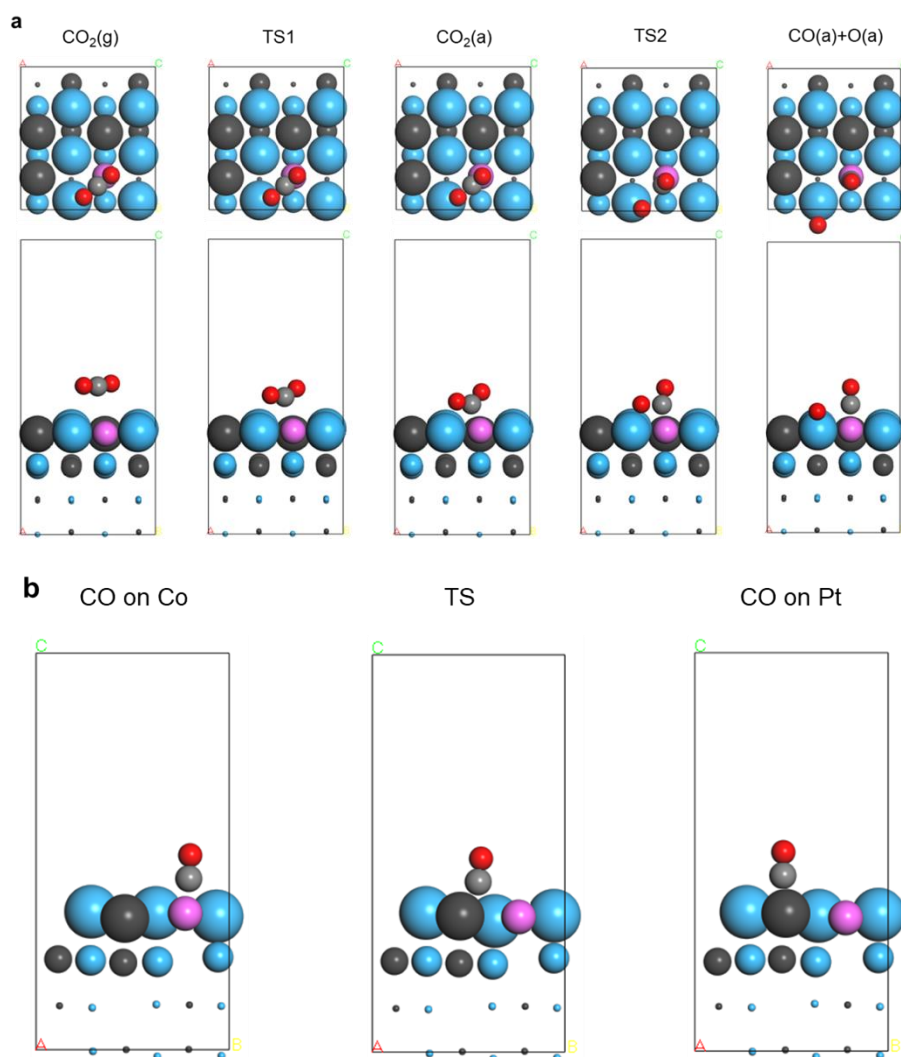


Figure 2.32. Structures of initial (IS), transition (TS), and final states (FS) in (a) CO_2 adsorption, CO_2 activation, and (b) CO migration on the Co site of $\text{Pt}_2\text{In}_3(012)\text{-Co}$. Atoms in the bulk was shown in smaller sizes for better visibility.

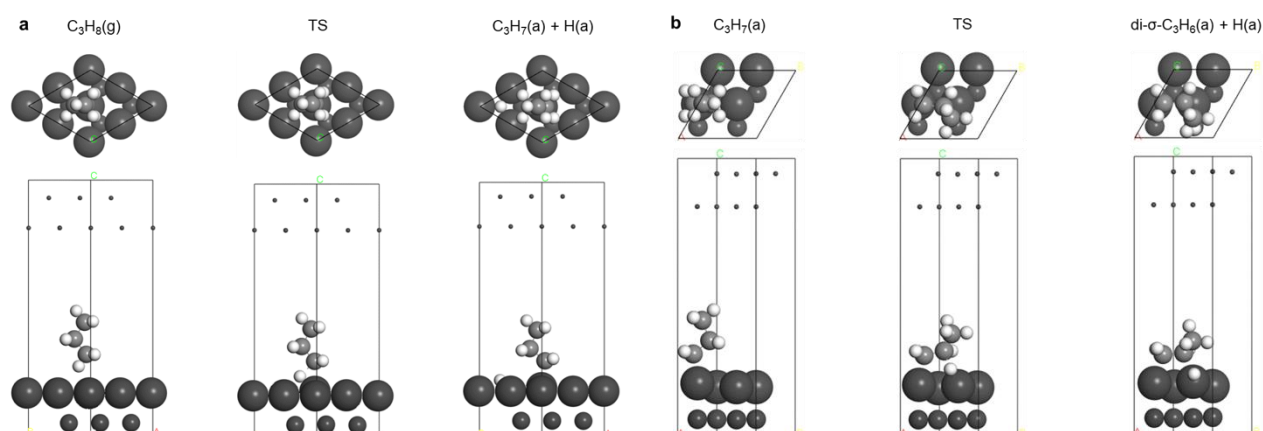


Figure 2.33. Structures of initial (IS), transition (TS), and final states (FS) in (a) the first and (b) second C–H scissions on $\text{Pt}(111)$. Atoms in the bulk was shown in smaller sizes for better visibility.

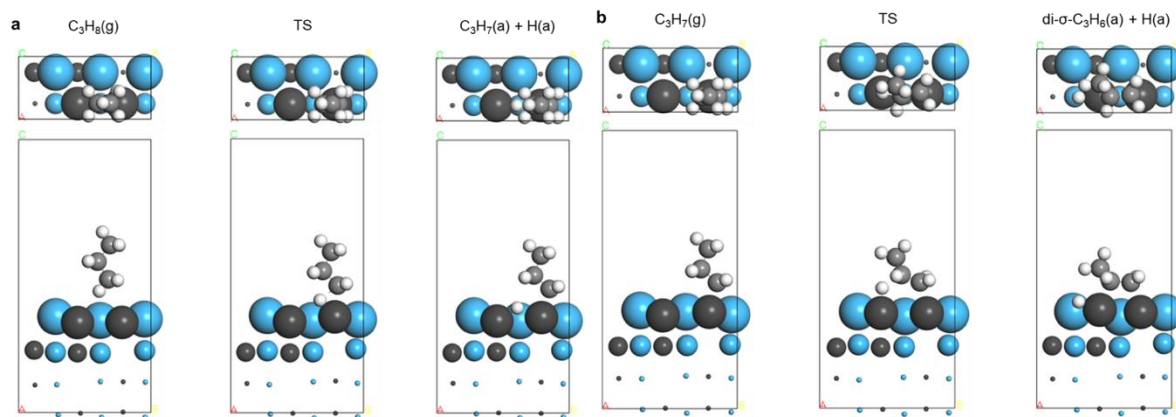


Figure 2.34. Structures of initial (IS), transition (TS), and final states (FS) in (a) the first and (b) second C–H scissions on $\text{Pt}_2\text{In}_3(012)$. Atoms in the bulk was shown in smaller sizes for better visibility.

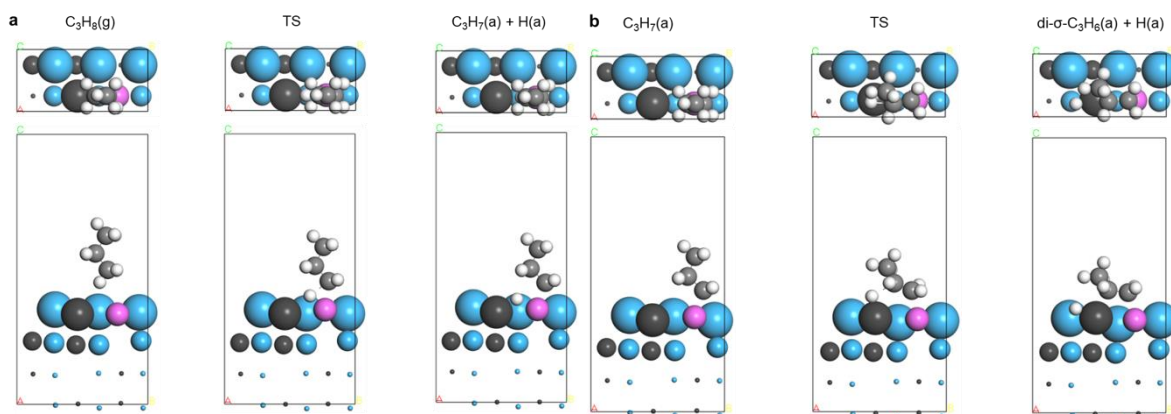


Figure 2.35. Structures of initial (IS), transition (TS), and final states (FS) in (a) the first and (b) second C–H scissions on the Co site of $\text{Pt}_2\text{In}_3(012)\text{-Co}$. Atoms in the bulk was shown in smaller sizes for better visibility.

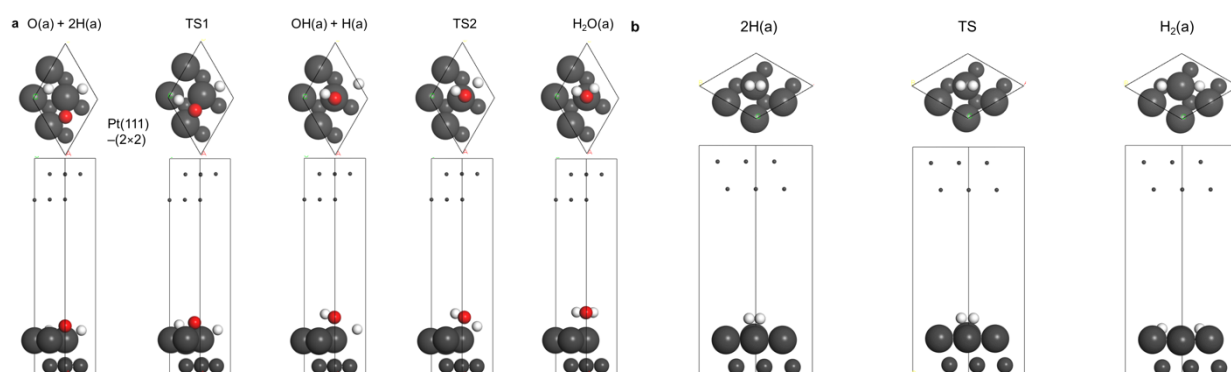


Figure 2.36. Structures of initial (IS), transition (TS), and final states (FS) in (a) H_2O formation and (b) H_2 recombination on $\text{Pt}(111)$. Atoms in the bulk was shown in smaller sizes for better visibility.

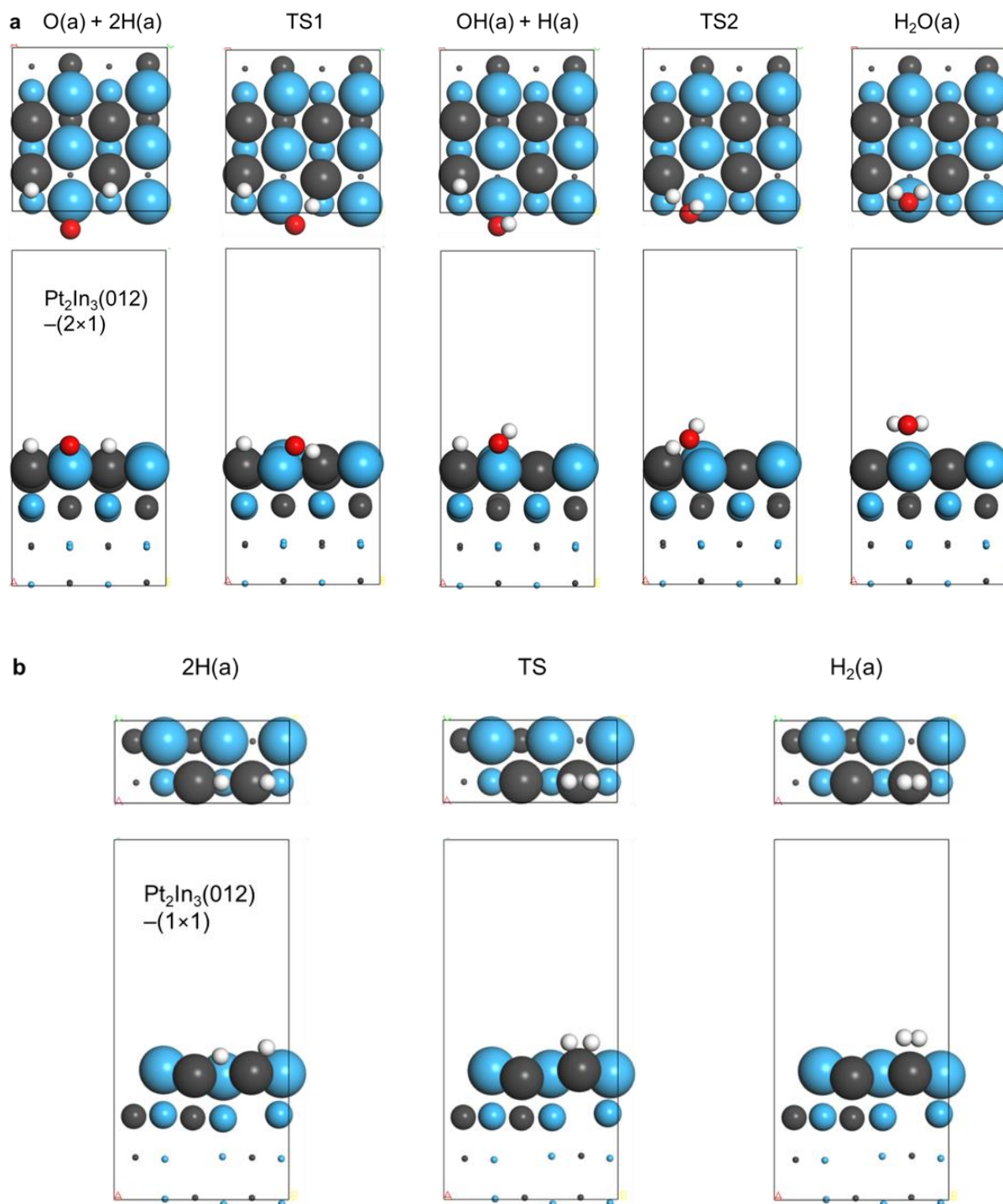


Figure 2.37. Structures of initial (IS), transition (TS), and final states (FS) in (a) H_2O formation and (b) H_2 recombination on $Pt_2In_3(012)$. Atoms in the bulk was shown in smaller sizes for better visibility.

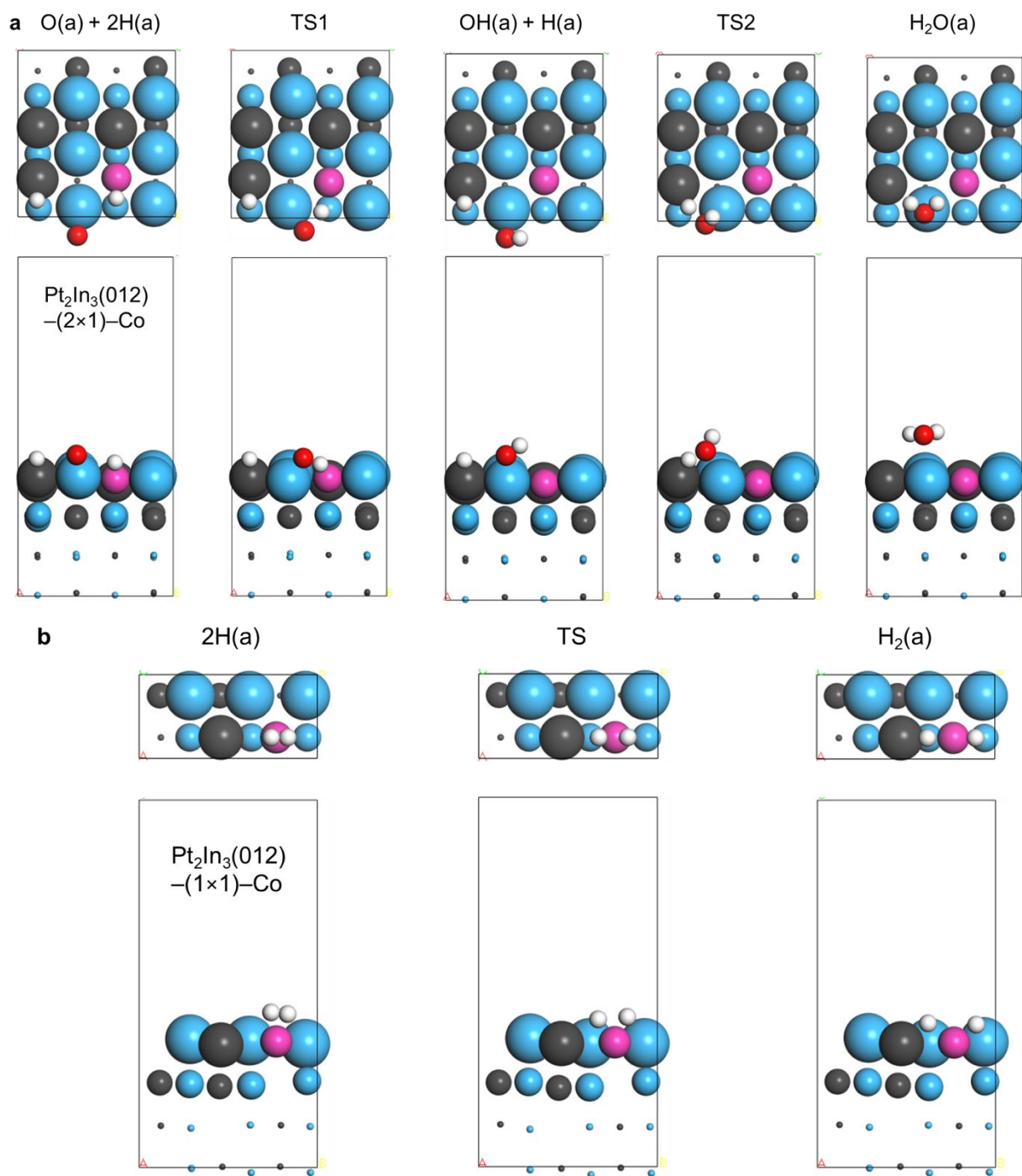


Figure 2.38. Structures of initial (IS), transition (TS), and final states (FS) in **(a)** H_2O formation and **(b)** H_2 recombination on the Co site of $Pt_2In_3(012)-Co$. Atoms in the bulk was shown in smaller sizes for better visibility.

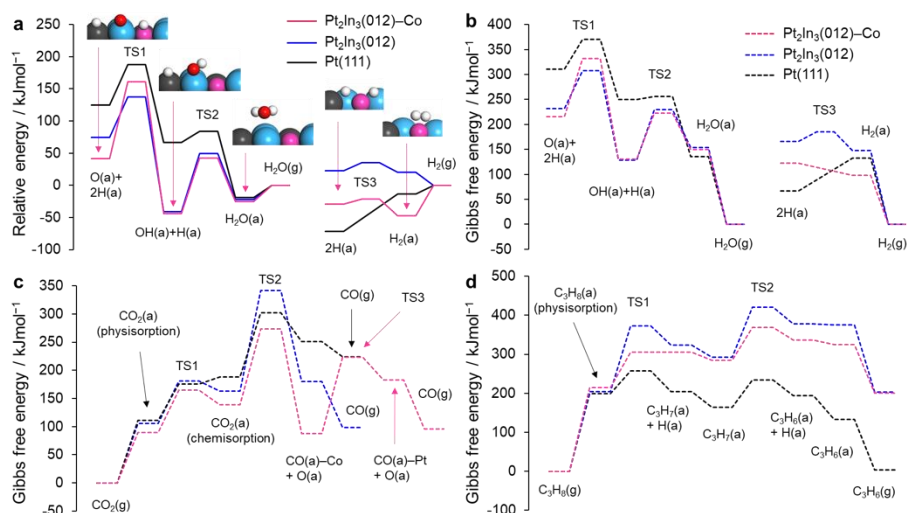


Figure 2.39. Energy diagrams for CO₂-ODP on Pt₂In₃(012), Pt₂In₃(012)-Co, and Pt(111) surfaces. **a, b** changes in **(a)** Electronic and **(b)** Gibbs free energies for H₂O formation and H₂ recombination. **c, d** Gibbs free energy changes for **(c)** CO₂ reduction and **(d)** C₃H₈ dehydrogenation. For Gibbs free energy profiles, adsorption and desorption showed large free energy gain and release, respectively, due to the significant contribution of translational entropy of gas-phase molecules at high temperature, of which trend is consistent with those reported in literature.^[75,76]

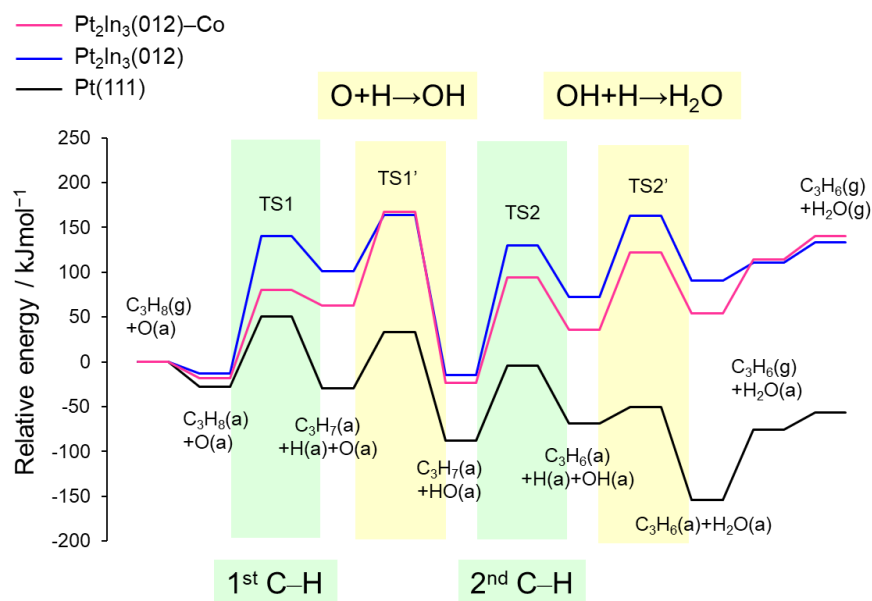


Figure 2.40. Energy diagrams for ODP (C₃H₈ + O → C₃H₆ + H₂O, as an integration of Figures 2.29b and 3.37a) on Pt₂In₃(012), Pt₂In₃(012)-Co, and Pt(111) surfaces. Compared with Figure 2.29b, the high amount of energy is released by consuming the eliminated H atom by O atom to form OH, resulting in a decrease in the overall energy barrier.

Table 2.8. Summary of electronic and Gibbs free energies for elementary steps of CO₂-ODP on Pt₂In₃(012) surface.^a

elementary step	energy (kJ/mol)			
	E_A	ΔE	G_A	ΔG
CO ₂ physisorption	0	−8.0	105.5	105.5
CO ₂ chemisorption	55.1	48.9	75.6	57.2
CO ₂ activation	169.1	21.8	179.2	17.3
CO desorption	83.4	83.4	0	−82.0
C ₃ H ₈ physisorption	0.0	−13.2	204.3	204.3
1st C–H activation	153.3	114.1	167.5	119.1
2nd C–H activation	148.5	87.0	133.6	85.7
C ₃ H ₆ desorption	19.9	19.9	0	−171.5
OH formation	62.8	−115.2	76.2	−103.4
H ₂ O formation	89.9	18.4	101.1	25.6
H ₂ O desorption	22.4	22.4	0	−175.8
H ₂ recombination	12.4	−2.3	19.5	−18.0
H ₂ desorption	0	−20.3	0	−147.6

^a E_A : activation energy, ΔE : reaction energy, G_A : activation Gibbs free energy, ΔG : reaction Gibbs free energy.

Table 2.9. Summary of electronic and Gibbs free energies for elementary steps of CO₂-ODP on Pt₂In₃(012)–Co surface. ^a

elementary step	energy (kJ/mol)			
	E_A	ΔE	G_A	ΔG
CO ₂ physisorption	0	−17.3	89.7	89.7
CO ₂ chemisorption	56.5	29.7	78.0	48.8
CO ₂ activation	135.1	−50.5	134.8	−50.9
CO desorption (Co)	182.3	182.3	8.5	8.5
CO migration	125.2	95.3	135.7	95.4
CO desorption (Pt)	87.0	87.0	0	−86.9
C ₃ H ₈ physisorption	0	−27.6	214.6	214.6
1st C–H activation	99.0	81.6	90.7	90.9
2nd C–H activation	117.6	58.9	85.0	52.4
C ₃ H ₆ desorption	60.2	60.2	0	−123.6
OH formation	119.1	−86.1	115.8	−85.0
H ₂ O formation	86.3	18.6	91.9	19.1
H ₂ O desorption	25.6	25.6	0	−149.8
H ₂ recombination	8.3	−17.4	0	−23.9
H ₂ desorption	47.0	47.0	0	−98.5

^a E_A : activation energy, ΔE : reaction energy, G_A : activation Gibbs free energy, ΔG : reaction Gibbs free energy.

Table 2.10. Summary of electronic and Gibbs free energies for elementary steps of CO₂-ODP on Pt(111) surface. ^a

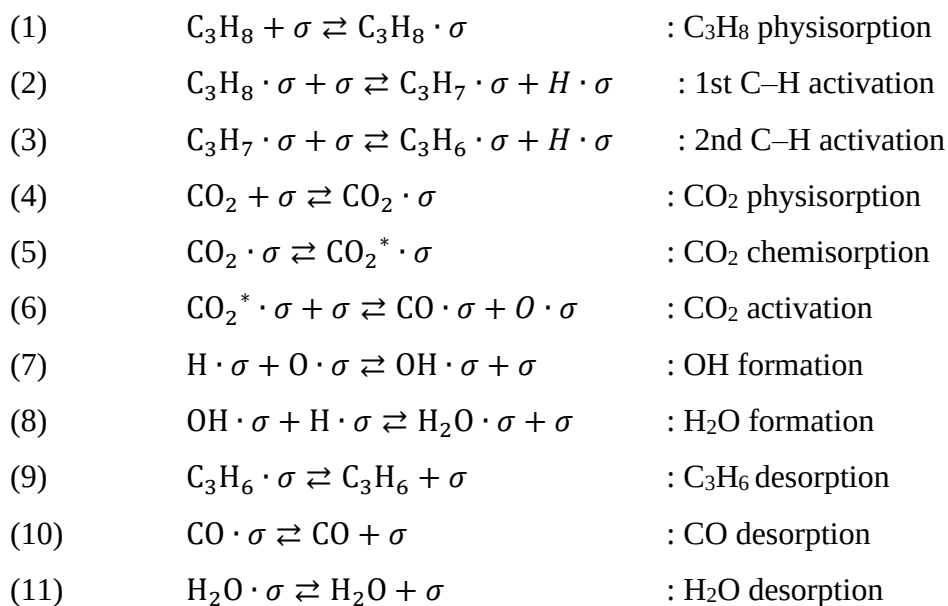
elementary step	energy (kJ/mol)			
	E_A	ΔE	G_A	ΔG
CO ₂ physisorption	0	−10.3	111.1	111.1
CO ₂ chemisorption	60.8	57.6	65.4	77.4
CO ₂ activation	114.2	85.6	114.0	62.4
CO desorption	129.3	129.3	0	−26.6
C ₃ H ₈ physisorption	0	−27.6	198.7	198.7
1st C–H activation	78.4	−2.1	59.1	6.2
2nd C–H activation	83.8	19.4	71.2	30.6
C ₃ H ₆ desorption	78.6	78.6	0	−129.0
OH formation	63.0	−58.3	60.1	−59.9
H ₂ O formation	17.7	−85.7	5.7	−114.8
H ₂ O desorption	19.3	19.3	0	−135.6
H ₂ recombination	58.0	58.0	66.8	66.8
H ₂ desorption	13.8	13.8	0	−133.0

^a E_A : activation energy, ΔE : reaction energy, G_A : activation Gibbs free energy, ΔG : reaction Gibbs free energy.

Supplementary Note 1

Kinetic analysis

We conducted two different approaches for kinetic analysis to understand the RDS of CO₂-ODP on Pt–Co–In/CeO₂ catalyst: (a) conventional quasi-stationary approximation and (b) microkinetic modeling using DFT-derived parameters. The former estimates the possible ranges of reaction orders, which can be verified by the experimental values. The latter can provide the reaction rate of each step by first principle. In both cases, we considered the following Langmuir-Hinshelwood type mechanism for CO₂-ODP:



For this model, the direct dehydrogenation pathway with no involvement of CO₂ was not considered because its contribution to the overall propylene production was considerably low. The reaction rate of each elementary step was described based the raw of mass action as follows:^[77]

$$r_i = \vec{r}_i - \tilde{r}_i = \vec{k}_i \prod_j \vec{P}_j \prod_j \vec{\theta}_j - \tilde{k}_i \prod_j \tilde{P}_j \prod_j \tilde{\theta}_j \quad (12)$$

where, $\vec{k}_i$ and $\tilde{k}_i$ are the rate constants for forward and reverse reactions in step i , respectively. $\vec{P}_j(\vec{\theta}_j)$ and $\tilde{P}_j(\tilde{\theta}_j)$ are the pressure (coverage) of the reactant and product species in step i ,

respectively. Pressure and coverage were used for gas-phase molecules and surface adsorbates, respectively. The specific representation of each reaction rate is shown below:

$$r_1 = \vec{k}_1 P_{C_3H_8} (1 - \theta) - \overleftarrow{k}_1 \theta_{C_3H_8} \quad (13) \quad r_2 = \vec{k}_2 \theta_{C_3H_8} (1 - \theta) -$$

$$\overleftarrow{k}_2 \theta_{C_3H_7} \theta_H \quad (14)$$

$$r_3 = \vec{k}_3 \theta_{C_3H_7} (1 - \theta) - \overleftarrow{k}_3 \theta_{C_3H_6} \theta_H \quad (15) \quad r_4 = \vec{k}_4 P_{CO_2} (1 - \theta) - \overleftarrow{k}_4 \theta_{CO_2} \quad (16)$$

$$r_5 = \vec{k}_5 \theta_{CO_2} - \overleftarrow{k}_5 \theta_{CO_2}^* \quad (17) \quad r_6 = \vec{k}_6 \theta_{CO_2}^* (1 - \theta) - \overleftarrow{k}_6 \theta_{CO} \theta_O \quad (18)$$

$$r_7 = \vec{k}_7 \theta_O \theta_H - \overleftarrow{k}_7 \theta_{OH} (1 - \theta) \quad (19) \quad r_8 = \vec{k}_8 \theta_{OH} \theta_H - \overleftarrow{k}_8 \theta_{H_2O} (1 - \theta) \quad (20)$$

$$r_9 = \vec{k}_9 \theta_{C_3H_6} - \overleftarrow{k}_9 P_{C_3H_6} (1 - \theta) \quad (21) \quad r_{10} = \vec{k}_{10} \theta_{CO} - \overleftarrow{k}_{10} P_{CO} (1 - \theta) \quad (22)$$

$$r_{11} = \vec{k}_{11} \theta_{H_2O} - \overleftarrow{k}_{11} P_{H_2O} (1 - \theta) \quad (23)$$

where, P_x , θ_x , and $1 - \theta$ are the relative pressure of x to the standard pressure, coverage of x , and the fraction of vacant adsorption site, respectively. Note that these are dimensionless values.

Kinetic Analysis based on quasi-stationary approximation

Outline:

According to the quasi-stationary approximation, when a certain step is considered as the rate-determining step, other steps can be regarded to be in equilibrium. Therefore, the equilibrium constants are provided as follows:

$$K_1 = \frac{\theta_{C_3H_8} \theta_H}{P_{C_3H_8} (1 - \theta)} \quad (24) \quad K_2 = \frac{\theta_{C_3H_7} \theta_H}{\theta_{C_3H_8} (1 - \theta)} \quad (25) \quad K_3 = \frac{\theta_{C_3H_6} \theta_H}{\theta_{C_3H_7} (1 - \theta)} \quad (26) \quad K_4$$

$$= \frac{\theta_{CO_2}}{P_{CO_2} (1 - \theta)} \quad (27)$$

$$K_5 = \frac{\theta_{CO_2}^*}{\theta_{CO_2}} \quad (28) \quad K_6 = \frac{\theta_{CO} \theta_O}{\theta_{CO_2}^* (1 - \theta)} \quad (29) \quad K_7 = \frac{\theta_{OH} (1 - \theta)}{\theta_O \theta_H} \quad (30) \quad K_8$$

$$= \frac{\theta_{H_2O} (1 - \theta)}{\theta_{OH} \theta_H} \quad (31)$$

$$K_9 = \frac{P_{C_3H_6} (1 - \theta)}{\theta_{C_3H_6}} \quad (32) \quad K_{10} = \frac{P_{CO} (1 - \theta)}{\theta_{CO}} \quad (33) \quad K_{11} = \frac{P_{H_2O} (1 - \theta)}{\theta_{H_2O}} \quad (33)$$

Note that K_i cannot be defined when the step i is considered as the RDS (ten equilibrium constants can be used). Besides, the conservation of the number of adsorption site is considered as follows:

$$\sum \theta_x + (1 - \theta) = 1 \quad (34)$$

$$\theta_{C_3H_8} + \theta_{C_3H_7} + \theta_{C_3H_6} + \theta_{CO_2} + \theta_{CO_2}^* + \theta_{CO} + \theta_O + \theta_H + \theta_{OH} + \theta_{H_2O} + (1 - \theta) = 1 \quad (35)$$

Each θ_x except $(1 - \theta)$ is expressed as a function of K_i , P_j , and $(1 - \theta)$, then the site conservation equation is solved for $(1 - \theta)$. Thus, each coverage and reaction rate can be expressed as a function of K_i and P_j :

$$\theta_n = f_n(K_i, P_j), r_n = \vec{r}_n - \overleftarrow{r}_n = \vec{k}_n \prod_n \vec{P}_n \prod_n f_n(K_i, P_j) - \overleftarrow{k}_n \prod_n \overleftarrow{P}_n \prod_n g_n(K_i, P_j) \quad (36)$$

Then, K_i and P_j except $P_{C_3H_8}$ or P_{CO_2} are regarded as constants in a series of catalytic experiments, which makes r_n a function of $P_{C_3H_8}$ or P_{CO_2} . This function can be approximated to a simplified form at a certain limit of coefficients included in the equation as follows:

$$r_n = k P_{C_3H_8}^\alpha P_{CO_2}^\beta \quad (37)$$

where, k is an apparent rate constant. The range of α (β) is obtained assuming their higher and lower limits using some approximations that ignore less important terms. When the step n is truly the RDS, r_n is equal to the overall reaction rate. Therefore, the ranges of α and β should be consistent with the experimental results (the reverse is not always true). If the predicted reaction order ranges do not agree with the experimental values, assuming the step n as the RDS should be false.

In the following section, full derivation of the rate equation and the range of possible reaction orders are shown for steps (1) and (6) as examples for better understanding. For other steps, summarized results derived in a similar manner are shown. The contribution of each reverse reaction was ignored because the experimental reactions were done in differential conditions (at very low conversion level: 5~10%, where $P_{C_3H_8}, P_{CO_2} \gg P_{C_3H_6}, P_{CO}, P_{H_2O}$).

