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Title	Ternary platinum-cobalt-indium nanoalloy on ceria as a highly efficient catalyst for the oxidative dehydrogenation of propane using CO ₂
Author(s)	Xing, Feilong; Nakaya, Yuki; Yasumura, Shunsaku et al.
Citation	Nature Catalysis, 5(1), 55-65 https://doi.org/10.1038/s41929-021-00730-x
Issue Date	2022-01-27
Doc URL	https://hdl.handle.net/2115/86382
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Type	journal article
File Information	PtCoIn_MS.pdf



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2 Platinum–cobalt–indium nanoalloy on ceria as a highly
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Abstract

The oxidative dehydrogenation of propane using CO₂ (CO₂-ODP) is a promising technique for high-yield propylene production and CO₂ utilization. Developing a highly efficient catalyst for CO₂-ODP is of great interest and benefit to the chemical industry and for carbon recycling. However, the efficiency of the existing catalysts is limited. Here, we report a Pt–Co–In ternary nanoalloy on CeO₂ having a (Pt_{1-x}Co_x)₂In₃ pseudo-binary alloy structure, which exhibits a considerably high catalytic activity, C₃H₆ selectivity, stability, and CO₂ utilization efficiency at 550 °C. Alloying Pt with In and Co significantly improves the C₃H₆ selectivity and CO₂ reduction ability, respectively. The Co species provide a high density of states near the Fermi level, which lowers the energy barrier of CO₂ reduction. The catalyst stability is drastically enhanced by combining the strong CO₂ activation ability of the alloy and the CeO₂ support capable of oxygen release, which facilitate Mars-van Krevelen-type coke combustion.

Keywords: propane dehydrogenation, CO₂, ternary alloy, intermetallic, CeO₂

42 Propylene is a very important raw materials for the production of a variety of petrochemicals in several
43 industries.¹ The recent shift in the feedstock for steam crackers from oil-based naphtha to shale-based
44 ethane has resulted in a significant gap between the limited supply of propylene and its increasing
45 demand globally.² Therefore, the development of highly efficient technologies to meet the rising global
46 demand for propylene is greatly desired.³ Although the direct dehydrogenation of propane (DDP) has
47 been studied and industrialized for this purpose, high reaction temperatures (typically ≥ 650 °C) are
48 required to obtain a sufficiently high propylene yield due to the process's endothermicity.⁴ Furthermore,
49 the harsh conditions inevitably induce severe catalyst deactivation and the thermal decomposition of
50 propylene, limiting the applicability of the approach. The oxidative dehydrogenation of propane using
51 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
52 solving such issues.^{5, 6} The equilibrium conversion of propane increases when dry reforming of C₃H₈
53 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
54 required to achieve a high propane conversion.⁷ Moreover, CO₂ can remove the coke deposited on the
55 catalyst surface via the Boudouard reaction ($\text{CO}_2 + \text{C} \rightarrow 2\text{CO}$).¹⁰ Unlike strong oxidants such as O₂,
56 CO₂ suppresses the over-oxidation of propylene and the catalyst itself, thus potentially providing an
57 efficient catalytic system for propylene production. Moreover, the catalytic conversion of CO₂ into a
58 value-added chemical is beneficial for carbon recycling and greenhouse gas reduction.^{11, 12}

59 The previous studies on the CO₂-ODP focused predominantly on early transition or typical metal
60 oxides (Cr₂O₃, V₂O₅, Ga₂O₃, and In₂O₃)^{5, 13, 14, 15, 16} and late transition metals (Pd, and Fe₃Ni)^{7, 17} as the
61 main active species. Among these materials, chromium oxide species dispersed on mesoporous
62 silica^{18,19} showed the highest specific activity and good propylene selectivity (ca. 80%) at high propane
63 conversion regions. However, these catalysts showed very low CO₂ conversion and rapid deactivation
64 within a few hours. Although the transition metal catalysts exhibited much longer catalyst life, the
65 conversions of propane and CO₂ were quite low (typically, <12%). In this context, to date, no catalyst
66 has been reported that exhibits at the same time a high catalytic activity, selectivity, stability, and CO₂
67 utilization efficiency. The challenge is that the catalyst should simultaneously activate both propane and
68 CO₂ without undesired side reactions and catalyst deactivation. Therefore, a multifunctional active
69 material that successfully meets these requirements should be developed as an innovative catalyst for
70 the CO₂-ODP. Possible candidates are multimetallic alloys.^{20, 21, 22} A highly efficient CO₂-ODP may be
71 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.

Results

Characterization

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. Figs 1a and b 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, Fig. 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 reaction³⁰ and propane dehydrogenation^{31, 32} 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 (Figs. 1d–h). The Pt:Co:In atomic ratios of the nanoparticles (regions 1–4, designated by dashed yellow squares in Figs. 1a and b) were approximately 1:0.5:2 (Fig. 1i), where the Co content was lower than that supplied in the catalyst preparation (Pt:Co:In = 1:1:2).

