HOKKAIDO UNIVERSITY

Title	Optimal mixing method of ZnZrO and MOR-type zeolite to prepare a bifunctional catalyst for CO2 hydrogenation to lower olefins
Author(s)	Tada, Shohei; Kinoshita, Hiroka; Li, Duanxing et al.
Citation	Advanced Powder Technology, 34(10), 104174 https://doi.org/10.1016/j.apt.2023.104174
Issue Date	2023-10
Doc URL	https://hdl.handle.net/2115/95741
Rights	© <2023>. This manuscript version is made available under the CC-BY-NC-ND 4.0 license https://creativecommons.org/licenses/by-nc-nd/4.0/
Rights(URL)	https://creativecommons.org/licenses/by-nc-nd/4.0/
Type	journal article
File Information	Revised Manuscript.pdf

Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP

Optimal mixing method of $ZnZrO_x$ and MOR-type zeolite to prepare a bifunctional catalyst for CO_2 hydrogenation to lower olefins

Shohei Tada [a,*], Hiroka Kinoshita [b], Duanxing Li [c], Masahiko Nishijima [d], Harune Yamaguchi [a], Ryuji Kikcuhi [a], Noriko Yamauchi [e], Yoshio Kobayashi [e], Kenta Iyoki [c,*]

a Division of Applied Chemistry, Hokkaido University, N13 W8, Kita-ku, Sapporo, Hokkaido 060-8628, Japan.
b Institute of Quantum Beam Science, Ibaraki University, 4-12-1 Nakanarusawa-cho, Hitachi, Ibaraki 316-8511, Japan.
c Department of Chemical System Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan.
d Flexible 3D System Integration Laboratory, Sanken, Osaka University, Ibaraki, Osaka 567-0047, Japan.
e Department of Materials Science and Engineering, Ibaraki University, 4-12-1 Nakanarusawa-cho, Hitachi, Ibaraki 316-8511, Japan.

*Corresponding authors: Shohei Tada (shohei.tada.st@eng.hokudai.ac.jp)
Kenta Iyoki (k_iyoki@chemsys.t.u-tokyo.ac.jp)

Keywords
Carbon dioxide hydrogenation, Mordenite, Bifunctional catalyst, Physical mixing

Abstract
In recent years, the issue of global warming caused by CO_2 emissions has become a critical problem and poses a worldwide challenge. To address this issue, we have developed a bifunctional catalyst that can convert CO_2 to lower olefins in a single stage. Our bifunctional catalysts are a combination of two catalysts, a CO_2-to-methanol hydrogenation catalyst (Zn-doped ZrO_2, named $ZnZrO_x$) and a methanol-to-olefin catalyst (MOR-type zeolite, named MOR104). In this research, we examined the impact of various mixing modes of the two catalysts on product distribution. We tested four different mixing modes using a down-flow fixed bed reactor: (a) $ZnZrO_x$ in the upper layer and MOR104 in the lower layer, (b) catalysts were mixed randomly after being pelletized separately, (c) MOR104 in the upper layer and $ZnZrO_x$ in the lower layer, and (d) granulated catalyst produced by physically mixing both catalyst powders. Our findings indicated that the best performance was achieved with catalyst (d), where the two catalysts were mixed in close proximity. This proximity resulted in efficient supply of

methanol produced on $ZnZrO_x$ to MOR104. In other words, the MTO reaction in MOR104 efficiently consumed methanol molecules produced via equilibrium-limited CO_2-to-methanol hydrogenation. When $ZnZrO_x$ and MOR104 were thoroughly mixed, the conversion of CO_2 to methanol shifted towards the product side, resulting in a greater overall utilization of CO_2. Furthermore, the bifunctional catalyst we developed was stable for six hours. Since there have been few studies of bifunctional catalysts containing zeolites other than ZSM-5 and SAPO-34, this study opens up new opportunities for bifunctional catalysts specialized for one-pass hydrocarbon synthesis through CO_2 hydrogenation.