Assuming step (1) as the RDS (full derivation):

When C_3H_8 physisorption (1) is the RDS, the overall reaction rate can be expressed using the rate constants $\vec{k}_1$ and $\overleftarrow{k}_1$ as follows:

$$r = \vec{k}_1 P_{C_3H_8} (1 - \theta) - \overleftarrow{k}_1 \theta_{C_3H_8} \quad (38)$$

Here, equilibrium constants K_i except K_1 can be defined assuming quasi-stationary approximation and used for solvation. Some θ_x can be obtained directly by K_i as follows:

$$\theta_{\text{H}_2\text{O}} = K_{11}^{-1} P_{\text{H}_2\text{O}} (1 - \theta) \quad (39) \quad , \quad \theta_{\text{CO}} = K_{10}^{-1} P_{\text{CO}} (1 - \theta) \quad (40) \quad , \quad \theta_{\text{C}_3\text{H}_6} = K_9^{-1} P_{\text{C}_3\text{H}_6} (1 - \theta) \quad (41),$$

$$\theta_{\text{CO}_2} = K_4 P_{\text{CO}_2} (1 - \theta) \quad (42)$$

$\theta_{\text{CO}_2}^*$ is obtained using the equations about K_4 and K_5 as follows:

$$\theta_{\text{CO}_2}^* = K_5 \theta_{\text{CO}_2} = K_4 K_5 P_{\text{CO}_2} (1 - \theta) \quad (43)$$

Similarly, θ_{O} is described using the equations about K_4 , K_5 , K_6 , and K_{10} as follows:

$$\begin{aligned} \theta_{\text{O}} &= K_6 \theta_{\text{CO}_2}^* \theta_{\text{CO}}^{-1} (1 - \theta) = K_6 K_4 K_5 P_{\text{CO}_2} (1 - \theta) \theta_{\text{CO}}^{-1} (1 - \theta) \\ &= K_4 K_5 K_6 K_{10} P_{\text{CO}}^{-1} P_{\text{CO}_2} (1 - \theta) \quad (44) \end{aligned}$$

θ_{H} can be derived by multiplying the equations about K_7 and K_8 , followed by assigning θ_{O} and $\theta_{\text{H}_2\text{O}}$ as follows:

$$\begin{aligned} K_7 \times K_8 &= \frac{\theta_{\text{H}_2\text{O}} (1 - \theta)^2}{\theta_{\text{O}} \theta_{\text{H}}^2} \quad \therefore \theta_{\text{H}} = \left(\frac{\theta_{\text{H}_2\text{O}}}{K_7 K_8 \theta_{\text{O}}} \right)^{0.5} (1 - \theta) \\ &= \left(\frac{K_{11}^{-1} P_{\text{H}_2\text{O}}}{K_7 K_8 K_4 K_5 K_6 K_{10} P_{\text{CO}_2} P_{\text{CO}}^{-1}} \right)^{0.5} (1 - \theta) \\ &= (K_4 K_5 K_6 K_7 K_8 K_{10} K_{11})^{-0.5} P_{\text{CO}}^{0.5} P_{\text{H}_2\text{O}}^{0.5} P_{\text{CO}_2}^{-0.5} (1 - \theta) \quad (45) \end{aligned}$$

θ_{OH} is obtained by assigning θ_{H} to the equations about K_8 , then θ_{H} again and $\theta_{\text{H}_2\text{O}}$ as follows:

$$\begin{aligned} \theta_{\text{OH}} &= \frac{\theta_{\text{H}_2\text{O}}}{K_8 \theta_{\text{H}}} (1 - \theta) = \frac{K_{11}^{-1} P_{\text{H}_2\text{O}}}{K_8 (K_4 K_5 K_6 K_7 K_8 K_{10} K_{11})^{-0.5} P_{\text{CO}}^{0.5} P_{\text{H}_2\text{O}}^{0.5} P_{\text{CO}_2}^{-0.5}} (1 - \theta) \\ &= (K_4 K_5 K_6 K_7 K_8^{-1} K_{10} K_{11}^{-1})^{0.5} P_{\text{CO}}^{-0.5} P_{\text{H}_2\text{O}}^{0.5} P_{\text{CO}_2}^{0.5} (1 - \theta) \quad (46) \end{aligned}$$

Similarly, $\theta_{\text{C}_3\text{H}_7}$ is obtained by assigning θ_{H} to the equations about K_3 , then θ_6 as follows:

$$\begin{aligned} \theta_{\text{C}_3\text{H}_7} &= \frac{\theta_{\text{C}_3\text{H}_6} \theta_{\text{H}}}{K_3 (1 - \theta)} = \frac{K_9^{-1} P_{\text{C}_3\text{H}_6} (K_4 K_5 K_6 K_7 K_8 K_{10} K_{11})^{-0.5} P_{\text{CO}}^{0.5} P_{\text{H}_2\text{O}}^{0.5} P_{\text{CO}_2}^{-0.5}}{K_3} (1 - \theta) \\ &= (K_3^2 K_4 K_5 K_6 K_7 K_8 K_9^2 K_{10} K_{11})^{-0.5} P_{\text{C}_3\text{H}_6} P_{\text{CO}}^{0.5} P_{\text{H}_2\text{O}}^{0.5} P_{\text{CO}_2}^{-0.5} (1 - \theta) \quad (47) \end{aligned}$$

Finally, $\theta_{\text{C}_3\text{H}_8}$ is derived by assigning θ_{H} to the equations about K_2 :

$$\begin{aligned} \theta_{\text{C}_3\text{H}_8} &= \frac{\theta_{\text{C}_3\text{H}_7} \theta_{\text{H}}}{K_2 (1 - \theta)} \\ &= \frac{(K_3^2 K_4 K_5 K_6 K_7 K_8 K_9^2 K_{10} K_{11})^{-0.5} P_{\text{C}_3\text{H}_6} P_{\text{CO}}^{0.5} P_{\text{H}_2\text{O}}^{0.5} P_{\text{CO}_2}^{-0.5} (K_4 K_5 K_6 K_7 K_8 K_{10} K_{11})^{-0.5} P_{\text{CO}}^{0.5} P_{\text{H}_2\text{O}}^{0.5} P_{\text{CO}_2}^{-0.5}}{K_2} (1 - \theta) \\ &= (K_2 K_3 K_4 K_5 K_6 K_7 K_8 K_9 K_{10} K_{11})^{-1} P_{\text{C}_3\text{H}_6} P_{\text{CO}} P_{\text{H}_2\text{O}} P_{\text{CO}_2}^{-1} (1 - \theta) \quad (48) \end{aligned}$$

Then, the site conservation equation is solved for $(1 - \theta)$.

$$\sum \theta_x + (1 - \theta) = \sum A_x(1 - \theta) + (1 - \theta) = 1 \quad (49)$$

where, A_x is the member of θ_x except $(1 - \theta)$, that is, the **blue-colored part** for each θ_x .

Therefore,

$$\left(1 + \sum A_x\right)(1 - \theta) = 1 \quad \therefore (1 - \theta) = \left(1 + \sum A_x\right)^{-1} \quad (50)$$

Now, the rate equation is expressed as follows:

$$\begin{aligned} r &= \overrightarrow{k_1}P_{C_3H_8}(1 - \theta) - \overleftarrow{k_1}\theta_{C_3H_8} \\ &= \frac{\overrightarrow{k_1}P_{C_3H_8} - (K_2K_3K_4K_5K_6K_7K_8K_9K_{10}K_{11})^{-1}P_{C_3H_6}P_{CO}P_{H_2O}P_{CO_2}^{-1}}{1 + \sum A_x} \\ &\approx \frac{\overrightarrow{k_1}P_{C_3H_8}}{1 + \sum A_x} \quad (51) \end{aligned}$$

where, the contribution of the reverse reaction was ignored because of the differential condition (very low conversion: $P_{C_3H_8}, P_{CO_2} \gg P_{C_3H_6}, P_{CO}, P_{H_2O}, P_{C_3H_6}P_{CO}P_{H_2O}P_{CO_2}^{-1} \lll 1$).

Next, this equation is regarded as a function of the single valuable, $P_{C_3H_8}$ or P_{CO_2} .

Each A_x is decomposed into P_{CO_2} and a constant B_x as follows:

$$A_{H_2O} = B_{H_2O} = K_{11}^{-1}P_{H_2O} \quad (52) \quad A_{CO} = B_{CO} = K_{10}^{-1}P_{CO} \quad (53) \quad A_{C_3H_6} = B_{C_3H_6}$$

$$= K_9^{-1}P_{C_3H_6} \quad (54)$$

$$A_{CO_2} = B_{CO_2}P_{CO_2} \quad (B_{CO_2} = K_4) \quad (55) \quad A_{CO_2}^* = B_{CO_2}^*P_{CO_2} \quad (B_{CO_2}^* = K_4K_5) \quad (56)$$

$$A_O = B_O P_{CO_2} \quad (B_O = K_4K_5K_6K_{10}P_{CO}^{-1}) \quad (57)$$

$$A_H = B_H P_{CO_2}^{-0.5} \quad (B_H = (K_4K_5K_6K_7K_8K_{10}K_{11})^{-0.5}P_{CO}^{0.5}P_{H_2O}^{0.5}) \quad (58)$$

$$A_{OH} = B_{OH} P_{CO_2}^{0.5} \quad (B_{OH} = (K_4K_5K_6K_7K_8^{-1}K_{10}K_{11})^{0.5}P_{CO}^{-0.5}P_{H_2O}^{0.5}) \quad (59)$$

$$A_{C_3H_7} = B_{C_3H_7} P_{CO_2}^{-0.5} \quad (B_{C_3H_7} = (K_3^2K_4K_5K_6K_7K_8K_9^2K_{10}K_{11})^{-0.5}P_{C_3H_6}P_{CO}^{0.5}P_{H_2O}^{0.5}) \quad (60)$$

$$A_{C_3H_8} = B_{C_3H_8} P_{CO_2}^{-1} \quad (B_{C_3H_8} = (K_2K_3K_4K_5K_6K_7K_8K_9K_{10}K_{11})^{-1}P_{C_3H_6}P_{CO}P_{H_2O}) \quad (61)$$

For $P_{C_3H_8}$, there is no factor of $P_{C_3H_8}$ in all A_x ; therefore, the rate equation is obviously first-order dependent on $P_{C_3H_8}$, that is, $\alpha = 1$.

For P_{CO_2} , the rate equation can be expressed as the function of P_{CO_2} as follows:

r

$$= \frac{\overrightarrow{k_1} P_{C_3H_8}}{1 + B_{H_2O} + B_{CO} + B_{C_3H_6} + (B_{CO_2} + B_{CO_2}^* + B_O) P_{CO_2} + B_{OH} P_{CO_2}^{0.5} + (B_H + B_{C_3H_7}) P_{CO_2}^{-0.5} + B_{C_3H_8} P_{CO_2}^{-1}} \quad (62)$$

Here, two limits of this equation are considered such that the order dependence of P_{CO_2} become the largest and smallest, which provides the possible range of reaction order β .

When $B_{C_3H_8} \gg 1 + B_{H_2O} + B_{CO} + B_{C_3H_6}, B_{CO_2} + B_{CO_2}^* + B_O, B_{OH}, B_H + B_{C_3H_7}$, this equation can be simplified as follows:

r

$$= \frac{B_{C_3H_8}^{-1} \overrightarrow{k_1} P_{C_3H_8}}{\frac{1 + B_{H_2O} + B_{CO} + B_{C_3H_6}}{B_{C_3H_8}} + \frac{B_{CO_2} + B_{CO_2}^* + B_O}{B_{C_3H_8}} P_{CO_2} + \frac{B_{OH}}{B_{C_3H_8}} P_{CO_2}^{0.5} + \frac{B_H + B_{C_3H_7}}{B_{C_3H_8}} P_{CO_2}^{-0.5} + P_{CO_2}^{-1}}$$

$$\approx \frac{\overrightarrow{k_1} P_{C_3H_8} P_{CO_2}}{B_{C_3H_8}}$$

$$\therefore \left(\frac{1 + B_{H_2O} + B_{CO} + B_{C_3H_6}}{B_{C_3H_8}}, \frac{B_{CO_2} + B_{CO_2}^* + B_O}{B_{C_3H_8}}, \frac{B_{OH}}{B_{C_3H_8}}, \frac{B_H + B_{C_3H_7}}{B_{C_3H_8}} \ll 1 \right) \quad (63)$$

On the contrary, when $B_{CO_2} + B_{CO_2}^* + B_O \gg 1 + B_{H_2O} + B_{CO} + B_{C_3H_6}, B_{OH}, B_H + B_{C_3H_7}, B_{C_3H_8}$,

this equation can be simplified as follows:

r

$$= \frac{(B_{CO_2} + B_{CO_2}^* + B_O)^{-1} \overrightarrow{k_1} P_{C_3H_8}}{\frac{1 + B_{H_2O} + B_{CO} + B_{C_3H_6}}{B_{CO_2} + B_{CO_2}^* + B_O} + P_{CO_2} + \frac{B_{OH}}{B_{CO_2} + B_{CO_2}^* + B_O} P_{CO_2}^{0.5} + \frac{B_H + B_{C_3H_7}}{B_{CO_2} + B_{CO_2}^* + B_O} P_{CO_2}^{-0.5} + \frac{B_{C_3H_8}}{B_{CO_2} + B_{CO_2}^* + B_O} P_{CO_2}^{-1}}$$

$$\approx \frac{\overrightarrow{k_1} P_{C_3H_8} P_{CO_2}^{-1}}{B_{CO_2} + B_{CO_2}^* + B_O}$$

$$\therefore \left(\frac{1 + B_{H_2O} + B_{CO} + B_{C_3H_6}}{B_{CO_2} + B_{CO_2}^* + B_O}, \frac{B_{OH}}{B_{CO_2} + B_{CO_2}^* + B_O}, \frac{B_H + B_{C_3H_7}}{B_{CO_2} + B_{CO_2}^* + B_O}, \frac{B_{C_3H_8}}{B_{CO_2} + B_{CO_2}^* + B_O} \ll 1 \right) \quad (64)$$

Therefore, the reaction order β can be 1 and -1 at the higher and lower limit and should always fall into this range. Based on this derivation, the reaction orders for $P_{C_3H_8}$ (α) and P_{CO_2} (β) on the overall reaction rate should be described as follows: $\alpha = 1, -1 < \beta < 1$. Since this does not agree with the experimental results, the step (1) should not be the RDS.

Assuming step (2) as the RDS (summary):

When the 1st C-H activation (2) is the RDS, the overall reaction rate can be expressed using the rate constants $\overrightarrow{k_2}$ and $\overleftarrow{k_2}$ as follows:

$$r = \overrightarrow{k_2} \theta_{C_3H_8} (1 - \theta) - \overleftarrow{k_2} \theta_{C_3H_7} \theta_H \approx \frac{\overrightarrow{k_2} K_1 P_{C_3H_8}}{(1 + \sum A_x)^2} \quad (65)$$

Where, A_x are expressed using B_x and $P_{C_3H_8}$ or P_{CO_2} as follows:

$$A_{H_2O} = B_{H_2O} = K_{11}^{-1} P_{H_2O} \quad (66) \quad A_{CO} = B_{CO} = K_{10}^{-1} P_{CO} \quad (67) \quad A_{C_3H_6} = B_{C_3H_6} = K_9^{-1} P_{C_3H_6} \quad (68)$$

$$A_{C_3H_8} = B_{C_3H_8} P_{C_3H_8} \quad (B_{C_3H_8} = K_1) \quad (69) \quad A_{CO_2} = B_{CO_2} P_{CO_2} \quad (B_{CO_2} = K_4) \quad (70)$$

$$A_{CO_2}^* = B_{CO_2}^* P_{CO_2} \quad (B_{CO_2}^* = K_4 K_5) \quad (71) \quad A_O = B_O P_{CO_2} \quad (B_H = K_4 K_5 K_6 K_{10} P_{CO}^{-1}) \quad (72)$$

$$A_H = B_H P_{CO_2}^{-0.5} \quad (B_H = (K_4 K_5 K_6 K_7 K_8 K_{10} K_{11})^{-0.5} P_{CO}^{0.5} P_{H_2O}^{0.5}) \quad (73)$$

$$A_{OH} = B_{OH} P_{CO_2}^{0.5} \quad (B_{OH} = (K_4 K_5 K_6 K_7 K_8^{-1} K_{10} K_{11}^{-1})^{0.5} P_{CO}^{-0.5} P_{H_2O}^{0.5}) \quad (74)$$

$$A_{C_3H_7} = B_{C_3H_7} P_{CO_2}^{-0.5} \quad (B_{C_3H_7} = (K_3^2 K_4 K_5 K_6 K_7 K_8 K_9^2 K_{10} K_{11})^{-0.5} P_{C_3H_6} P_{CO}^{0.5} P_{H_2O}^{0.5}) \quad (75)$$

(note that all the A_x except $A_{C_3H_8}$ are identical to those when the step (1) is assumed as the RDS)

The reaction orders for $P_{C_3H_8}$ (α) and P_{CO_2} (β) on the overall reaction rate should be described as follows: $-1 < \alpha < 1$, $-2 < \beta < 1$. Since this does not agree with the experimental results, the step (2) should not be the RDS.

Assuming step (3) as the RDS (summary):

When the 2nd C-H activation (3) is the RDS, the overall reaction rate can be expressed using the rate constants $\overrightarrow{k_3}$ and $\overleftarrow{k_3}$ as follows:

$$r = \overrightarrow{k_3} \theta_{C_3H_7} (1 - \theta) - \overleftarrow{k_3} \theta_{C_3H_6} \theta_H \approx \frac{\overrightarrow{k_3} (K_1^2 K_2^2 K_4 K_5 K_6 K_7 K_8 K_{10} K_{11})^{0.5} P_{CO}^{-0.5} P_{H_2O}^{-0.5} P_{C_3H_8} P_{CO_2}^{0.5}}{(1 + \sum A_x)^2} \quad (76)$$

Where, A_x are expressed using B_x and $P_{C_3H_8}$ or P_{CO_2} as follows:

$$A_{H_2O} = B_{H_2O} = K_{11}^{-1} P_{H_2O} \quad (77) \quad A_{CO} = B_{CO} = K_{10}^{-1} P_{CO} \quad (78) \quad A_{C_3H_6} = B_{C_3H_6} = K_9^{-1} P_{C_3H_6} \quad (79)$$

$$A_{C_3H_8} = B_{C_3H_8} P_{C_3H_8} (B_{C_3H_8} = K_1) \quad (80) \quad A_{CO_2} = B_{CO_2} P_{CO_2} (B_{CO_2} = K_4) \quad (81)$$

$$A_{CO_2}^* = B_{CO_2}^* P_{CO_2} (B_{CO_2}^* = K_4 K_5) \quad (82) \quad A_O = B_O P_{CO_2} (B_H = K_4 K_5 K_6 K_{10} P_{CO}^{-1}) \quad (83)$$

$$A_H = B_H P_{CO_2}^{-0.5} (B_H = (K_4 K_5 K_6 K_7 K_8 K_{10} K_{11})^{-0.5} P_{CO}^{0.5} P_{H_2O}^{0.5}) \quad (84)$$

$$A_{OH} = B_{OH} P_{CO_2}^{0.5} (B_{OH} = (K_4 K_5 K_6 K_7 K_8^{-1} K_{10} K_{11}^{-1})^{0.5} P_{CO}^{-0.5} P_{H_2O}^{0.5}) \quad (85)$$

$$A_{C_3H_7} = B_{C_3H_7} P_{C_3H_8} P_{CO_2}^{0.5} (B_{C_3H_7} = (K_1^2 K_2^2 K_4 K_5 K_6 K_7 K_8 K_{10} K_{11})^{0.5} P_{CO}^{-0.5} P_{H_2O}^{-0.5}) \quad (86)$$

(all the A_x except $A_{C_3H_8}$ and $A_{C_3H_7}$ are identical to those when the step (1) is assumed as the RDS)

The reaction orders for $P_{C_3H_8}$ (α) and P_{CO_2} (β) on the overall reaction rate should be described as follows: $-1 < \alpha < 1$, $-1.5 < \beta < 1.5$. Since this does not agree with the experimental results, the step (3) should not be the RDS.

Assuming step (4) as the RDS (summary):

When the CO_2 physisorption (4) is the RDS, the overall reaction rate can be expressed using the rate constants $\vec{k}_4$ and $\overleftarrow{k}_4$ as follows:

$$r = \vec{k}_4 P_{CO_2} (1 - \theta) - \overleftarrow{k}_4 \theta_{CO_2} \approx \frac{\vec{k}_4 P_{CO_2}}{1 + \sum A_x} \quad (87)$$

Where, A_x are expressed using B_x and $P_{C_3H_8}$ or P_{CO_2} as follows:

$$A_{H_2O} = B_{H_2O} = K_{11}^{-1} P_{H_2O} \quad (88) \quad A_{CO} = B_{CO} = K_{10}^{-1} P_{CO} \quad (89) \quad A_{C_3H_6} = B_{C_3H_6}$$

$$= K_9^{-1} P_{C_3H_6} \quad (90)$$

$$A_{C_3H_8} = B_{C_3H_8} P_{C_3H_8} (B_{C_3H_8} = K_1) \quad (91) \quad A_H = B_H P_{C_3H_8}^{0.5} (B_H = (K_1 K_2 K_3 K_9)^{0.5} P_{C_3H_6}^{-0.5}) \quad (92)$$

$$A_{C_3H_7} = B_{C_3H_7} P_{C_3H_8}^{0.5} (B_{C_3H_7} = (K_1 K_2 K_3^{-1} K_9^{-1})^{0.5} P_{C_3H_6}^{0.5}) \quad (93)$$

$$A_{OH} = B_{OH} P_{C_3H_8}^{-0.5} (B_{OH} = (K_1 K_2 K_3 K_8^2 K_9 K_{11}^2)^{-0.5} P_{C_3H_6}^{0.5} P_{H_2O}) \quad (94)$$

$$A_O = B_O P_{C_3H_8}^{-1} (B_H = (K_1 K_2 K_3 K_7 K_8 K_9 K_{11})^{-1} P_{C_3H_6} P_{H_2O}) \quad (95)$$

$$A_{CO_2}^* = B_{CO_2}^* P_{C_3H_8}^{-1} (B_H = (K_1 K_2 K_3 K_6 K_7 K_8 K_9 K_{10} K_{11})^{-1} P_{C_3H_6} P_{CO} P_{H_2O}) \quad (96)$$

$$A_{CO_2} = B_{CO_2} P_{C_3H_8}^{-1} (B_H = (K_1 K_2 K_3 K_5 K_6 K_7 K_8 K_9 K_{10} K_{11})^{-1} P_{C_3H_6} P_{CO} P_{H_2O}) \quad (97)$$

The reaction orders for $P_{C_3H_8}$ (α) and P_{CO_2} (β) on the overall reaction rate should be described as follows: $-1 < \alpha < 1$, $\beta = 1$. Since this does not agree with the experimental results, the step (4) should not be the RDS.

Assuming step (5) as the RDS (summary):

When the CO₂ chemisorption (5) is the RDS, the overall reaction rate can be expressed using the rate constants $\overrightarrow{k_5}$ and $\overleftarrow{k_5}$ as follows:

$$r = \overrightarrow{k_5}\theta_{\text{CO}_2} - \overleftarrow{k_5}\theta_{\text{CO}_2}^* \approx \frac{\overrightarrow{k_5}K_4P_{\text{CO}_2}}{1 + \sum A_x} \quad (98)$$

Where, A_x are expressed using B_x and $P_{\text{C}_3\text{H}_8}$ or P_{CO_2} as follows:

$$A_{\text{H}_2\text{O}} = B_{\text{H}_2\text{O}} = K_{11}^{-1}P_{\text{H}_2\text{O}} \quad (99) \quad A_{\text{CO}} = B_{\text{CO}} = K_{10}^{-1}P_{\text{CO}} \quad (100) \quad A_{\text{C}_3\text{H}_6} = B_{\text{C}_3\text{H}_6} = K_9^{-1}P_{\text{C}_3\text{H}_6} \quad (101)$$

$$A_{\text{CO}_2} = B_{\text{CO}_2}P_{\text{CO}_2} \quad (B_{\text{CO}_2} = K_4) \quad (102) \quad A_{\text{C}_3\text{H}_8} = B_{\text{C}_3\text{H}_8}P_{\text{C}_3\text{H}_8} \quad (B_{\text{C}_3\text{H}_8} = K_1) \quad (103)$$

$$A_{\text{H}} = B_{\text{H}}P_{\text{C}_3\text{H}_8}^{0.5} \quad (B_{\text{H}} = (K_1K_2K_3K_9)^{0.5}P_{\text{C}_3\text{H}_6}^{-0.5}) \quad (104)$$

$$A_{\text{C}_3\text{H}_7} = B_{\text{C}_3\text{H}_7}P_{\text{C}_3\text{H}_8}^{0.5} \quad (B_{\text{C}_3\text{H}_7} = (K_1K_2K_3^{-1}K_9^{-1})^{0.5}P_{\text{C}_3\text{H}_6}^{0.5}) \quad (105)$$

$$A_{\text{OH}} = B_{\text{OH}}P_{\text{C}_3\text{H}_8}^{-0.5} \quad (B_{\text{OH}} = (K_1K_2K_3K_8^2K_9K_{11}^2)^{-0.5}P_{\text{C}_3\text{H}_6}^{0.5}P_{\text{H}_2\text{O}}) \quad (106)$$

$$A_{\text{O}} = B_{\text{O}}P_{\text{C}_3\text{H}_8}^{-1} \quad (B_{\text{O}} = (K_1K_2K_3K_7K_8K_9K_{11})^{-1}P_{\text{C}_3\text{H}_6}P_{\text{H}_2\text{O}}) \quad (107)$$

$$A_{\text{CO}_2}^* = B_{\text{CO}_2}^*P_{\text{C}_3\text{H}_8}^{-1} \quad (B_{\text{CO}_2}^* = (K_1K_2K_3K_6K_7K_8K_9K_{10}K_{11})^{-1}P_{\text{C}_3\text{H}_6}P_{\text{CO}}P_{\text{H}_2\text{O}}) \quad (108)$$

(note that all the A_x except A_{CO_2} are identical to those when the step (4) is assumed as the RDS)

The reaction orders for $P_{\text{C}_3\text{H}_8}$ (α) and P_{CO_2} (β) on the overall reaction rate should be described as follows: $-1 < \alpha < 1$, $0 < \beta < 1$. Since this does not agree with the experimental results, the step (5) should not be the RDS.

Assuming step (6) as the RDS (full derivation):

When CO₂ activation (6) is the RDS, the overall reaction rate can be expressed using the rate constants $\overrightarrow{k_6}$ and $\overleftarrow{k_6}$ as follows:

$$r = \overrightarrow{k_6}\theta_{\text{CO}_2}^*(1 - \theta) - \overleftarrow{k_6}\theta_{\text{CO}}\theta_{\text{O}} \quad (109)$$

Here, equilibrium constants K_i except K_6 can be defined assuming quasi-stationary approximation and used for solvation. Some θ_x can be obtained directly by K_i as follows:

$$\theta_{\text{H}_2\text{O}} = K_{11}^{-1}P_{\text{H}_2\text{O}}(1 - \theta) \quad (110), \quad \theta_{\text{CO}} = K_{10}^{-1}P_{\text{CO}}(1 - \theta) \quad (111), \quad \theta_{\text{C}_3\text{H}_6} = K_9^{-1}P_{\text{C}_3\text{H}_6}(1 - \theta) \quad (112),$$

$$\theta_{\text{C}_3\text{H}_8} = K_1P_{\text{C}_3\text{H}_8}(1 - \theta) \quad (113), \quad \theta_{\text{CO}_2} = K_4P_{\text{CO}_2}(1 - \theta) \quad (114)$$

$\theta_{\text{CO}_2}^*$ is obtained using the equations about K_4 and K_5 as follows:

$$\theta_{\text{CO}_2}^* = K_5\theta_{\text{CO}_2} = K_4K_5P_{\text{CO}_2}(1 - \theta) \quad (115)$$

θ_H can be derived by multiplying the equations about K_2 and K_3 , followed by assigning $\theta_{C_3H_8}$ and $\theta_{C_3H_6}$ as follows:

$$K_2 \times K_3 = \frac{\theta_{C_3H_6}}{\theta_{C_3H_8}} \frac{\theta_H^2}{(1-\theta)^2} \quad \therefore \theta_H = \left(\frac{K_2 K_3 \theta_{C_3H_8}}{\theta_{C_3H_6}} \right)^{0.5} (1-\theta) = \left(\frac{K_2 K_3 K_1 P_{C_3H_8}}{K_9^{-1} P_{C_3H_6}} \right)^{0.5} (1-\theta)$$

$$= (K_1 K_2 K_3 K_9)^{0.5} P_{C_3H_6}^{-0.5} P_{C_3H_8}^{0.5} (1-\theta) \quad (116)$$

$\theta_{C_3H_7}$ is obtained by assigning θ_H to the equations about K_3 , then θ_6 as follows:

$$\theta_{C_3H_7} = \frac{\theta_{C_3H_6} \theta_H}{K_3 (1-\theta)} = \frac{K_9^{-1} P_{C_3H_6} (K_1 K_2 K_3 K_9)^{0.5} P_{C_3H_6}^{-0.5} P_{C_3H_8}^{0.5}}{K_3} (1-\theta)$$

$$= (K_1 K_2 K_3^{-1} K_9^{-1})^{0.5} P_{C_3H_6}^{0.5} P_{C_3H_8}^{0.5} (1-\theta) \quad (117)$$

Similarly, θ_{OH} is derived by assigning θ_H and θ_{H_2O} to the equations about K_8 as follows:

$$\theta_{OH} = \frac{\theta_{H_2O}}{K_8 \theta_H} (1-\theta) = \frac{K_{11}^{-1} P_{H_2O}}{K_8 (K_1 K_2 K_3 K_9)^{0.5} P_{C_3H_6}^{-0.5} P_{C_3H_8}^{0.5}} (1-\theta)$$

$$= (K_1 K_2 K_3 K_8^2 K_9 K_{11}^2)^{-0.5} P_{C_3H_6}^{0.5} P_{H_2O} P_{C_3H_8}^{-0.5} (1-\theta) \quad (118)$$

Finally, θ_O is derived by assigning θ_{OH} and θ_H to the equations about K_7 as follows:

$$\theta_O = \frac{\theta_{OH}}{K_7 \theta_H} (1-\theta) = \frac{(K_1 K_2 K_3 K_8^2 K_9 K_{11}^2)^{-0.5} P_{C_3H_6}^{0.5} P_{H_2O} P_{C_3H_8}^{-0.5}}{K_7 (K_1 K_2 K_3 K_9)^{0.5} P_{C_3H_6}^{-0.5} P_{C_3H_8}^{0.5}} (1-\theta)$$

$$= (K_1 K_2 K_3 K_7 K_8 K_9 K_{11})^{-1} P_{C_3H_6} P_{H_2O} P_{C_3H_8}^{-1} (1-\theta) \quad (119)$$

Then, the site conservation equation is solved for $(1-\theta)$ as shown in step (1).

$$(1-\theta) = \left(1 + \sum A_x \right)^{-1} \quad (120)$$

Now, the rate equation is expressed as follows:

$$r = \vec{k}_6 \theta_{CO_2}^* (1-\theta) - \overleftarrow{k}_6 \theta_{CO} \theta_O$$

$$= \frac{\vec{k}_6 K_4 K_5 P_{CO_2} - \overleftarrow{k}_6 (K_1 K_2 K_3 K_7 K_8 K_9 K_{10} K_{11})^{-1} P_{C_3H_6} P_{CO} P_{H_2O} P_{C_3H_8}^{-1}}{(1 + \sum A_x)^2}$$

$$\approx \frac{\vec{k}_6 K_4 K_5 P_{CO_2}}{(1 + \sum A_x)^2} \quad (121)$$

where, the contribution of the reverse reaction was ignored because of the differential condition (very low conversion: $P_{C_3H_8}, P_{CO_2} \gg P_{C_3H_6}, P_{CO}, P_{H_2O}, P_{C_3H_6} P_{CO} P_{H_2O} P_{C_3H_8}^{-1} \lll 1$).

Next, this equation is regarded as a function of the single valuable, $P_{C_3H_8}$ or P_{CO_2} .

Each A_x is decomposed into a constant B_x and $P_{C_3H_8}$ or P_{CO_2} as follows:

$$A_{H_2O} = B_{H_2O} = K_{11}^{-1}P_{H_2O} \quad (122) \quad A_{CO} = B_{CO} = K_{10}^{-1}P_{CO} \quad (123) \quad A_{C_3H_6} = B_{C_3H_6} = K_9^{-1}P_{C_3H_6} \quad (124)$$

$$A_{C_3H_8} = B_{C_3H_8}P_{C_3H_8}^{0.5} (B_{C_3H_8} = K_1) \quad (125) \quad A_{CO_2} = B_{CO_2}P_{CO_2}^{0.5} (B_{CO_2} = K_4) \quad (126)$$

$$A_{CO_2}^* = B_{CO_2}^*P_{CO_2}^{0.5} (B_{CO_2}^* = K_4K_5) \quad (127) \quad A_H = B_HP_{C_3H_8}^{0.5} (B_H = (K_1K_2K_3K_9)^{0.5}P_{C_3H_6}^{-0.5}) \quad (128)$$

$$A_{C_3H_7} = B_{C_3H_7}P_{C_3H_8}^{0.5} (B_{C_3H_7} = (K_1K_2K_3^{-1}K_9^{-1})^{0.5}P_{C_3H_6}^{0.5}) \quad (129)$$

$$A_{OH} = B_{OH}P_{C_3H_8}^{0.5} (B_{OH} = (K_1K_2K_3K_8^2K_9K_{11}^2)^{-0.5}P_{C_3H_6}^{0.5}P_{H_2O}) \quad (130)$$

$$A_O = B_OP_{C_3H_8}^{-1} (B_O = (K_1K_2K_3K_7K_8K_9K_{11})^{-1}P_{C_3H_6}P_{H_2O}) \quad (131)$$

For $P_{C_3H_8}$, the rate equation can be expressed as the function of $P_{C_3H_8}$ as follows: (132)

$$r = \frac{\vec{k}_6 K_4 K_5 P_{CO_2}}{(1 + B_{H_2O} + B_{CO} + B_{C_3H_6} + (B_{CO_2} + B_{CO_2}^*)P_{CO_2} + B_{C_3H_8}P_{C_3H_8}^{0.5} + (B_H + B_{C_3H_7})P_{C_3H_8}^{0.5} + B_{OH}P_{C_3H_8}^{-0.5} + B_OP_{C_3H_8}^{-1})^2}$$

Here, two limits of this equation are considered such that the order dependence of $P_{C_3H_8}$ become the largest and smallest, which provides the possible range of reaction order α .

When $B_O \gg 1 + B_{H_2O} + B_{CO} + B_{C_3H_6} + (B_{CO_2} + B_{CO_2}^*)P_{CO_2}, B_{C_3H_8}, B_H + B_{C_3H_7}, B_{OH}$, this equation can be simplified as follows:

$$r = \frac{B_O^{-2}\vec{k}_6 K_4 K_5 P_{CO_2}}{\left(\frac{1 + B_{H_2O} + B_{CO} + B_{C_3H_6} + (B_{CO_2} + B_{CO_2}^*)P_{CO_2}}{B_O} + \frac{B_{C_3H_8}}{B_O}P_{C_3H_8}^{0.5} + \frac{B_H + B_{C_3H_7}}{B_O}P_{C_3H_8}^{0.5} + \frac{B_{OH}}{B_O}P_{C_3H_8}^{-0.5} + \frac{P_{C_3H_8}^{-1}}{B_O}\right)^2}$$

$$\approx \frac{\vec{k}_6 K_4 K_5 B_O^{-2} P_{CO_2} P_{C_3H_8}^2}{\left(\frac{1 + B_{H_2O} + B_{CO} + B_{C_3H_6} + (B_{CO_2} + B_{CO_2}^*)P_{CO_2}}{B_O}, \frac{B_{C_3H_8}}{B_O}, \frac{B_H + B_{C_3H_7}}{B_O}, \frac{B_{OH}}{B_O}\right)} \ll 1 \quad (133)$$

On the contrary, when $B_{C_3H_8} \gg 1 + B_{H_2O} + B_{CO} + B_{C_3H_6} + (B_{CO_2} + B_{CO_2}^*)P_{CO_2}, B_H + B_{C_3H_7}, B_{OH}, B_O$, this equation can be simplified as follows:

r

$$\begin{aligned}
&= \frac{B_{C_3H_8}^{-2} \overrightarrow{k_6 K_4 K_5} P_{CO_2}}{\left(\frac{1 + B_{H_2O} + B_{CO} + B_{C_3H_6} + (B_{CO_2} + B_{CO_2}^*) P_{CO_2}}{B_{C_3H_8}} + P_{C_3H_8} + \frac{B_H + B_{C_3H_7}}{B_{C_3H_8}} P_{C_3H_8}^{0.5} + \frac{B_{OH}}{B_{C_3H_8}} P_{C_3H_8}^{-0.5} + \frac{B_O}{B_{C_3H_8}} P_{C_3H_8}^{-1} \right)^2} \\
&\approx \frac{\overrightarrow{k_6 K_4 K_5} B_{C_3H_8}^{-2} P_{CO_2} P_{C_3H_8}^{-2}}{\left(\frac{1 + B_{H_2O} + B_{CO} + B_{C_3H_6} + (B_{CO_2} + B_{CO_2}^*) P_{CO_2}}{B_{C_3H_8}}, \frac{B_H + B_{C_3H_7}}{B_{C_3H_8}}, \frac{B_{OH}}{B_{C_3H_8}}, \frac{B_O}{B_{C_3H_8}} \right)} \\
&\ll 1 \quad (134)
\end{aligned}$$

Therefore, the reaction order α can be 2 and -2 at the higher and lower limit and should always fall into this range.

For $P_{C_3H_8}$, the rate equation can be expressed as the function of P_{CO_2} as follows: (135)

r

$$= \frac{\overrightarrow{k_6 K_4 K_5} P_{CO_2}}{\left(1 + B_{H_2O} + B_{CO} + B_{C_3H_6} + B_{C_3H_8} P_{C_3H_8} + (B_H + B_{C_3H_7}) P_{C_3H_8}^{0.5} + B_{OH} P_{C_3H_8}^{-0.5} + B_O P_{C_3H_8}^{-1} + (B_{CO_2} + B_{CO_2}^*) P_{CO_2} \right)^2}$$

Here, two limits of this equation are considered such that the order dependence of P_{CO_2} become the largest and smallest, which provides the possible range of reaction order β .