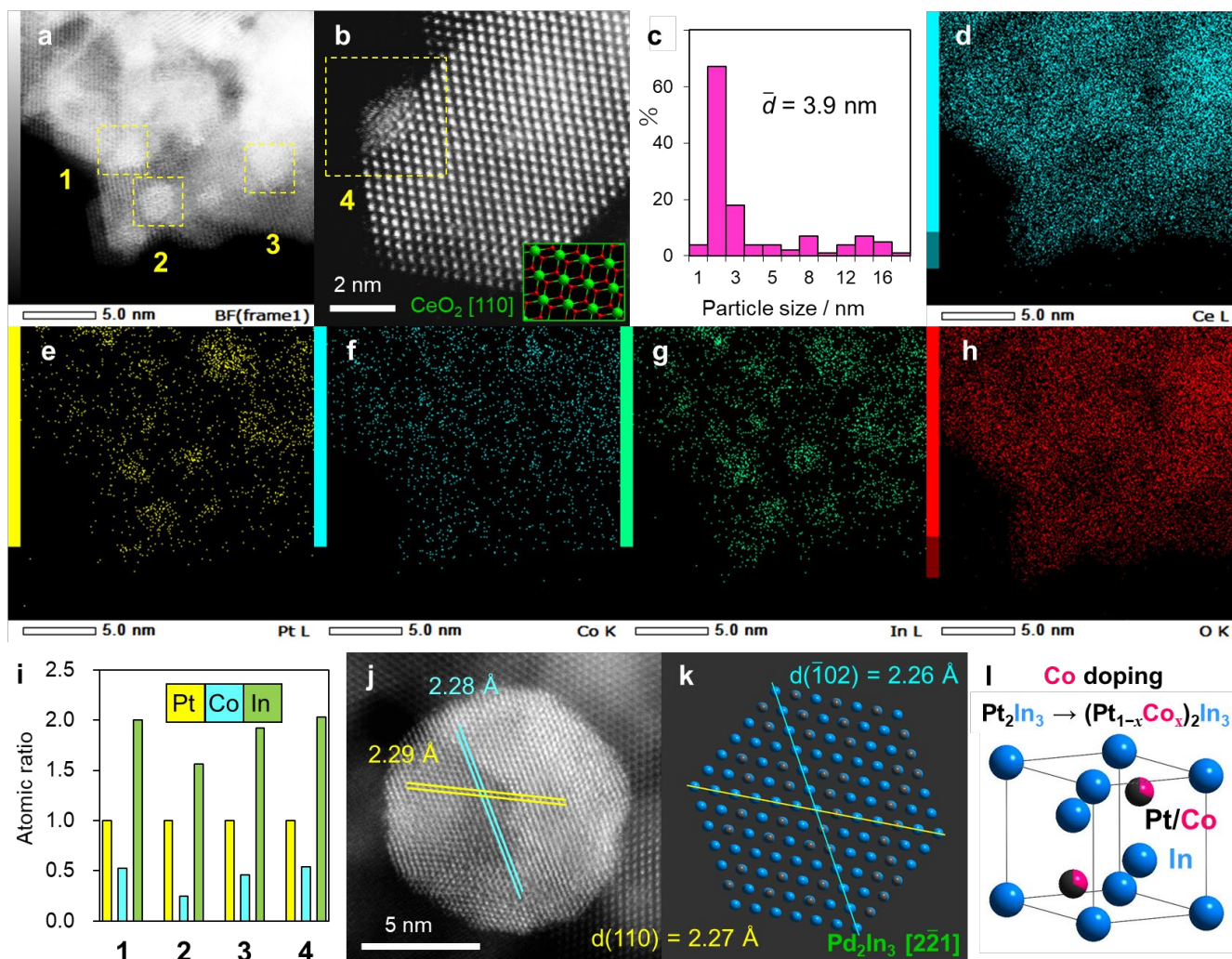


Fig. 1: Characterization of Pt-Co-In/CeO₂. **a, b** HAADF-STEM image of Pt-Co-In/CeO₂ (Pt:Co:In =1:1:2). **c** Particle-size distribution. **d-h**, Elemental maps of **(d)** Ce, **(e)** Pt, **(f)** Co, **(g)** In, and **(h)** O in **a**, acquired by EDX. **i** Atomic ratios of Pt, Co, and, In present 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 Pt₂In₃ viewed along the [221] direction. **l** Model of the (Pt_{1-x}Co_x)₂In₃ pseudo-binary alloy structure with the crystal structure unit.

Therefore, some of the Co species appear to not be included in the nanoparticles and are highly dispersed on the CeO₂ support. Fig. 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 (Figs. 1j and k).³³ 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 (Fig. 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 (Supplementary Fig. 1). 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 (Supplementary Fig. 2). A small contribution of In₂O₃ was observed in the In K-edge XANES (Supplementary Fig. 2) and extended XAFS (EXAFS) spectra (Supplementary Fig. 3, the Fourier transform of EXAFS is shown in Supplementary Fig. 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 (Supplementary Fig. 5 and Supplementary Table 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 (Supplementary Fig. 6a).³⁴ 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 (Supplementary Fig. 6b, In⁽⁰⁾: 443.5 eV and In³⁺: 444.5 eV),³⁴ which can be attributed to the ternary alloy phase and residual In₂O₃, respectively, as suggested by the XAFS study.

Catalytic Reactions

Afterward, the Pt–Co–In/CeO₂ catalyst was tested for the CO₂-ODP at 550°C. Some Pt-based binary

146 alloy catalysts (Pt–M/CeO₂ : M = Co, In, and Sn), of which the Pt dispersion is similar to that of Pt–Co–
 147 In/CeO₂ (Supplementary Table 2), and monometallic Pt/CeO₂ were examined to understand the
 148 individual effect of each second metal. For all the catalysts, the products were CO, C₃H₆, C₂H₄, C₂H₆,
 149 CH₄, H₂O, and H₂. No other byproducts such as oxygenates were detected in the outlet gas
 150 (Supplementary Fig. 7). Figs. 2a–c show the time course of C₃H₈ conversion, C₃H₆ selectivity in
 151 hydrocarbons (C_xH_y), and CO₂ conversion, respectively (see Supplementary Fig. S8 for details of
 152 equilibrium conversion). Although the Pt/CeO₂ and Pt–M/CeO₂ catalysts showed a high initial C₃H₈
 153 conversion (52–68%), rapid deactivation occurred within 5–10 h. Pt–Sn, which is known to be selective
 154 and stable for DDP,²⁸ was not effective for CO₂-ODP.