1. Introduction

Since the 18th century's Industrial Revolution, humanity has advanced by utilizing fossil fuels such as coal, oil, and natural gas. However, burning these fuels releases CO_2, causing a rise in atmospheric CO_2 concentration that's believed to be responsible for global warming and altering the Earth's climate. To safeguard the global environment and achieve a sustainable future, it is essential to decrease fossil fuel usage and simultaneously encourage capturing and reusing CO_2 to limit atmospheric CO_2 concentration as much as possible. The topic of CO_2 recycling has garnered significant attention from researchers in recent years, and our team has been among those studying bifunctional catalysts that can facilitate the synthesis of lower hydrocarbons using CO_2 and H_2 obtained from renewable energy sources.

We focus on the process of synthesizing lower olefins from CO_2 by using methanol as an intermediate. This is the two-step process involving the hydrogenation of CO_2 to methanol ($CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$), followed by the conversion of methanol to lower olefins, commonly known as an MTO (methanol-to-olefins) reaction. Typically, Cu-based catalysts are used for the first step. [1] Subsequently, zeolites serve as solid acid catalysts to convert methanol into lower olefins.[2] When lower olefins are synthesized via CO_2 hydrogenation, the equilibrium limitations of the methanol synthesis reaction have a significant impact. As the methanol synthesis reaction is a molecule-reducing reaction, high-pressure condition is preferred according to Le Chatelier's principle. In practice, many methanol synthesis plants are operated under high-pressure conditions ranging from 3 to 5 MPa.

In recent years, researchers have studied the development of a single-stage reactor that combines both reactions for the direct conversion of CO_2 to lower olefins. By utilizing the methanol produced on-site in the MTO reaction, it is expected that the CO_2-to-methanol hydrogenation will shift towards the product side to minimize the decrease in methanol partial pressure. This means that the one-pass reaction will become more financially viable and energy-efficient. However, one of the challenges is the discrepancy in optimal operating temperatures between existing catalysts for methanol synthesis and MTO reactions. The conventional methanol synthesis catalysts, such as $Cu/ZnO/Al_2O_3$ and $Cu/ZnO/ZrO_2$, operate at around 250 ℃. [2, 3] In contrast, the zeolite such as SAPO-34 and HZSM-5, used as an MTO catalyst, requires a reaction temperature of > 400 °C. [2] To overcome this

challenge, the operating temperatures of the two reactions need to be brought closer together.

Metal oxide catalysts (Zn-,[4-6] In-,[7] Ga-,[8, 9] and Cd-doped ZrO_2[9]) that operate at temperatures higher than Cu-based catalysts, specifically at temperatures above 300 °C, are crucial in the one-pass process of hydrocarbon synthesis. In the case of Zn-doped ZrO_2, for example, H_2 and CO_2 are activated on Zn^{2+} and Zr^{4+} sites, respectively. [6] At the interfacial sites, Zn^{2+}-O- Zr^{4+}, CO_2 molecules are hydrogenated through formate and methoxy species to methanol. In recent studies, bifunctional catalysts, which are produced by combining metal oxide catalysts with zeolite such as SAPO-34 and HZSM-5, have shown promising results in hydrocarbon synthesis at a temperature range of about 350-400 °C. Researchers have investigated various bifunctional catalysts using SAPO-34 and HZSM-5 zeolites. For example, Zhang et al. synthesized light aromatics using bifunctional catalysts composed of Cr-doped ZrO_2 and HZSM-5.[10] Li et al. developed bifunctional catalysts with ZnO-ZrO_2 supported on SAPO-34, successfully synthesizing lower olefins with more than 80% of the produced hydrocarbon species. [11] Ramirez et al. reported the use of a ZrS/SAPO-34 system for methanol synthesis.[12] Wang et al. proposed Cr_2O_3/HZSM-5 and ZrO_2/HZSM-5 as specialized catalysts for hydrocarbon synthesis with more than two carbons. [13] The effectiveness of these bifunctional catalysts was not only determined by the individual physicochemical properties of the metal oxide catalyst and HZSM-5 but also by the distance and interaction between the two catalysts. [13] Different mixing methods of Zn-doped ZrO_2 and HZSM-5 were investigated by Li et al. to determine how they affect product distribution in the CO_2 hydrogenation reaction. [14] Their results show that when both catalysts were thoroughly mixed, aromatic hydrocarbons were selectively synthesized, while C_{5+} hydrocarbons were the main products when the mixing was insufficient. However, few bifunctional catalysts containing zeolites other than SAPO-34 and HZSM-5 have been reported. [15]