When $B_{CO_2} + B_{CO_2}^* \ll 1 + B_{H_2O} + B_{CO} + B_{C_3H_6} + B_{C_3H_8} P_{C_3H_8} + (B_H + B_{C_3H_7}) P_{C_3H_8}^{0.5} + B_{OH} P_{C_3H_8}^{-0.5} + B_O P_{C_3H_8}^{-1}$,

this equation can be simplified as follows: (136)

r

$$\begin{aligned}
&= \frac{(1 + B_{H_2O} + B_{CO} + B_{C_3H_6} + B_{C_3H_8} P_{C_3H_8} + (B_H + B_{C_3H_7}) P_{C_3H_8}^{0.5} + B_{OH} P_{C_3H_8}^{-0.5} + B_O P_{C_3H_8}^{-1})^{-2} \overrightarrow{k_6 K_4 K_5} P_{CO_2}}{\left(1 + \frac{B_{CO_2} + B_{CO_2}^*}{1 + B_{H_2O} + B_{CO} + B_{C_3H_6} + B_{C_3H_8} P_{C_3H_8} + (B_H + B_{C_3H_7}) P_{C_3H_8}^{0.5} + B_{OH} P_{C_3H_8}^{-0.5} + B_O P_{C_3H_8}^{-1}} P_{CO_2} \right)^2} \\
&\approx \frac{\overrightarrow{k_6 K_4 K_5} P_{CO_2}}{(1 + B_{H_2O} + B_{CO} + B_{C_3H_6} + B_{C_3H_8} P_{C_3H_8} + (B_H + B_{C_3H_7}) P_{C_3H_8}^{0.5} + B_{OH} P_{C_3H_8}^{-0.5} + B_O P_{C_3H_8}^{-1})^2} \\
&\ll 1
\end{aligned}$$

When $B_{\text{CO}_2} + B_{\text{CO}_2}^* \gg 1 + B_{\text{H}_2\text{O}} + B_{\text{CO}} + B_{\text{C}_3\text{H}_6} + B_{\text{C}_3\text{H}_8}P_{\text{C}_3\text{H}_8} + (B_{\text{H}} + B_{\text{C}_3\text{H}_7})P_{\text{C}_3\text{H}_8}^{0.5} + B_{\text{OH}}P_{\text{C}_3\text{H}_8}^{-0.5} + B_{\text{O}}P_{\text{C}_3\text{H}_8}^{-1}$,

this equation can be simplified as follows: (137)

r

$$= \frac{(B_{\text{CO}_2} + B_{\text{CO}_2}^*)^{-2} \vec{k}_6 K_4 K_5 P_{\text{CO}_2}}{\left(\frac{1 + B_{\text{H}_2\text{O}} + B_{\text{CO}} + B_{\text{C}_3\text{H}_6} + B_{\text{C}_3\text{H}_8}P_{\text{C}_3\text{H}_8} + (B_{\text{H}} + B_{\text{C}_3\text{H}_7})P_{\text{C}_3\text{H}_8}^{0.5} + B_{\text{OH}}P_{\text{C}_3\text{H}_8}^{-0.5} + B_{\text{O}}P_{\text{C}_3\text{H}_8}^{-1} + P_{\text{CO}_2}}{B_{\text{CO}_2} + B_{\text{CO}_2}^*} \right)^2}$$

$$\approx \frac{\vec{k}_6 K_4 K_5 P_{\text{CO}_2}^{-1}}{(B_{\text{CO}_2} + B_{\text{CO}_2}^*)^2}$$

$$\because \left(\frac{1 + B_{\text{H}_2\text{O}} + B_{\text{CO}} + B_{\text{C}_3\text{H}_6} + B_{\text{C}_3\text{H}_8}P_{\text{C}_3\text{H}_8} + (B_{\text{H}} + B_{\text{C}_3\text{H}_7})P_{\text{C}_3\text{H}_8}^{0.5} + B_{\text{OH}}P_{\text{C}_3\text{H}_8}^{-0.5} + B_{\text{O}}P_{\text{C}_3\text{H}_8}^{-1}}{B_{\text{CO}_2} + B_{\text{CO}_2}^*} \ll 1 \right)$$

Based on this derivation, the reaction orders for $P_{\text{C}_3\text{H}_8}$ (α) and P_{CO_2} (β) on the overall reaction rate should be described as follows: $-2 < \alpha < 2$, $-1 < \beta < 1$. This is consistent with the experimental reaction orders, suggesting that the CO_2 activation is the RDS of CO_2 -ODP.

Assuming step (7) as the RDS (summary):

When the OH formation (7) is the RDS, the overall reaction rate can be expressed using the rate constants $\vec{k}_7$ and $\overleftarrow{k}_7$ as follows:

$$r = \vec{k}_7 \theta_{\text{CO}_2}^* (1 - \theta) - \overleftarrow{k}_7 \theta_{\text{CO}} \theta_{\text{O}} \approx \frac{\vec{k}_7 K_1 K_2 K_3 K_4^2 K_5^2 K_6^2 K_9 K_{10}^2 P_{\text{C}_3\text{H}_6}^{-0.5} P_{\text{CO}}^{-1} P_{\text{C}_3\text{H}_8}^{0.5} P_{\text{CO}_2}}{(1 + \sum A_x)^2} \quad (138)$$

Where, A_x are expressed using B_x and $P_{\text{C}_3\text{H}_8}$ or P_{CO_2} as follows:

$$A_{\text{H}_2\text{O}} = B_{\text{H}_2\text{O}} = K_{11}^{-1} P_{\text{H}_2\text{O}} \quad (139) \quad A_{\text{CO}} = B_{\text{CO}} = K_{10}^{-1} P_{\text{CO}} \quad (140) \quad A_{\text{C}_3\text{H}_6} = B_{\text{C}_3\text{H}_6}$$

$$= K_9^{-1} P_{\text{C}_3\text{H}_6} \quad (141)$$

$$A_{\text{C}_3\text{H}_8} = B_{\text{C}_3\text{H}_8} P_{\text{C}_3\text{H}_8} \quad (B_{\text{C}_3\text{H}_8} = K_1) \quad (142) \quad A_{\text{CO}_2} = B_{\text{CO}_2} P_{\text{CO}_2} \quad (B_{\text{CO}_2} = K_4) \quad (143)$$

$$A_{\text{CO}_2}^* = B_{\text{CO}_2}^* P_{\text{CO}_2} \quad (B_{\text{CO}_2}^* = K_4 K_5) \quad (144) \quad A_{\text{O}} = B_{\text{O}} P_{\text{CO}_2} \quad (B_{\text{H}} = K_4 K_5 K_6 K_{10} P_{\text{CO}}^{-1}) \quad (145)$$

$$A_{\text{H}} = B_{\text{H}} P_{\text{C}_3\text{H}_8}^{0.5} \quad (B_{\text{H}} = (K_1 K_2 K_3 K_9)^{0.5} P_{\text{C}_3\text{H}_6}^{-0.5}) \quad (146)$$

$$A_{\text{C}_3\text{H}_7} = B_{\text{C}_3\text{H}_7} P_{\text{C}_3\text{H}_8}^{0.5} \quad (B_{\text{C}_3\text{H}_7} = (K_1 K_2 K_3^{-1} K_9^{-1})^{0.5} P_{\text{C}_3\text{H}_6}^{0.5}) \quad (147)$$

$$A_{\text{OH}} = B_{\text{OH}} P_{\text{C}_3\text{H}_8}^{-0.5} \quad (B_{\text{OH}} = (K_1 K_2 K_3 K_8^2 K_9 K_{11}^2)^{-0.5} P_{\text{C}_3\text{H}_6}^{0.5} P_{\text{H}_2\text{O}}) \quad (148)$$

(note that all the A_x except A_{O} are identical to those when the step (6) is assumed as the RDS)

The reaction orders for $P_{C_3H_8}$ (α) and P_{CO_2} (β) on the overall reaction rate should be described as follows: $-1.5 < \alpha < 1.5$, $-1 < \beta < 1$. Since this does not agree with the experimental results, the step (7) should not be the RDS.

Assuming step (8) as the RDS (summary):

When the H_2O formation (8) is the RDS, the overall reaction rate can be expressed using the rate constants $\overrightarrow{k_8}$ and $\overleftarrow{k_8}$ as follows:

$$r = \overrightarrow{k_8}\theta_{CO}\theta_H - \overleftarrow{k_8}\theta_{H_2O}(1 - \theta) \approx \frac{\overrightarrow{k_8}K_1K_2K_3K_4K_5K_6K_7K_9K_{10}P_{C_3H_6}^{-1}P_{CO}^{-1}P_{C_3H_8}P_{CO_2}}{(1 + \sum A_x)^2} \quad (149)$$

Where, A_x are expressed using B_x and $P_{C_3H_8}$ or P_{CO_2} as follows:

$$A_{H_2O} = B_{H_2O} = K_{11}^{-1}P_{H_2O} \quad (150) \quad A_{CO} = B_{CO} = K_{10}^{-1}P_{CO} \quad (151) \quad A_{C_3H_6} = B_{C_3H_6} = K_9^{-1}P_{C_3H_6} \quad (152)$$

$$A_{C_3H_8} = B_{C_3H_8}P_{C_3H_8} \quad (B_{C_3H_8} = K_1) \quad (153) \quad A_{CO_2} = B_{CO_2}P_{CO_2} \quad (B_{CO_2} = K_4) \quad (154)$$

$$A_{CO_2}^* = B_{CO_2}^*P_{CO_2} \quad (B_{CO_2}^* = K_4K_5) \quad (155) \quad A_O = B_O P_{CO_2} \quad (B_H = K_4K_5K_6K_{10}P_{CO}^{-1}) \quad (156)$$

$$A_H = B_H P_{C_3H_8}^{0.5} \quad (B_H = (K_1K_2K_3K_9)^{0.5}P_{C_3H_6}^{-0.5}) \quad (157)$$

$$A_{C_3H_7} = B_{C_3H_7}P_{C_3H_8}^{0.5} \quad (B_{C_3H_7} = (K_1K_2K_3^{-1}K_9^{-1})^{0.5}P_{C_3H_6}^{0.5}) \quad (158)$$

$$A_{OH} = B_{OH}P_{C_3H_8}^{0.5}P_{CO_2} \quad (B_{OH} = (K_1K_2K_3K_4^2K_5^2K_6^2K_7^2K_9K_{10}^2)^{0.5}P_{C_3H_6}^{-0.5}P_{CO}^{-1}) \quad (159)$$

(note that all the A_x except A_{OH} are identical to those when the step (7) is assumed as the RDS)

The reaction orders for $P_{C_3H_8}$ (α) and P_{CO_2} (β) on the overall reaction rate should be described as follows: $-1 < \alpha < 1$, $-1 < \beta < 1$. Since this does not agree with the experimental results, the step (8) should not be the RDS.

Assuming step (9) as the RDS (summary):

When the C_3H_6 desorption (9) is the RDS, the overall reaction rate can be expressed using the rate constants $\overrightarrow{k_9}$ and $\overleftarrow{k_9}$ as follows:

$$r = \overrightarrow{k_9}\theta_{C_3H_6} - \overleftarrow{k_9}P_{C_3H_6}(1 - \theta) \approx \frac{\overrightarrow{k_9}K_1K_2K_3K_4K_5K_6K_7K_8K_{10}K_{11}P_{CO}^{-1}P_{H_2O}^{-1}P_{C_3H_8}P_{CO_2}}{1 + \sum A_x} \quad (160)$$

Where, A_x are expressed using B_x and $P_{C_3H_8}$ or P_{CO_2} as follows:

$$A_{H_2O} = B_{H_2O} = K_{11}^{-1}P_{H_2O} \quad (161) \quad A_{CO} = B_{CO} = K_{10}^{-1}P_{CO} \quad (162)$$

$$A_{C_3H_8} = B_{C_3H_8}P_{C_3H_8} \quad (B_{C_3H_8} = K_1) \quad (163) \quad A_{CO_2} = B_{CO_2}P_{CO_2} \quad (B_{CO_2} = K_4) \quad (164)$$

$$A_{\text{CO}_2}^* = B_{\text{CO}_2}^* P_{\text{CO}_2} (B_{\text{CO}_2}^* = K_4 K_5) \quad (165) \quad A_{\text{O}} = B_{\text{O}} P_{\text{CO}_2} (B_{\text{H}} = K_4 K_5 K_6 K_{10} P_{\text{CO}}^{-1}) \quad (166)$$

$$A_{\text{H}} = B_{\text{H}} P_{\text{CO}_2}^{-0.5} (B_{\text{H}} = (K_4 K_5 K_6 K_7 K_8 K_{10} K_{11})^{-0.5} P_{\text{CO}}^{0.5} P_{\text{H}_2\text{O}}^{0.5}) \quad (167)$$

$$A_{\text{C}_3\text{H}_7} = B_{\text{C}_3\text{H}_7} P_{\text{C}_3\text{H}_8} P_{\text{CO}_2}^{0.5} (B_{\text{C}_3\text{H}_7} = (K_1^2 K_2^2 K_4 K_5 K_6 K_7 K_8 K_{10} K_{11})^{0.5} P_{\text{CO}}^{-0.5} P_{\text{H}_2\text{O}}^{-0.5}) \quad (168)$$

$$A_{\text{OH}} = B_{\text{OH}} P_{\text{CO}_2} (B_{\text{OH}} = (K_4 K_5 K_6 K_7 K_8^{-1} K_{10} K_{11}^{-1})^{0.5} P_{\text{CO}}^{-0.5} P_{\text{H}_2\text{O}}^{0.5}) \quad (169)$$

$$A_{\text{C}_3\text{H}_6} = B_{\text{C}_3\text{H}_6} P_{\text{C}_3\text{H}_8} P_{\text{CO}_2} (B_{\text{C}_3\text{H}_6} = K_1 K_2 K_3 K_4 K_5 K_6 K_7 K_8 K_{10} K_{11} P_{\text{CO}} P_{\text{H}_2\text{O}}) \quad (170)$$

The reaction orders for $P_{\text{C}_3\text{H}_8}$ (α) and P_{CO_2} (β) on the overall reaction rate should be described as follows: $0 < \alpha < 1$, $0 < \beta < 1.5$. Since this does not agree with the experimental results, the step (9) should not be the RDS.

Assuming step (10) as the RDS (summary):

When the CO desorption (10) is the RDS, the overall reaction rate can be expressed using the rate constants $\overrightarrow{k}_{10}$ and $\overleftarrow{k}_{10}$ as follows:

$$r = \overrightarrow{k}_{10} \theta_{\text{CO}} - \overleftarrow{k}_{10} P_{\text{CO}} (1 - \theta) \approx \frac{\overrightarrow{k}_{10} K_1 K_2 K_3 K_4 K_5 K_6 K_7 K_8 K_9 K_{11} P_{\text{C}_3\text{H}_6}^{-1} P_{\text{H}_2\text{O}}^{-1} P_{\text{C}_3\text{H}_8} P_{\text{CO}_2}}{1 + \sum A_x} \quad (171)$$

Where, A_x are expressed using B_x and $P_{\text{C}_3\text{H}_8}$ or P_{CO_2} as follows:

$$A_{\text{H}_2\text{O}} = B_{\text{H}_2\text{O}} = K_{11}^{-1} P_{\text{H}_2\text{O}} \quad (172) \quad A_{\text{C}_3\text{H}_6} = B_{\text{C}_3\text{H}_6} = K_9^{-1} P_{\text{C}_3\text{H}_6} \quad (173)$$

$$A_{\text{C}_3\text{H}_8} = B_{\text{C}_3\text{H}_8} P_{\text{C}_3\text{H}_8} (B_{\text{C}_3\text{H}_8} = K_1) \quad (174)$$

$$A_{\text{CO}_2} = B_{\text{CO}_2} P_{\text{CO}_2} (B_{\text{CO}_2} = K_4) \quad A_{\text{CO}_2}^* = B_{\text{CO}_2}^* P_{\text{CO}_2} (B_{\text{CO}_2}^* = K_4 K_5) \quad (175)$$

$$A_{\text{H}} = B_{\text{H}} P_{\text{C}_3\text{H}_8}^{0.5} (B_{\text{H}} = (K_1 K_2 K_3 K_9)^{0.5} P_{\text{C}_3\text{H}_6}^{-0.5}) \quad (176)$$

$$A_{\text{C}_3\text{H}_7} = B_{\text{C}_3\text{H}_7} P_{\text{C}_3\text{H}_8}^{0.5} (B_{\text{C}_3\text{H}_7} = (K_1 K_2 K_3^{-1} K_9^{-1})^{0.5} P_{\text{C}_3\text{H}_6}^{0.5}) \quad (177)$$

$$A_{\text{OH}} = B_{\text{OH}} P_{\text{C}_3\text{H}_8}^{-0.5} (B_{\text{OH}} = (K_1 K_2 K_3 K_8^2 K_9 K_{11}^2)^{-0.5} P_{\text{C}_3\text{H}_6}^{0.5} P_{\text{H}_2\text{O}}) \quad (178)$$

$$A_{\text{O}} = B_{\text{O}} P_{\text{C}_3\text{H}_8}^{-1} (B_{\text{H}} = (K_1 K_2 K_3 K_7 K_8 K_9 K_{11})^{-1} P_{\text{C}_3\text{H}_6} P_{\text{H}_2\text{O}}) \quad (179)$$

$$A_{\text{CO}} = B_{\text{CO}} P_{\text{C}_3\text{H}_8} P_{\text{CO}_2} (B_{\text{H}} = K_1 K_2 K_3 K_4 K_5 K_6 K_7 K_8 K_9 K_{11} P_{\text{C}_3\text{H}_6}^{-1} P_{\text{H}_2\text{O}}^{-1}) \quad (180)$$

The reaction orders for $P_{\text{C}_3\text{H}_8}$ (α) and P_{CO_2} (β) on the overall reaction rate should be described as follows: $0 < \alpha < 2$, $0 < \beta < 1$. Since this does not agree with the experimental results, the step (10) should not be the RDS.

Assuming step (11) as the RDS (summary):

When the H₂O desorption (11) is the RDS, the overall reaction rate can be expressed using the rate constants $\overrightarrow{k_{11}}$ and $\overleftarrow{k_{11}}$ as follows:

$$r = \overrightarrow{k_{11}}\theta_{\text{H}_2\text{O}} - \overleftarrow{k_{11}}P_{\text{H}_2\text{O}}(1 - \theta) \approx \frac{\overrightarrow{k_{11}}K_1K_2K_3K_4K_5K_6K_7K_8K_9K_{10}P_{\text{C}_3\text{H}_6}^{-1}P_{\text{CO}}^{-1}P_{\text{C}_3\text{H}_8}P_{\text{CO}_2}}{1 + \sum A_x} \quad (181)$$

Where, A_x are expressed using B_x and $P_{\text{C}_3\text{H}_8}$ or P_{CO_2} as follows:

$$A_{\text{CO}} = B_{\text{CO}} = K_{10}^{-1}P_{\text{CO}} \quad (182) \quad A_{\text{C}_3\text{H}_6} = B_{\text{C}_3\text{H}_6} = K_9^{-1}P_{\text{C}_3\text{H}_6} \quad (183)$$

$$A_{\text{C}_3\text{H}_8} = B_{\text{C}_3\text{H}_8}P_{\text{C}_3\text{H}_8} \quad (B_{\text{C}_3\text{H}_8} = K_1) \quad (184) \quad A_{\text{CO}_2} = B_{\text{CO}_2}P_{\text{CO}_2} \quad (B_{\text{CO}_2} = K_4) \quad (185)$$

$$A_{\text{CO}_2}^* = B_{\text{CO}_2}^*P_{\text{CO}_2} \quad (B_{\text{CO}_2}^* = K_4K_5) \quad (186) \quad A_{\text{O}} = B_{\text{O}}P_{\text{CO}_2} \quad (B_{\text{H}} = K_4K_5K_6K_{10}P_{\text{CO}}^{-1}) \quad (187)$$

$$A_{\text{H}} = B_{\text{H}}P_{\text{C}_3\text{H}_8}^{0.5} \quad (B_{\text{H}} = (K_1K_2K_3K_9)^{0.5}P_{\text{C}_3\text{H}_6}^{-0.5}) \quad (188)$$

$$A_{\text{C}_3\text{H}_7} = B_{\text{C}_3\text{H}_7}P_{\text{C}_3\text{H}_8}^{0.5} \quad (B_{\text{C}_3\text{H}_7} = (K_1K_2K_3^{-1}K_9^{-1})^{0.5}P_{\text{C}_3\text{H}_6}^{0.5}) \quad (189)$$

$$A_{\text{OH}} = B_{\text{OH}}P_{\text{C}_3\text{H}_8}^{0.5}P_{\text{CO}_2} \quad (B_{\text{OH}} = (K_1K_2K_3K_4^2K_5^2K_6^2K_7^2K_9K_{10}^2)^{0.5}P_{\text{C}_3\text{H}_6}^{-0.5}P_{\text{CO}}^{-1}) \quad (190)$$

$$A_{\text{H}_2\text{O}} = B_{\text{H}_2\text{O}}P_{\text{C}_3\text{H}_8}P_{\text{CO}_2} \quad (B_{\text{H}_2\text{O}} = K_1K_2K_3K_4K_5K_6K_7K_8K_9K_{10}P_{\text{C}_3\text{H}_6}^{-1}P_{\text{CO}}^{-1}) \quad (191)$$

The reaction orders for $P_{\text{C}_3\text{H}_8}$ (α) and P_{CO_2} (β) on the overall reaction rate should be described as follows: $0 < \alpha < 1$, $0 < \beta < 1$. Since this does not agree with the experimental results, the step (11) should not be the RDS.

Thus, the theoretical reaction orders were consistent with the experimental orders only when CO₂ activation (6) was assumed as the RDS. Based on these results, we concluded that the RDS of CO₂-ODP on Pt–Co–In/CeO₂ was CO₂ activation.

One may think that this conclusion looks counterintuitive, because P_{CO_2} negatively contributes to the overall reaction rate even though CO₂ activation is the RDS. However, this is explained by the following interpretations. First, since adsorption of CO₂ should be stronger than C₃H₈, surface concentration of CO₂ should be much higher than C₃H₈. Note that C₃H₈ is a saturated light alkane, of which adsorption is physisorption and typically very weak, whereas CO₂ can be chemisorbed as shown in the DFT study (energy barrier: C₃H₈ desorption; 17 kJmol⁻¹, chemisorbed to physisorbed CO₂; 24 kJmol⁻¹). When the surface concentration of CO₂ is high, its dependence on P_{CO_2} and the rate dependence on P_{CO_2} (β) should become low. Second, the reverse reaction of the RDS, CO+O→CO₂, can be accelerated by consuming O atom by reacting with eliminated H atoms from C₃H₈. Therefore, the competitive and stronger

adsorption of CO₂ than C₃H₈ inhibits C₃H₈ activation and H release, which negatively contributes to the overall reaction rate.

Kinetic Analysis based on Microkinetic modeling

To construct microkinetic modeling for CO₂-ODP, we calculated the rate constant of each elementary step as follows. The rate constant, k , is expressed as:

$$k = A \exp\left(-\frac{E_A}{k_B T}\right) \quad (192)$$

where A and E_A is the pre-exponential factor and the activation energy of the reaction, respectively. According to the transition state theory, the rate constant is also expressed by using the partition functions of the initial and transition states (q_{IS} and q_{TS} , respectively) and E_A :

$$k = \frac{k_B T}{h} \frac{q_{TS}}{q_{IS}} \exp\left(-\frac{E_A}{k_B T}\right) \quad (193)$$

Comparing of these equations, the pre-exponential factor, A can be expressed as:

$$A = \frac{k_B T}{h} \frac{q_{TS}}{q_{IS}} \quad (194)$$

The partition function, q is expressed as:

$$q = q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} \quad (195)$$

where q_{trans} , q_{rot} , and q_{vib} are the translational, rotational, and vibrational partition functions, respectively (see p.S6, Computational details, for the expression of q_{trans} and q_{rot}).

The vibrational partition function, q_{vib} , is expressed as:

$$q_{\text{vib}} = \prod_n \frac{1}{1 - \exp(-h\nu_n/k_B T)} \quad (196)$$

where, ν_n is the vibrational frequency of the n 'th vibrational mode. For surface species, the rotational and translational contributions were converted into vibrational modes; therefore, the total partition function can be written only by vibrational modes: $q = q_{\text{vib}}$. Spurious frequencies lower than 100 cm⁻¹ were replaced with 50 cm⁻¹ in a similar manner mentioned in p.S6. For physisorption of molecules, q_{TS}/q_{IS} was considered to be unity.

At a steady-state, the coverage of each adsorbate reaches constant and can be regarded as time-invariant, which satisfies the following equations:

$$\frac{\partial}{\partial t}\theta_x = 0 \quad (197)$$

$$\begin{aligned} \frac{\partial}{\partial t}\theta_{\text{C}_3\text{H}_8} &= r_1 - r_2 = \vec{k}_1 P_{\text{C}_3\text{H}_8}(1 - \theta) - \overleftarrow{k}_1 \theta_{\text{C}_3\text{H}_8} - \vec{k}_2 \theta_{\text{C}_3\text{H}_8}(1 - \theta) + \overleftarrow{k}_2 \theta_{\text{C}_3\text{H}_7} \theta_{\text{H}} \\ &= 0 \quad (198) \end{aligned}$$

$$\begin{aligned} \frac{\partial}{\partial t}\theta_{\text{C}_3\text{H}_7} &= r_2 - r_3 = \vec{k}_2 \theta_{\text{C}_3\text{H}_8}(1 - \theta) - \overleftarrow{k}_2 \theta_{\text{C}_3\text{H}_7} \theta_{\text{H}} - \vec{k}_3 \theta_{\text{C}_3\text{H}_7}(1 - \theta) + \overleftarrow{k}_3 \theta_{\text{C}_3\text{H}_6} \theta_{\text{H}} \\ &= 0 \quad (199) \end{aligned}$$

$$\begin{aligned} \frac{\partial}{\partial t}\theta_{\text{C}_3\text{H}_6} &= r_3 - r_9 = \vec{k}_3 \theta_{\text{C}_3\text{H}_7}(1 - \theta) - \overleftarrow{k}_3 \theta_{\text{C}_3\text{H}_6} \theta_{\text{H}} - \vec{k}_9 \theta_{\text{C}_3\text{H}_6} + \overleftarrow{k}_9 P_{\text{C}_3\text{H}_6}(1 - \theta) \\ &= 0 \quad (200) \end{aligned}$$

$$\frac{\partial}{\partial t}\theta_{\text{CO}_2} = r_4 - r_5 = \vec{k}_4 P_{\text{CO}_2}(1 - \theta) - \overleftarrow{k}_4 \theta_{\text{CO}_2} - \vec{k}_5 \theta_{\text{CO}_2} + \overleftarrow{k}_5 \theta_{\text{CO}_2}^* = 0 \quad (201)$$

$$\frac{\partial}{\partial t}\theta_{\text{CO}_2}^* = r_5 - r_6 = \vec{k}_5 \theta_{\text{CO}_2} - \overleftarrow{k}_5 \theta_{\text{CO}_2}^* - \vec{k}_6 \theta_{\text{CO}_2}^*(1 - \theta) + \overleftarrow{k}_6 \theta_{\text{CO}} \theta_{\text{O}} = 0 \quad (202)$$

$$\frac{\partial}{\partial t}\theta_{\text{OH}} = r_7 - r_8 = \vec{k}_7 \theta_{\text{O}} \theta_{\text{H}} - \overleftarrow{k}_7 \theta_{\text{OH}}(1 - \theta) - \vec{k}_8 \theta_{\text{OH}} \theta_{\text{H}} + \overleftarrow{k}_8 \theta_{\text{H}_2\text{O}}(1 - \theta) = 0 \quad (203)$$

$$\frac{\partial}{\partial t}\theta_{\text{O}} = r_6 - r_7 = \vec{k}_6 \theta_{\text{CO}_2}^*(1 - \theta) - \overleftarrow{k}_6 \theta_{\text{CO}} \theta_{\text{O}} - \vec{k}_7 \theta_{\text{O}} \theta_{\text{H}} + \overleftarrow{k}_7 \theta_{\text{OH}}(1 - \theta) = 0 \quad (204)$$

$$\frac{\partial}{\partial t}\theta_{\text{CO}} = r_6 - r_{10} = \vec{k}_6 \theta_{\text{CO}_2}^*(1 - \theta) - \overleftarrow{k}_6 \theta_{\text{CO}} \theta_{\text{O}} - \vec{k}_{10} \theta_{\text{CO}} + \overleftarrow{k}_{10} P_{\text{CO}}(1 - \theta) = 0 \quad (205)$$

$$\frac{\partial}{\partial t}\theta_{\text{H}_2\text{O}} = r_8 - r_{11} = \vec{k}_8 \theta_{\text{OH}} \theta_{\text{H}} - \overleftarrow{k}_8 \theta_{\text{H}_2\text{O}}(1 - \theta) - \vec{k}_{11} \theta_{\text{H}_2\text{O}} + \overleftarrow{k}_{11} P_{\text{H}_2\text{O}}(1 - \theta) = 0 \quad (206)$$

$$\begin{aligned} \frac{\partial}{\partial t}\theta_{\text{H}} &= r_2 + r_3 - r_7 - r_8 = \vec{k}_2 \theta_{\text{C}_3\text{H}_8}(1 - \theta) - \overleftarrow{k}_2 \theta_{\text{C}_3\text{H}_7} \theta_{\text{H}} + \vec{k}_3 \theta_{\text{C}_3\text{H}_7}(1 - \theta) - \overleftarrow{k}_3 \theta_{\text{C}_3\text{H}_6} \theta_{\text{H}} \\ &\quad - \vec{k}_7 \theta_{\text{O}} \theta_{\text{H}} + \overleftarrow{k}_7 \theta_{\text{OH}}(1 - \theta) - \vec{k}_8 \theta_{\text{OH}} \theta_{\text{H}} + \overleftarrow{k}_8 \theta_{\text{H}_2\text{O}}(1 - \theta) \\ &= 0 \quad (207) \end{aligned}$$

Besides, the number of adsorption site was considered to be conserved.

$$\begin{aligned} \theta_{\text{C}_3\text{H}_8} + \theta_{\text{C}_3\text{H}_7} + \theta_{\text{C}_3\text{H}_6} + \theta_{\text{CO}_2} + \theta_{\text{CO}_2}^* + \theta_{\text{CO}} + \theta_{\text{O}} + \theta_{\text{H}} + \theta_{\text{OH}} + \theta_{\text{H}_2\text{O}} + (1 - \theta) \\ = 1 \quad (208) \end{aligned}$$

We obtained a set of simultaneous equations for θ_x (11 variables and equations) by assigning the DFT-derived rate constants of each forward/reverse reactions and the relative pressures of gas molecules ($P_{C_3H_8} = P_{CO_2} = 0.24$ and $P_{C_3H_6} = P_{CO} = P_{H_2O} = 0.01$, dimensionless values) to each equation. Note that these values are identical to those used in the free-energy calculation in the DFT study and assume a differential condition as observed in the experimental kinetic study. They were numerically solved by the Newton's method to obtain the surface coverages. The forward and reverse reaction rates of each elementary step at a steady-state were obtained as the products of thus calculated surface coverages and the corresponding rate constants based on each rate equation (Tables 2.6. and 2.7.). The forward and reverse reaction rates are identical or very close to each other in all the steps except the RDS (CO_2 activation), which is consistent with the steady-state approximation.

For the simulation of a macroscopic reaction rate R ($mLmin^{-1}$, as a flow rate at room temperature under an atmospheric pressure for the comparison with the experimental condition), the predicted overall reaction rate of the RDS ($\vec{r}_6 - \overleftarrow{r}_6/s^{-1}$) was multiplied with the total amount of Pt included in the catalyst (M_{Pt}/mol), Pt dispersion (D_{Pt}), and the pressure calibration factor (P_{exp}/P°) as follows:

$$R(mL \cdot min^{-1}) = (\vec{r}_6 - \overleftarrow{r}_6)(s^{-1}) \times M_{Pt}(mol) \times D_{Pt} \times \frac{P_{exp}(Pa)}{P^\circ(Pa)} \\ \times \frac{8.31(Pa \cdot m^3/(mol \cdot K)) \times 298.15(K)}{101325(Pa)} \times 60 \left(\frac{min^{-1}}{s^{-1}} \right) \times 10^6 \left(\frac{mL}{m^3} \right) \quad (209)$$

Where, P_{exp} and P° are the experimental total pressure (in this study, $P_{exp} = 101325$ Pa) and the unit pressure in the SI unit system ($P^\circ = 1$ Pa), respectively. The pressure calibration factor is necessary to convert the reaction rate under the dimension less condition (the relative pressure terms have no information about the absolute pressure) to that under an experimental absolute pressure. The Pt dispersion was regarded as the half of metal dispersion (Pt+Co, Pt/Co =1) measured by CO chemisorption because CO adsorbs on Co sites as well as Pt sites. For the simulation of temperature-dependence, all the partition functions, rate constants, and reaction rates were calculated individually for each temperature (500°C–540°C).

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Chapter Three

High-entropy intermetallics on ceria as efficient catalysts
for the oxidative dehydrogenation of propane using CO₂

3.1 Introduction

Global demand for propylene, a raw material for petrochemicals, has resulted in a significant supply-demand gap as the feedstock has shifted from naphtha to shale gas production. As a result, increasing the supply of propylene from shale gas is currently highly desired in highly efficient technologies.^{[1],[2],[3]} Direct dehydrogenation of propane (DDP) is an appealing on-purpose approach in principle. However, high propylene yields are typically obtained at high reaction temperatures (typically $\geq 600^\circ\text{C}$) owing to its endothermicity.^[4] Furthermore, under such harsh conditions, undesired side reactions (over-dehydrogenation and C–C cracking) occur, resulting in coke accumulation and, eventually, the catalysts in use must be regenerated by coke combustion in a short period, decreasing productivity for a stable and continuous supply of propylene.^[2] The oxidative dehydrogenation of propane using CO_2 as a soft oxidant (CO_2 -ODP: $\text{C}_3\text{H}_8 + \text{CO}_2 \rightarrow \text{C}_3\text{H}_6 + \text{CO} + \text{H}_2\text{O}$)^{[5],[6]} is a promising alternative to DDP, where CO_2 can remove carbon via the reverse Boudouard reaction ($\text{CO}_2 + \text{C} \rightarrow 2\text{CO}$).^[7] In comparison to ODP using O_2 , CO_2 -ODP avoids oxidation of propylene and the catalyst. Moreover, converting CO_2 into a value-added chemical is an appealing approach for a carbon neutral and green sustainable society.

Many researchers have focused in recent decades on the use of metal oxides such as V_2O_5 ,^[8] Cr_2O_3 ,^{[9],[10]} Ga_2O_3 ,^[11] and In_2O_3 ^[12] as good CO_2 -ODP catalysts. Despite the fact that chromium oxide species dispersed on mesoporous silica showed the highest catalytic activity with moderate propylene selectivity (ca. 80%), the CO_2 utilization efficiency (excess CO_2 is necessary) and catalyst stability were low. Transition metal-based catalysts like Pd, Fe_3Ni , and Pt–Co–In^{[5],[13],[14]} have been receiving more attention in CO_2 -ODP, owing to their multifunctional properties for simultaneous activation of propane and CO_2 .^{[15],[16],[17]} C–H activation of propane and CO_2 reduction can be mediated by noble metals (Pt and Pd)^{[18],[19]} and the late 3d transition metals (Co, Ni, and Cu),^{[20],[21]} respectively; thus, an appropriate combination of these metals allows for the construction of a dual functional catalyst for propane and CO_2 conversion. Using CeO_2 or Ce-based oxides as a support of the metallic phase is also a promising way for CO_2 -ODP owing to various promotional effects such as Mars-van Kreveren-type CO_2 activation^[22–24] or coke combustion,^{[14],[25]} and strong metal-support interaction to tune the character of the active phase.^{[26],[27]} We recently reported that the Pt–Co–In/ CeO_2 catalyst exhibited remarkably high catalytic activity and CO_2 utilization efficiency.^[14] However, irreversible catalyst deactivation still occurred, which was likely caused by the accumulation of incombustible coke and nanoparticle sintering. Therefore, it is highly desired

to develop a more efficient catalyst that is stable at high temperatures, very selective to minimize side reactions, and can burn coke more efficiently.

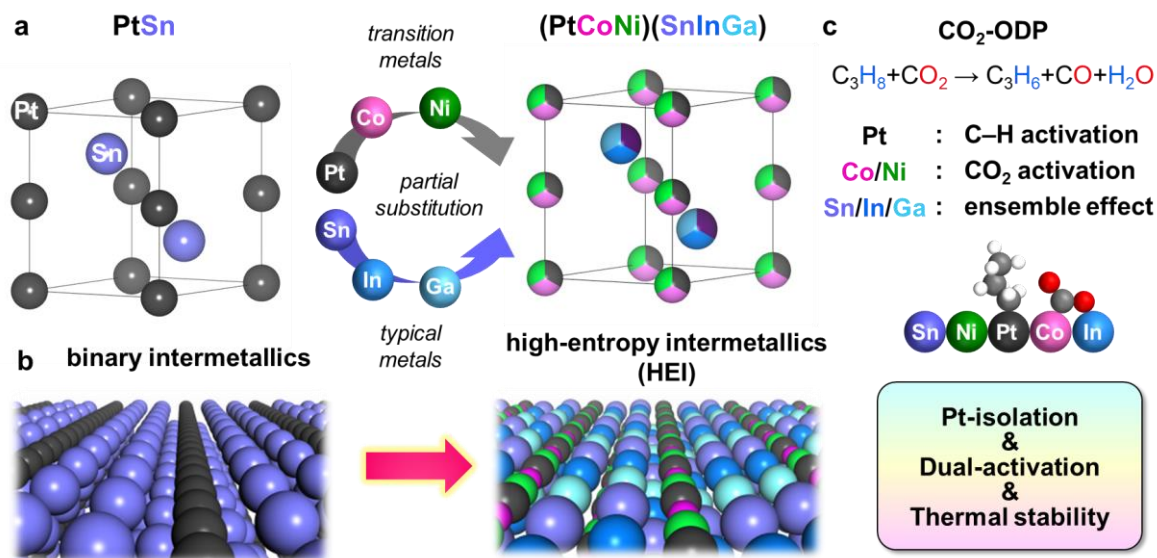


Figure 3.1.: Aim of this work. **a** Catalyst design concept based on HEI. Pt and Sn sites in intermetallic PtSn (hexagonal NiAs-type structure, space group: $P6_3/mmc$) are partially substituted by Co/Ni and In/Ga, respectively, forming a PtSn-type HEI (PtCoNi)(SnInGa). **b** Atomic arrangement of the most stable (110) surfaces of PtSn (left) and (PtCoNi)(SnInGa) HEI (right). **c** The role of each metal and the effect of multi-metallization on the catalysis of CO₂-ODP.