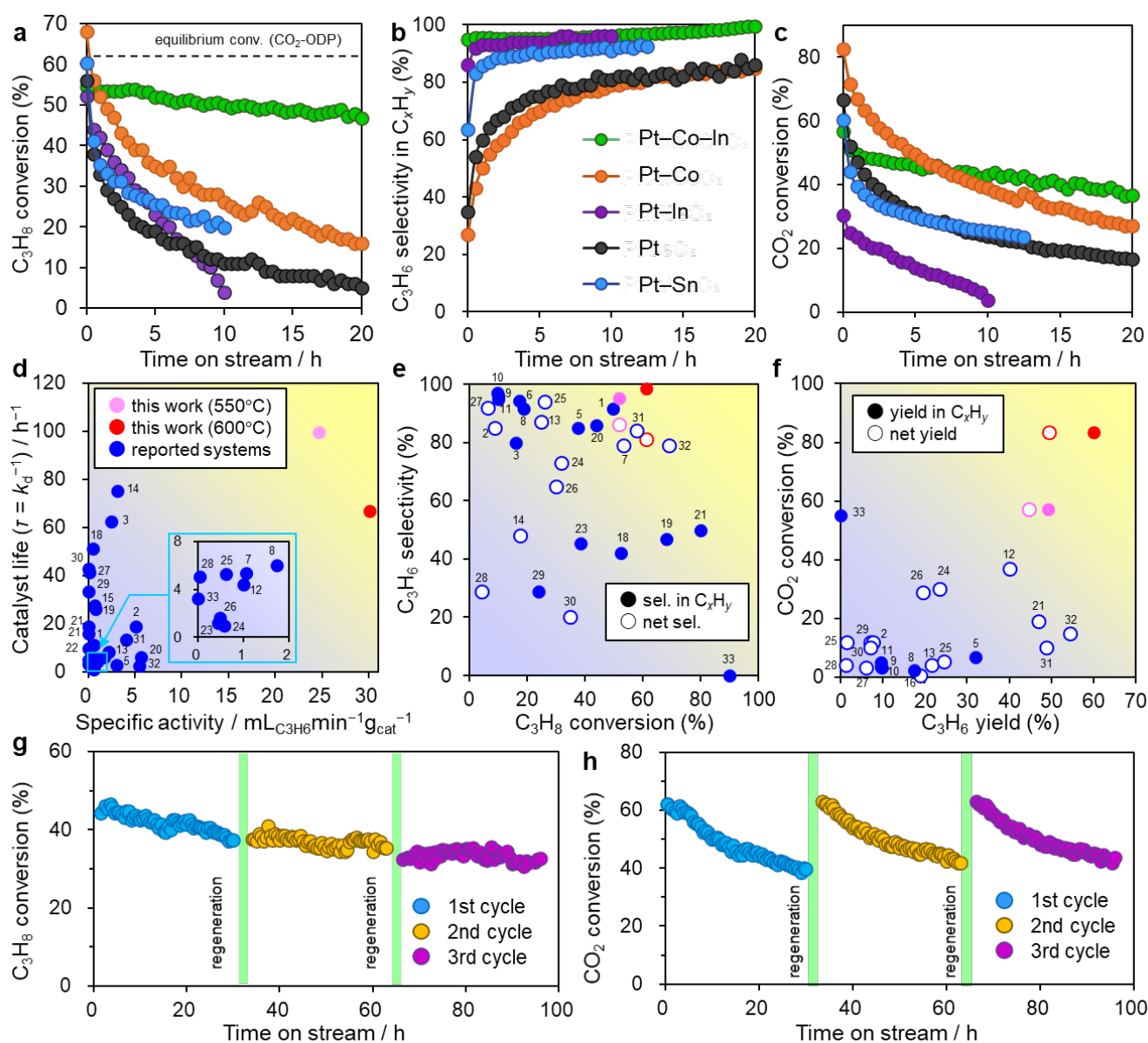


Fig. 2: Catalytic performance of Pt–Co–In/CeO₂ in the CO₂-ODP. Reaction conditions: catalyst amount, 100 mg; gas feed, C₃H₈:CO₂:He = 5:5:10 mL·min⁻¹; temperature, 550 °C. **a, b, c** Time course of **(a)** C₃H₈ conversion, **(b)** C₃H₆ selectivity, and **(c)** CO₂ conversion. **d, e, f** Comparison of 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 Supplementary Tables 4 and 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.