Here, we are focusing on MOR-type zeolite which is a relatively inexpensive zeolite with 12-membered rings. Beside these large pores, there are 8-membered ring side pockets, where Brønsted acid sites contribute greatly to the activation of methanol [16] and dimethyl ether.[17] We reported the first time synthesizing lower olefins using a bifunctional catalyst composed of $ZnZrO_x$ mixed with MOR-type zeolite. [18] The developed catalyst demonstrated significant potential for synthesizing lower olefins via CO_2 hydrogenation in comparison to $ZnZrO_x$ + SAPO-34 and $ZnZrO_x$ + HZSM-5. [18] In addition, we found that MOR-type zeolite with a high Si/Al ratio (Si/Al ratio = 104) was suitable for the synthesis of lower olefins. [19] As described above, fundamental studies for bifunctional catalysts based on MOR-type zeolite are scarce. The present study is centered on the distance between $ZnZrO_x$ and MOR-type zeolite and assessing the variations in the products yielded by each catalyst when subjected to different mixing methods. Our objective is to contribute to the expansion of the field of bifunctional catalysts based on MOR-type zeolites.

2. Results and Discussion

We synthesized $ZnZrO_x$ using an incipient wetness impregnation method, and as-received proton-form MOR zeolite (MOR104), as shown in ESI. The XRD patterns of the synthesized samples are illustrated in **Figure 1a**. The $ZnZrO_x$ pattern exhibits a discernible peak related to *t*-ZrO_2 and a weak peak attributed to ZnO. According to our previous research [6], Zn species can be wholly incorporated into the *t*-ZrO_2 lattice when the Zn/Zr atomic ratio is lower than 0.23. However, since the Zn/Zr atomic ratio in the $ZnZrO_x$ sample in this study was 0.42, it can be inferred that some Zn species failed to integrate into the solid solution and instead formed ZnO particles. The selection of $ZnZrO_x$ with a high Zn/Zr ratio was based on its established propensity for demonstrating a comparatively elevated performance for methanol production. [6] The MOR104 peaks align with the typical peak of MOR-type zeolites.[19] The pattern of the physical mixture involving $ZnZrO_x$ and MOR104 displayed characteristic patterns corresponding to $ZnZrO_x$, specifically *t*-ZrO_2 and ZnO, as well as MOR104.

The morphological characteristics of the synthesized samples were analyzed using scanning transmission electron microscopy (STEM, **Figure 1b**). The Zn and Zr species were uniformly dispersed within the $ZnZrO_x$ particles with an average size of about 10 nm. The particle of MOR104 displayed an irregular shape with a smooth surface and was ca. 500 nm. According to a scanning electron micrscopy observation in previous study, they had a size distribution ranging from 0.1 to 2 μm, which formed aggregates of a few micrometers in size through close binding. [19] In addition, MOR104 surface exhibited the attachment of multiple ZnZrOx particles in the STEM image of ZnZrOx + MOR104.

Figure 1c shows the N_2 adsorption-desorption isotherms for two different samples, along with the calculation of specific surface area and total pore volume. The specific surface area of $ZnZrO_x$ was 42 $m^2\ g^{-1}$, which was lower than the specific surface areas of MOR104 (603 $m^2\ g^{-1}$), as shown in **Table S1**. The isotherm of MOR104 was classified as type I, indicating the presence of micropores (< 2 nm). Based on the specific surface areas of $ZnZrO_x$ and MOR104 and their mixing weight ratios, the specific surface area of the composite sample was estimated to be 270 $m^2\ g^{-1}$. Remarkably, this estimated value closely approximates the actual measured value of 280 $m^2\ g^{-1}$ (**Table S1**).