To address this challenge, we developed a novel catalyst design concept based on high-entropy intermetallics (HEIs).^{[28],[29]} HEIs are multi-metallic alloys with five or more elements and specific crystal structures originating from the parent binary intermetallics (Figure 3.1). HEIs, as opposed to high-entropy alloys (HEAs) with random atomic distribution, can provide ordered reaction environments suitable for CO₂-ODP. To minimize unwanted side reactions, the intermetallic PtSn, which is a highly selective DDP catalyst, was chosen as the parent platform of HEI to minimize undesired side reactions. However, alloying with typical metals is known to significantly decrease the CO₂ activation ability of Pt. Therefore, PtSn's Pt site was then partially substituted with Ni and Co to incorporate metals more capable of CO₂ activation. This has another merit to further dilute Pt–Pt sites for higher selectivity. On the other hand, the Sn site of PtSn was partially replaced with In and Ga, increasing mixing entropy and the resulting thermodynamic stability. When the formation entropy of the parent intermetallics is significantly negative (PtSn: $\Delta H_f = -74.0 \text{ kJmol}^{-1}$),^[30] site-specific multi-

metallization is possible. The higher number of constituent metals also enhances the kinetic stability of nanoparticles owing to the sluggish diffusion effect, which prevents sintering or segregation.^[31] Furthermore, CeO₂ was used as a catalyst support for facile CO₂ capture and coke combustion because it is basic and can release oxygen, which is advantageous for these purposes.^{[5],[32]} In this case, we demonstrate that a PtCoNiInGaSn/CeO₂ catalyst with a HEI structure (donated as HEI/CeO₂) based on intermetallic PtSn can act as a highly efficient CO₂-ODP catalyst, exhibiting exceptional catalytic activity, C₃H₆ selectivity, coke resistance, thermal stability, and CO₂ utilization stability.

3.2 Experimental section

3.2.1 Catalyst preparation

Pt/CeO₂, Pt–Co–In/CeO₂, HEI/CeO₂, Pt–Sn/CeO₂, Pt–Co–In/CeO₂, quinary, HEA and HEI/CeO₂ (Pt: 1 wt%) were prepared by a conventional impregnation method using H₂PtCl₆ (aqueous solution, Kojima Chemicals, Pt 3.71 wt%), In(NO₃)₃·3H₂O, Co(NO₃)₂·6H₂O, Ni(NO₃)₂·6H₂O, Ga(NO₃)₃·6H₂O and SnCl₂ as metal precursors. The CeO₂ support (JRC-CEO-2, S_{BET} = 123.1 m²g⁻¹) was added to a vigorously stirred aqueous solution (50 ml H₂O per gram of CeO₂) containing Pt and the corresponding second and/or third metal precursor(s) (Pt:Co:Ni:Sn:In:Ga=1:1:1:1:1:1, Pt:Ni=1:1, Pt:Co =1:1, Pt:In =1:1, Pt:Ga =1:1, Pt:Sn = 1:1, and Pt:Co:In =1:1:2), followed by stirring for 3 h at room temperature. The mixture was dried under a reduced pressure at 50 °C using a rotary evaporator, followed by calcination under flowing air at 500°C for 1 h and reduction under flowing H₂ (50 ml/min) at 600 °C for 1 h. HEI/ Al₂O₃ catalysts (Al₂O₃ prepared by calcination of boehmite [γ -AlOOH, supplied by SASOL chemicals] at 900 °C for 3 h, γ -phase), Pt:Co:Ni:Sn:In:Ga=1:1:1:1:1:1, Pt: 1 wt%) was also prepared by the same method mentioned above. HEI/SiO₂ was synthesized by the pore-filling co-impregnation method, which can deposit all the metal components on the SiO₂ support without loss^[17].

3.2.2 Catalytic test

Under atmospheric pressure, CO₂-ODP was performed in a quartz fixed-bed reactor with a 6 mm internal diameter. Prior to the catalytic reactions, the catalyst (0.10 g) diluted with sea sand (0.90 g, Miyazaki Chemical, 99.9%) was treated with flowing hydrogen (10 mL/min) at 600°C for 0.5 hours. The catalysts were then evaluated by feeding a reactant gas mixture (C₃H₈: CO₂: He = 1:1:2, a total flow rate of 20 mL/min) through them. The gas phase was analyzed and

quantified using a downstream-equipped online thermal conductivity detection gas chromatograph (Shimadzu GC-8A, column: Gaskuropack 54, 80/100 SUS 2m×3mm I.D.). C₃H₈, C₃H₆, C₂H₄, C₂H₆, CH₄, CO, and CO₂ could be separated under the following condition (see Figure 3.35 for a GC chart): carrier gas; He 30mL min⁻¹, column temperature; 50°C (constant). The conversions of C₃H₈ and CO₂ were defined as follows:

$$\text{C}_3\text{H}_8 \text{ conversion: } X_{\text{C}_3\text{H}_8} (\%) = \frac{F_{\text{C}_3\text{H}_8}^{\text{in}} - F_{\text{C}_3\text{H}_8}^{\text{out}}}{F_{\text{C}_3\text{H}_8}^{\text{in}}} \times 100 \quad (1)$$

$$\text{CO}_2 \text{ conversion: } X_{\text{CO}_2} (\%) = \frac{F_{\text{CO}_2}^{\text{in}} - F_{\text{CO}_2}^{\text{out}}}{F_{\text{CO}_2}^{\text{in}}} \times 100 \quad (2)$$

where, F_x^{in} and F_x^{out} indicate the x (mL min⁻¹), inlet and outlet flow rates of respectively.

In this reaction, CO can be formed from C_xH_y by dry reforming as well as from CO₂ via the reverse water gas shift reaction, which was distinguished as follows:

$$\text{CO formed from CO}_2: F_{\text{CO}}^{\text{CO}_2} = F_{\text{CO}_2}^{\text{in}} - F_{\text{CO}_2}^{\text{out}} \quad (\text{mL} \cdot \text{min}^{-1}) \quad (3)$$

$$\text{CO formed from C}_x\text{H}_y: F_{\text{CO}}^{\text{C}_x\text{H}_y} = F_{\text{CO}}^{\text{out}} - F_{\text{CO}}^{\text{CO}_2} \quad (\text{mL} \cdot \text{min}^{-1}) \quad (4)$$

Then, two different expressions of C₃H₆ selectivity and yield were defined in order to compare them to those reported in the literature.

$$\text{C}_3\text{H}_6 \text{ sel. in C}_x\text{H}_y: S_{\text{C}_3\text{H}_6}^{\text{C}_x\text{H}_y} (\%) = \frac{F_{\text{C}_3\text{H}_6}^{\text{out}}}{F_{\text{C}_3\text{H}_6}^{\text{out}} + \frac{2}{3}F_{\text{C}_2\text{H}_6}^{\text{out}} + \frac{2}{3}F_{\text{C}_2\text{H}_4}^{\text{out}} + \frac{1}{3}F_{\text{CH}_4}^{\text{out}}} \times 100 \quad (5)$$

$$\text{net C}_3\text{H}_6 \text{ sel.: } S_{\text{C}_3\text{H}_6} (\%) = \frac{F_{\text{C}_3\text{H}_6}^{\text{out}}}{F_{\text{C}_3\text{H}_6}^{\text{out}} + \frac{2}{3}F_{\text{C}_2\text{H}_6}^{\text{out}} + \frac{2}{3}F_{\text{C}_2\text{H}_4}^{\text{out}} + \frac{1}{3}F_{\text{CH}_4}^{\text{out}} + \frac{1}{3}F_{\text{CO}}^{\text{C}_x\text{H}_y}} \times 100 \quad (6)$$

$$\text{C}_3\text{H}_6 \text{ yield in C}_x\text{H}_y: Y_{\text{C}_3\text{H}_6}^{\text{C}_x\text{H}_y} (\%) = \frac{X_{\text{C}_3\text{H}_8} \cdot S_{\text{C}_3\text{H}_6}^{\text{C}_x\text{H}_y}}{100} \quad (7)$$

$$\text{net C}_3\text{H}_6 \text{ yield: } Y_{\text{C}_3\text{H}_6} (\%) = \frac{X_{\text{C}_3\text{H}_8} \cdot S_{\text{C}_3\text{H}_6}}{100} \quad (8)$$

Material balance was considered using the following scales:

$$\text{material balance in } C_xH_y = \frac{F_{C_3H_8}^{out} + F_{C_3H_6}^{out} + \frac{2}{3}F_{C_2H_6}^{out} + \frac{2}{3}F_{C_2H_4}^{out} + \frac{1}{3}F_{CH_4}^{out}}{F_{C_3H_8}^{in}} \times 100 \quad (9)$$

$$\text{material balance in } CO_x = \frac{F_{CO_2}^{out} + F_{CO}^{out}}{F_{CO_2}^{in}} \times 100 \quad (10)$$

total material balance =

$$\frac{F_{C_3H_8}^{out} + F_{C_3H_6}^{out} + \frac{2}{3}F_{C_2H_6}^{out} + \frac{2}{3}F_{C_2H_4}^{out} + \frac{1}{3}F_{CH_4}^{out} + F_{CO_2}^{out} + \frac{1}{3}F_{CO}^{C_xH_y} + F_{CO}^{CO_2}}{F_{C_3H_8}^{in} + F_{CO_2}^{in}} \times 100 \quad (11)$$

The deactivation constant, mean catalyst life, CO₂ utilization efficiency, turnover frequency (TOF), average coke selectivity, and turnover number of coke were defined as follows.

$$\text{Deactivation constant: } k_d = \left\{ \ln \left(\frac{1 - X_{C_3H_8}^f}{X_{C_3H_8}^f} \right) - \ln \left(\frac{1 - X_{C_3H_8}^i}{X_{C_3H_8}^i} \right) \right\} (t^f - t^i)^{-1} \quad (12)$$

$$\text{Mean catalyst life: } \tau = \frac{1}{k_d} \quad (13)$$

$$\text{CO}_2 \text{ utilization efficiency (\%)} = X_{CO_2} \left(1 - \frac{|X_{CO_2} - Y_{C_3H_6}|}{X_{CO_2} + Y_{C_3H_6}} \right) \quad (14)$$

$$\text{TOF}_{C_3H_8/CO_2} (\text{site}^{-1} \text{min}^{-1}) = \frac{M_{C_3H_8/CO_2}^{in} \times X_{C_3H_8/CO_2}^i}{n_{Pt+Co+Ni} \times D} \quad (15)$$

$$\text{average coke selectivity: } S_C (\%) = \frac{\frac{1}{3}n_C^t}{\int_0^t (F_{C_3H_8}^{in} - F_{C_3H_8}^{out}) dt} \times 100 \quad (16)$$

$$\text{TON}_{\text{coke}} (\text{site}^{-1}) = \frac{n_C^t}{n_{Pt+Co+Ni} \times D} \quad (17)$$

$$\text{specific activity (mL}_{C_3H_6} \text{min}^{-1} \text{g}_{AM}^{-1}) = \frac{F_{C_3H_8}^{in} \times Y_{C_3H_6}}{W_{AM}} \quad (18)$$

where, $X_{C_3H_8}^i$ and $X_{C_3H_8}^f$ indicate the initial (t^i : 0.5 h) and final (t^f : 50 h) $X_{C_3H_8}$, respectively. The CO₂ utilization efficiency was used as the scale of how much CO₂ is converted (X_{CO_2}) and how close to the 1:1 stoichiometry the consumption of CO₂ and the formation of C₃H₆ (the latter term: maximum (unity) at the 1:1 stoichiometry) are. The CO₂ utilization efficiency becomes high when CO₂ conversion is high and when the stoichiometry of CO₂ conversion and C₃H₆ formation is close to unity, i.e., CO₂ is solely used for CO₂-ODP. Conversely, it

becomes low when CO₂ conversion is much higher than C₃H₆ yield or when excess CO₂ is used. $M_{C_3H_8/CO_2}^{in}$ and $M_{C_3H_8/CO_2}^{out}$ are the inlet and outlet molar flow rates (mol/min) of C₃H₈ or CO₂, respectively. $n_{Pt+Co+Ni}$ and D corresponds to the mole of active metal in the catalyst and its dispersion estimated by CO chemisorption, respectively. We confirmed by DFT calculation that CO can strongly adsorb on Pt, Co, and Ni sites (Figure 3.36). n_C^t indicates the mole of coke accumulated at a time on a stream of t ($x = C$). W_{AM} is the weight (g) of the active metal component included in the catalyst. The second term in the parenthesis of eq (14) represents the degree of deviation between X_{CO_2} and $Y_{C_3H_6}$. All catalytic tests for kinetic analysis were performed under different conditions by adjusting the amount of catalyst used, where the reactant conversion was lower than 15% (typically 5%~10%).

3.2.3 Characterization

The crystal structure of the prepared catalyst was investigated using powder XRD on a Rigaku MiniFlex II/AP diffractometer with Cu Ka radiation. A JEOL JEM-ARM200 M microscope equipped with an EDX analyzer was used for high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) (EX24221M1G5T). The STEM analysis was performed at a 200 kV accelerating voltage. To prepare the TEM specimen, all samples were sonicated in ethanol and then dispersed on a Mo grid supported by an ultrathin carbon film.

A TPO experiment was performed using BELCAT II (MicrotracBEL) to determine the amount of coke deposited on spent catalysts after 20 and 50 hours of CO₂-ODP at 600°C (0.1g of the catalyst with 0.9g of quartz sand). The spent catalyst was placed in a quartz tube reactor and treated with flowing He (30 mL/min) at 150°C for 30 minutes before cooling to room temperature. While O₂/He (50%, 40 mL/min) was flowing, the catalyst bed temperature was increased (40°C–900°C, ramping rate: 5°C min⁻¹). An online mass spectrometer was used to determine the amount of CO₂ in the outlet gas. CO₂- and He-TPSR experiments were performed for coked catalysts in a similar fashion using the flow of CO₂/He (10%, 30 mL/min) and pure He (30 mL/min). The dispersion of Pt and Co in the catalysts (the percentage of exposed Pt + Co to the total amount of Pt + Co) was measured by the chemisorption of CO at room temperature. Prior to chemisorption, the catalyst (40 mg) was treated with 5% H₂/Ar (30 mL/min) at 600°C for 0.5 hours, followed by cooling to ca -110°C by liquid nitrogen with an He purge (30 mL/min). Then, introduced a pulse of 10% CO/He into the reactor and quantified the CO that passed through the catalyst bed using a TCD detector. This pulse measurement was

repeated until no more CO was adsorbed. The dispersion was estimated assuming a 1:1 stoichiometry of CO adsorption on Pt and/or Co. In our ionization condition, the signal intensity of $m/z = 28$ is only about 6% of that of $m/z = 44$ when CO₂ alone is flowed without catalyst as shown below. However, for He-TPSR, the signal intensity of $m/z = 28$ is comparable to or higher than that of $m/z = 44$, indicating that the contribution of CO₂ to the signal of $m/z = 28$ is negligible. For CO₂-TPSR, the peak feature in the signal of $m/z = 28$ was not observed in that of $m/z = 44$, which purely indicates the evolution of CO.

XAFS spectra of the prepared catalysts were collected at the BL01B14 beamline of SPring-8, Japan Synchrotron Radiation Research Institute (JASRI) using Si(111) (for Co K-, Ni K-, Ga K-, and Pt L_{III}-edges) and Si(311) (for Sn K- and In K-edge) double-crystals as monochromators. Prior to the measurement, the catalyst was pelletized (ca. 150 mg with a diameter of 10 mm) and pretreated by H₂/N₂ (20%, 40 mL/min) at 600°C for 0.5 hours in an in-situ quartz cell, followed by cooling to room temperature with an N₂ purge (32 mL/min). At room temperature, the XAFS spectra were recorded in transmission (Sn K- and In K-edge) and fluorescence (Pt L_{III}-, Ga K-, Ni K-, and Co K-edge: using a 19-element Ge solid-state detector) modes. The XAFS spectra were analyzed using the Athena and Artemis software versions 0.9.25, which are included in the Demeter package. The back-scattering amplitude and phase shift functions were calculated using FEFF8.^[33] The R-factor (R^2) for curve-fitting is defined as follows:

$$R^2 = \frac{\sum_i \{k^3 \chi_i^{exp}(k) - k^3 \chi_i^{fit}(k)\}^2}{\sum_i \{k^3 \chi_i^{exp}(k)\}^2} \quad (19)$$

3.2.4 Computational details

Periodic DFT calculations were performed using the CASTEP code^[34] with Vanderbilt-type ultrasoft pseudopotentials as well as the revised version of Perdew–Burke–Ernzerhof exchange–correlation functional based on the generalized gradient approximation.^[35] At a kinetic energy of 360 eV, the plane-wave basis set was truncated. A 0.1 eV Fermi smearing was utilized. The Tkatchenko–Scheffler method was used to analyze dispersion correlations with a scaling coefficient of $s_R = 0.94$ and a damping parameter of $d = 20$.^[36] The reciprocal space was sampled using a k -point mesh with a spacing of typically 0.04 Å⁻¹, as generated by the Monkhorst–Pack scheme.^[37] Geometry optimizations and transition state (TS) searches were performed on supercell structures using periodic boundary conditions. The surfaces were modeled using metallic slabs with a thickness of four atomic layers with 13 Å of vacuum spacing. We chose Pt–Sn(110) as the most stable surface, which has the highest surface atom

density and diffraction intensity. Geometry optimizations were performed using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm.^[38] The unit cell size of the bulk material (Pt–Sn, Pt–Co–In and HEI) was firstly optimized, followed by modeling the slab structure and surface relaxation with the size of the supercell fixed. The convergence criteria for structure optimization and energy calculation were set to (a) an SCF tolerance of 1.0×10^{-6} eV per atom, (b) an energy tolerance of 1.0×10^{-5} eV per atom, (c) a maximum force tolerance of 0.05 eV $\text{\AA}^{-1}$, and (d) a maximum displacement tolerance of 1.0×10^{-3} $\text{\AA}$.

As the parent structure of HEI, a PtSn–(2×2×2) supercell was constructed so that the (110) plane of PtSn corresponded to the (001) plane of the supercell. The distribution of each constituent metal in HEI was determined with the following restrictions: (1) Pt/Co/Ni occupy the Pt sites while Sn/In do the Sn sites (Ga was not included in this model for simplicity because of the low concentration mentioned above), (2) Pt atoms do not neighbor each other on all the (110) layers, and (3) the number of each metal in each (110) layer is fixed to 2 or 3 (Pt/Ni/Co) and 4 (Sn/In). The distribution of each atom was determined using random numbers. Then, we generated ten different bulk (2×2×2) unit cells, of which energy difference was < 0.5 eV, indicating that the distribution does not strongly influence the stability of bulk structure. Among them, we chose the most stable structure as an energetically likely model as shown in Table 3.7 and Figure 3.24.

The adsorption energy was defined as follows: $E_{\text{ad}} = E_{\text{A-S}} - (E_{\text{S}} + E_{\text{A}})$, where $E_{\text{A-S}}$ is the energy of the slab together with the adsorbate, E_{A} is the total energy of the free adsorbate, and E_{S} is the total energy of the bare slab. The adsorption energy for an oxygen-preadsorbed slab was calculated using E_{SH} , which is the total energy of the oxygen-adsorbed slab, instead of using E_{S} . The d band center (ε_{d}) was defined as the average energy of the occupied d band relative to the Fermi level as follows:

$$\varepsilon_{\text{d}} = \int_{-\infty}^0 E \rho_{\text{d}}(E) \text{d}E / \int_{-\infty}^0 \rho_{\text{d}}(E) \text{d}E \quad (20)$$

where ρ_{d} is the density of states projected to d orbitals.

The transition state (TS) search was performed using the complete linear synchronous transit/quadratic synchronous transit (LST/QST) method.^{[39],[40]} Linear synchronous transit maximization was performed, followed by energy minimization in the directions conjugating to the reaction pathway. The approximated TS was used to perform QST maximization with conjugate gradient minimization refinements. This cycle was repeated until a stationary point

was found. Convergence criterion for the TS calculations were set to root-mean-square forces on an atom tolerance of $0.05 \text{ eV } \text{\AA}^{-1}$.

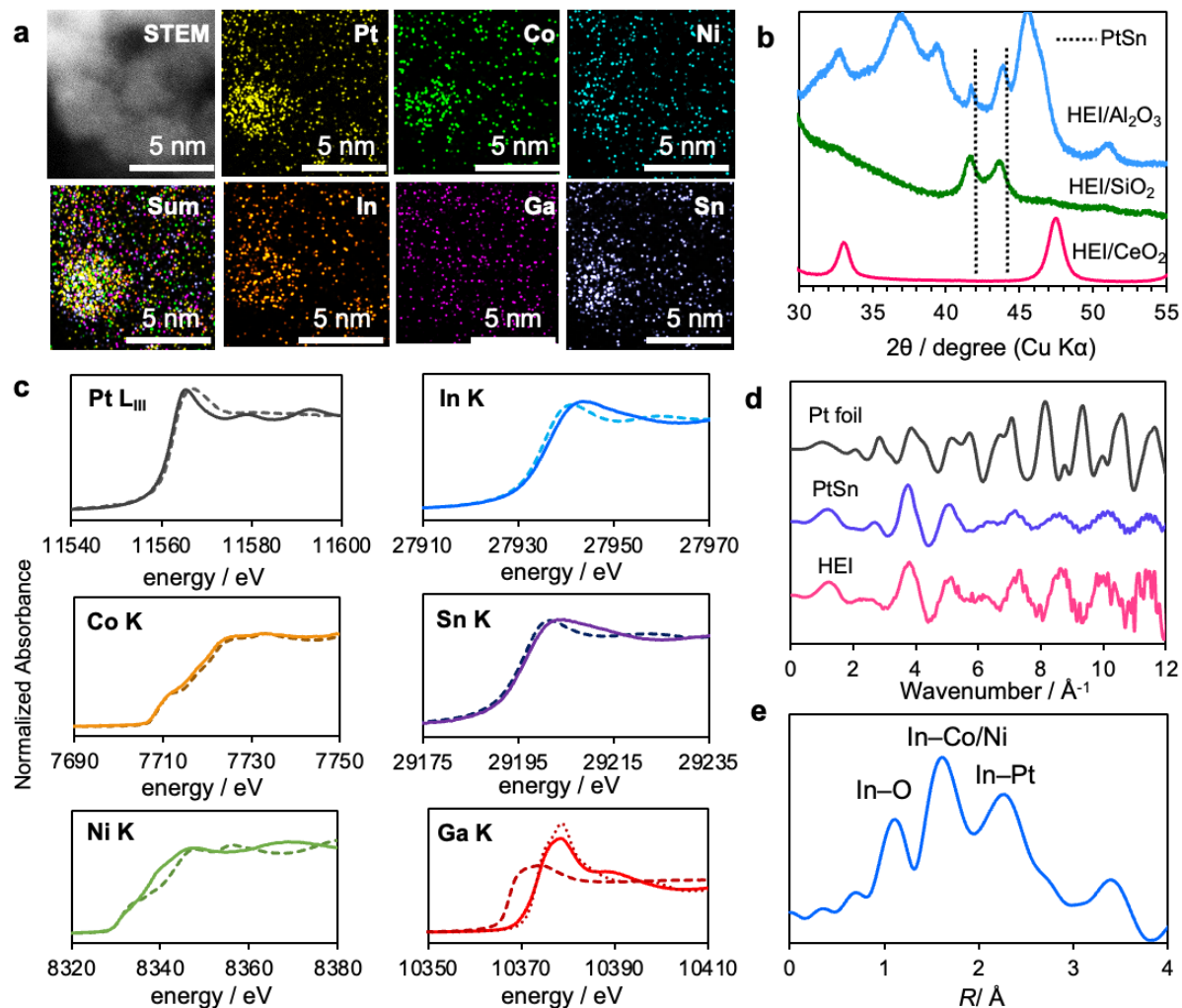


Figure 3.2. Characterization of the HEI catalyst. **a** HAADF-STEM image and the corresponding elemental maps of HEI/CeO₂. **b** XRD patterns of HEI supported on Al₂O₃, SiO₂ and CeO₂. **c** Pt L_{III}, Co K, Ni K, In K, Sn K and Ga K-edge XANES spectra of the in-situ reduced catalysts (solid lines) and reference foils (dashed lines) or oxides (dotted lined). **d** Pt L_{III}-edge EXAFS oscillations of Pt foil, Pt–Sn and HEI/CeO₂. **e** Fourier transform of the In K-edge EXAFS of HEI/CeO₂.

3.3 Results

3.3.1 Structure characterization of the catalysts

The HEI/CeO₂ catalyst was prepared using a conventional co-impregnation method with CeO₂ as the support. Figure 3.2a shows a high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image of HEI/CeO₂ as well as the corresponding elemental maps obtained through energy-dispersive X-ray (EDX) analysis. Metallic nanoparticles were not visible in the HAADF-STEM image, most likely due to insufficient Z-contrast between Ce and the other metals. The elemental maps of Pt, Co, Ni, Sn, In, and Ga, on the other hand, clearly indicated the presence of a small (~4 nm) multi-metallic nanoparticle on the CeO₂ support.

In the multi-metallic nanoparticles, the transition and typical metals atomic ratios ((Pt + Co + Ni)/(Sn + In + Ga)) were approximately 1:1 (Figures 3.3, 3.4, and 3.5). The crystal structures of the HEI catalysts were then analyzed using X-ray diffraction (XRD). When Al₂O₃ or SiO₂ was used as a catalyst support for HEI, two intense peaks appeared at 41.8° and 44.1°, which corresponded to the 102 and 110 diffractions of intermetallic PtSn (Figure 3.2b). The shifts in diffraction angles from pristine PtSn can be attributed to changes in the lattice constant caused by site-specific multi-metallization. However, the corresponding diffractions were not observed for HEI/CeO₂. One possible interpretation is that the reflection of X-ray on the nanoparticles was significantly weakened by the strong X-ray scattering by Ce, of which atomic weight and the scattering factor are much larger than Si and Al. Thus, HAADF-STEM and XRD did not provide convincing information for the CeO₂-supported catalyst, as is commonly reported in the literature. As a result, X-ray adsorption fine structure (XAFS) analysis was performed to obtain additional structural information. The Pt L_{III}-, Co K-, Ni K-, Sn K-, and In K-edge X-ray absorption near edge spectra (XANES) of HEI/CeO₂ matched those of the corresponding reference foils, indicating that these metals are reduced to zero-valent states (Figure 3.2c). In contrast, the Ga K-edge XANES of HEI/CeO₂ were similar to those of Ga₂O₃, indicating that Ga species in HEI were mostly oxidized. We also performed H₂ temperature-programmed reduction, in which the metal precursors were reduced below 600°C (Figure 3.6). Considering the order of reduction potentials ($\text{Ga}^{3+} + 3e^- \rightarrow \text{Ga}^{(0)} : -0.55$ V vs. SHE < $\text{CeO}_2 + e^- \rightarrow \text{Ce}_2\text{O}_3 : -0.36$ V < $\text{In}^{3+} + 3e^- \rightarrow \text{In}^{(0)} : -0.34$ V, see Table 3.1 on other metals), it is likely that only oxophilic Ga was reoxidized by CeO₂ lattice oxygen, even if it could be reduced by H₂. Figure 3.2d shows the Pt L_{III}-edge EXAFS oscillation of Pt foil, PtSn/SiO₂, and HEI/CeO₂. The oscillation feature of HEI/CeO₂ was similar to that of intermetallic PtSn but completely different from that of fcc Pt, indicating that Pt species in HEI are present in a PtSn-like structure. Figure 3.2e shows the Fourier transform of the In K-edge

EXAFS of HEI/CeO₂, where three peaks assignable to In–O, In–Co/Ni, and In–Pt were distinctly observed (see [Figures. 3.7, 3.8, and 3.9](#) [Table 3.3](#) for details of curve-fitting). The observation of In–Pt and In–Co/Ni scatterings suggests that In is also present in the PtSn-like structure (at the Sn site) and that Co(Ni) is doped into the Pt site. The small contribution of oxygen could be attributed to interactions with CeO₂’s lattice oxygen. We also conducted extensive curve-fitting analysis on other adsorption edges, assigning the corresponding transition metal–typical metal scatterings (Pt–Sn/In, Co–Sn/In, Ni–Sn/In, Sn–Pt, and Sn–Co/Ni). Although metallic bonds with Ga were suggested, their coordination numbers were small (~1.0), whereas the coordination number of Ga–O was high (7.4), which is consistent with the XANES result. Based on these findings, PtSn-based HEI nanoparticles, i.e., (PtCoNi)(SnInGa), were most likely formed on CeO₂, with the Pt and Sn sites being partially replaced primarily with Co/Ni and In/Ga, respectively. Notably, the fraction of metallic Ga in the HEI nanoparticles appears to be lower than suggested by XANES and EXAFS because the Ga species are present primarily as oxides (they do not participate in alloy formation).

Table 3.1. Reduction potentials of metals cations involved in this study.^{[41],[42]}

Reduction	E_0 (V) vs. SHE
$\text{Pt}^{2+} + 2e^- \rightarrow \text{Pt}^{(0)}$	+1.18
$\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}^{(0)}$	−0.236
$\text{Co}^{2+} + 2e^- \rightarrow \text{Co}^{(0)}$	−0.282
$\text{Sn}^{2+} + 2e^- \rightarrow \text{Sn}^{(0)}$	−0.141
$\text{In}^{3+} + 3e^- \rightarrow \text{In}^{(0)}$	−0.338
$\text{CeO}_2 + e^- \rightarrow \text{Ce}_2\text{O}_3$	−0.364
$\text{Ga}^{3+} + 3e^- \rightarrow \text{Ga}^{(0)}$	−0.549

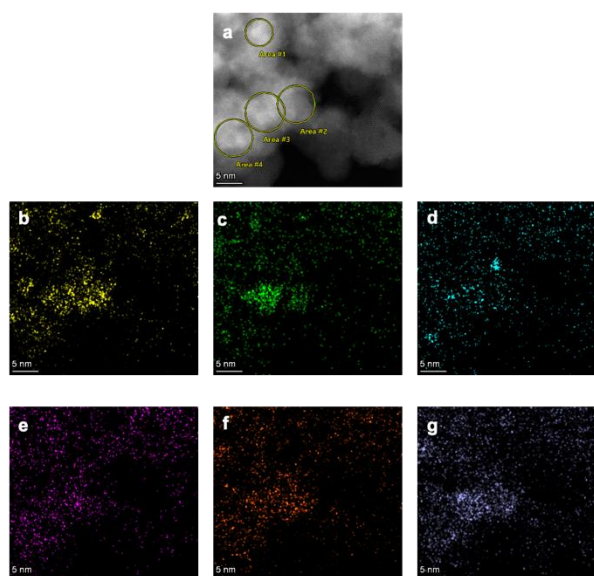


Figure 3.3. HAADF-STEM-EDX analysis on HEI. **a** HAADF-STEM image of HEI/CeO₂ (PtCoNiInGaSn/CeO₂). Atomic ratios in the regions designated by dotted yellow circles **1-4** were calculated and shown in Figure 3. **b-g** Elemental maps of **(b)** Pt, **(c)** Ni, **(d)** Co, **(e)** Ga, **(f)** In, and **(g)** Sn on HEI/CeO₂ acquired using EDX analysis.

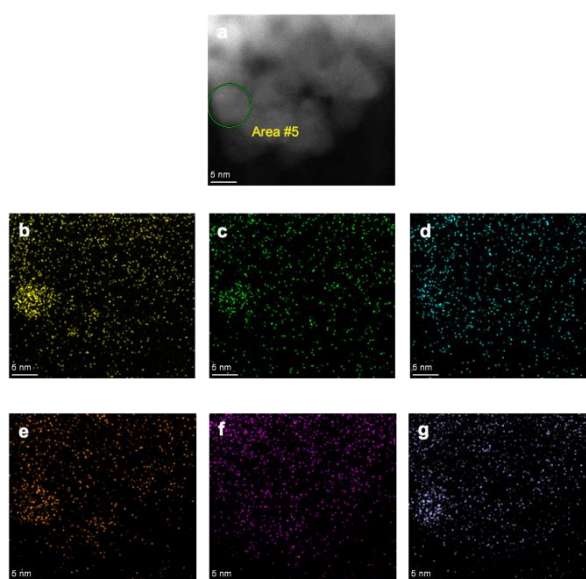


Figure 3.4. HAADF-STEM-EDX analysis on HEI. **a** HAADF-STEM image of HEI/CeO₂ (PtCoNiInGaSn/CeO₂). Atomic ratio in the region designated by dotted yellow circle **5** was calculated and shown in Figure 3. **b-g** Elemental maps of **(b)** Pt, **(c)** Ni, **(d)** Co, **(e)** Ga, **(f)** In, and **(g)** Sn on HEI/CeO₂ acquired using EDX analysis.

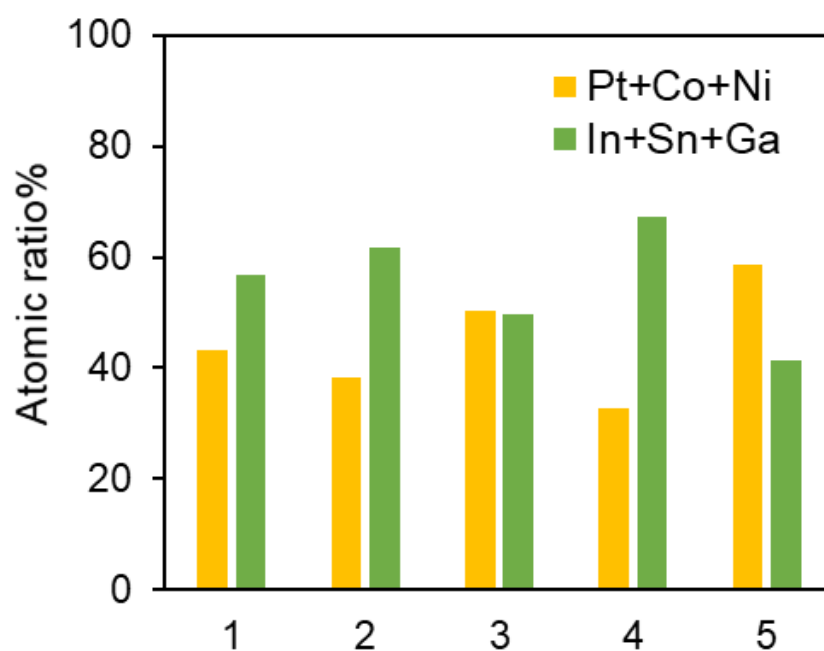


Figure 3.5. Elemental analysis on HEI. Atomic ratios of Pt+Co+Ni and Sn+In+Ga in the regions 1–5 designated by dotted circles in Figure 3.3 and Figure 3.4.

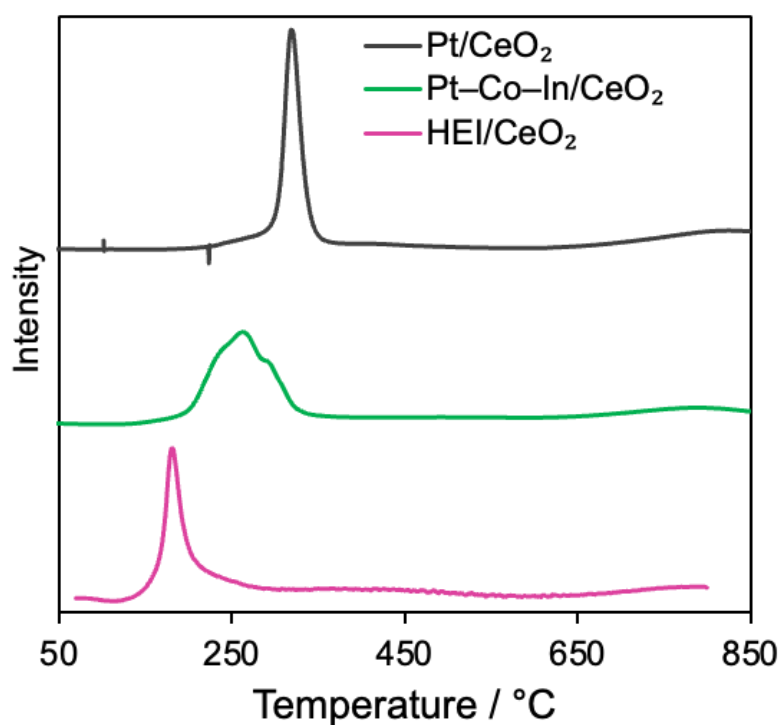


Figure 3.6. H₂-TPR analysis. H₂-TPR profiles of unreduced Pt/CeO₂, Pt-Co-In/CeO₂, and HEI/CeO₂.

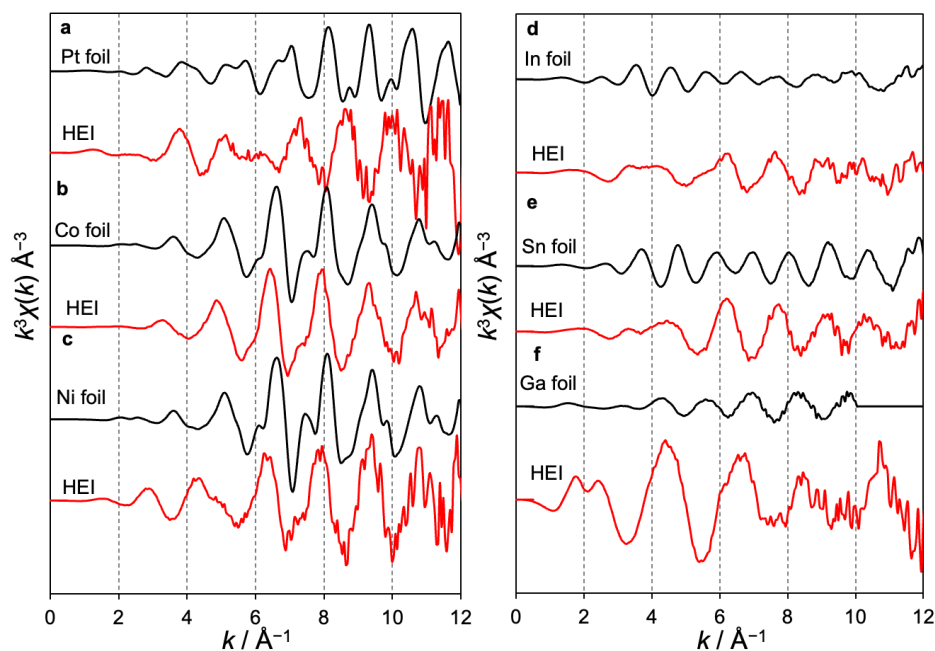
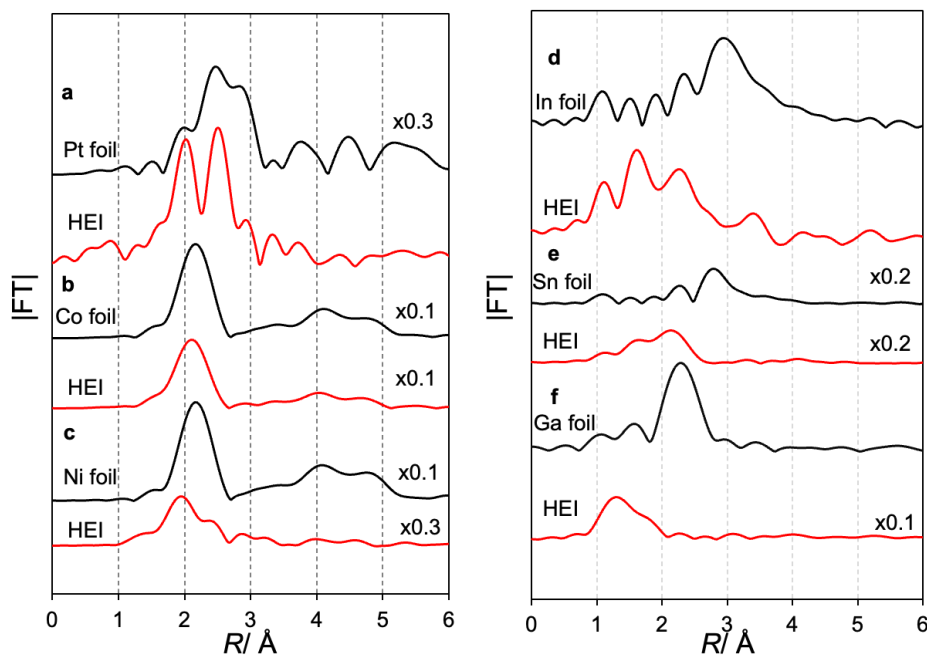


Figure 3.7. EXAFS oscillations of HEI. **a** Pt L_{III}-, **b** Co K-, **c** Ni K-, **d** In K-, **e** Sn K-, and **f** Ga K-edge EXAFS spectra of the in-situ reduced HEI/CeO₂ catalysts and reference compounds.