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, Fig. S9). 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, Fig. S8), 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 (Supplementary Fig. 10). The net C₃H₆ selectivity and yield, which consider CO from C₃H₈ as a byproduct, were still high (86–97%, Supplementary Fig. 11 and 47–44%, Supplementary Fig. 12, respectively). H₂ yield for Pt–Co–In was less than 5% (Supplementary Fig. 13), 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,³⁵ 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 (Fig. 2c), 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 (Supplementary Fig. 14). 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^{36,37} (Co/SiO₂ was not fully reduced by reduction at 600°C; see H₂-TPR, Supplementary Fig. 15). 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 (Supplementary Figs. 16–18), 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, Supplementary Fig. 19) and Raman analysis (Supplementary Fig. 20) 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% (Supplementary Table 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 (Supplementary Tables 4–5 and Supplementary Fig. 21 for details with references). For a better comparison, the catalytic performance of Pt–Co–In/CeO₂ at 600°C (Supplementary Fig. 22) 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.³⁸ 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 ($\text{mL}_{\text{C}_3\text{H}_8} \cdot \text{min}^{-1} \cdot g_{\text{cat}}^{-1}$) and the conversion–selectivity relationship were considered (Figs. 2d and 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 C_3H_6 selectivity) or not (C_3H_6 selectivity in C_xH_y). Our catalyst exhibited the highest C_3H_6 selectivity (86% and 95% for open and filled circles, respectively) at a high C_3H_8 conversion region ($> 50\%$), indicating its significant ability to suppress undesired side reactions. Fig. 2f shows the plot of the CO_2 conversion versus the C_3H_6 yield, which reflects the CO_2 utilization efficiency. A high CO_2 conversion with C_3H_6 production in 1:1 stoichiometry (the upper-right direction in Fig. 2f) is preferred for a high CO_2 utilization efficiency (see Equation 16 for the definition of CO_2 utilization efficiency). In this context, our catalyst exhibited the highest CO_2 conversion and C_3H_6 yield with near 1:1 stoichiometry among the typical systems ever reported, where the CO_2 utilization efficiency was 53% at 550 °C and 70% at 600 °C (Supplementary Fig. 21c). 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, CO_2 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 C_3H_8 was cut off to feed CO_2/He for 5 h, followed by H_2 reduction for 0.5 h at the same temperature. By this process, the CO_2 conversion was fully recovered, and it had no negative effect on the C_3H_8 conversion (Figs. 2g and h, see Supplementary Fig. 23 for C_3H_6 selectivity). Although a slight decrease in C_3H_8 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 Fig. 2g, 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/CeO₂, 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 (Supplementary Fig. 24). Thus, the Pt–Co–In/CeO₂ catalyst is highly capable of coke combustion by CO_2 , which enables continuous coke removal and long-term stability in CO_2 -ODP.

Mechanistic study

249 Next, we performed a mechanistic study to profoundly understand the functions of Co, In, and CeO₂
 250 in the catalysis. First, a kinetic analysis was conducted to understand the rate-determining step (RDS) of
 251 the CO₂-ODP on Pt–Co–In/CeO₂. The following reaction rate equation was considered for the
 252 CO₂-ODP: $r_x = kP_{\text{C}_3\text{H}_8}^\alpha P_{\text{CO}_2}^\beta$, where r_x is the consumption rate of x ($x = \text{C}_3\text{H}_8$ or CO_2), and $P_{\text{C}_3\text{H}_8}$
 253 and P_{CO_2} are the pressures of C₃H₈ and CO₂, respectively. The experimental reaction orders were
 254 positive and could be higher than unity for $P_{\text{C}_3\text{H}_8}$, while they were negative for P_{CO_2} (Table 1, see
 255 Supplementary Fig. 25 for details). Here, we considered a Langmuir–Hinshelwood mechanism
 256 involving the two-step dehydrogenation of C₃H₈ to C₃H₆, CO₂ reduction to CO, and oxidation of the
 257 eliminated hydrogen to form water (Table 1). We solved the rate equation of each step by applying
 258 quasi-stationary approximation and site conservation condition (see Supplementary Note 1 for details).
 259 The ranges of predicted reaction orders were fully consistent with the experimental orders only when
 260 the CO₂ activation to form CO and O was regarded as the RDS (step 6 in Table 1). Besides, we
 261 conducted microkinetic modeling based on the transition state theory and steady-state approximation to
 262 estimate the forward and reverse reaction rates for each step (Supplementary Note 1 and Supplementary
 263 Table 6). For this modeling, some parameters calculated using density functional theory (DFT), such as
 264 activation energy (to be described later) and vibrational frequency, were used. As shown in Table 1
 265 (calculated reaction rate), step 6 showed the lowest rate. These results showed that the RDS of
 266 CO₂-ODP on Pt–Co–In/CeO₂ was the CO₂ activation. Subsequently, the apparent activation energy
 267 (E_A^*) was estimated for Pt–In/CeO₂ and Pt–Co–In/CeO₂ by Arrhenius-type plots. The E_A of CO₂
 268 activation was significantly reduced by the incorporation of Co to Pt–In (168.8→138.3 kJ·mol^{−1}, Table
 269 1 and Supplementary Fig. 26), which is consistent with the experimental trend of the CO₂ conversion
 270 and turnover frequency (TOF), as shown in Fig. 2c and Supplementary Fig. 27, respectively. We also
 271 simulated the dependences of the reaction rate on $P_{\text{C}_3\text{H}_8}$ and temperature using the kinetic modeling,
 272 both of which agreed finely with the experimental trends (Supplementary Fig. 28; only slight deviations
 273 from the experimental values were observed, which may be due to errors in the DFT calculation). This
 274 result strongly supports the validity of our kinetic model. Thus, the kinetic analysis revealed that
 275 alloying with Co kinetically promoted the CO₂ activation, which is the RDS of the CO₂-ODP.
 276 Compared with reported systems, Pt–Co–In/CeO₂ showed comparable E_A^* : for C₃H₈ dehydrogenation
 277 (WO_x–VO_x/SiO₂: 127–145 kJ·mol^{−1}, Fe₃Ni/CeO₂: 115 kJ·mol^{−1}), for CO₂ activation (Fe₃Ni/CeO₂: 135
 278 kJ·mol^{−1}).

Table 1: 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	$E_A / \text{kJ} \cdot \text{mol}^{-1}$	experiment		DFT calculation	
				Pt–In	Pt–Co–In	Pt ₂ In ₃	Pt ₂ In ₃ –Co
$x = C_3H_8$	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	$\vec{r}_f / \text{s}^{-1}$	$\vec{r}_l / \text{s}^{-1}$		
(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: $\vec{r}_f$ and $\vec{r}_r$ 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.