Figure 1d depicts the NH_3-TPD profile for MOR104 wherein two peaks are identified: one on the low-temperature side (100-200 °C) and the other on the high-temperature side (350-550 °C). The low-temperature peak denotes the desorption of physically adsorbed NH_3 on the surface of the solid acid, which is not the focus of this paper. [20, 21] The peak temperature of the peak observed on the high-temperature side is directly proportional to the acid strength. Moreover, a larger peak implies a higher acid amount. For MOR104, a small peak is observed at approximately 408 °C, which means that MOR104 possessed a small number of strong acid sites. [21]

The oxidation states of Zn species in $ZnZrO_x$ and $ZnZrO_x$ + MOR104 were analyzed by X-ray photoelectron spectroscopy (XPS). **Figure S1** provide comprehensive details, confirming the presence

of Zn species in the form of Zn^{2+} ions.

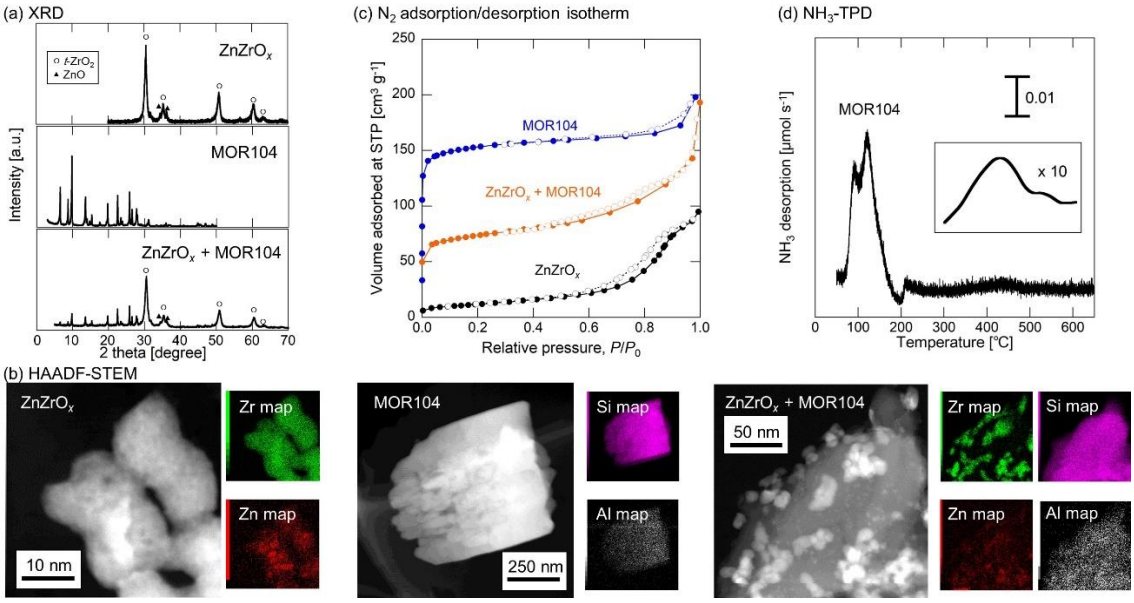


Figure 1 (a) XRD patterns of $ZnZrO_x$, MOR104, and $ZnZrO_x$ + MOR104, (b) STEM image of $ZnZrO_x$, MOR104, and $ZnZrO_x$ + MOR104 with elemental mapping, (c) N_2 adsorption/desorption isotherms of $ZnZrO_x$, MOR104, and $ZnZrO_x$ + MOR104 at -196°C, and (d) NH_3-TPD profiles of MOR104. For (c), the data points for adsorption and desorption are denoted by filled and blank symbols, respectively.