Figure 3.8. Fourier transforms of EXAFS of HEI. Fourier transforms of **a** Pt L_{III}-, **b** Co K-,



c Ni K-, **d** In K-, **e** Sn K-, and **f** Ga K-edge EXAFS of the in-situ reduced HEI/CeO₂ catalysts and reference compounds.

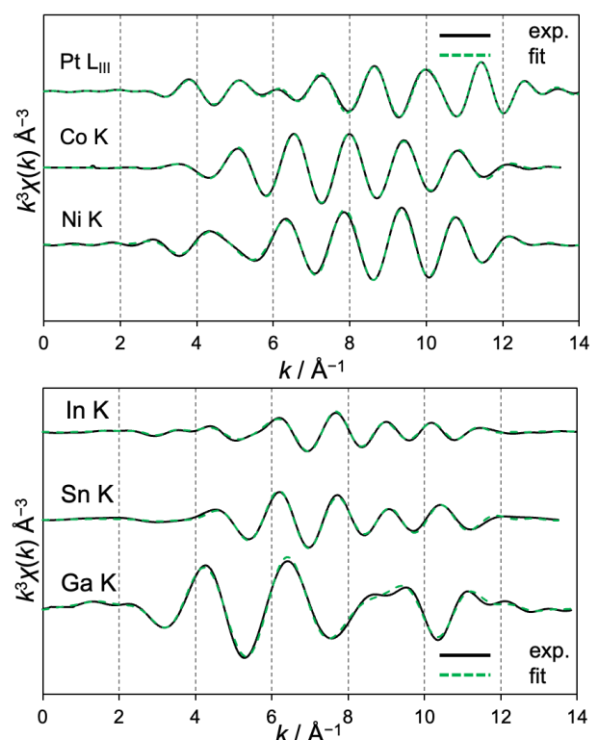


Figure 3.9. Curve-fitting analysis for HEI. Curve-fitting for the Pt L_{III}-, Co K-, Ni K-, In K-, Sn K-, and Ga K-edge k^3 -weighted EXAFS oscillations of HEI/CeO₂. The k^3 -weighted EXAFS oscillation was Fourier-transformed in the k range of 3–12 Å⁻¹ for all edges. Curve-fitting was performed using the back Fourier-transforms of the coordination peaks ranging between 1.3–3.7 Å, 1.0–3.0 Å, 1.0–3.0 Å, 1.2–4.0 Å, 1.0–3.0 Å, and 1.0–3.0 Å for Pt L_{III}-, Co K-, Ni K-, In K-, Sn K-, and Ga K-edge, respectively.

Table 3.2. Information about coke on the spent catalyst. ^a

catalyst	coke wt% ^b	average coke sel. (%) ^c	coke TON ^d
Pt/CeO ₂	0.3	0.004	17.0
Pt–Co–In/CeO ₂	0.2	0.003	11.6
HEI/CeO ₂	0.1	0.001	2.9

^a The catalysts after 50 h of catalytic run were used. ^b Gram coke per gram catalyst × 100. ^c Mole of accumulated coke / total mole of converted C₃H₈ × 3. See Equation (16) for details. Since the coke selectivity was too low to change the net C₃H₆ selectivity, we ignored coke in the calculation of C₃H₆ selectivity. ^d See Equation (17) for details.

Table 3.3. Results of EXAFS curve-fitting for HEI/CeO₂ and the reference foils

Sample	Edge	Shell	S ₀ ² ^a	CN ^b	R (Å) ^c	ΔE ₀ (eV) ^d	σ ² (Å ²) ^e	R-factor
Pt foil	Pt L _{III}	Pt–Pt	0.95	12 (fix)	2.77 ± 0.00	7.9 ± 1.4	0.005	0.005
Co foil	Co K	Co–Co	0.80	12 (fix)	2.50 ± 0.00	-5.2 ± 0.4	0.006	0.003
Ni foil	Ni K	Ni–Ni	0.84	12 (fix)	2.77 ± 0.00	6.0 ± 0.6	0.006	0.003
Sn foil	Sn K	Sn–Sn	1.04	4 (fix)	3.02 ± 0.00	3.4 ± 1.1	0.010	0.013
		Sn–Sn		2 (fix)	3.18 ± 0.00			
		Ga–O		1 (fix)	1.87 ± 0.00			
Ga ₂ O ₃	Ga K	Ga–O	1.03	3 (fix)	2.02 ± 0.00	8.0 ± 2.4	0.001	0.015
		Ga–Ga		2 (fix)	3.06 ± 0.00			
In foil	In K	In–In	0.87	4 (fix)	3.16 ± 0.01	2.1 ± 0.7	0.016	0.003
		In–In		8 (fix)	3.32 ± 0.04			
HEI/CeO ₂	Pt L _{III}	Pt–Ga		0.7 ± 0.0	2.57 ± 0.02		0.008	0.009
		Pt–Sn/In	0.82	2.6 ± 0.3	2.63 ± 0.01	0.8 ± 1.1	0.008	
		Pt–Pt		1.9 ± 0.2	2.71 ± 0.01		0.008	
	Co K	Co–Co	0.80	7.6 ± 0.6	2.49 ± 0.00	5.1 ± 0.7	0.007	0.002
		Co–In/Sn		3.8 ± 0.6	2.68 ± 0.00		0.040	
	Ni K	Ni–Ni	0.84	2.0 ± 0.5	2.48 ± 0.03	-9.5 ± 2.1	0.009	0.008
		Ni–Sn/In		3.7 ± 3.3	2.61 ± 0.04		0.007	
		Sn–O		1.4 ± 0.3	2.12 ± 0.02		0.005	
	Sn K	Sn–Co/Ni	1.04	1.1 ± 0.4	2.61 ± 0.00	5.4 ± 2.9	0.005	0.003
		Sn–Pt		3.4 ± 2.2	2.73 ± 0.02		0.016	
	Ga K	Ga–O	1.03	1.8 ± 1.6	1.74 ± 0.02	-10.0 ± 2.9	0.012	0.003
		Ga–Ni/Co		3.1 ± 3.3	1.93 ± 0.03		0.007	
		In–O		1.6 ± 0.7	2.14 ± 0.02		0.007	
	In K	In–Co/Ni	0.87	0.3 ± 0.3	2.63 ± 0.03	4.5 ± 4.0	0.001	0.016
		In–Pt		3.3 ± 1.9	2.71 ± 0.04		0.011	

^a Amplitude factor. ^b Coordination number. ^c Distance between absorber and backscatterer atoms. ^d Correction term in the absorption edge. ^e Debye–Waller factor.

Table 3.4. Metal dispersions of CeO₂-supported Pt-based catalysts.^a

Catalyst	Active metal (Pt and Co) dispersion (%) estimated by CO chemisorption
Pt/CeO ₂	25.4
PtSn/CeO ₂	70.0
Pt–Co–In/CeO ₂	29.6
HEI/CeO ₂	30.3
PtSn/CeO ₂ spent	15.0
Pt–Co–In/CeO ₂ spent	6.9
HEI/CeO ₂ spent	30.2
HEI/Al ₂ O ₃	34.2
HEI/SiO ₂	19.7

^a The loading amount of Pt was fixed at 1 wt% for all the catalysts.

3.3.2 Catalytic performance in CO₂-ODP

The catalytic performance of HEI/CeO₂ in CO₂-ODP was then tested at 600°C. Additionally, control catalysts such as Pt/CeO₂, Pt–Co–In/CeO₂, and PtSn/CeO₂ were also tested. [Figure 3.10a](#), [3.10b](#), and [3.10c](#) show the time-course of C₃H₈ conversion, C₃H₆ selectivity in hydrocarbons (see [Figure 3.11](#) for the net C₃H₆ selectivity, which includes CO formed from hydrocarbons via dry reforming), and CO₂ conversions, respectively. With the exception of Pt/CeO₂ (72% sel.), all catalysts converted C₃H₈ by approximately 30% with a high C₃H₆ selectivity (90%–94%). The net C₃H₆ selectivity was comparable to that in hydrocarbons for PtSn and HEI, whereas it was lower for Pt and Pt–Co–In, indicating that dry reforming of propane was inhibited on the PtSn-based structure. Although Pt, PtSn, and Pt–Co–In showed rapid deactivation within 5–20 hours, HEI/CeO₂ mostly retained the initial conversion at least for 30 hours. Similar trends were observed for C₃H₆ selectivity and CO₂ conversion, with HEI/CeO₂ retaining the highest C₃H₆ selectivity (90%) and the lowest deactivation rate for 50 hours, as well as the highest stability for CO₂ conversion. The trends in catalyst stability can be explained roughly by the amount of coke on the catalyst as estimated by temperature-programmed oxidation (TPO, [Figure 3.10d](#)), where the relative coke amount on HEI was much lower than that on Pt, PtSn, and Pt–Co–In even after 50 hours of catalytic run. The coke selectivity, which was calculated by dividing the mole of accumulated coke by the total mole of the converted C₃H₈ and the carbon number of C₃H₈, was only 0.001% ([Table 3.2](#)),

highlighting its outstandingly high coke resistance (material balance was also close to unity, [Figure 3.12](#)). The loss of C_3H_6 selectivity at the later stage of the reaction for PtSn and Pt–Co–In might be due to the segregation of Pt from the alloy phase because the final selectivity was close to that for Pt. Furthermore, we used CO chemisorption on spent catalysts to evaluate whether the metal dispersion was retained following the reaction. The spent catalyst was regenerated through oxidation–reduction treatment before the CO chemisorption. As shown in [Figure 3.10e](#) (for details see [Table 4](#)), the metal dispersion of PtSn and Pt–Co–In decreased significantly following the reaction, implying that nanoparticles sinter irreversibly. On the other hand, HEI retained the original metal dispersion, which demonstrated that no aggregation occurred even under the harsh conditions. Thus, the HEI/CeO₂ catalyst demonstrated remarkably high thermal stability and coke resistance, enabling long-term stability in CO₂-ODP.

We also tested the catalytic performance of other Pt-based binary alloy catalysts (Pt–M/CeO₂: M = Co, Ni, In, and Ga, [Figure 3.13](#)) to confirm the role of constituent metals. Although Pt–Co and Pt–Ni exhibited higher initial C_3H_8 and CO₂ conversions than Pt, C_3H_6 selectivity was quite low (20%–40%) because of a large contribution of dry reforming of propane (DRP) to CO. This suggests that typical metals are necessary to inhibit DRP. However, Pt–Ga/CeO₂ and Pt–In/CeO₂ demonstrated very low CO₂ conversion and higher C_3H_6 selectivity; thus, Ni and Co are required for CO₂ activation as expected. We also investigated the effect of multi-metallization at the Sn site with PtCoNiSn/CeO₂ (Pt: Ni: Co: Sn = 1:1:1:3) and PtCoNiSnIn/CeO₂ (Pt: Ni: Co: Sn = 1:1:1:1.5:1.5), which resulted in lower catalyst stability than HEI/CeO₂, respectively ([Figures 3.14 and 3.15](#)). As a result, the formation of the HEI structure is a key factor in achieving high stability. Using HEI/Al₂O₃ and HEI/SiO₂ catalysts, the effect of CeO₂ support was also investigated ([Figure 3.16](#)). Although high C_3H_8 conversion (50%~60%) and C_3H_6 selectivity (>95%) were obtained at the beginning of the reaction, deactivation occurred rapidly due to coke accumulation within a few hours. This demonstrates that while the PtSn-based HEI has an intrinsically high performance for CO₂-ODP, CeO₂ is also required to maintain long-term stability.

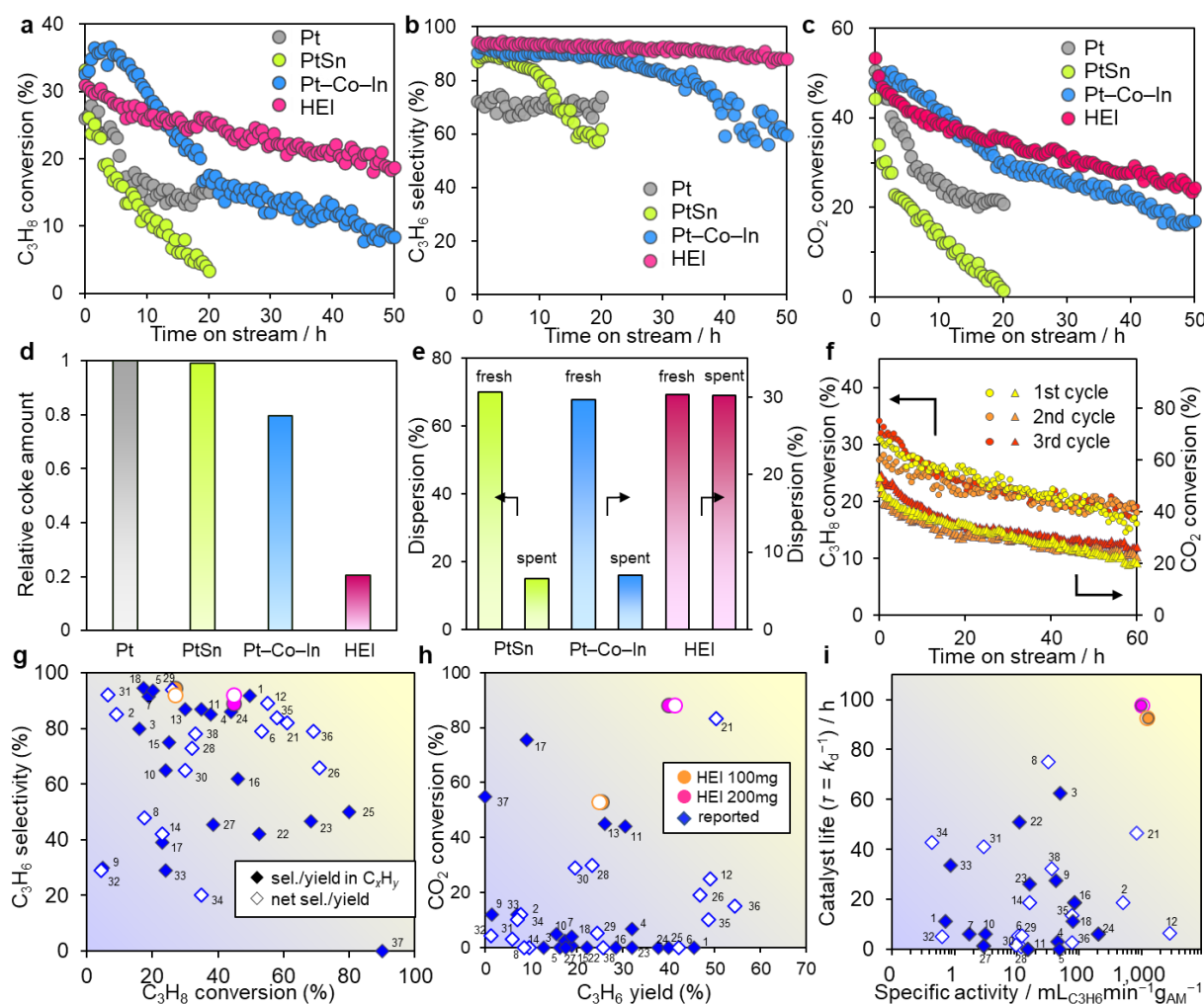


Figure 3.10. Catalytic performance of HEI/CeO₂ in the CO₂-ODP. Reaction conditions: catalyst amount, 100 mg; gas feed, C₃H₈:CO₂:He = 5:5:10 mL·min⁻¹; temperature, 600 °C. **a,b,c** Time course of (a) C₃H₈ conversion, (b) C₃H₆ selectivity in hydrocarbons, and (c) CO₂ conversion. **d** Relative coke amount accumulated by O₂-TPO of the spent catalysts after the time stream of Figure 3.10.a in CO₂-ODP at 600°C. **e** Metal dispersions comparison of fresh and spent catalysts. **f** Reusability of HEI/CeO₂ in repeated long catalytic runs with regeneration procedure (CO₂:He = 5:10 mLmin⁻¹ for 2 h, then H₂:He = 5:10 mLmin⁻¹ for 0.5 h at 600 °C between each cycle). **g,h,i** Comparison of the catalytic performances with those of reported systems (values indicate references in Tables 3.5 and 3.6): (g) C₃H₈ conversion vs. C₃H₆ selectivity, (h) C₃H₆ yield vs CO₂ conversion, (i) specific activity of C₃H₆ production (mL_{C₃H₆} min⁻¹ g_{AM(active metal)}⁻¹) vs. mean catalyst life ($\tau = k_d^{-1}$: reciprocal deactivation constant).

The reusability of HEI/CeO₂ was then tested. The spent catalyst was regenerated by flowing CO₂ at 600°C, followed by H₂ reduction. Both C₃H₈ and CO₂ conversions were fully recovered after the repeated regeneration processes (Figure 3.10f). Thus, the HEI/CeO₂ catalyst

demonstrated exceptional stability, regenerability, and coke resistance in CO₂-ODP. When the spent PtSn/CeO₂ catalyst underwent the regeneration process including H₂ reduction, C₃H₆ selectivity was recovered to the original level (Figure 3.17), indicating that the segregated Pt–SnO_x composite was alloyed again. However, the conversion of C₃H₈ and CO₂ was not recovered, which is consistent with the increase in the size of nanoparticles by sintering. In terms of activity, selectivity, stability, reusability, and CO₂ utilization efficiency, the catalytic performance of HEI/CeO₂ was compared to that of previously reported systems for the CO₂-ODP (Figures 3.10g, 3.10h, and 3.10i; see Figures 3.18, 3.19 and Tables 3.5–3.6 for details with references). Here, two selectivity/yield descriptions (filled: in hydrocarbons, open: including CO via dry reforming) are shown for better comparison with those in literature because the description differs depending on literature. The HEI/CeO₂ catalyst demonstrated exceptional catalytic activity, excellent C₃H₆ selectivity, high CO₂ utilization efficiency, and long-term stability. Notably, the mean catalyst life ($\tau = k_d^{-1}$) was 13 times that of the PtSn/CeO₂ catalyst and twice that of the Pt–Co–In/CeO₂ catalyst.

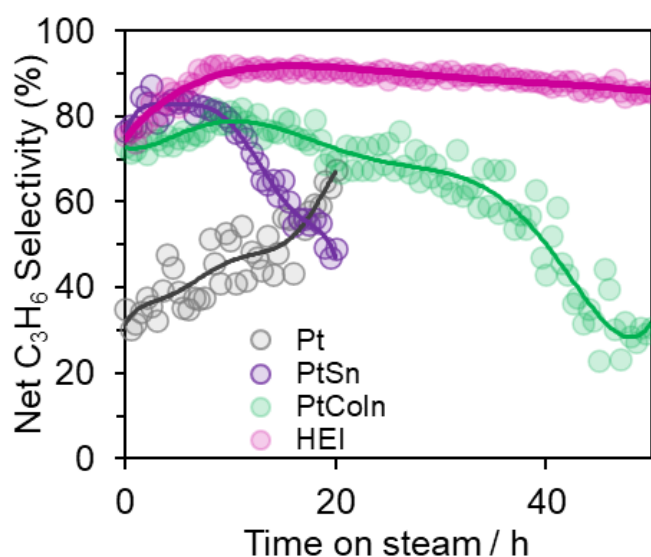


Figure 3.11. Net C₃H₆ selectivity. Net C₃H₆ selectivity considering CO formed from C_xH_y via dry reforming obtained in CO₂-ODP over monometallic Pt/CeO₂, PtSn/CeO₂, PtCoIn/CeO₂, and HEI/CeO₂. Pt/CeO₂ showed an increase in the net C₃H₆ selectivity, even though C₃H₆ selectivity in HC was constant, indicating that dry reforming was inhibited as the reaction proceeded.

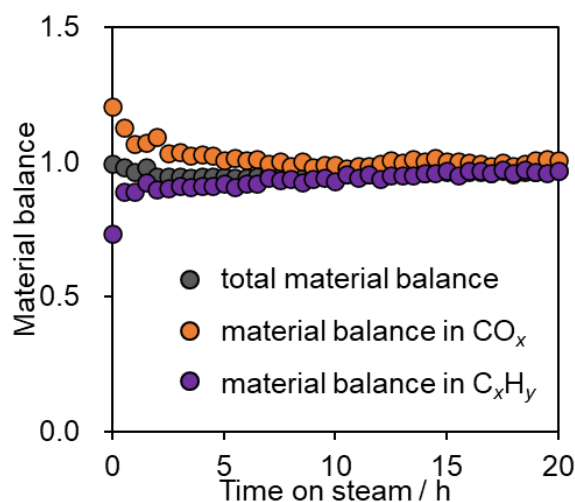


Figure 3.12. Material balances in CO₂-ODP over the HEI/CeO₂ catalyst. Material balance in CO_x was higher than unity while that in C_xH_y was lower, indicating that dry reforming of propane occurred as a side reaction. Although this trend was prominent at the initial stage of the reaction (<5 h), it became minor with time. However, total material balance was always close to unity, which is consistent with the very low coke selectivity.

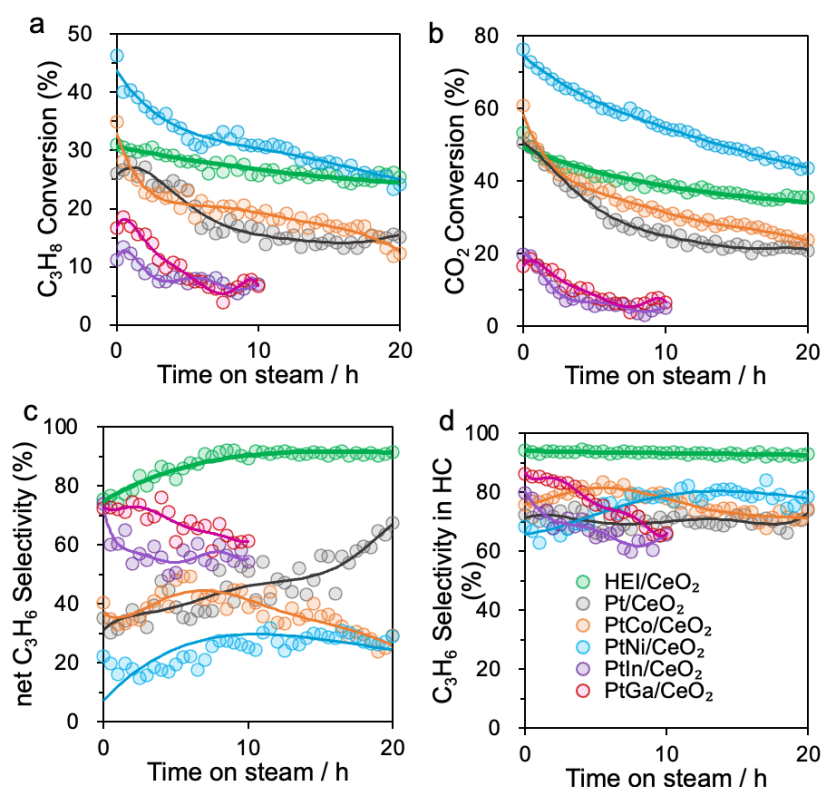


Figure 3.13. Catalytic performance of monometallic Pt/CeO₂, PtCo/CeO₂, PtNi/CeO₂, PtIn/CeO₂, PtGa/CeO₂, and HEI/CeO₂ in CO₂-ODP. **a** C₃H₈ conversion, **b** CO₂ conversion, **c** net C₃H₆ selectivity considering CO formed from C_xH_y, and **d** C₃H₆ selectivity in C_xH_y.

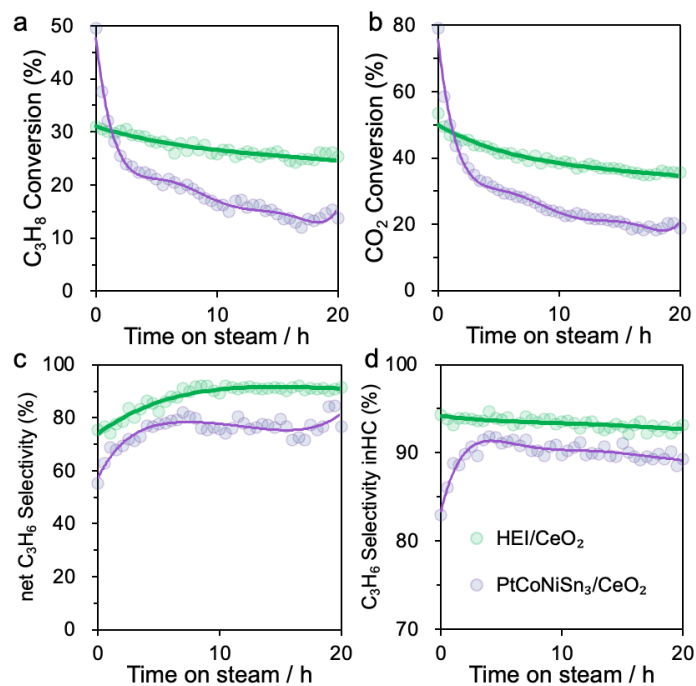


Figure 3.14. Catalytic performance of PtCoNiSn₃/CeO₂ and HEI/CeO₂ in CO₂–ODP. **a C₃H₈ conversion, **b** CO₂ conversion, **c** net C₃H₆ selectivity considering CO formed from C_xH_y, and **d** C₃H₆ selectivity in C_xH_y.**

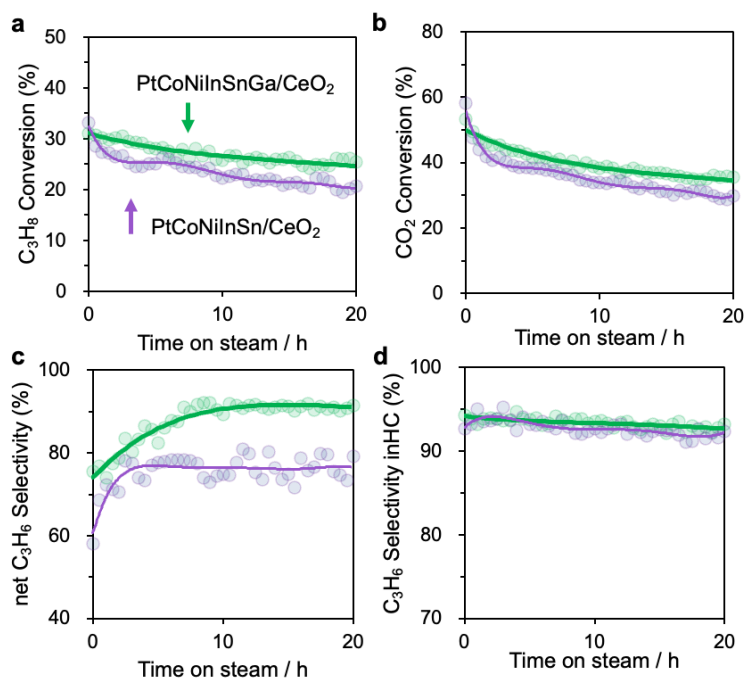


Figure 3.15. Catalytic performance of PtCoNiSnIn/CeO₂ (Pt:Co:Ni:Sn:In = 1:1:1:1.5:1.5) and HEI/CeO₂ in CO₂–ODP. **a C₃H₈ conversion, **b** CO₂ conversion, **c** net C₃H₆ selectivity considering CO formed from C_xH_y, and **d** C₃H₆ selectivity in C_xH_y.**

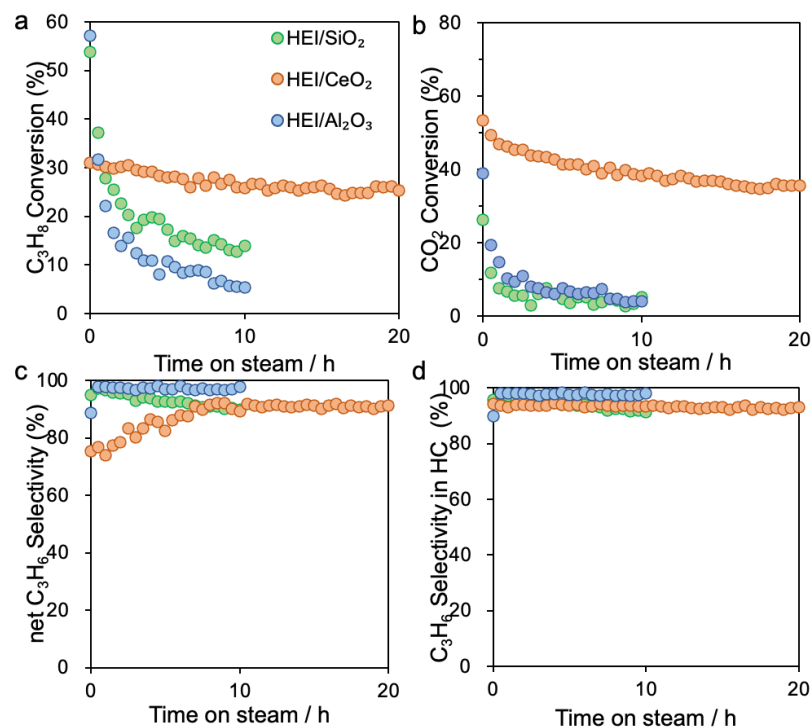


Figure 3.16. Catalytic performance of HEI/Al₂O₃, HEI/SiO₂, and HEI/CeO₂ in CO₂-ODP. **a C₃H₈ conversion, **b** CO₂ conversion, **c** net C₃H₆ selectivity considering CO formed from C_xH_y, and **d** C₃H₆ selectivity in C_xH_y.**

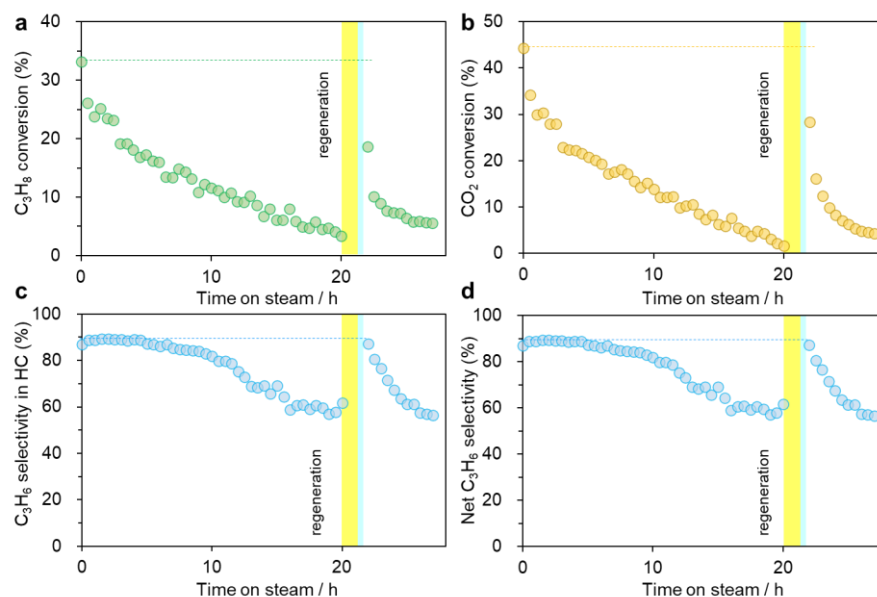


Figure 3.17. Catalytic performance of PtSn/CeO₂ catalyst in the CO₂-ODP before and after regeneration procedure. **a C₃H₈ conversion, **b** CO₂ conversion, **c** C₃H₆ selectivity in HC, and **d** net C₃H₆ selectivity.**

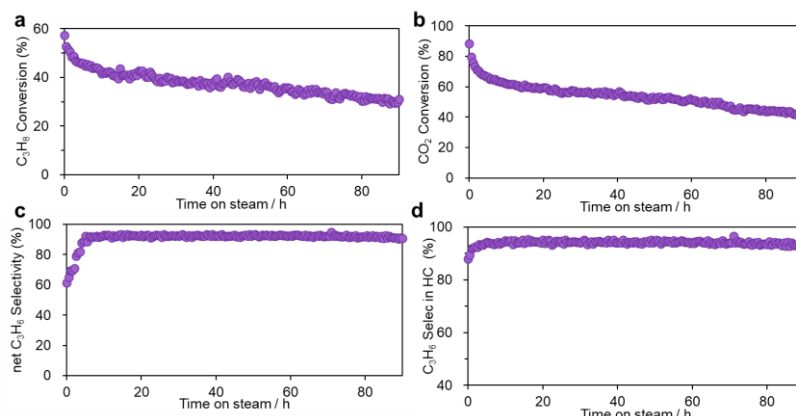


Figure 3.18. Catalytic performance of HEI/CeO₂ (200mg) in the CO₂-ODP. **a** C₃H₈ conversion, **b** CO₂ conversion, **c** net C₃H₆ selectivity, and **d** C₃H₆ selectivity in C_xH_y.

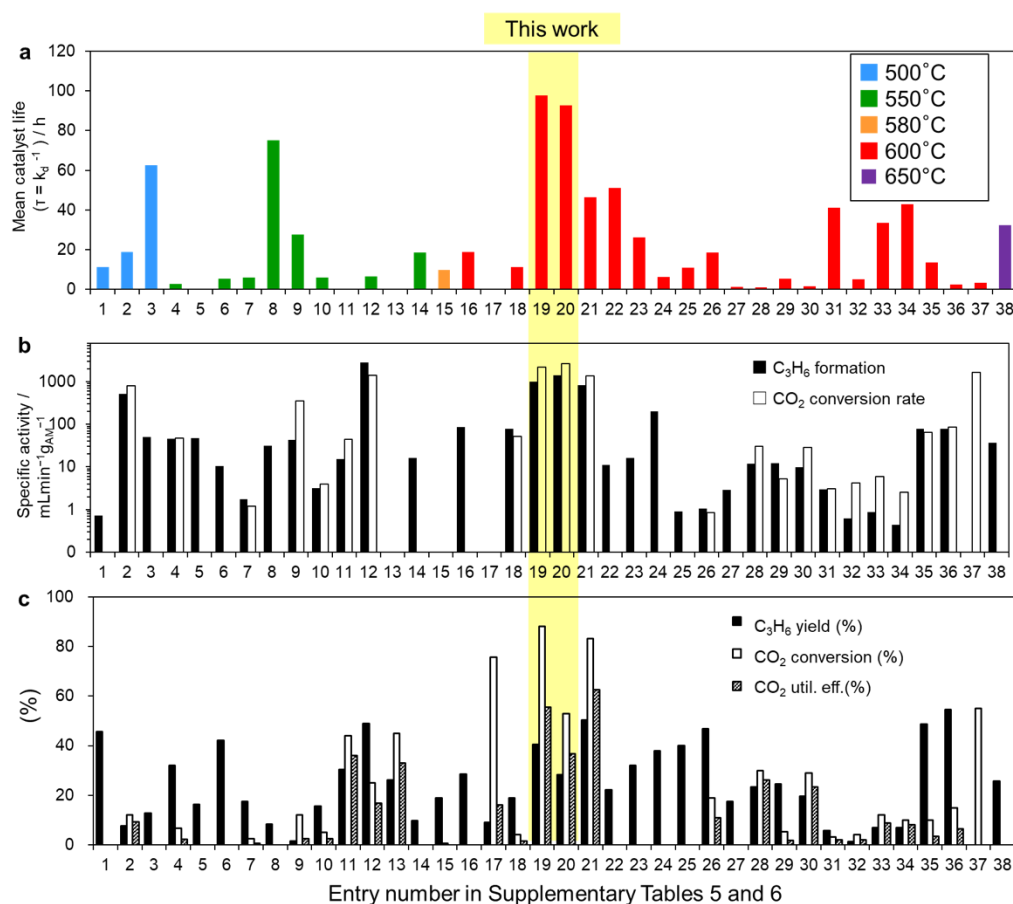


Figure 3.19. Catalytic performance of HEI/CeO₂ and reported systems for CO₂-ODP. **a** Mean catalyst life ($\tau = k_d^{-1}$). **b** Specific activity (mL_{C₃H₆}/CO₂·min⁻¹·g_{AM}⁻¹) for C₃H₆ formation and CO₂ conversion. **c** C₃H₆ yield CO₂ conversion, and CO₂ utilization efficiency. See Tables 3.5 and 3.6 for which selectivity/yield description (net or in hydrocarbons) was used for each entry. For entries 19 and 20 (HEI, this study), selectivity/yield in hydrocarbons are shown.