280

281 We subsequently examined a series of Pt-Co-In catalysts using various supports, such as Al₂O₃,
 282 TiO₂, and ZrO₂, so that the role of the CeO₂ support was clarified. Although these catalysts showed
 283 moderate initial conversions of C₃H₈ and CO₂, rapid deactivation occurred within 1–2 h (Figs. 3a and b).
 284 This result strongly indicates that the role of CeO₂ is to significantly enhance the catalyst stability; this
 285 is probably attributed to its coke combustion ability, as mentioned above. To confirm this ability,
 286 temperature-programmed surface reactions (TPSRs) were conducted using the coked catalysts under He
 287 and CO₂ flows. The coked Pt-Co-In/CeO₂ evolved CO from 500 °C even in the absence of CO₂
 288 (He-TPSR, Fig. 3c), whereas the coked Pt-Co-In/Al₂O₃ showed almost no CO evolution up to 600°C.

289

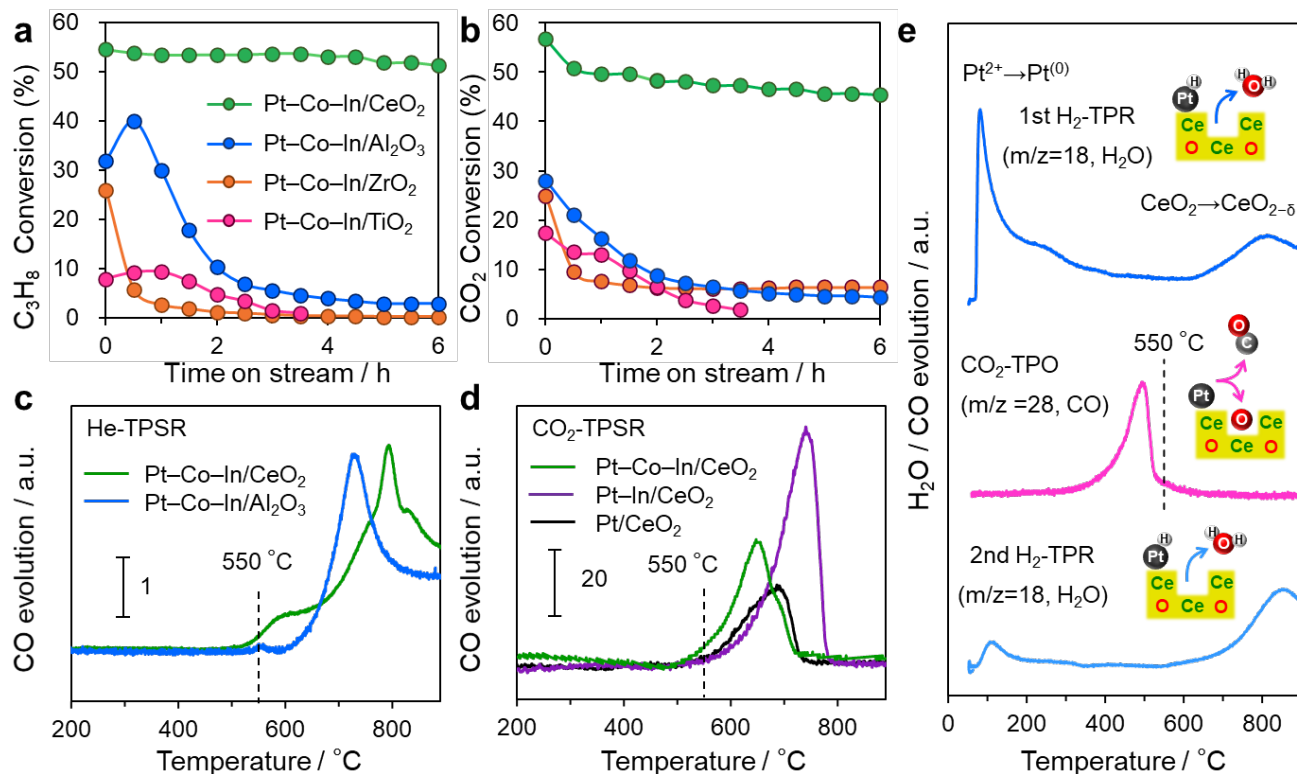


Fig. 3: Effect of the catalyst support and TPSR on the coked catalysts. **a, b** (a) C_3H_8 and (b) CO_2 conversions in CO_2 -ODP on the Pt–Co–In catalysts using various supports. **c** He-TPSR on the coked Pt–Co–In/CeO₂ (used in DDP for 2 h) and Pt–Co–In/Al₂O₃ (used in CO_2 -ODP for 2 h) catalysts. **d** CO_2 -TPSR on the coked Pt/CeO₂, Pt–In/CeO₂ (used in CO_2 -ODP for 2 h), and Pt–Co–In/CeO₂ (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 CeO₂ using Pt/CeO₂.