Figures S2 and **2** displays the results of reaction tests performed on bifunctional catalysts with different methods of packing them into the catalyst layer. The experiments were conducted under a pressure of 1.0 MPa due to the constraints imposed by the Japanese high pressure gas safety act. For the tests, 500 mg of $ZnZrO_x$ and 350 mg of MOR104 were packed into the catalyst layer using the following methods: (a) $ZnZrO_x$ in the upper layer and MOR104 in the lower layer, (b) catalysts were mixed randomly after being packed separately, (c) MOR104 in the upper layer and $ZnZrO_x$ in the lower layer, and (d) granulated catalyst produced by physically mixing both catalyst powders. For comparison, the catalytic performance using only 500 mg of $ZnZrO_x$ packed into the catalyst layer is shown in (e). We have checked that CO_2 are hardly hydrogenated over MOR104 alone (**Table S2**).

In **Figure S2**, CO_2 conversion increased with the reaction temperature in spite of the types of catalysts. Of note, mixing of $ZnZrO_x$ with solid acid catalysts gradually decreased CO_2 conversion, in line with our previous report. [18]

Next, we focused on the case where only $ZnZrO_x$ was introduced into the catalyst bed (**Figure 2e**). Using an FID detector, we observed only methanol in the products. Other than methanol, we confirmed the CO by-production. With increasing the reaction temperature from 325 to 400 °C, the methanol yield decreased from *ca*. 3% to 1%, and simultaneously, the CO yield increased (**Figure S2**).

Third, we considered case (a) where $ZnZrO_x$ and MOR104 were packed in the upper and lower

layer, respectively (**Figure 2a**). The overall hydrocarbon yield at 325 °C was *ca*. 3% and gradually decreased with increasing reaction temperature. In addition, the tendency of CO yield was like that for $ZnZrO_x$ (**Figure S2**). The behavior was almost the same to the case where only $ZnZrO_x$ was introduced to the catalyst bed (**Figure 2e**). With the catalyst packing method in case (a), the activity of $ZnZrO_x$ determined the overall yield. The difference between cases (a) and (e) was the product distribution. For case (a), light olefines ($C_2^=$-$C_4^=$) were mainly produced, where for case (e), methanol was produced. Hence, the presence of MOR104 in the catalyst bed proceeded the MTO reaction, which was also confirmed by an *in-situ* infrared study (see ESI, **Figure S3**).

Fourth, when MOR104 were used in the upper layer and $ZnZrO_x$ in the lower layer (**Figure 2c**), the yield of C_2-C_4 hydrocarbons was low, with methanol and CH_4 being the main products. Conditions such as (c) were expected to produce mainly the products produced by $ZnZrO_x$ because MOR104 is inactive in CO_2 hydrogenation. Although the yields of C_{5+} and $C_2^=$-$C_4^=$ appeared high at some temperatures, this is probably due to the mixing of the two catalysts by the thermocouple inserted from above in the catalyst bed. Therefore, from now on, we have decided not to discuss the case (c).

Fifth, we focused on cases (b) and (d) where the catalysts were mixed randomly (**Figures 2b** and **2d**). The difference in the packing of (b) and (d) determined the performance of the bifunctional catalysts. In case (b), the $C_2^=$-$C_4^=$ yield was higher. On the other hand, in case (d), the total yield was higher. Of note, the total yield of methanol and hydrocarbons at 350-375 °C (approximately 6-8 %) was higher than those for cases (a) and (e). In other words, the CO yield in the same temperature range was much lower than that for the cases (a) and (e), as shown in **Figure S2**. These results suggest that the highest yield of lower olefins is achieved when $ZnZrO_x$ and MOR104 are randomly mixed together. The durability of the catalyst (case (d) in **Figure 2**) has undergone prior assessment, as shown in **Figure S4**.[19] In 6 hours, almost no degradation of the catalyst was observed.