Table 3.5. Summary of the catalytic performance of HEI/CeO₂ and other reported catalysts for CO₂-ODP.

No	catalyst	temp. (°C)	gas feed ratio C ₃ H ₈ :CO ₂ :He	time (h)		C ₃ H ₈ conv. (%)		C ₃ H ₆ sel. (%) ^a		k _d (h ⁻¹)	τ (h)	ref.
				initial	final	initial	final	initial	final			
1	Ga ₈ Al ₂ O ₁₅	500	2.5: 5:92.5	0.25	8	49.7	33.1	91.7	98	0.089	11.2	[43]
2	Ru ₁ Cr ₁₀ O _x /SiO ₂	500	1:1:1	0.67	7	9	6.5	(85)	(90)	0.053	18.8	[44]
3	Pd/CeZrAlO _x	500	26:37:37	0.17	140	16	2	80	98	0.016	62.6	[13]
4	7%Cr/SBA-1	550	1:5:9	0.17	4	37.7	16	85	91	0.347	2.9	[45]
5	Cr-O/SiO ₂	550	1:5	0.17	0	17.2	—	94.4	—	—	—	[46]
6	Cr ₂ O ₃ —ZrO ₂ 180	550	2.5:5:92.5	0.17	6	53.3	27.8	(79)	(90.8)	0.186	5.4	[47]
7	Ga ₂ O ₃ —M	550	1:5:9	0.17	4	19	11	91.6	95	0.167	6.0	[48]
8	FeCeO ₂	550	1:1:2	0.10	20	17.5	14	(48)	(53)	0.013	75.2	[49]
9	Fe ₃ Ni/CeO ₂	550	1:1:2	0.10	10	4.8	3.4	30	58.2	0.036	27.5	[50]
10	20%ZnO-ZrO ₂	550	1:4:20	0.08	2	24	20	65	70	0.165	6.1	[51]
11	15V-15Zr@ZSM-5	550	2.5:5:92.5	1.0	6	35	39	87	90	—	—	[52]
12	0.5%PtSnCe/SiO ₂	550	1:1:5	0.08	6	55	33	(89.1)	(93.4)	0.154	6.5	[53]
13	Ga ₂ O ₃ V ₂ O ₅ /ZSM-5	550	—	0.50	6	30	35	87	90	—	—	[54]
14	FeNi/Ceria-Vo-R	550	2.4:4.8:10	0.33	3	23	21	(42)	(42)	0.054	18.6	[55]
15	12% In/HZSM-5	580	1:4:5	1.0	6	25.2	17.6	75	70	0.101	9.9	[56]
16	GaN/NaZSM-5	600	1:2:7	0.08	10	46	34	62	78	0.053	18.7	[57]
17	CaO/ZSM-5	600	5:5:90	0.08	—	23.1	—	39	—	—	—	[58]
18	2Cr-Ca/ZrO ₂	600	1:3:6	0.08	10	20.2	9.5	93.5	94.6	0.089	11.3	[59]
19	HEI/CeO ₂ 200mg	600	1:1:2	8 (0.5) ^b	90	44	31	92 (89)	93 (91)	0.010	97.7	This work
20	HEI/CeO ₂ 100mg	600	1:1:2	8 (0.5) ^b	50	30	20	94 (92)	90 (89)	0.011	92.6	
21	Pt—Co—In/CeO ₂	600	1:1:2	0.08	50	61	35	(82)	(94)	0.022	46.3	[14]
22	Ga ₂ O ₃ /HZSM-48	600	2.5:5:92.5	1.0	10	52.6	48.2	42.2	45.6	0.020	51.1	[60]
23	ZnO/HZSM-5	600	2.5:5:92.5	1.0	30	68.3	41.5	46.8	62.1	0.038	26.1	[61]
24	Cr-MSU-28	600	1:1:08	0.17	2	44	36.8	86	90.4	0.163	6.1	[62]
25	5%Cr/SiO ₂	600	15:30:55	0.55	20	80	53	50	90.6	0.078	12.8	[63]
26	2%Cr ₂ O ₃ /SiO ₂	600	15:30:55	0.3	17	71	50	(66)	(90)	0.055	18.3	[64]
27	15%Ga/ZrO ₂	600	2.5:5:92.5	0.17	3	38.6	6	45.4	77	0.807	1.2	[65]
28	Ga ₂ O ₃ /TiO ₂	600	2.5:5:92.5	0.17	3	32	2.5	(73)	—	1.027	1.0	[11]
29	Ga ₂ O ₃ /Al ₂ O ₃	600	2.5:5:92.5	0.17	3	26	17	(94)	—	0.190	5.2	[11]
30	Ga ₂ O ₃ /ZrO ₂	600	2.5:5:92.5	0.17	3	30	7	(65)	—	0.614	1.6	[11]
31	Ga ₂ O ₃ /SiO ₂	600	2.5:5:92.5	0.17	3	6.4	6	(92)	—	0.024	41.2	[11]
32	Ga ₂ O ₃ /MgO	600	2.5:5:92.5	0.17	3	4.3	2.5	(29)	—	0.198	5.1	[11]
33	10%In ₂ O ₃ /Al ₂ O ₃	600	2.5:10:87.5	0.17	8	24	20	29	84	0.030	33.5	[12]
34	In-Al-20	600	2.5:10:87.5	0.17	12	35	29	(20)	(78)	0.023	42.8	[66]
35	5.2V-MSNS	600	1:4:4	0.17	24	58	19	(84)	(89)	0.074	13.4	[67]
36	Cr/MSS-2	600	1:4:4	0.17	4	69	33	(79)	(90)	0.394	2.5	[68]
37	0.5 Ni-Cr/Si	600	1:1:8	0.17	12	90	19	0	90	0.308	3.2	[69]
38	7 Ga/SiO ₂ -A	650	1:2	0.08	20	33	21	(78)	(77)	0.031	32.3	[70]

^a Values with and without parenthesis indicate net C₃H₆ selectivity and C₃H₆ selectivity in hydrocarbon, respectively. ^b The data at time on stream of 8 h was used for the initial values of C₃H₈₍₆₎ because the induction period was observed in net C₃H₆ selectivity as shown in Figure 3.11. For the initial values of CO₂, time on stream of 0.5 h was employed.

Table 3.6. Summary of the catalytic performance of HEI/CeO₂ and other reported catalysts for CO₂-ODP. ^a

No	catalyst	active species (wt%)	C ₃ H ₈ conc. (%)	CO ₂ conv. (%)		catalyst amount (g)	total flow (mL/min)	CO ₂ rateutil. eff. (%)	F _(C₃H₆) / W _{AM} ^b		F _(CO₂) / W _{AM}	
				initial	final				initial	final	initial	final
1	Ga ₈ Al ₂ O ₁₅	80	2.5	—	—	0.20	10	—	0.7	0.5	—	—
2	Ru ₁ Cr ₁₀ O _x /SiO ₂	1	33.3	12	9	0.15	30	9	(510)	(390)	800	600
3	Pd/CeZrAlO _x	5	26.0	—	—	0.20	15	—	49.9	7.6	—	—
4	7%Cr/SBA-1	7	6.7	6.7	—	0.20	30	2	45.8	20.8	47.9	—
5	Cr-O/SiO ₂	3.4	16.7	—	—	0.50	30	—	47.8	0.0	—	—
6	Cr ₂ O ₃ -ZrO ₂ 180	10	2.5	—	—	0.20	20	—	(10.5)	(6.3)	—	—
7	Ga ₂ O ₃ -M	100	6.7	2.4	—	0.20	30	1	1.7	1.0	1.2	—
8	FeCeO ₂	10	25.0	—	—	0.20	30	—	(31.5)	(27.8)	—	—
9	Fe ₃ Ni/CeO ₂	1.7	25.0	12	5.7	0.10	20	3	42.4	58.2	353	168
10	20%ZnO-ZrO ₂	20	4.0	5	4	0.50	50	2	3.1	2.8	4.0	3.2
11	15V-15Zr@ZSM-5	15	2.5	44	49	0.20	60	36	15.2	17.6	44.0	49.0
12	0.5%PtSnCe/SiO ₂	0.5	14.3	25	20	0.25	50	17	(2800)	(1761)	1429	1143
13	Ga ₂ O ₃ V ₂ O ₅ /ZSM-5	4	—	45	47	0.20	15	33	—	—	—	—
14	FeNi/Ceria-Vo-R	1.43	14.0	—	—	1.00	17.2	—	(16.2)	(14.8)	—	—
15	12% In/HZSM-5	12	10.0	0.6	3	—	20	—	—	—	—	—
16	GaN/NaZSM-5	5	10.0	—	—	0.20	30	—	85.6	79.6	—	—
17	CaO/ZSM-5	50	5.0	75.7	—	—	100	16	—	—	—	—
18	2Cr-Ca/ZrO ₂	2	10.0	4.1	0.7	0.30	25	1	78.7	37.4	51.3	8.8
19	HEI/CeO ₂ 200mg	1	25.0	88	42	0.20	20	61	1012	720	2200	1050
20	HEI/CeO ₂ 100mg	1	25.0	53	24	0.10	20	37	1414 (1380)	900 (890)	2650	1200
21	Pt-Co-In/CeO ₂	3	25.0	83	45	0.10	20	70	(837)	(548)	1385	750
22	Ga ₂ O ₃ /HZSM-48	5	2.5	—	—	0.20	20	—	11.1	11.0	—	—
23	ZnO/HZSM-5	5	2.5	—	—	0.20	20	—	16.0	12.9	—	—
24	Cr-MSU-28	2.8	10.0	—	—	0.20	30	—	203	178	—	—
25	5%Cr/SiO ₂	2	15.0	—	—	—	—	—	0.9	1.1	—	—
26	2%Cr ₂ O ₃ /SiO ₂	2	15.0	19	—	—	—	11	(1.1)	(1.0)	0.9	—
27	15%Ga/ZrO ₂	15	2.5	0	—	0.20	20	0	2.9	0.8	—	—
28	Ga ₂ O ₃ /TiO ₂	5	2.5	30	—	0.20	20	26	(11.7)	—	30.0	—
29	Ga ₂ O ₃ /Al ₂ O ₃	5	2.5	5.2	—	0.20	20	2	(12.2)	—	5.2	—
30	Ga ₂ O ₃ /ZrO ₂	5	2.5	29	—	0.20	20	23	(9.8)	—	29.0	—
31	Ga ₂ O ₃ /SiO ₂	5	2.5	3.1	—	0.20	20	2	(2.9)	—	3.1	—
32	Ga ₂ O ₃ /MgO	5	2.5	4.2	—	0.20	20	2	(0.6)	—	4.2	—
33	10%In ₂ O ₃ /Al ₂ O ₃	10	2.5	12	10	0.20	10	9	0.9	2.1	6.0	5.0
34	In-Al-20	20	2.5	10	8	0.20	10	8	(0.4)	(1.4)	2.5	2.0
35	5.2V-MSNS	5.2	11.1	10	—	0.20	15	3	(78.1)	(27.1)	64.1	—
36	Cr/MSS-2	7	11.1	15	5	0.20	18	6	(77.9)	(42.4)	85.7	28.6
37	0.5 Ni-Cr/Si	0.5	10.0	55	15	0.20	30	—	0.0	513	1650	450
38	7 Ga/SiO ₂ -A	7	33.3	—	—	1.00	30	—	(36.8)	(23.1)	—	—

^a The time on stream for the initial and final values are the same with those in Table 3.5. The initial time was used for calculating CO₂ utilization efficiency. ^b Values with and without parenthesis indicate those based on net C₃H₆ yield and C₃H₆ yield in hydrocarbon, respectively.

3.3.3 Mechanistic study

A mechanistic study was performed to better understand the roles of the HEI structure in enhanced catalysis. Arrhenius-type plots were used to compare the apparent activation energy (E_A^*) for the PtSn/CeO₂, Pt–Co–In/CeO₂, and HEI/CeO₂. The E_A of C₃H₈ dehydrogenation for PtSn/CeO₂ was 143.9 kJ·mol⁻¹ and Pt–Co–In/CeO₂ was 138.3 kJ·mol⁻¹, whereas HEI/CeO₂ was 128.0 kJ·mol⁻¹ (Figure 3.20a). A similar trend was also observed for the E_A of CO₂ reduction (Figure 3.20b, PtSn: 141.5 kJ·mol⁻¹, Pt–Co–In: 130.3 kJ·mol⁻¹, and HEI: 102.5 kJ·mol⁻¹). Thus, the activation of C₃H₈ and CO₂ are both kinetically promoted in the HEI structure. To investigate the reactivity of coke accumulated on the catalyst surface, we also conducted temperature-programmed surface reactions (TPSRs) on spent Pt–Co–In/CeO₂ and HEI/CeO₂ catalysts. When the temperature was elevated under flowing He, CO was produced, indicating that coke was combusted by CeO₂ lattice oxygen. (He-TPSR, Figure 3.20c). Notably, the combustion temperature for HEI was lower than that of Pt–Co–In, demonstrating that the coke combustion ability of HEI/CeO₂ is superior to that of Pt–Co–In/CeO₂. This may be explained by the enhanced redox property of CeO₂ by multi-metallization (see Figure 3.21 for details). When TPSR was performed on coked HEI/CeO₂ in the presence of CO₂ (CO₂-TPSR, Figure 3.20d), a large amount of CO evolved from 600°C and was completely combusted at 700°C. On the other hand, when coked Pt–Co–In/CeO₂ was used, CO evolution occurred at higher temperatures (from 650°C), which is consistent with the trend in E_A of CO₂ activation. Based on these results, we concluded that the high coke resistance of HEI/CeO₂ originated from the enhancement in the redox property of CeO₂ and the CO₂ activation ability of the alloy phase by multi-metallization. We further tested the catalytic performance of HEI in DDP as a control experiment without CO₂. As shown in Figure 3.20e, rapid deactivation occurred within 0.5 h even for HEI/CeO₂, indicating that simultaneous CO₂ supply is necessary for the continuous coke combustion. This is because the oxygen vacancy of CeO₂ must be refilled for the continuous combustion. In this regard, we previously confirmed by H₂-TPR and CO₂-TPO that the oxygen atoms derived from CO₂ refilled the oxygen vacancy of CeO₂.^[71] Then, C₃H₈ conversion was fully recovered when HEI/CeO₂ was regenerated under flowing CO₂ and the subsequent H₂ reduction, demonstrating that coke accumulated on the catalyst can be completely removed. Conversely, the catalytic activity of HEI/SiO₂ (Figure 3.20f) and HEI/Al₂O₃ (Figure 3.22) was not fully recovered after the regeneration process. Therefore, the oxygen releasing ability of CeO₂ is essential for the coke combustion and the high

regenerability. HEI/SiO₂ showed slower deactivation rate than HEI/CeO₂, which may be due to much higher specific surface area of SiO₂ than CeO₂.

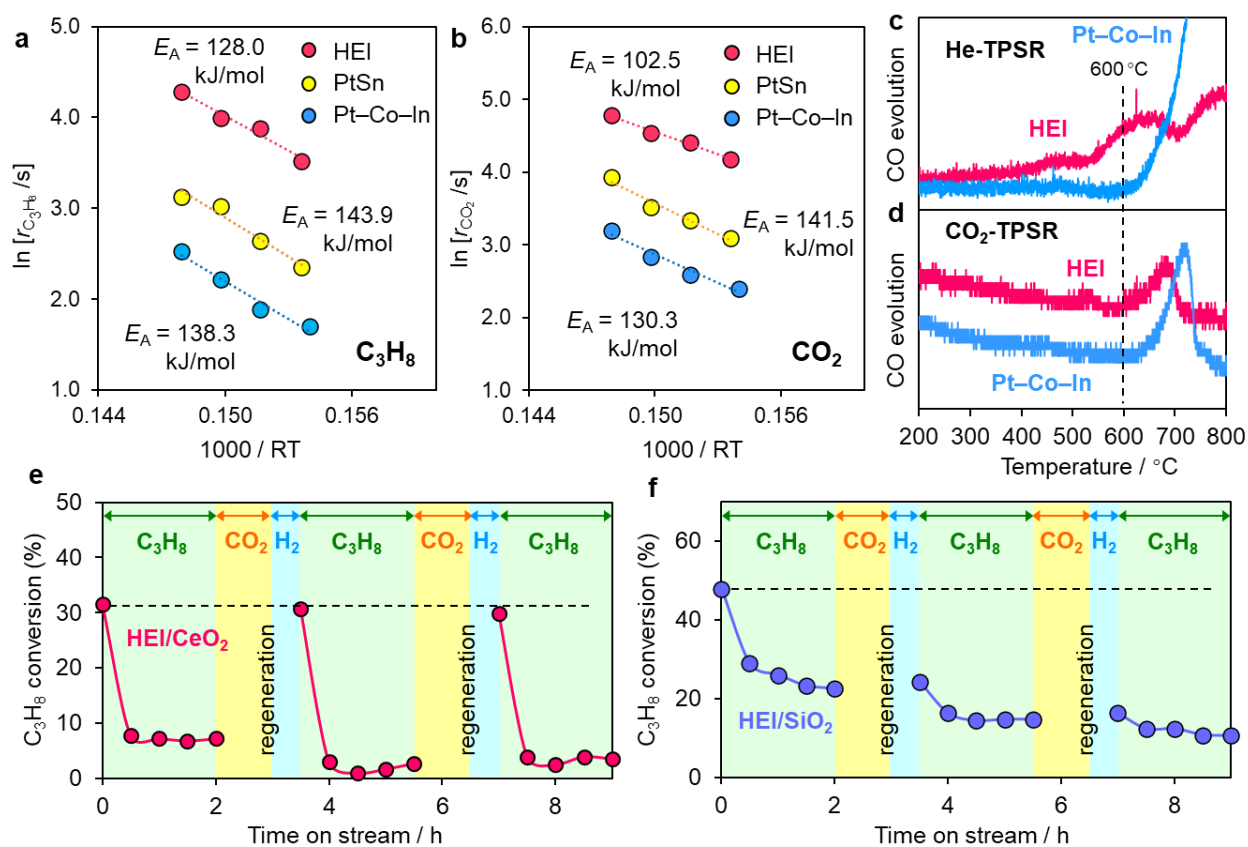


Figure 3.20. Mechanistic study. Arrhenius-type plots for **a** C_3H_8 and **b** CO_2 conversion rates obtained in CO_2 -ODP on HEI/CeO₂. **c** He- and **d** CO_2 -TPSR on the coked Pt-Co-In/CeO₂ and HEI/CeO₂ catalysts (used in CO_2 -ODP for 50 h). CO evolution was quantified by the mass intensity of $m/z = 28$, respectively. Changes in C_3H_8 conversion in the DDP-regeneration cycles over **e** HEI/CeO₂ and **f** HEI/SiO₂. Reaction conditions: DDP; C_3H_8 :He = 5:10 mLmin⁻¹ (2 h), regeneration; CO_2 :He = 10:10 mLmin⁻¹ (1 h), then H_2 :He = 5:10 mLmin⁻¹ (0.5 h) at 600 $^{\circ}C$.

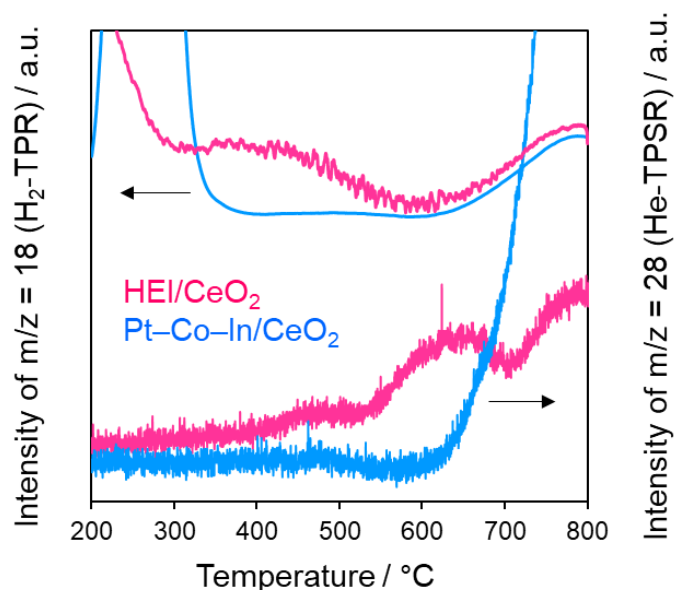


Figure 3.21. H₂-TPR and He-TPSR. H₂-TPR profiles of unreduced HEI/CeO₂ and Pt-Co-In/CeO₂ (magnification of Figure 3.6) and He-TPSR on the coked Pt-Co-In/CeO₂ and HEI/CeO₂ (magnification of Figure 3.20c). The reduction of CeO₂ was promoted by the multi-metallization as well as the reduction of the alloy phase shown in Figure 3.6 (a new reduction peak assignable to the reduction of CeO₂ appeared around at 400~550°C). The starting temperature of CO evolution in the He-TPSR on HEI/CeO₂ roughly agreed with this region. A similar trend was also observed for Pt-Co-In/CeO₂ (both started from 600°C). Thus, the coke combustion ability of the lattice oxygen of CeO₂ seems to follow the reducibility of CeO₂.

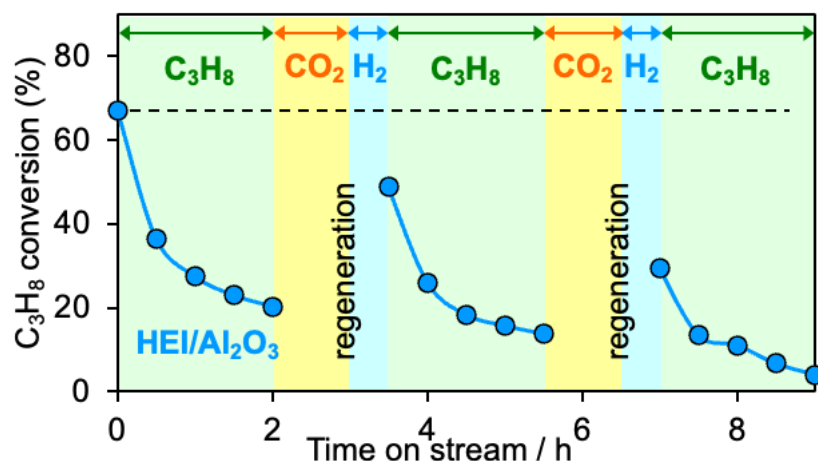


Figure 3.22. Changes in C₃H₈ conversion in the DDP-regeneration cycles over HEI/Al₂O₃. Reaction conditions: DDP; C₃H₈:He = 5:10 mLmin⁻¹ (2 h), regeneration; CO₂:He = 10:10 mLmin⁻¹ (1 h), then H₂:He = 5:10 mLmin⁻¹ (0.5 h) at 600°C.

3.3.4 DFT calculation

Finally, DFT calculations were conducted to better understand the role of the HEI phase in the CO₂-ODP's high catalytic performance. As the parent structure of HEI, a PtSn-(2×2×2) supercell was constructed, and then the Pt and Sn sites were partially and randomly replaced with Ni/Co and In, respectively (Figure 3.23a, see method paragraph and Table 3.7 for further details in modeling). Because of the low concentration mentioned above, Ga was not included in this model for simplicity. Two (110) surfaces (corresponding to the supercell's (004) layer) were cleaved for surface slab models (Figure 3.24). Adsorption (E_{ad}) and C–H activation energies (E_A) of propylene were calculated using eight different adsorption sites and conformations (Figure 3.23b, see Figures. 20–24 for details). E_{ad} and E_A have narrow ranges (E_{ad} : -51 ~ -35 kJmol⁻¹, E_A : 137 ~ 147 kJmol⁻¹), suggesting that reactivity is not strongly dependent on local structure and elemental distribution. Figure 3.23c compares the E_A and E_{ad} for PtSn, Pt–Co–In, and HEI. We also demonstrated ΔE ($\Delta E = E_A + E_{ad} = E_A - E_d$ (propylene desorption energy)), which is widely used as a scale that reflects propylene selectivity. The ΔE of HEI (98.9 kJmol⁻¹) was much higher than that of Pt–Co–In (45.7 kJmol⁻¹) and indicates that propylene desorption is significantly enhanced, which is consistent with the experimental trend in C₃H₆ selectivity (90% and 60% at 40 hours, respectively). When compared to Pt–Co–In and PtSn, HEI demonstrated much higher E_A , indicating that isolating Pt effectively inhibits the third C–H activation, which causes side effects. This property significantly reduces the formation of coke as a result of side reactions. The E_A of propane to propylene and CO₂ reduction was also calculated on each of the three surfaces (see Figures. 3.25–3.34 for details). The summary of E_A and the corresponding energy diagrams are shown in Figures. 3.23d and 3.23e, respectively. HEI showed lower E_A of propane dehydrogenation than PtSn and Pt–Co–In, indicating that the desired C–H activation was enhanced by multi-metallization while the undesired was inhibited. The order of E_A (HEI < Pt–Co–In < PtSn) was consistent with that of the experimental apparent E_A shown in Figure 3.23a. For CO₂ reduction, CO₂ is first chemisorbed on the metallic surface to form a bidentate sp^2 -like conformation, then C–O cleavage occurs to generate CO and O (Figure 3.23e and Figures. 3.30–33). Although the chemisorption step showed moderate energy barriers (~ 0.7 eV), they were much lower than those of the CO₂ activation step (1.0~1.3 eV), indicating that CO₂ activation is the rate-determining step (RDS) in CO₂ reduction. In this regard, we recently revealed by microkinetic modeling that CO₂ activation was the RDS in CO₂-ODP over Pt–Co–In. Among the three surfaces, PtSn had the highest E_A of CO₂ activation (Figure 3.23d). This is consistent with the low CO₂ conversion rate and is most likely due to a lack of 3d transition metals. The E_A of HEI

was exhibited to be lower than that of Pt–Co–In, which corresponded to the experimental order of apparent activation energies shown in [Figure 3.23a](#). We also considered the effect the electronic structure changes upon multi-metallization on the catalytic activity. [Figure 3.23f](#) shows the density of states projected on d orbitals (d-DOS) of the surface transition metals on HEI(004):B and PtSn(110). PtSn had low d-DOS near the Fermi level due to alloying with Sn, which may have resulted in the high E_A . Conversely, HEI showed an intense peak near the Fermi level owing to the Ni and Co 3d states. Therefore, the d band was significantly upshifted near the Fermi level by doping Ni and Co. The enhanced activity in propane dehydrogenation and CO₂ reduction can be explained by the modification of the d band by the introduction of Ni and Co. This demonstrates our catalyst design concept mentioned in the introduction paragraph ([Figure 3.1](#)).

As a result, the experimental trends in C₃H₈ activation, C₃H₆ selectivity, CO₂ conversion, and stability were reproduced by our DFT calculation. The enhanced CO₂ activation capability improves oxygen supply for coke combustion. Thus, the HEI phase is capable of inhibiting coke formation while also promoting coke combustion, which enhances coke resistance and the long-term stability of the catalyst.

3.4 Discussion

In summary, we designed and prepared a PtSn-based HEI catalyst in the CO₂-ODP using CeO₂ as a highly coke resistant and thermally stable catalyst. The Pt and Sn sites of intermetallic PtSn were partially substituted with Ni/Co and In/Ga, resulting in nanoparticles with a HEI structure of (PtCoNi)(SnInGa). The multi-metallization sufficiently isolates Pt atoms, preventing propylene decomposition and coke formation. The incorporation of Ni and Co significantly enhanced the ability to activate CO₂. Doping In(Ga) into the Sn site improved catalyst stability, probably due to the enhanced entropy effect. The combination of these abilities significantly enhances coke resistance and catalyst lifetime. Furthermore, because of the increased thermal stability, multi-metallization also prevents nanoparticle sintering. The HEI/CeO₂ catalyst shows 2- and 1.5-times higher catalyst life and specific activity than those of the best catalyst ever reported. Moreover, the catalyst can be reused by performing a simple regeneration procedure with CO₂ alone without any loss of original performance. This work not only demonstrated outstanding catalytic performance, but it also opened up a new window of catalyst design concepts based on HEI. The obtained insights and technology will contribute to carbon-neutralization of industrial processes for light alkane conversions.

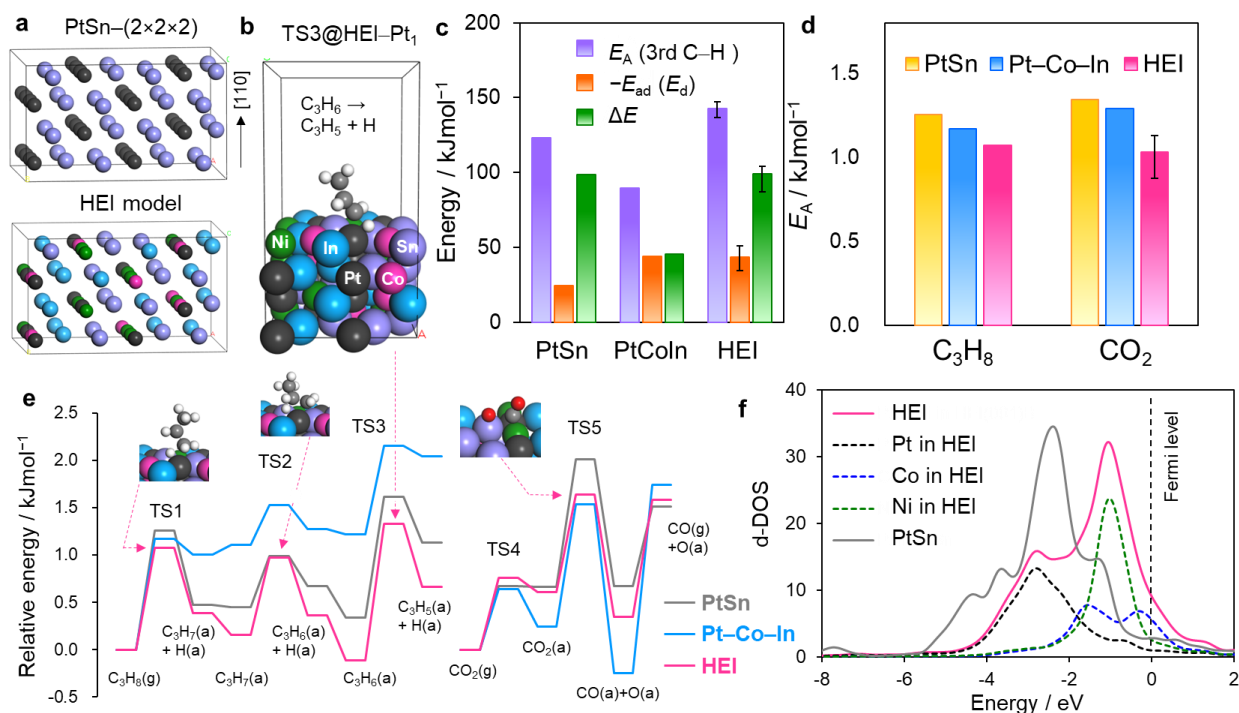


Figure 3.23. DFT calculations. **a** Model structures of PtSn and the PtSn-based HEI for DFT calculations. **b** An example of the HEI slab model for CO₂-ODP for the over dehydrogenation: C₃H₆→C₃H₅+H at a Pt₁-HEI site on (110) surface (HEI(001):B3). **c** Comparison of E_A of the third C–H activation (overdehydrogenation of C₃H₆), $-E_{ad}$ (E_d) of C₃H₆, and ΔE ($= E_A + E_{ad}$) on the surface of PtSn, Pt–Co–In, and HEI (average). **d** E_A of propane dehydrogenation and CO₂ activation. For propane dehydrogenation, E_A of the first C–H scission was shown. **e** Energy diagrams of propane dehydrogenation and CO₂ reduction on the surface of PtSn, Pt–Co–In and HEI. **f** d-DOS of the surface transition metals on HEI(004):B and PtSn(110).

Table3.7. Structural information of HEI optimized by DFT.

lattice parameters / Å					cell angles / degree				
a	10.6585	b	13.9152	c	8.0341	$\alpha = \beta = \gamma = 90$			
fractional coordinates									
element	No.	a	b	c	element	No.	a	b	c
Pt	1	0.4989	0.253349	0.000127	In	1	0.132369	0.418577	-0.006663
Pt	2	1.000477	0.249699	-0.001157	In	2	0.36528	0.08387	0.000168
Pt	3	1.002695	0.499398	0.253125	In	3	0.631272	0.169734	0.256446
Pt	4	1.001279	0.250256	0.499994	In	4	0.621183	0.41374	0.491502
Pt	5	0.74544	0.50098	0.750795	In	5	0.629955	0.169242	0.744043
Pt	6	0.49888	1.002084	0.253777	In	6	0.86185	0.084153	0.000376
Pt	7	0.498532	1.001659	0.746333	In	7	0.861619	0.333782	0.25085
Pt	8	0.250743	0.745421	0.499885	In	8	0.864185	0.084005	0.499741
Pt	9	1.000779	1.001602	0.246267	In	9	0.131015	0.917392	0.500279
Pt	10	1.000476	1.001863	0.753671	In	10	0.120321	0.662932	0.756175
Pt	11	0.7492	0.745824	0.000406	In	11	0.375859	0.831994	0.242164
Pt	12	0.748351	0.745198	0.499531	In	12	0.374635	0.831214	0.758154
Co	1	0.251136	0.25239	0.000323	In	13	0.625435	0.916319	-0.000185
Co	2	0.254296	0.251967	0.499585	In	14	0.629601	0.916115	0.500172
Co	3	1.001574	0.498301	0.745568	In	15	0.878691	0.83321	0.250131
Co	4	0.746549	0.505096	0.247824	In	16	0.878862	0.832705	0.750004
Co	5	0.747527	0.252256	0.504361	Sn	1	0.136645	0.168034	0.249815
Co	6	0.496455	0.743425	0.001942	Sn	2	0.133174	0.41767	0.5072
Co	7	0.249256	1.001212	0.250091	Sn	3	0.138995	0.16718	0.749708
Co	8	0.249884	1.000828	0.749765	Sn	4	0.368666	0.334153	0.255663
Ni	1	0.495723	0.499376	0.247625	Sn	5	0.365006	0.086589	0.499847
Ni	2	0.49708	0.250441	0.49985	Sn	6	0.370782	0.333711	0.743915
Ni	3	0.493691	0.498495	0.753772	Sn	7	0.625469	0.419795	0.010118
Ni	4	0.254886	0.501631	0.251652	Sn	8	0.870837	0.332846	0.748453
Ni	5	0.252996	0.501038	0.748815	Sn	9	0.136246	0.913398	-0.000215
Ni	6	0.747909	0.252918	-0.003828	Sn	10	0.126128	0.668767	0.242931
Ni	7	0.498359	0.745527	0.497899	Sn	11	0.372679	0.583871	0.000053
Ni	8	0.249845	0.746757	0.000898	Sn	12	0.379299	0.577801	0.500735
Ni	9	1.004776	0.750115	0.001698	Sn	13	0.615324	0.661817	0.248051
Ni	10	1.001298	0.746294	0.497492	Sn	14	0.609215	0.666945	0.751557
Ni	11	0.748825	0.999573	0.249371	Sn	15	0.882207	0.58152	-0.002066
Ni	12	0.748987	0.999642	0.75073	Sn	16	0.878052	0.581137	0.502133

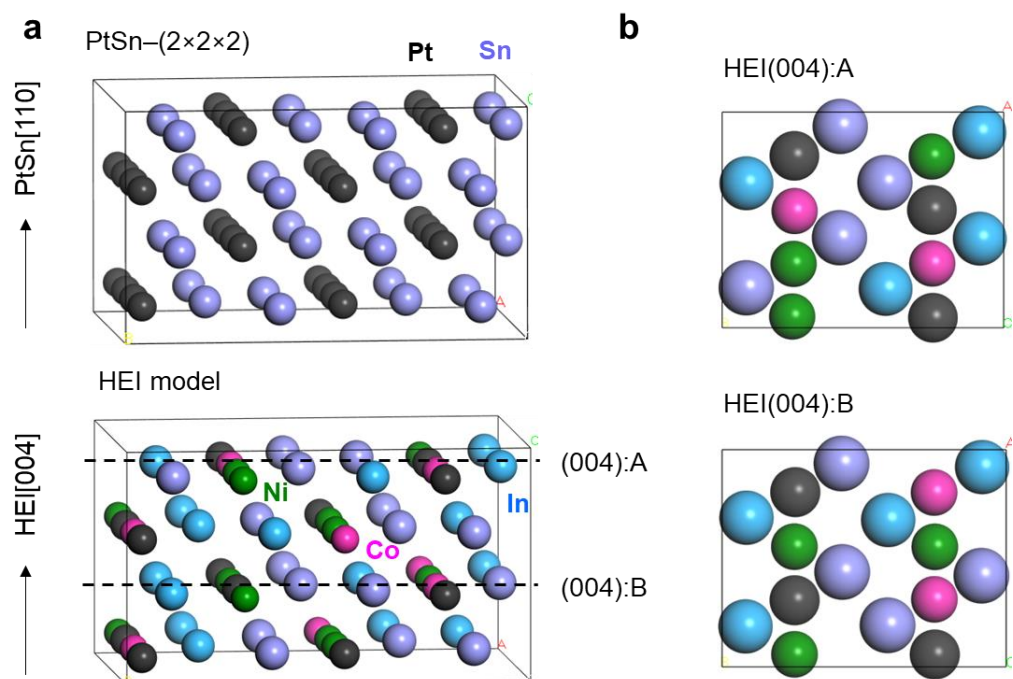


Figure 3.24. Structural details for DFT calculations. **a** The optimized structure of the (2×2×2) supercell of PtSn and the corresponding HEI model. The first (A) and third (B) top layers of the (004) plane were selected as representative surfaces for catalysis. **b** Atomic arrangement of the HEI(004): A and B surfaces.