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 CO_2 -ODP (550 °C), while Al₂O₃ cannot, which agrees with the stability trend in CO_2 -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 CO_2 (CO_2 -TPSR, Fig. 3d), 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 CO_2 . 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, Fig. 2a)

309 and the CO₂ reducing ability (Pt–Co–In, Pt > Pt–In, Fig. 2c), which reflects the coke combustion
310 abilities of these catalysts. Based on these results, we concluded that the coke combustion ability
311 depended on the CO₂ reducing ability of the metal nanoparticles, as well as the oxygen-releasing ability
312 of CeO₂. The concert of the ternary alloy and the specific character of the CeO₂ support enabled the
313 continuous self-regeneration function and the remarkably high coke resistance. Furthermore, we verified
314 the filling of oxygen vacancy after the lattice oxygen consumption of CeO₂ using a CO₂-titration (TPO)
315 technique and Pt/CeO₂. As shown in Fig. 3e, oxygen vacancies of CeO₂ were obtained by H₂-TPR,
316 followed by cooling and subsequent CO₂-TPO. CO evolution was completed by 550 °C, indicating that
317 CO₂ was divided into CO and O. The oxygen atoms were left on the catalyst. H₂-TPR was repeated after
318 CO₂-TPO and cooling, where the reduction peak of CeO₂ appeared again (Fig. 3e). These results
319 strongly support that the oxygen atoms derived from CO₂ refill the oxygen vacancies of CeO₂.

320 Finally, we conducted DFT calculations to understand the role of the Pt–Co–In ternary alloy in the
321 enhanced catalysis. As a model of the Pt–Co–In alloy surface, the stable (012) surface of intermetallic
322 Pt₂In₃ was considered and one of the surface Pt atoms was replaced with Co, hereafter denoted as
323 Pt₂In₃(012)–Co. Unmodified Pt₂In₃(012) and monometallic Pt(111) surfaces were also considered for
324 comparison. CO₂ reduction to CO, C₃H₈ dehydrogenation to C₃H₆, H₂O formation, and H₂
325 recombination were considered on these surfaces (see Supplementary Figs. 29–37 for detailed structures
326 and Supplementary Fig. 38 for Gibbs free energy changes). Fig. 4a shows the energy diagram of CO₂
327 reduction, where CO₂ was first physisorbed, then chemisorbed with a bent sp²-like conformation,
328 followed by C–O bond scission to form CO and O, and lastly, CO desorption. The chemisorption was
329 endothermic and required moderate energy barriers of 55–57 kJ·mol^{−1}. For Pt₂In₃ and Pt₂In₃–Co, the
330 subsequent C–O scission generated CO on a top site of Pt/Co and O at an In–In bridge site, which was
331 more stable than those on Pt(111), probably due to the oxophilicity of In. CO was considerably more
332 stable on Co than on Pt; therefore, the direct desorption of CO from the Co site required a high amount
333 of energy (182.3 kJ·mol^{−1}). Relatively-low energy desorption is still allowed when CO migrates to the
334 neighboring Pt site. However, the microkinetic modeling showed that the constant and reaction rate for
335 the desorption of product molecules were considerably high (Table 1 and Supplementary Table 6) due
336 to the huge contribution of the translational partition function of gas-phase molecules at high
337 temperatures.

338

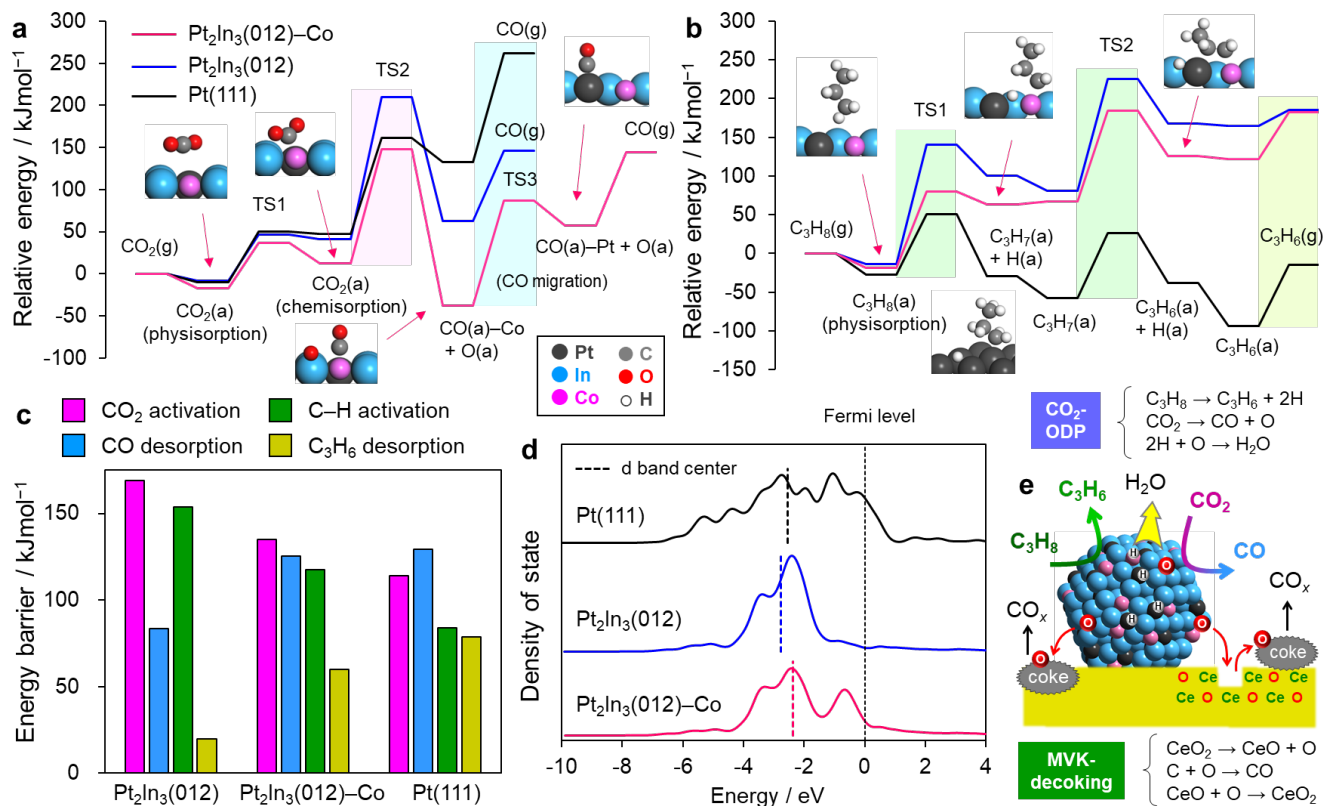


Fig. 4: DFT calculations and reaction mechanism: a, b Energy diagrams of (a) CO₂ reduction to CO and O and (b) C₃H₈ dehydrogenation to C₃H₆ on Pt(111), Pt₂In₃(012), and Pt₂In₃(012)-Co. **c** Summary of the energy barriers on each surface. For Pt₂In₃(012)-Co, the energy barrier of CO migration was regarded 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.