When $ZnZrO_x$ and MOR104 are in contact with each other, the methanol produced is immediately used for the MTO reaction, and the formation of by-products can be minimized. This means that the MTO reaction on the zeolite utilizes the methanol, causing the methanol synthesis reaction to shift towards the product side. Consequently, using bifunctional catalysts to generate useful substances like hydrocarbons from CO_2 in a one-pass process significantly increases CO_2 conversion efficiency. We have already reported this phenomenon using a bifunctional catalyst produced by physical mixing of $ZnZrO_x$ and MFI-type zeolite. [18] Using the bifunctional catalyst at 375 °C and 1.0 MPa, a 9 % hydrocarbon yield was achieved. In contrast, the equilibrium methanol yield that can be achieved under limited conditions of 1.0 MPa is 1.7 % at 250 °C (the optimal operating temperature for commercial Cu-based catalysts) and less than 0.1 % at 375 °C. The physical mixture of $ZnZrO_x$ and MFI-type zeolite has demonstrated significant catalytic potential in the conversion of CO_2 to olefins through the methanol intermediate, because of its ability to efficiently convert the methanol intermediate well beyond the equilibrium yield in the process of CO_2-to-methanol hydrogenation.

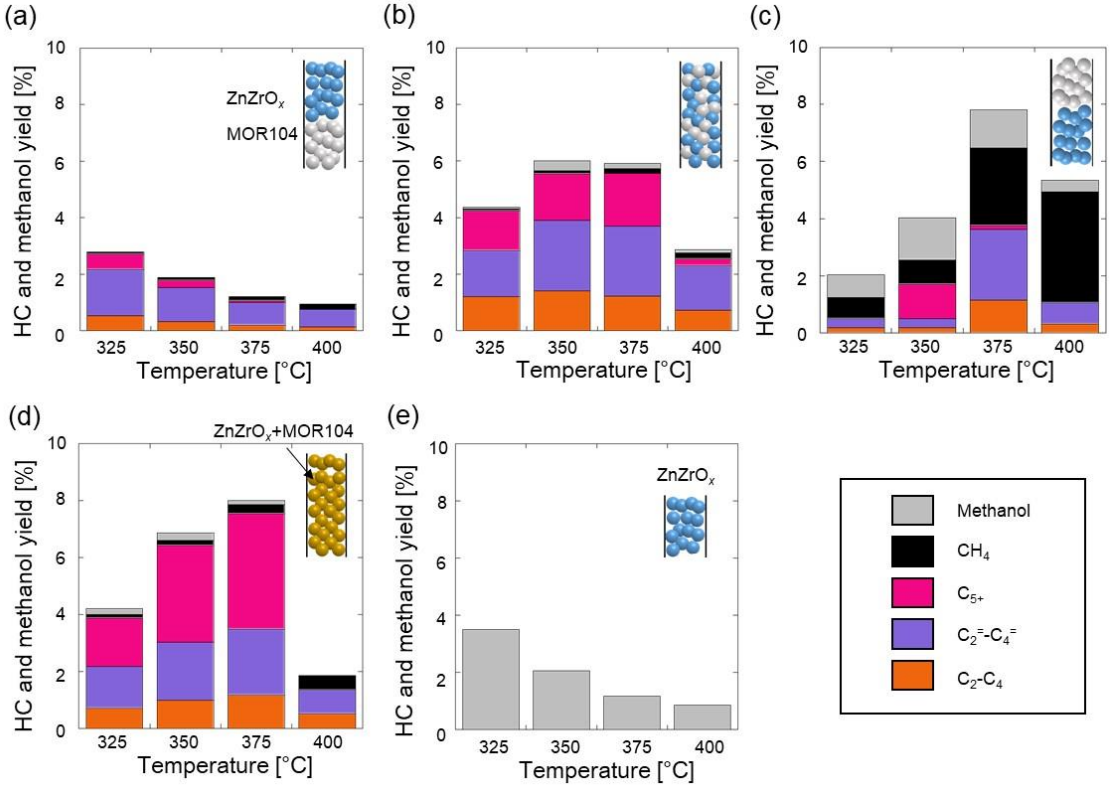


Figure 2 Yields of hydrocarbons and methanol over (a-d) $ZnZrO_x$-MOR104 bifunctional catalysts and (e) a $ZnZrO_x$ catalyst at 1.0 MPa.