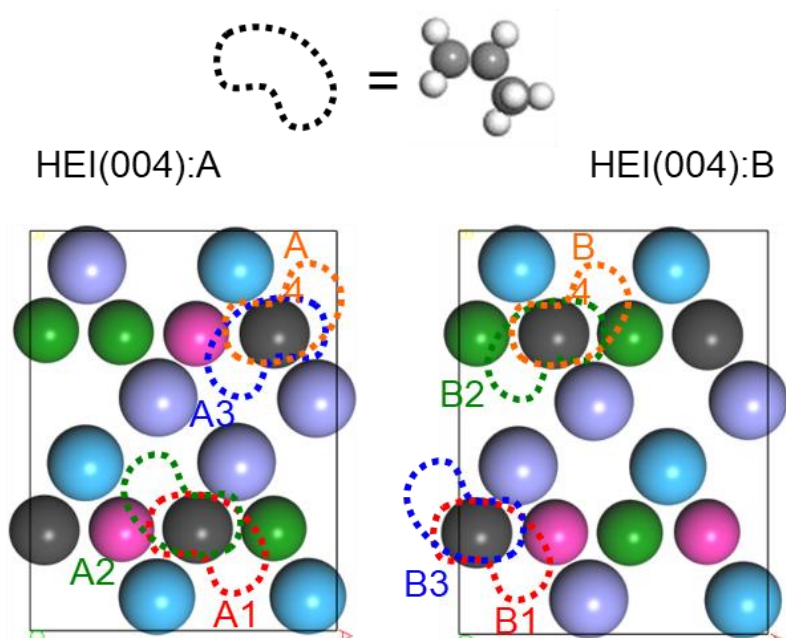


Figure 3.25. Adsorption sites and conformations of C₃H₆ on the HEI(004) surfaces considered in this study. Dotted lines indicate the conformations of C₃H₆.

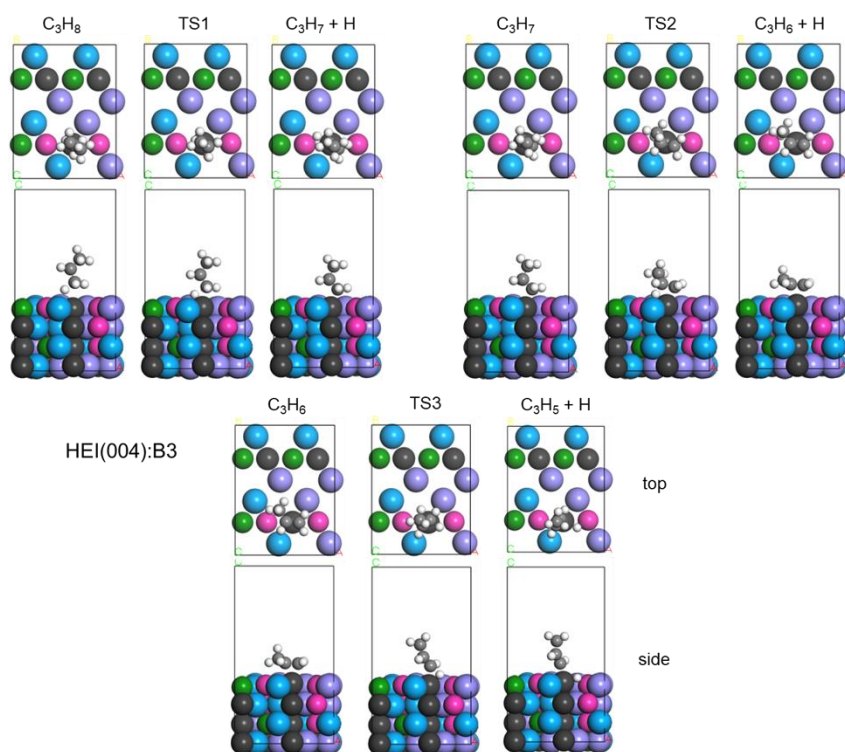


Figure 3.26. DFT-optimized structures of C_3H_x on HEI. Structures of initial (IS), transition (TS), and final states (FS) in the C–H activation of C_3H_6 on the B3 site of HEI(004).

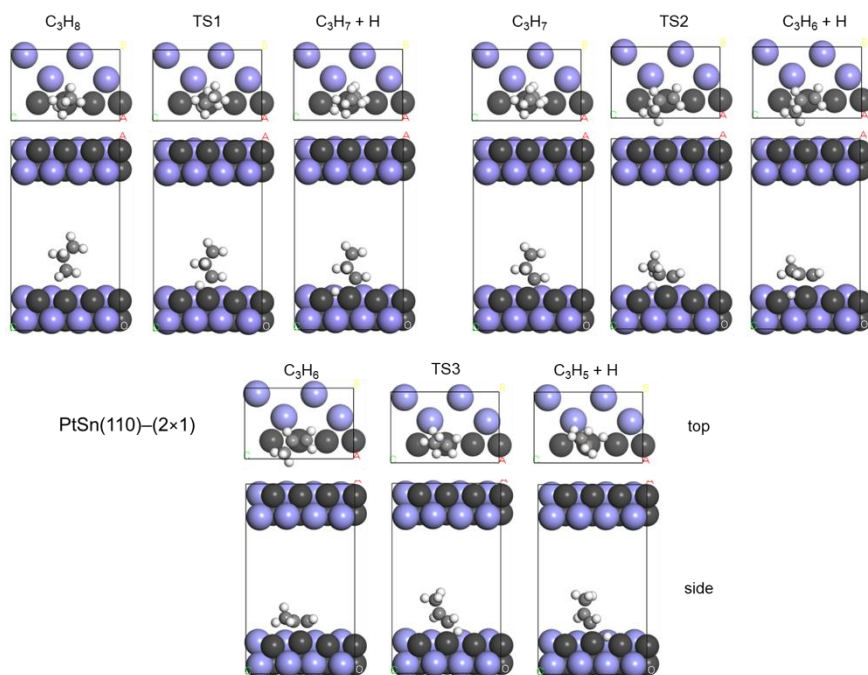


Figure 3.27. DFT-optimized structures of C_3H_x on PtSn. Structures of initial (IS), transition (TS), and final states (FS) in the C–H activation of C_3H_6 on PtSn(110).

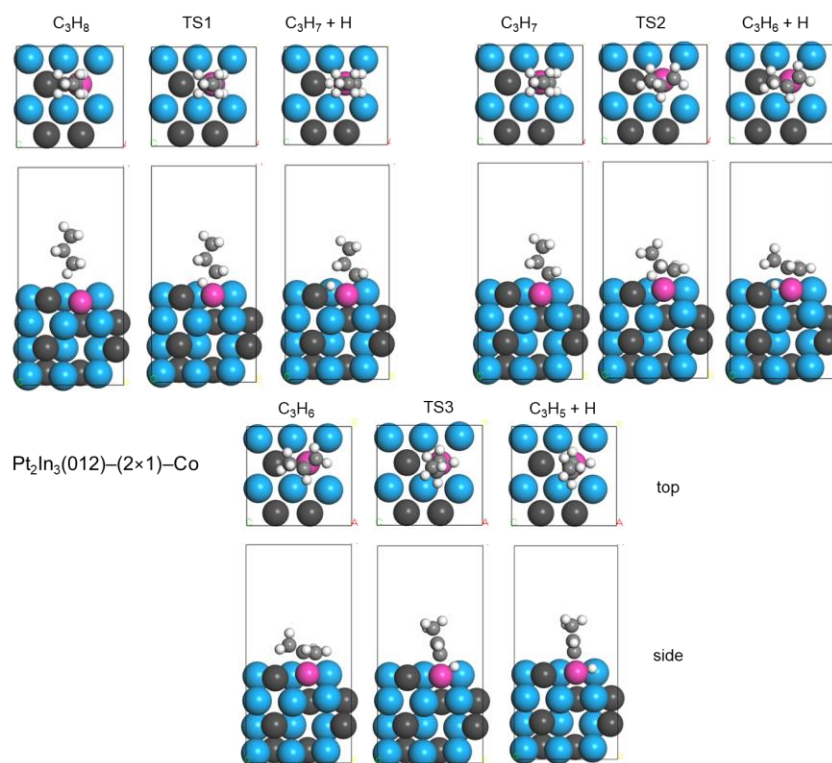


Figure 3.28. DFT-optimized structures of C_3H_x on Pt-Co-In. Structures of initial (IS), transition (TS), and final states (FS) in the C-H activation of C_3H_6 on $Pt_2In_3(012)-Co$.

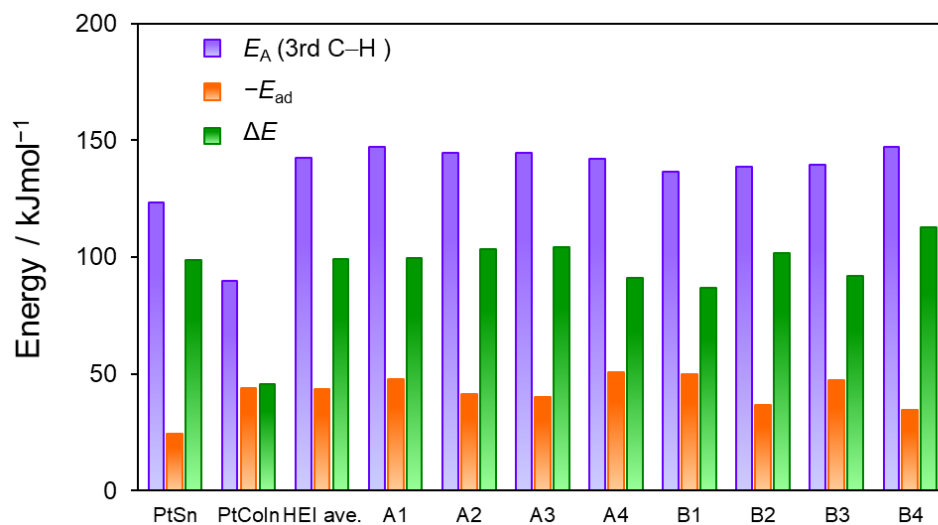


Figure 3.29. Comparison of DFT-calculated energies. E_A of 3rd C-H activation, ΔE , and E_{ad} of C_3H_6 on the surface of PtSn, PtCoIn, and HEI with eight different adsorption sites and conformations. Average of A1 to B4 is shown as “HEI ave.”

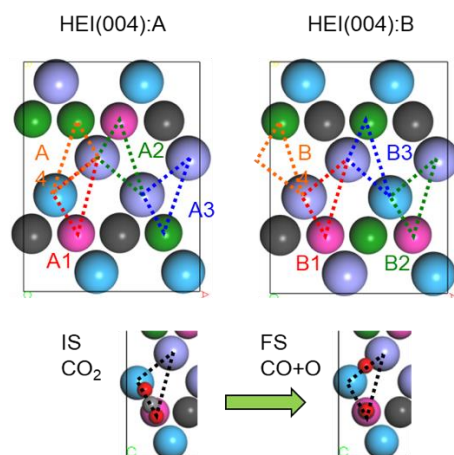


Figure 3.30. Adsorption sites and conformations of CO₂, CO, and O on the HEI(004) surfaces. Dotted triangles indicate the region where the adsorbates are involved.

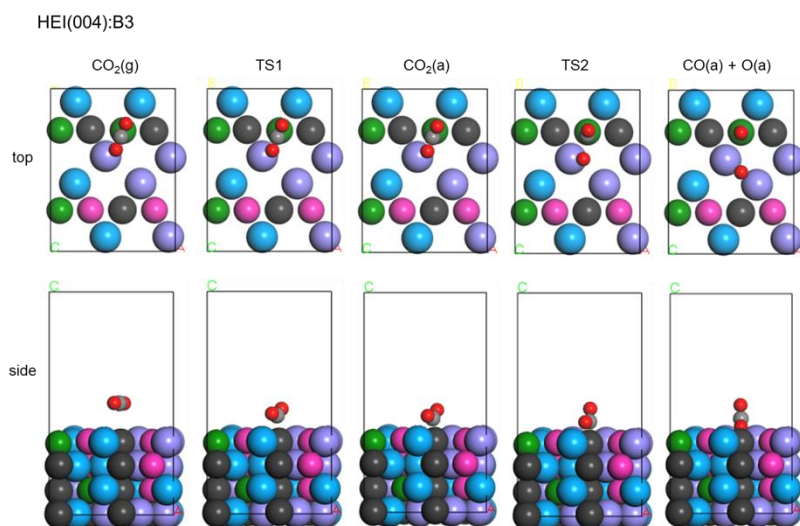


Figure 3.31. DFT-optimized structures of CO_x on HEI. Structures of initial (IS), transition (TS), and final states (FS) in CO₂ activation on the B3 site of HEI(004).

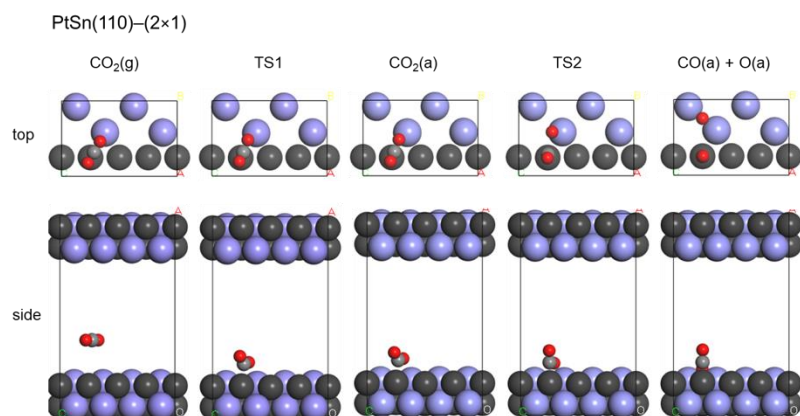


Figure 3.32. DFT-optimized structures of CO₂ on PtSn. Structures of initial (IS), transition (TS), and final states (FS) in CO₂ activation on PtSn(110).

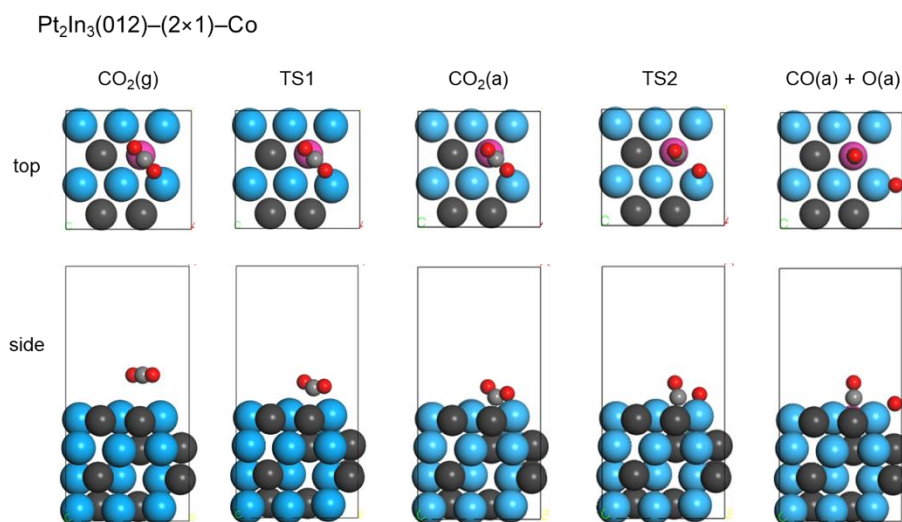


Figure 3.33. DFT-optimized structures of CO_2 on Pt–Co–In. Structures of initial (IS), transition (TS), and final states (FS) in CO_2 activation on the Co site of $\text{Pt}_2\text{In}_3(012)\text{-Co}$.

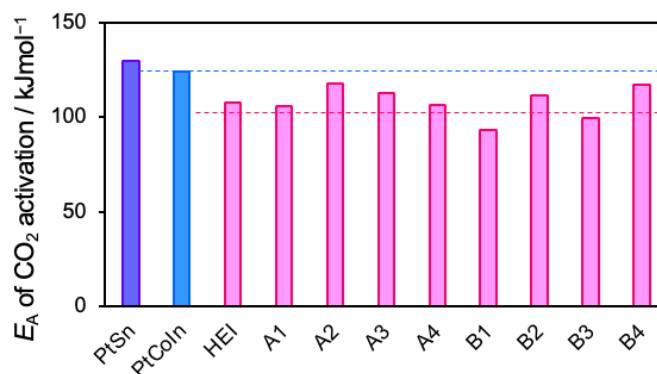


Figure 3.34. Comparison of CO_2 activation energy. E_A of CO_2 activation on the surface of PtSn, PtCoIn, and HEI with eight different adsorption sites and conformations. Average of A1 to B4 is shown as red dotted lines.

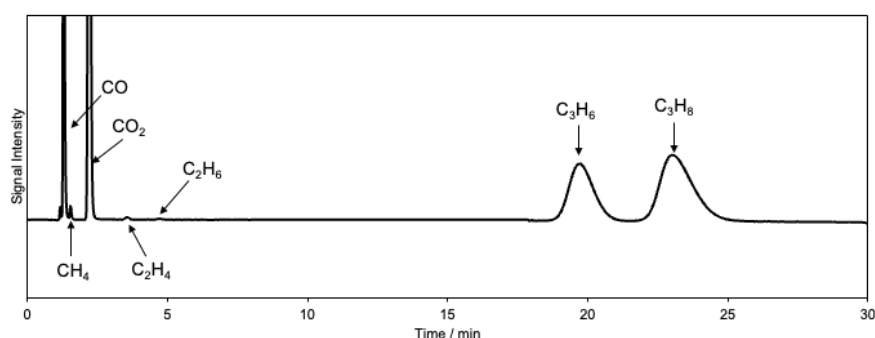


Figure 3.35. An example of the GC chart. A GC chart obtained from the outlet gas in CO_2 -ODP over HEI/ CeO_2 .

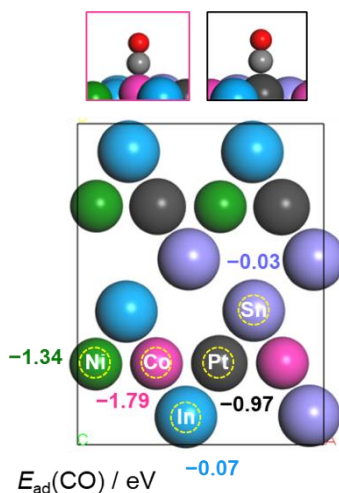


Figure 3.36. DFT calculation for CO adsorption. E_{ad} (eV) of CO on some atop sites of HEI(004):B. Yellow dotted circles indicate the adsorption sites of CO. Upper insets show the optimized structure of CO on Co and Pt atop sites. Sn and In showed very small negative values corresponding to only physisorption. The largely negative values for Pt, Ni, and Co indicate that they are active for CO pulse chemisorption and should be included in the estimation of metal dispersion and TOF.

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Chapter Four

Design of Pt-based Pseudo-binary Intermetallic Catalysts
for Dry Reforming of Propane using CO₂

4.1 Introduction

Syngas (syngas; a mixture of H_2 and CO) production is an important industrial process for the conversion of natural gas into liquid fuels and essential components of petrochemicals and chemicals.^[1] In this regard, thermochemical reforming has attracted a lot of attention as a technology for syngas production of liquid fuels and oxygenated chemicals with low H_2/CO ratio.^[2–4] Conventional syngas production via steam reforming often yields products with $H_2:CO > 3$, which is higher than required for further downstream processing of olefins (Fischer-Tropsch reaction) or synthesis of oxygenated compounds. Therefore, as an option, dry reforming of methane with CO_2 is of elevated importance and thus has been extensively studied.^[5–8] In recent years, the dry reforming of light hydrocarbons such as ethane and propane has also received considerable attention.^[9–13] Compared to methane, the use of ethane and propane can consume more CO_2 stoichiometrically, therefore, it has a great potential for greenhouse gas emission reduction and energy savings. In particular, propane is more easily activated than methane at lower reaction temperatures. Propane is a major component of natural gas and is also produced in various petroleum processing operations and it can be stored as a compressible liquid and is easier to transport.^[13] On the other hand, due to its high carbon atom content, propane is expected to produce more surface carbon species than other natural gases, so an efficient catalyst design is challenging.

Many previous studies on catalytic dry reforming of propane (DRP) using precious metals such as Pt, Ru, Rh, and Re have been reported.^[9,14–16] Precious metals exhibit high catalytic activity and selectivity in thermochemical reforming processes, but their high cost have limited their application in industry. Transition metal-based catalysts such as nickel are a cost-effective alternative to precious metal-based catalysts, and many researchers have confirmed the activity of nickel-based catalysts for dry reforming reactions.^[13,17–20] However, nickel-based catalysts can be rapidly deactivated by sintering and coke formation, which can be more severe especially for DRP reactions. Inspired by this, alloys of noble and transition metals are potential ways to develop efficient coke resistant catalysts while reducing costs in large-scale processes. In our previous study, we reported that the Pt–Co–In/ CeO_2 catalyst exhibited remarkably high catalytic activity and CO_2 utilization efficiency in oxidative dehydrogenation of propane using CO_2 .^[21] It demonstrates that the performance of the reaction can be well tuned in controlling the structure of the catalyst.

Here, we report a highly efficient ternary PtCo₂In₃/ CeO_2 catalyst for the DRP reaction with high selectivity and stability even for 100 h reaction. The result showed that the catalytic behavior of these catalysts is highly sensitive to the doping amount of cobalt. By controlling

the amount of cobalt doping, the catalytic activity of the Pt-Co-In/CeO₂ catalyst can be improved and the C-H/C-C bond of propane can be selectively cleaved in the presence of CO₂. The origin of the altered catalytic behavior is analyzed using X-ray powder diffraction (XRD), transmission electron microscopy (TEM), and temperature programmed-mass spectrometry measurements (TP-MS). The PtCo₂In₃/CeO₂ catalysts reported in this work demonstrates great advantages over conventional reported catalysts for the DRP reaction.

4.2 Experiment

4.2.1 Catalysts preparation. Pt/CeO₂, Pt-Co/CeO₂, Pt-In/CeO₂, and Pt-Co-In/CeO₂ (Pt: 3 wt%) were prepared by a conventional impregnation method using H₂PtCl₆ (aqueous solution, Kojima Chemicals, Pt 8.77 wt%), In(NO₃)₃·3H₂O, and Co(NO₃)₂·6H₂O, as metal precursors. The CeO₂ support (JRC-CEO-2, $S_{\text{BET}} = 123.1 \text{ m}^2\text{g}^{-1}$) was added to a vigorously stirred aqueous solution (50 ml H₂O per gram of CeO₂) containing Pt and the corresponding second and/or third metal precursor(s) (Pt:Co = 1:1, Pt:In = 1:1, and Pt:Co:In = 1:2:3 or 2:1:3), followed by stirring for 3 h at room temperature. The mixture was dried under a reduced pressure at 50 °C using a rotary evaporator, followed by calcination under flowing air at 500°C for 1 h and reduction under flowing H₂ (50 ml/min) at 600 °C for 1 h. Co/CeO₂, CoIn/CeO₂, and In/CeO₂ were prepared by a similar method, where the amounts of Co and In were adjusted to be equal to those included in Pt-Co-In/CeO₂.

4.2.2 Catalytic test. DRP was performed in a quartz fixed-bed reactor with 6 mm of internal diameter under an atmospheric pressure. The catalyst (0.10 g) diluted with sea sand (0.90 g, Miyazaki Chemical, 99.9%) was treated under flowing hydrogen (10 mL/min) at 550°C for 0.5 h prior to the catalytic reactions. Then, the catalysts were evaluated by feeding reactant gas mixture (C₃H₈: CO₂: He = 1:3:2, a total flow rate of 30 mL/min). The long-time stability reaction was test by feeding reactant gas mixture (C₃H₈: CO₂: He = 1:3:26, a total flow rate of 30 mL/min). The gas phase was analyzed and quantified using an online thermal conductivity detection gas chromatograph (Shimadzu GC-8A, column: Gaskuropack 54) equipped downstream. For all the catalysts, C₃H₆, C₂H₄, C₂H₆, CH₄, CO, CO₂, H₂O, and H₂ were detected as reaction products in outlet gas.

$$\text{C}_3\text{H}_8 \text{ conversion: } X_{\text{C}_3\text{H}_8} (\%) = \frac{F_{\text{C}_3\text{H}_8}^{\text{in}} - F_{\text{C}_3\text{H}_8}^{\text{out}}}{F_{\text{C}_3\text{H}_8}^{\text{in}}} \times 100 \quad (1)$$

$$\text{CO}_2 \text{ conversion: } X_{\text{CO}_2} (\%) = \frac{F_{\text{CO}_2}^{\text{in}} - F_{\text{CO}_2}^{\text{out}}}{F_{\text{CO}_2}^{\text{in}}} \times 100 \quad (2)$$

where, F_x^{in} and F_x^{out} indicate the x (mL min⁻¹), inlet and outlet flow rates of respectively.

$$C_3H_6 \text{ sel. in } C_xH_y: S_{C_3H_6}^{C_xH_y} (\%) = \frac{F_{C_3H_6}^{out}}{F_{C_3H_6}^{out} + \frac{2}{3}F_{C_2H_6}^{out} + \frac{2}{3}F_{C_2H_4}^{out} + \frac{1}{3}F_{CH_4}^{out} + \frac{1}{3}F_{CO}^{C_xH_y}} \times 100 \quad (3)$$

$$CO \text{ selectivity: } S_{CO} (\%) = \frac{(\frac{1}{3}F_{CO}^{C_xH_y} - F_{C_3H_6}^{out})/2}{F_{C_3H_6}^{out} + \frac{2}{3}F_{C_2H_6}^{out} + \frac{2}{3}F_{C_2H_4}^{out} + \frac{1}{3}F_{CH_4}^{out} + \frac{1}{3}F_{CO}^{C_xH_y}} \times 100 \quad (4)$$

4.2.3 Characterization

The crystal structure of the prepared catalyst was examined by powder X-ray diffraction (XRD) using a Rigaku MiniFlex II/AP diffractometer with Cu Ka radiation. High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) was carried out using a JEOL JEM-ARM200 M microscope equipped with an energy dispersive X-ray (EDX) analyzer (EX24221M1G5T). STEM analysis was performed at an accelerating voltage of 200 kV. To prepare the TEM specimen, all samples were sonicated in ethanol and then dispersed on a Mo grid supported by an ultrathin carbon film.

TPO experiment was performed using BELCAT II (MicrotracBEL) to quantify the amount of coke deposited on the spent catalysts after 50 h of DRP at 550 °C (0.1g of the catalyst with 0.9g quartz sand). The spent catalyst placed in a quartz tube reactor was treated under flowing He (30 mL/min) at 150 °C for 30 min, followed by cooling to room temperature. Then, the catalyst bed temperature was increased (40–900 °C, ramping rate: 5 °C min⁻¹) under flowing O₂/He (2%, 50 mL/min). The amount of CO₂ in the outlet gas was quantified by an online mass spectrometer. C₃H₆ and CO₂ temperature-programmed desorption were performed. Prior to the C₃H₆-TPD, the as-reduced catalyst (100 mg) was heated to 600°C under 5%H₂/Ar gas mixture (20 mL min⁻¹) with a ramping rate of 20 °C min⁻¹, then kept at same temperature for 0.5 h. After the reduction, the catalyst was cooled to -35°C using CATCryo-II under a He flow (20 mL min⁻¹), then kept at -35°C for 0.5 h, subsequently exposed to 5% C₃H₆/He gas mixture (20 mL min⁻¹) at same temperature for 5 mins. The catalyst was then purged under He (50 mL min⁻¹) at -35°C for 1.5 h, subsequently heated from -35°C to 300°C with a ramping rate of 2 °C min⁻¹. The outlet gas (C₃H₆; m/z = 41) was analyzed online by quadrupole mass spectrometer (BELMASS). For CO₂-TPD, the catalyst was pre-treated and then purged under He (50 mL min⁻¹) at 50°C for 0.5 h, subsequently heated from 50°C to 600°C with a ramping rate of 5 °C min⁻¹ equipped downstream. The outlet gas (CO₂; m/z = 44) was analyzed online by quadrupole mass spectrometer (BELMASS).

X-ray absorption fine structure (XAFS) spectra of the prepared catalysts were collected at the BL01B14 beamline of SPring-8, Japan Synchrotron Radiation Research Institute (JASRI) using Si(111) (for Co K- and Pt L_{III}-edges) and Si(311) (for In K-edge) double-crystals as monochromators. Prior to the measurement, the catalyst was pelletized (ca. 150 mg with a diameter of 10 mm) and pretreated by H₂/N₂ (20%, 40 mL/min) at 550 °C for 0.5 h in an in-situ quartz cell, followed by cooling to room temperature with N₂ purge (50 mL/min). The XAFS spectra were recorded in a transmission (In K-edge) and a fluorescence (Pt L_{III}-, and Co K-edge: using a 19-element Ge solid-state detector) modes at room temperature. Athena and Artemis softwares ver. 0.9.25 implemented in the Demeter package were used for the analysis of the obtained XAFS spectra. FEFF8 was used for the calculation of the back-scattering amplitude and phase shift functions.^[22] We defined the R-factor (R^2) for curve-fitting as follows: $R^2 = \sum_i \{k^3 \chi_i^{exp}(k) - k^3 \chi_i^{fit}(k)\}^2 / \sum_i \{k^3 \chi_i^{exp}(k)\}^2$.

4.3 Results

4.3.1 Structure characterization of the catalysts

The Pt–Co–In/CeO₂ (Pt: 3wt%, Pt:Co:In = 1:2:3 and 2:1:3, hereafter, PtCo₂In₃ and Pt₂CoIn₃) catalysts were prepared using CeO₂ as the support by conversional impregnation method. The catalysts structure firstly characterized by high-angle annular dark field scanning transmission electron microscopy (HAADF–STEM) and energy dispersive X-ray (EDX) analyses (Figure 4.1a, Figures 4.2, and Figure 4.3). The elemental maps of platinum, cobalt, and indium confirmed that these three elements are highly dispersed on the support and comprised the nanoparticles with a diameter of ~5 nm. In the meantime, some cobalt species also seem to exist outside of the nanoparticles. To confirm whether cobalt is doped into the nanoparticles, X-ray diffraction (XRD) analysis (Figure 4.1b and Figure 4.4) was performed. The monometallic Pt/CeO₂ and bimetallic PtIn/CeO₂ catalysts were also prepared to better clarify the crystal structure. For the Pt/CeO₂ catalyst, no extra peaks were observed which may be due to the high dispersion of the nanoparticles, except for two peaks at 33.1 and 47.5 corresponding to the (200) and (220) planes of CeO₂. In contrast, PtIn/CeO₂ catalyst showed two peaks at around 39.7 and 40.0 which assigned to the (110) and (102) planes of intermetallic Pt₂In₃. For PtCo₂In₃/CeO₂ and Pt₂CoIn₃/CeO₂ catalysts containing cobalt components, the lattice expansion of Pt₂In₃ resulted in a slight shift in the diffraction angle of both peaks. It is confirmed the formation of Pt–Co–In pseudo-binary alloy structure. Furthermore, to confirm the displacement site of cobalt, X-ray absorption fine structure (XAFS) analysis was carried out subsequently. The Pt L_{III}-edge, Co K-edge and In K-edge X-ray adsorption near edge

structure (XANES) spectra of Pt based catalysts show similar white line intensities to those of the reference foil (Figure 4.1c and Figure 4.5), which confirms that these metals are in the metallic state. The Pt L_{III}-edge adsorption edges are shifted to the high energy, which may contribute to the electron transfer by alloying with cobalt and indium. A small fraction of In₂O₃ was observed in the K-edge XANES (Figure 4.5d) and extended XAFS (EXAFS) spectra (Figure 4.5e; the Fourier transform of the EXAFS is shown in Figure 4.5f). It could be caused by the interactions with CeO₂'s lattice oxygen. Figure 4.1d shows the Pt L_{III}-edge EXAFS raw oscillation features of Pt foil, PtIn/CeO₂, PtCo₂In₃/CeO₂ and Pt₂CoIn₃/CeO₂ catalysts. PtCo₂In₃/CeO₂ and Pt₂CoIn₃/CeO₂ exhibited the similar trend to that of PtIn/CeO₂, but were different from the reference fcc Pt foil. A similar trend was also showed in the Co K-edge and In K-edge of both trimetallic catalysts (Figure 4.5a and Figure 4.5d), which was quite different from the oscillation features of the reference foil and oxide. It indicated that these three elements in Pt–Co–In/CeO₂ catalysts are present in a PtIn structure, which is consistent with the XRD results (Figure 4.1b). Figure 1e showed the Fourier transform of the Pt L_{III}-edge EXAFS of Pt-based catalysts, whereas the peak assigned to Pt–In scattering distance of Pt–Co–In/CeO₂ is shorter than the PtIn/CeO₂, indicating that cobalt partially doped in the PtIn crystal structure. Moreover, EXAFS curve-fitting (Figure 4.6 and Table 4.1) suggested the presence of Pt–In (In–Pt) and Co–In (In–Co) scatterings. This is demonstrated that the formation of the (Pt_{1-x}Co_x)₂In₃ pseudo-binary alloy structure (Figure 4.1f). Although some Co–Co scattering were observed from Co K-edge fitting, it is confirmed that some metallic Co nanoparticles presents on the CeO₂ support and is consistent with the result of the HAADF-STEM-EDX analysis.

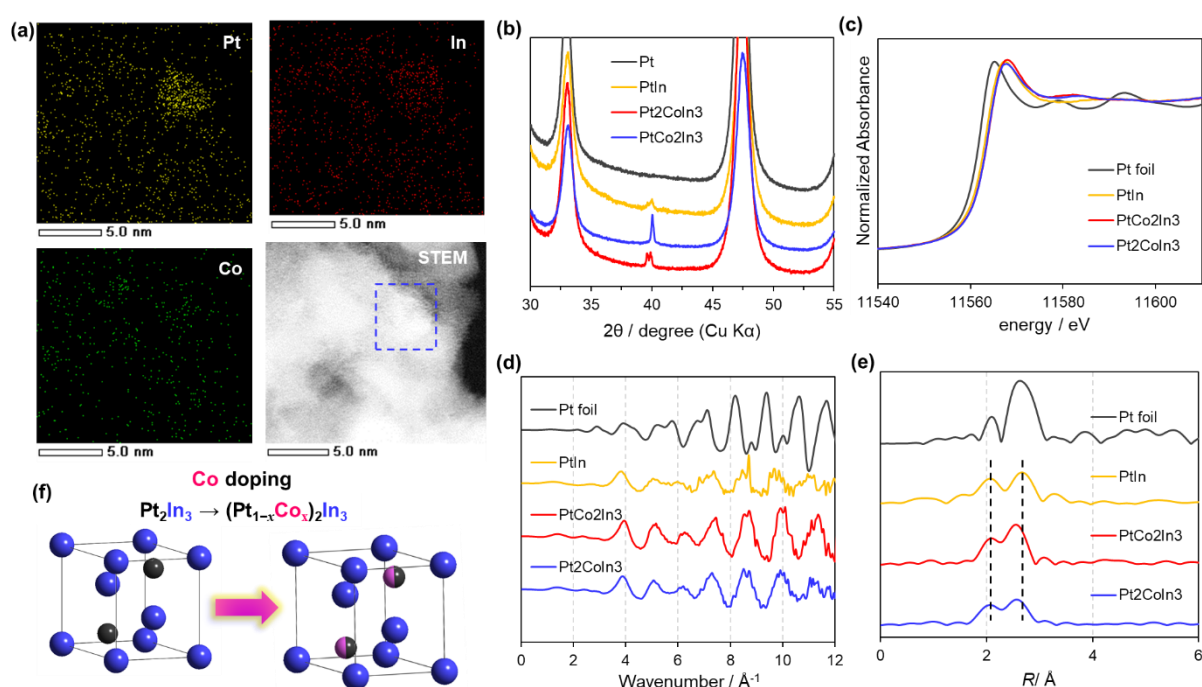


Figure 4.1: Characterization of Pt–Co–In/CeO₂. **a**, Elemental maps of Pt, Co, In, and HAADF-STEM image of Pt–Co–In/CeO₂ (Pt:Co:In = 1:2:3). **b** XRD patterns of for Pt/CeO₂, PtIn/CeO₂, Pt₂CoIn₃/CeO₂, and PtCo₂In₃/CeO₂ catalysts. **c**, Pt L_{III}-edge X-ray absorption near edge structure (XANES) spectra **d** extended X-ray absorption near edge structure (EXAFS) spectra, **e** Fourier transform of EXAFS of Pt foil, PtIn/CeO₂, Pt₂CoIn₃/CeO₂, and PtCo₂In₃/CeO₂ catalysts. **f** Model of the (Pt_{1-x}Co_x)₂In₃ pseudo-binary alloy structure with the crystal structure unit.

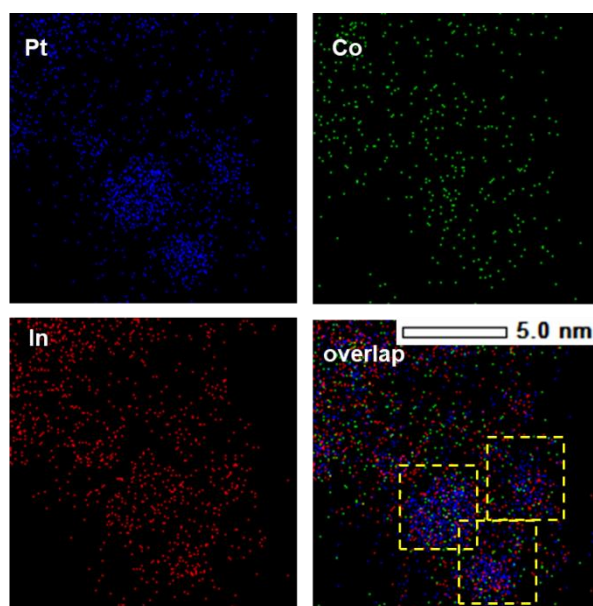


Figure 4.2: EDX analysis on PtCo₂In₃/CeO₂. Elemental maps of Pt, Co, In, and overlap of these three metal on PtCo₂In₃/CeO₂ acquired using EDX analysis.