Thus, the direct desorption of CO from the Co site can smoothly occur even with the large energy barrier. Fig. 4b 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, Supplementary Fig. 38a and Supplementary Tables 7–9). 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 (Supplementary Fig. 39). Fig. 4c. 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 1 and Supplementary Fig. 26) and with the low CO₂ conversion and TOF of Pt–In/CeO₂. (Figs. 2c and Supplementary Fig. 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 1) and the significantly improved CO₂ conversion/TOF (Figs. 2c and Supplementary Fig. 27) by Co-substitution. Good agreements were also obtained between the theoretical and experimental E_A^* values for C–H activation (Table 1), 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 (Fig. 4b) in line with the Brønsted–Evans–Polanyi relationship.³⁹ 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 Fig. 4d. 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.^{40,41} 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.

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 Fig. 4e. 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 Supplementary Fig. 24. 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%, Supplementary Fig. 1) 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.

Discussion

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.

Methods

Catalysts 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.

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.⁴² 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.

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.

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

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

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

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

503

504 H₂ yield was defined as follows:

$$505 \quad \text{H}_2 \text{ yield: } Y_{\text{H}_2} (\%) = \frac{F_{\text{H}_2}^{\text{out}}}{F_{\text{C}_3\text{H}_8}^{\text{in}}} \times 100 \quad (9)$$

506 Material balance was considered using the following scales:

507

$$508 \quad \text{carbon blance in } \text{C}_x\text{H}_y = \frac{F_{\text{C}_3\text{H}_8}^{\text{out}} + F_{\text{C}_3\text{H}_6}^{\text{out}} + \frac{2}{3}F_{\text{C}_2\text{H}_6}^{\text{out}} + \frac{2}{3}F_{\text{C}_2\text{H}_4}^{\text{out}} + \frac{1}{3}F_{\text{CH}_4}^{\text{out}}}{F_{\text{C}_3\text{H}_8}^{\text{in}}} \times 100 \quad (10)$$

$$509 \quad \text{carbon blance in } \text{CO}_x = \frac{F_{\text{CO}_2}^{\text{out}} + F_{\text{CO}}^{\text{out}}}{F_{\text{CO}_2}^{\text{in}}} \times 100 \quad (11)$$

510 total carbon blance =

$$511 \quad \frac{F_{\text{C}_3\text{H}_8}^{\text{out}} + F_{\text{C}_3\text{H}_6}^{\text{out}} + \frac{2}{3}F_{\text{C}_2\text{H}_6}^{\text{out}} + \frac{2}{3}F_{\text{C}_2\text{H}_4}^{\text{out}} + \frac{1}{3}F_{\text{CH}_4}^{\text{out}} + F_{\text{CO}_2}^{\text{out}} + \frac{1}{3}F_{\text{CO}}^{\text{out}} + F_{\text{C}_x\text{H}_y}^{\text{CO}_2}}{F_{\text{C}_3\text{H}_8}^{\text{in}} + F_{\text{CO}_2}^{\text{in}}} \times 100 \quad (12)$$

$$512 \quad \text{oxygen blance} = \frac{2F_{\text{CO}_2}^{\text{out}} + F_{\text{CO}}^{\text{out}} + F_{\text{H}_2\text{O}}^{\text{out}}}{2F_{\text{CO}_2}^{\text{in}}} \times 100 \quad (13)$$

513

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

516

$$517 \quad \text{Deactivation constant: } k_d = \left\{ \ln \left(\frac{1 - X_{\text{C}_3\text{H}_8}^f}{X_{\text{C}_3\text{H}_8}^f} \right) - \ln \left(\frac{1 - X_{\text{C}_3\text{H}_8}^i}{X_{\text{C}_3\text{H}_8}^i} \right) \right\} (t^f - t^i)^{-1} \quad (14)$$

$$518 \quad \text{Mean catalyst life: } \tau = \frac{1}{k_d} \quad (15)$$

$$519 \quad \text{CO}_2 \text{ utilization efficiency } (\%) = X_{\text{CO}_2} \left(1 - \frac{|X_{\text{CO}_2} - Y_{\text{C}_3\text{H}_6}|}{X_{\text{CO}_2} + Y_{\text{C}_3\text{H}_6}} \right) \quad (16)$$

$$520 \quad \text{TOF}_{\text{C}_3\text{H}_8/\text{CO}_2} (\text{site}^{-1}\text{min}^{-1}) = \frac{M_{\text{C}_3\text{H}_8/\text{CO}_2}^{\text{in}} \times X_{\text{C}_3\text{H}_8/\text{CO}_2}^i}{n_{\text{Pt+Co}} \times D} \quad (17)$$

$$521 \quad \text{average coke selectivity: } S_c (\%) = \frac{\frac{1}{3}n_c^t}{\int_0^t (F_{\text{C}_3\text{H}_8}^{\text{in}} - F_{\text{C}_3\text{H}_8}^{\text{out}}) dt} \times 100 \quad (18)$$

$$522 \quad \text{TON}_{\text{coke}} (\text{site}^{-1}) = \frac{n_c^t}{n_{\text{Pt+Co}} \times D} \quad (19)$$

523

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_{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%).

533

534 Computational details

Periodic DFT calculations were performed using the CASTEP code⁴³ with Vanderbilt-type ultrasoft pseudopotentials and the revised version of Perdew–Burke–Ernzerhof exchange–correlation functional based on the generalized gradient approximation.⁴⁴ 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 $d = 20$.⁴⁵ 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.⁴⁶ 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 $13 \text{ \AA}$ of vacuum spacing. We chose $Pt_2In_3(012)$ as the most stable surface, which has the highest surface atom density and diffraction intensity.^{47,48} $Pt_2In_3(012)$ –Co was constructed as a model of the surface $(Pt_{1-x}Co_x)_2In_3$ pseudo binary alloy by replacing one of the surface Pt atoms of $Pt_2In_3(012)$. The unit cells were (2×2) for $Pt(111)$, (1×1) for C_3H_8 dehydrogenation on $Pt_2In_3(012)$ (–Co), and (1×2) for CO_2 reduction on $Pt_2In_3(012)$ (–Co). Geometry optimizations were performed using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm.⁴⁹ The unit cell size of the bulk material (Pt and Pt_2In_3) 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 $1.0 \times 10^{-6} \text{ eV}$ per atom, (b) an energy tolerance of $1.0 \times 10^{-5} \text{ eV}$ per atom, (c) a maximum force

553 tolerance of 0.05 eV Å⁻¹, and (d) a maximum displacement tolerance of 1.0 × 10⁻³ Å.

554 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
555 the slab together with the adsorbate, E_{A} is the total energy of the free adsorbate, and E_{S} is the total
556 energy of the bare slab. The adsorption energy for an oxygen-preadsorbed slab was calculated using E_{SH} ,
557 which is the total energy of the oxygen-adsorbed slab, instead of using E_{S} . The d band center (ε_{d}) was
558 defined as the average energy of the occupied d band relative to the Fermi level as follows:

559

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

560

561

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

563 The transition state (TS) search was performed using the complete linear synchronous
564 transit/quadratic synchronous transit (LST/QST) method.^{50,51} Linear synchronous transit maximization
565 was performed, followed by energy minimization in the directions conjugating to the reaction pathway.
566 The approximated TS was used to perform QST maximization with conjugate gradient minimization
567 refinements. This cycle was repeated until a stationary point was found. Convergence criterion for the
568 TS calculations were set to root-mean-square forces on an atom tolerance of 0.05 eV Å⁻¹.

569 The activation energy (E_{A}) was determined as the largest energy barrier among all the focused steps:
570 for CO₂ conversion; CO₂ activation, for C₃H₈ conversion, the 1st or 2nd C–H activation. We also
571 consider theoretical apparent activation energy, E_{A}^* , for the comparison with the experimental values.
572 This is identical to E_{A} except when the initial state for E_{A} is a weakly adsorbed state, like physisorption,
573 where the apparent activation energy should be expressed as $E_{\text{A}}^* = E_{\text{A}} + E_{\text{ad}}$ as often considered in
574 literature.⁴³ In this study, the 1st C–H activation on Pt₂In₃ falls into this case: $E_{\text{A}}^* = E_{\text{A}}$ (153.3) + E_{ad}
575 (−13.2) = 140.1 kJ/mol.

576

577 Vibrational frequencies of the adsorbates were computed by phonon calculation based on harmonic
578 approximation using the finite displacement method in CASTEP. Fractional positions of all the metal
579 atoms were fixed so that only C, H, and O atoms were considered for phonon calculation. The
580 contribution of solid surface to the vibrational terms, which is typically much lower than that of
581 adsorbates, was ignored. The threshold for energy convergence for each iteration was set to 10⁻¹⁰ eV per
582 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:⁵²

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

where, E_e is the electronic energy,

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

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

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

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

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

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

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

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.⁵³ 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 °C and their translational and rotational contributions were evaluated at relative pressures (P/P^0) of 0.24 and 0.01, respectively.

Data Availability

All data is available from the authors upon reasonable request, because the authors need to confirm the purpose.

609

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Acknowledgement

This work was supported by JSPS KAKENHI (Grant Numbers 17H01341, 17H04965, and 20H02517), MEXT project Element Strategy Initiative (JPMXP0112101003), JST CREST (JPMJCR17J3), JST PRESTO (JPMJPR19T7), and the Collaborative Research Projects of Laboratory for Materials and Structures, Institute of Innovative Research, Tokyo Institute of Technology. The XAFS analysis was performed with the approval of JASRI (No. 2019B1620 and 2019B1469). We appreciate the technical staffs of Research Institute for Electronic Science, Dr. Yuta Nakasaka, and Mr. Kah Wei Ting, Hokkaido University for help with HAADF-STEM, Raman, and XPS analyses, respectively.

725 Computation time was provided by the supercomputer systems in Institute for Chemical Research,
726 Kyoto University.

727

728 **Author contributions**

729 S.F. and F.X. design the research and co-wrote the manuscript in discussion. F.X. performed all the
730 experimental works. Y.N. contributed to XAFS and XPS studies. S.F. conducted all the computational
731 and kinetic studies. S.Y. contributed to free energy calculation. S.F., F.X., Y.N., S.Y., and K.S.
732 discussed the data and commented on the manuscript.

733

734 **Competing interests**

735 The authors declare no competing interests.