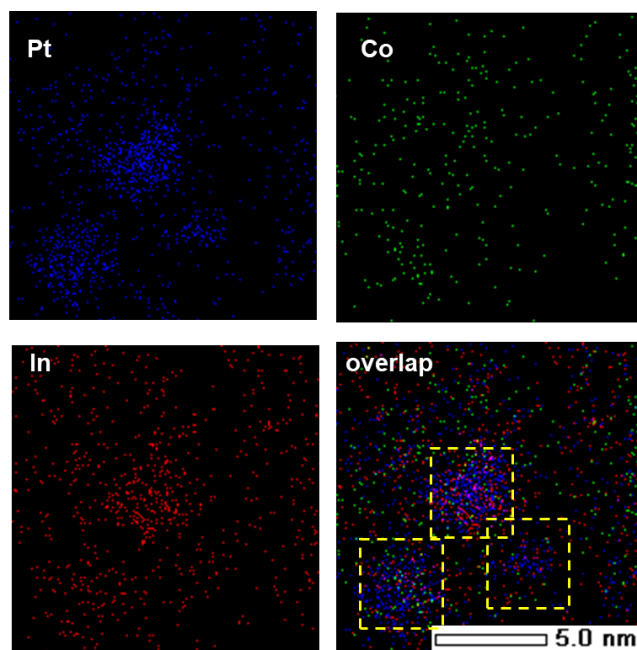


Figure 4.3: EDX analysis on PtCo₂In₃/CeO₂. Elemental maps of Pt, Co, In, and overlap of these three metal on PtCo₂In₃/CeO₂ acquired using EDX analysis.

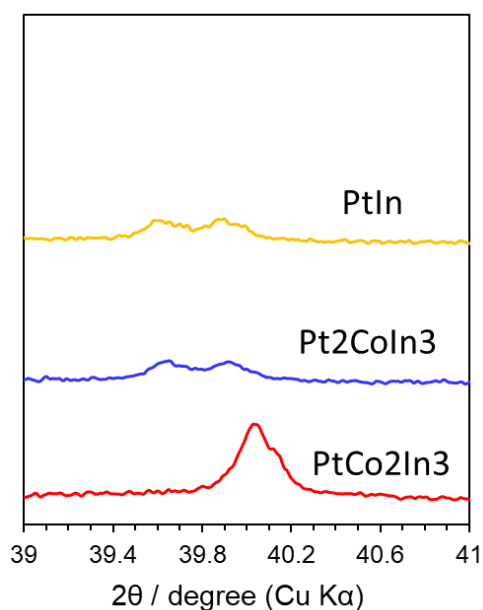


Figure 4.4: Expanded of XRD patterns of for Pt–In/CeO₂, Pt₂CoIn₃/CeO₂ and PtCo₂In₃/CeO₂ catalysts. Pt–In/CeO₂ showed the diffraction pattern assignable to that of intermetallic Pt₂In₃. In the corresponding diffraction pattern of Pt–Co–In/CeO₂ was shifted to higher angles, which suggests that the lattice constant of Pt₂In₃ was changed by doping of Co into Pt₂In₃.

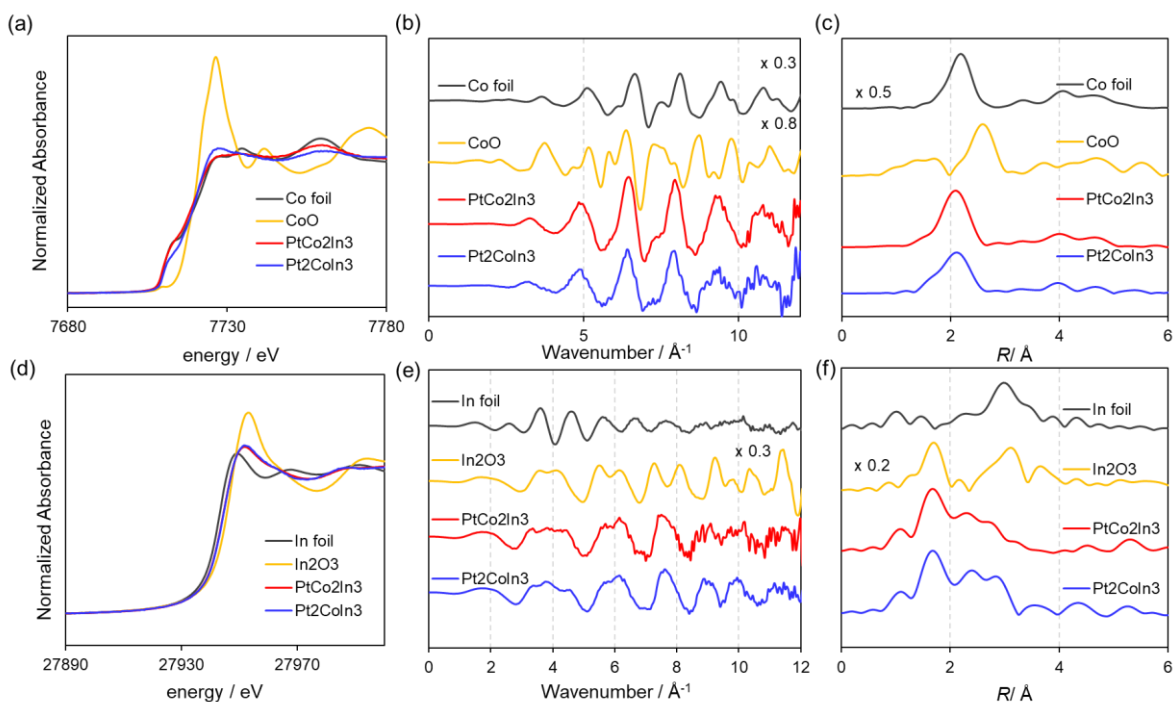


Figure 4.5: X-ray absorption near edge structure (XANES) spectra of Pt₂CoIn₃/CeO₂ and PtCo₂In₃/CeO₂ catalysts and reference compounds **(a)** Co K and **(d)** In K-edge. **EXAFS oscillations of (b)** Co K- and **(e)** In K-edge. Fourier transforms of EXAFS spectra **(c)** Co K- and **(f)** In K.

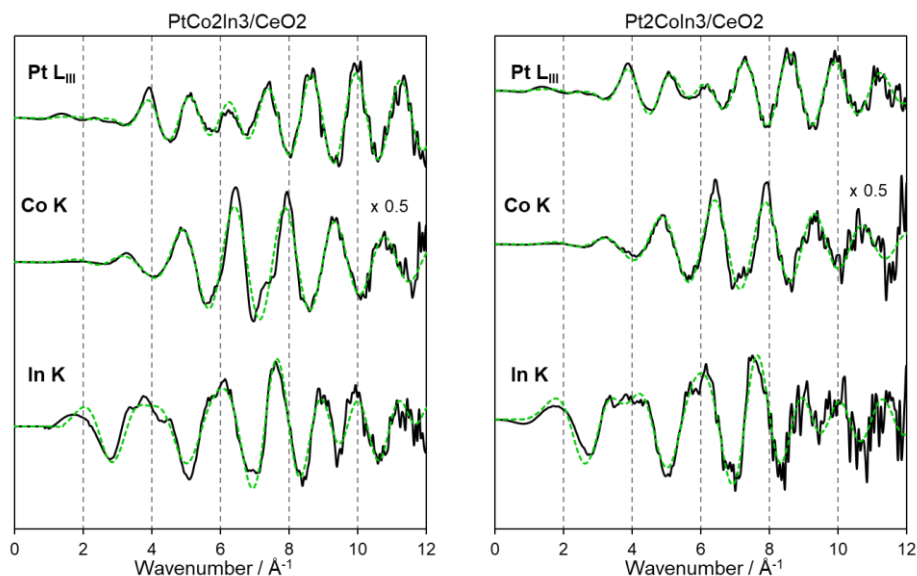


Figure 4.6: Curve-fitting analysis for Pt₂CoIn₃/CeO₂ and PtCo₂In₃/CeO₂ catalysts. Curve-fitting for the Pt L_{III}-, Co K-, and In K-edge k^3 -weighted EXAFS oscillations of Pt₂CoIn₃/CeO₂ and PtCo₂In₃/CeO₂. The k^3 -weighted EXAFS oscillation was Fourier-transformed in the k range of 3–12 Å⁻¹ for all edges. Curve-fitting was performed using the back Fourier-transforms of the coordination peaks ranging between 1.0–3.0 Å, 1.0–3.0 Å, and 1.0–3.5 Å, for Pt L_{III}-, Co K-, and In K-edge, respectively.

Table 4.1. Results of EXAFS curve-fitting for Pt₂CoIn₃/CeO₂ and Pt₂CoIn₃/CeO₂ and the reference foils

Sample	Edge	Shell	S_0^{-2} ^a CN ^b	r (Å) ^c	ΔE_0 (eV)	σ^2 (Å ²) ^d	R-factor ^e
Pt foil	Pt L _{III}	Pt–Pt	0.89 12 (fix)	2.76 ± 0.04	7.6 ± 0.7	0.005	0.003
Co foil	Co K	Co–Co	0.80 12 (fix)	2.49 ± 0.00	7.5 ± 0.1	0.007	0.000
In foil	In K	In–In	0.90 4 (fix)	3.11 ± 0.00	-2.9 ± 0.8	0.026	0.019
		In–In	8 (fix)	3.23 ± 0.00			
Pt ₂ CoIn ₃ /CeO ₂	Pt L _{III}	Pt–Co	0.89 0.9 ± 0.7	2.57 ± 0.01	3.6 ± 1.6	0.010	0.007
		Pt–In	4.3 ± 0.7	2.69 ± 0.00		0.008	
	Co K	Co–Co	0.80 5.5 ± 3.9	2.49 ± 0.04	-3.6 ± 5.8	0.011	0.019
		Co–In	0.3 ± 1.3	2.62 ± 0.05		0.003	
		In–O	2.4 ± 1.1	2.15 ± 0.02		0.012	
	In K	In–Pt	0.90 4.5 ± 3.1	2.70 ± 0.02	2.4 ± 3.1	0.014	0.029
		In–Co	0.7 ± 3.0	2.78 ± 0.05		0.021	
	Pt L _{III}	Pt–In	0.89 3.2 ± 0.5	2.72 ± 0.01	4.8 ± 1.2	0.008	0.017
	Co K	Co–Co	0.80 5.3 ± 0.7	2.48 ± 0.01	-2.4 ± 1.9	0.008	0.010
		Co–In	1.8 ± 1.7	2.69 ± 0.11		0.034	
PtCo ₂ In ₃ /CeO ₂		In–O	2.1 ± 0.6	2.15 ± 0.02		0.010	
	In K	In–Pt	0.90 3.6 ± 1.9	2.73 ± 0.01	3.6 ± 3.0	0.012	0.023
		In–Co	1.3 ± 1.2	2.79 ± 0.03		0.009	

^a Amplitude factor. ^b Coordination number. ^c Distance between absorber and backscatterer atoms. ^d Correction term in the absorption edge. ^e Debye–Waller factor.

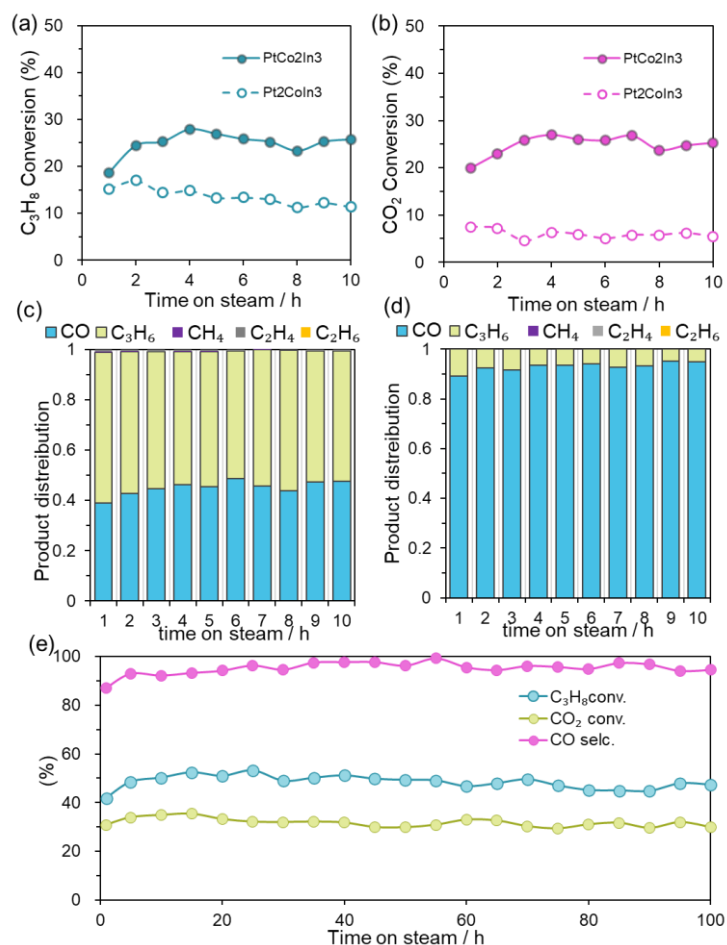


Figure. 4.7: Catalytic performance of Pt–Co–In/CeO₂ in the DRP. Reaction conditions: catalyst amount, 100 mg; gas feed, C₃H₈ : CO₂ : He = 5:15:10 mL·min⁻¹; temperature, 550 °C. Time course of (a) C₃H₈ conversion, (b) CO₂ conversion. (c) product distribution of Pt2CoIn3/CeO₂ and (d) product distribution of PtCo2In3/CeO₂ (e) Long-term stability test with of PtCo2In3/CeO₂ catalyst Time course of C₃H₈ and CO₂ conversions, and CO selectivity.

4.3.2 Catalytic performance in DRP

The prepared PtCo2In3/CeO₂ and Pt2CoIn3/CeO₂ were then tested for CO₂-assisted propane reaction with a molar ratio of propane to CO₂ of 1:3 at 550 °C, using helium as a balance gas. Figure 2a-d shows the time course of C₃H₈ conversion, CO₂ conversion and the product distribution of both catalysts, respectively. The Pt2CoIn3/CeO₂ catalyst gave a product distribution which consist of 60% C₃H₆, 39% CO, and the other C₁₋₂ products, and C₃H₆ selectivity remained at 52% for 10 h reaction. In contrast, PtCo2In3/CeO₂ catalyst like more favorable to generate CO, showed an 89% CO selectivity and even increased to 95% after 10 h reaction. This suggested that the PtCo2In3/CeO₂ has a superior activity in dry-reforming

reaction via C-C bond cleavage, whereas Pt₂CoIn₃/CeO₂ prefers to produce C₃H₆ via C-H bond cleavage. Same as the initial C₃H₈ conversion (~16%) of Pt₂CoIn₃/CeO₂ (Figure 4.7a), the C₃H₈ conversion of PtCo₂In₃/CeO₂ increased and stabilized at ~26% after 10 h reaction, whereas Pt₂CoIn₃/CeO₂ gradually decreased to ~10%. The initial C₃H₈ conversion of PtCo₂In₃/CeO₂ (~16%) is the same with Pt₂CoIn₃/CeO₂ (Figure 4.7a), but the C₃H₈ conversion of PtCo₂In₃/CeO₂ increased after 10 h of reaction and stabilized at ~26%, whereas that of Pt₂CoIn₃/CeO₂ gradually decreased to ~10%. PtCo₂In₃/CeO₂ and Pt₂CoIn₃/CeO₂ showed quite different C₃H₆ selectivity (25% and 5%, respectively, Figure 4.7c-d) at the whole reaction period. In order to understand the individual effect of each second metal, we also performed the reaction with corresponding monometallic Pt/CeO₂, bimetallic PtCo/CeO₂, and PtIn/CeO₂ catalysts (Figure 4.8). The C₃H₈ conversion of Pt/CeO₂, PtCo/CeO₂, and PtIn/CeO₂ were 40%, 33%, and 28%, meanwhile, the CO₂ conversion (Figure 4.7b), were followed as 38%, 40%, and 16%, respectively. These results show that alloying platinum with cobalt or indium decreases C₃H₈ conversion due to the ensemble effect, while adding a certain amount of cobalt could increase CO₂ conversion. Furthermore, Pt₂CoIn₃/CeO₂ showed the almost same product distribution with PtIn/CeO₂, it indicated that the small amount of cobalt doping has not changed the inherent performance of PtIn/CeO₂. Whereas the PtCo₂In₃/CeO₂ may change the reaction pathway from oxidative dehydrogenation to dry-reforming reaction. All these catalysts were also rapidly deactivated, suggesting that the PtCo₂In₃/CeO₂ catalyst not only shows superior activity in the dry reforming reaction, but also excellent stability. To identify the alloying effect of PtCo₂In₃/CeO₂, we further performed the control experiment (Figure 4.9) using physical mixture of the binary and monometallic catalysts (Pt/CeO₂+Co-In/CeO₂) and dual system catalysts (Pt/CeO₂+quartz wool+Co-In/CeO₂ and CoIn/CeO₂+quartz wool+Pt/CeO₂). The physical mixture catalyst showed lower catalytic activity than PtCo₂In₃/CeO₂ and the dual system catalysts exhibited lower stability, suggesting that the ternary alloy structure doped with cobalt in Pt-In alloy is essential for high catalytic performance. Then, we performed the long-term stability test on PtCo₂In₃/CeO₂ and showed that the conversion of C₃H₈ and CO₂ did not decrease even at 100h reaction while maintaining ~95% CO selectivity. A temperature-programmed oxidation (TPO, Figure 4.10a-b) and XRD analysis (Figure 4.12) of the spent catalysts after 50 h were performed. The XRD analysis of spent catalysts exhibited almost the same diffraction peaks as those of the fresh catalysts, indicating the absence of catalyst aggregation. On the other hand, compared to the PtCo₂In₃/CeO₂ and the physical mixture catalyst (Pt/CeO₂+Co-In/CeO₂), the mono-, bi-metallic catalysts showed 5-10 times higher coke accumulation after the reaction. The

combined results suggest that the coke accumulation is the main cause of catalyst deactivation, and PtCo2In3/CeO₂ exhibits superior coke resistance.

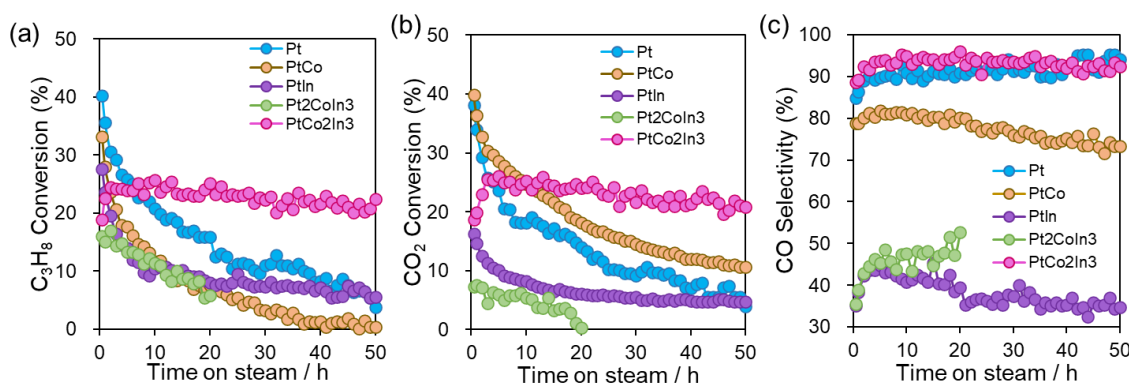


Figure 4.8: Catalytic performance of monometallic Pt/CeO₂, PtCo/CeO₂, PtIn/CeO₂, PtCo2In3/CeO₂, and Pt2CoIn3/CeO₂ in DRP. **a** C₃H₈ conversion, **b** CO₂ conversion, **c** CO selectivity.

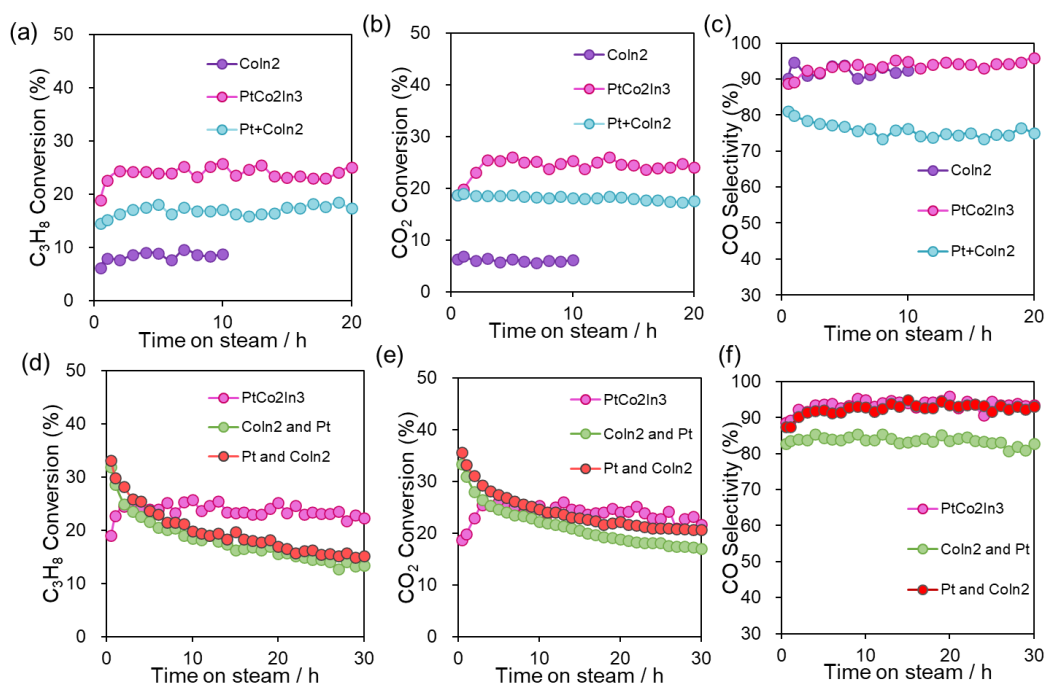


Figure 4.9: Catalytic performance of CoIn/CeO₂, PtCo2In3/CeO₂, and physical mixture catalysts (Pt/CeO₂+CoIn/CeO₂) in DRP. **(a)** C₃H₈ conversion, **(b)** CO₂ conversion, **(c)** CO selectivity. Catalytic performance of dual system (Pt/CeO₂ + quartz wool + Co-In/CeO₂,

donated as Pt and CoIn₂, and CoIn/CeO₂ + quartz wool + Pt/CeO₂ donated as CoIn₂ and Pt,). in DRP. **(d)** C₃H₈ conversion, **(e)** CO₂ conversion, **(f)** CO selectivity.

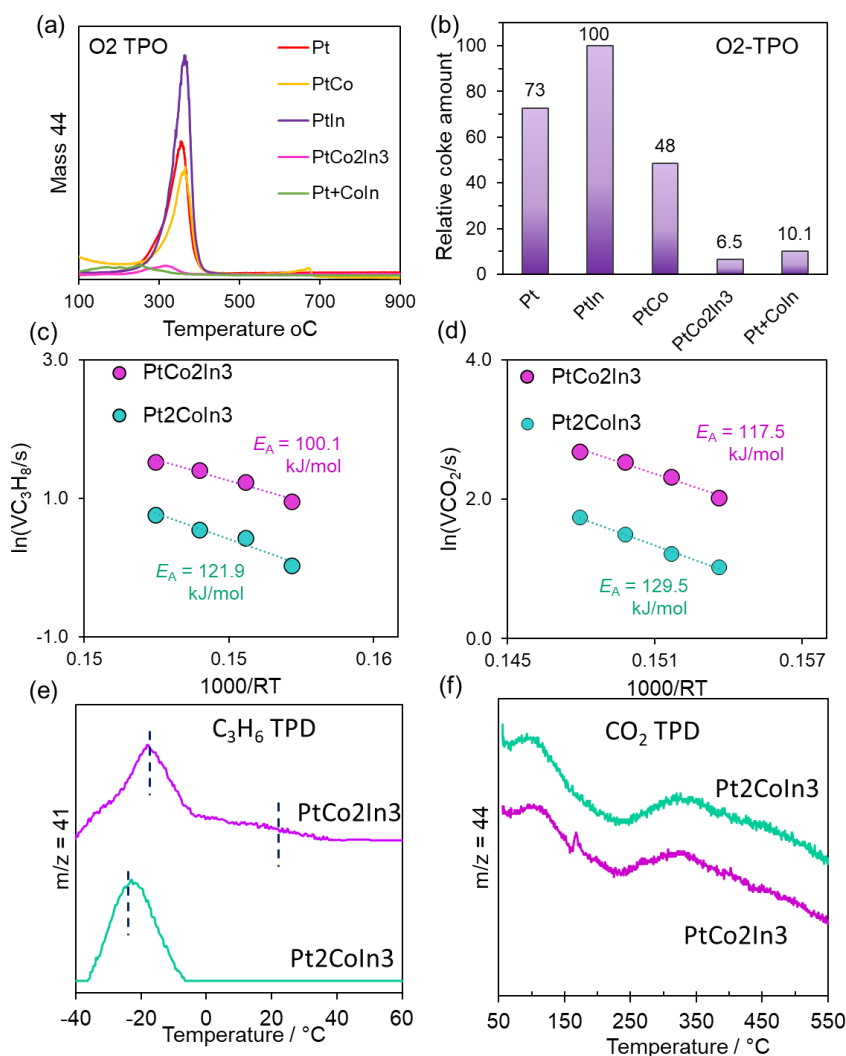


Figure. 4.10: Mechanistic study (a) O₂-TPO profiles of the spent catalysts after 50h of DRP at 550°C. **(b)** Relative coke amount accumulated on the catalysts estimated from **a**. Arrhenius-type plots for **(c)** C₃H₈ and **(d)** CO₂ conversion rates obtained in DRP on PtCo₂In₃/CeO₂ and Pt₂CoIn₃/CeO₂. catalysts. The catalyst amount was set to 20 mg so that the conversion became below 15%. **(e)** C₃H₆-TPD for PtCo₂In₃/CeO₂ and Pt₂CoIn₃/CeO₂. catalysts (adsorption temperature: -35 °C). **(f)** CO₂-TPD for PtCo₂In₃/CeO₂ and Pt₂CoIn₃/CeO₂. catalysts (adsorption temperature: 50 °C)

4.3.3 Mechanistic study

Next, a mechanistic study was conducted to elucidate the reason of the difference in performance between PtCo₂In₃/CeO₂ and Pt₂CoIn₃/CeO₂. The apparent activation energy

(Figure 4.10b-c) was evaluated by Arrhenius-type plots. The activation energies for C_3H_8 and CO_2 decreased from 121.9 to 100.1 kJ/mol and 129.5 to 117.5 kJ/mol, respectively, indicating that the addition of more cobalt to the PtIn crystal structure significantly reduced the activation barrier. This result may further explain the reason that PtCo₂In₃/CeO₂ is more active in both C_3H_8 and CO_2 than Pt₂CoIn₃/CeO₂. To further investigate the origin of the different selectivity between different catalysts, the temperature-programmed surface reactions (TPSRs) were conducted, including C_3H_6 desorption, CO_2 desorption, further oxidative of propene step ($C_3H_6 + CO_2$), and reverse water gas shift step (RWGS, $H_2 + CO_2$). From the C_3H_6 -TPD results (Figure 4.10e), PtCo₂In₃/CeO₂ exhibited broad desorption peaks between -40 and 40 °C, while Pt₂CoIn₃/CeO₂ showed one peak at around -30 °C and propene completely desorb at -30 °C. This suggests that Pt₂CoIn₃/CeO₂ is easier to desorb propylene than PtCo₂In₃/CeO₂, which is consistent with the selective trend of C_3H_6 . On the other hand, the CO_2 -TPD results (Figure 4.10f) for both catalysts showed almost the same trend, indicating that the same value of CO_2 adsorbed on the catalyst surface has less influence on the overall reaction. To further determine which step affected the different selectivity of these two catalysts, $C_3H_6 + CO_2$ TPSR and $H_2 + CO_2$ TPSR experiments were performed. Figure 4.11b shows the results of the $H_2 + CO_2$ TPSR experiment, indicating that the CO_2 hydrogenation step was not altered by these two different catalysts. On the contrary, the results of $C_3H_6 + CO_2$ TPSR experiments (Figure 4.11a), showed that C_3H_6 and CO_2 are much more active on PtCo₂In₃/CeO₂, which means that the oxidation of C_3H_6 by CO_2 occurs more easily on PtCo₂In₃/CeO₂, producing large amounts of H_2 and CO.

4.4 Discussion

Overall, we designed a highly efficient ternary PtCo₂In₃/CeO₂ catalyst for the DRP reaction with high selectivity and stability even for 100 h reaction. The result showed that the catalytic behavior of these catalysts is highly sensitive to the doping amount of cobalt. By controlling the amount of cobalt doping, the catalytic activity of the Pt-Co-In/CeO₂ catalyst can be improved and the C-H/C-C bond of propane can be selectively cleaved in the presence of CO_2 . This work not only demonstrated outstanding catalytic performance, but it also opened up a new window of catalyst design concepts based on multi-metallic catalysts. The obtained insights and technology will contribute to carbon-neutralization of industrial processes for light alkane conversions.

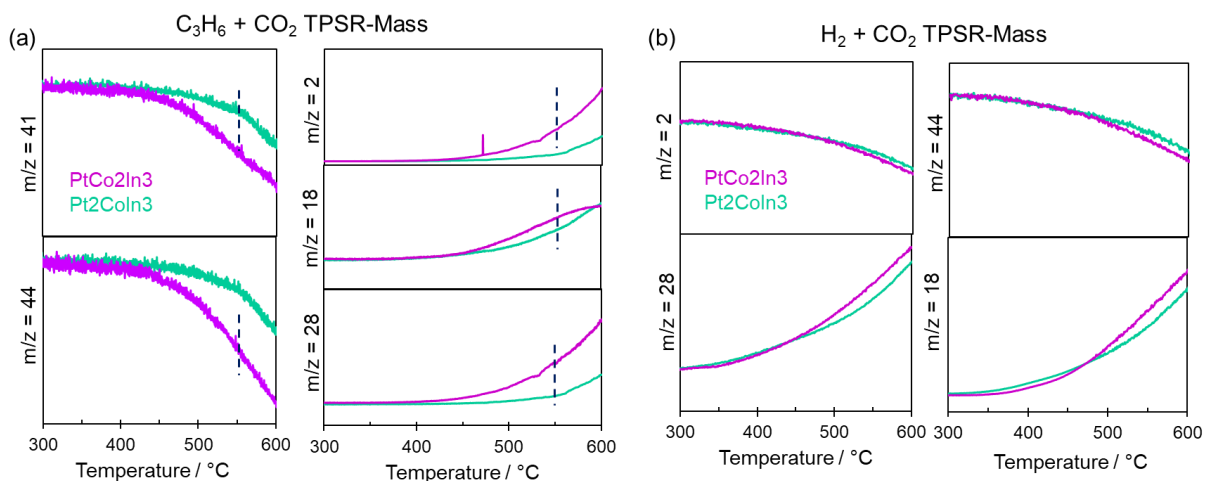


Figure. 4.11: TPSR on the PtCo2In3/CeO₂ and Pt2CoIn3/CeO₂ catalysts. **(a)** C₃H₆ + CO₂ TPSR-Mass experiments **(b)** and H₂ + CO₂ TPSR-Mass experiments. Dot line is the reaction temperature (550oC). The reactants and products were collected with mass intensity of m/z = 2 (H₂), m/z = 18(H₂O), m/z = 28(CO), 8 m/z = 41(C₃H₆), and m/z = 44(CO₂).

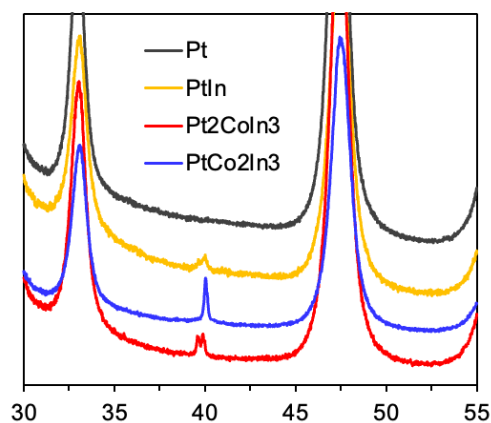


Figure. 4.12: XRD patterns of for Pt/CeO₂, PtIn/CeO₂, Pt2CoIn3/CeO₂, and PtCo2In3/CeO₂ catalysts after 50h reaction.

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Chapter Five

General Conclusion

In this research, I focused on developing a highly efficient catalyst for CO₂-assisted oxidative dehydrogenation and dry reforming of propane. For this purpose,

Chapter 2 concludes that Pt–Co–In ternary alloy on CeO₂ exhibited a highly efficient catalyst for the CO₂-ODP. This material comprises small nanoparticles (2–3 nm) with a (Pt_{1-x}Co_x)₂In₃ pseudo-binary alloy structure, where Pt, Co, and In are adjacent to each other on an atomic level. Both the C₃H₈ dehydrogenation and CO₂ reduction smoothly proceed on the Pt–Co active site to form 2H and O, as well as the main products: C₃H₆ and CO. Alloying with In enhances the C₃H₆ selectivity due to the ensemble effect and decreases the amount of coke that accumulates on the catalyst surface. The doped Co improves the adsorption strengths of the C and H species, which promotes the activation of C₃H₈ and CO₂. The O atoms oxidize the eliminated H to form H₂O or combust coke on the alloy surface or neighboring CeO₂ sites. Note that coke combustion is allowed when CO₂ conversion is higher than C₃H₈ conversion because of the stoichiometry of the CO₂-ODP. Coke can be combusted also by the lattice oxygen of CeO₂, where CeO₂ is partially reduced to form an oxygen vacancy. This oxygen vacancy is refilled by an O atom derived from CO₂ activation, enabling continuous coke combustion through the redox of CeO₂. Thus, CeO₂ can facilitate coke combustion via a Mars-van Krevelen-type mechanism, which significantly enhances the coke resistance and catalyst stability. Pt–Co–In/CeO₂ exhibits outstanding catalytic activity, C₃H₆ selectivity, long-term stability, and CO₂ utilization efficiency, all of which are greater than typical values ever reported.

Chapter 3 concludes that a PtSn-based HEI catalyst was designed and prepared in the CO₂-ODP as a highly coke resistant and thermally stable catalyst. The Pt and Sn sites of intermetallic PtSn were partially substituted with Ni/Co and In/Ga, resulting in nanoparticles with a HEI structure of (PtCoNi)(SnInGa). The multi-metallization sufficiently isolates Pt atoms, preventing propylene decomposition and coke formation. The incorporation of Ni and Co significantly enhanced the ability to activate CO₂. Doping In(Ga) into the Sn site improved catalyst stability, probably due to the enhanced entropy effect. The combination of these abilities significantly enhances coke resistance and catalyst lifetime. Furthermore, because of the increased thermal stability, multi-metallization also prevents nanoparticle sintering. The HEI/CeO₂ catalyst shows 2- and 1.5-times higher catalyst life and specific activity than those of the best catalyst ever reported. Moreover, the catalyst can be reused by performing a simple regeneration procedure with CO₂ alone without any loss of original performance.

Chapter 4 concludes that Pt–Co–In ternary alloy system to the CO₂-assisted dry-reforming of propane (DRP) reaction, which has attracted much attention as a syngas production technology for liquid fuels and oxygenated chemicals with a low H₂/CO ratio. Compared to the dry-reforming of methane, the use of propane can consume more carbon dioxide than methane, and in particular, propane can be activated more easily than methane at lower reaction temperatures. Considering the recent global demand for net-zero emissions, converting CO₂ into a value-added chemical is an appealing approach. The PtCo₂In₃/CeO₂ ternary catalyst for the DRP reaction with high selectivity and stability even over 100 h. The results show that the catalytic behavior of these catalysts is highly sensitive to the amount of cobalt doping. By controlling the amount of cobalt doping, the catalytic activity of PtCo₂In₃/CeO₂ catalysts can be improved, and the C-H/C-C bond of propane can be selectively cleaved in the presence of CO₂.

In conclusion, our work not only demonstrates excellent catalytic performance, but also opens a new window for the design of multi-metallic catalysts. The results obtained in this study can promote the carbon-neutralization of industrial processes for light alkane conversion.

Acknowledgments

I would like to acknowledge the Advance Graduate School and DX Doctoral Fellowship of Hokkaido University and Japan Society for the Promotion of Science for giving the precious opportunity and financial support to gain PhD degree in Institute for Catalysis, Faculty of Chemical Science and Engineering.

Firstly, I would like to express gratitude to my supervisor Professor Shinya Furukawa for guiding in an excellent way during my study and supervising the research so that we could achieve our goals. He gives me not only fundamental background of metallic alloy catalysts but also serves as a paragon, demonstrating the attitude of a true scientist. I would like to acknowledge the opportunity to study in Japan as a Ph.D. student.

I would also like to appreciate the advisory committee members, Professor Ken-ichi Shimizu, Professor Jun-ya Hasegawa, Professor Atsushi Fukuoka, and Professor Kenji Iida for the suggestions.

I am truly grateful to all the staff and laboratory member in Shimizu Group for the kind help on the daily experiment. Also, for the togetherness of the group member in Furukawa group as well.

Last, but not least, I would like to thank my parents and all my dear friends whom I could not mention for always standing beside me to get through the ups and down.