4. Conclusion

The present study examined a bifunctional catalyst that facilitates the production of hydrocarbons through CO_2 hydrogenation in a single-step process. Specifically, we investigated the optimal mixing method of two catalysts, namely $ZnZrO_x$ (a methanol synthesis catalyst) and MOR104 (solid acid catalyst, MOR-type zeolite with a Si/Al ratio = 104). Physically combining the two catalysts into grains resulted in the highest hydrocarbon yields. This finding suggests that the proximity of $ZnZrO_x$ and MOR104 is a critical factor in achieving maximum efficiency. Additionally, the developed catalyst exhibited stable performance for a period of 6 hours at a temperature of 350 °C.

Acknowledgements

This work was financially supported by the Uncharted Territory Challenge 2050 (No. 19101608-0), and Feasibility Study Program on Energy and New Environmental Technology (No. 22100386-0), New Energy and Industrial Technology Development Organization, Japan. We thank the Advanced Characterization Nanotechnology Platform, Nanotechnology Platform Program (Grant no.

JPMXP09A21OS0012) and Advanced Research Infrastructure for Materials and Nanotechnology in Japan (ARIM) program (Grant no. JPMXP1223OS0019) of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan, at the Research Center for Ultra High Voltage Electron Microscopy (Nanotechnology Open Facilities), Osaka University. In addition, a part of this work was conducted at Laboratory of XPS analysis, Joint-use facilities, Hokkaido university, supported by ARIM of MEXT (Grant No. JPMXP1223HK0103).

References

[1] A. Alvarez, A. Bansode, A. Urakawa, A.V. Bavykina, T.A. Wezendonk, M. Makkee, J. Gascon, F. Kapteijn, Challenges in the Greener Production of Formates/Formic Acid, Methanol, and DME by Heterogeneously Catalyzed CO_2 Hydrogenation Processes, Chemical Reviews, 117 (2017) 9804-9838.

[2] M. Stöcker, Methanol-to-hydrocarbons: catalytic materials and their behavior, Microporous and Mesoporous Materials, 29 (1999) 3-48.

[3] T.T.N. Hoang, Y.S. Lin, T.N.H. Le, T.K. Le, T.K.X. Huynh, D.H. Tsai, Cu-ZnO@Al_2O_3 hybrid nanoparticle with enhanced activity for catalytic CO_2 conversion to methanol, Advanced Powder Technology, 32 (2021) 1785-1792.

[4] J. Wang, G. Li, Z. Li, C. Tang, Z. Feng, H. An, H. Liu, T. Liu, C. Li, A highly selective and stable ZnO-ZrO_2 solid solution catalyst for CO_2 hydrogenation to methanol, Science Advances, 3 (2017) e1701290.

[5] C. Temvuttirojn, Y. Poo-arporn, N. Chanlek, C.K. Cheng, C.C. Chong, J. Limtrakul, T. Witoon, Role of Calcination Temperatures of ZrO_2 Support on Methanol Synthesis from CO_2 Hydrogenation at High Reaction Temperatures over ZnO_x/ZrO_2 Catalysts, Industrial & Engineering Chemistry Research, 59 (2020) 5525-5535.

[6] S. Tada, N. Ochiai, H. Kinoshita, M. Yoshida, N. Shimada, T. Joutsuka, M. Nishijima, T. Honma, N. Yamauchi, Y. Kobayashi, K. Iyoki, Active Sites on $Zn_XZr_{1-X}O_{2-X}$ Solid Solution Catalysts for CO_2-to-Methanol Hydrogenation, ACS Catalysis, 12 (2022) 7748-7759.

[7] O. Martin, A.J. Martin, C. Mondelli, S. Mitchell, T.F. Segawa, R. Hauert, C. Drouilly, D. Curulla-Ferre, J. Perez-Ramirez, Indium Oxide as a Superior Catalyst for Methanol Synthesis by CO_2 Hydrogenation, Angewandte Chemie International Edition, 55 (2016) 6261-6265.

[8] W.H. Feng, M.M. Yu, L.J. Wang, Y.T. Mia, M. Shakouri, J. Ran, Y. Hu, Z. Li, R. Huang, Y.L. Lu, D. Gao, J.F. Wu, Insights into Bimetallic Oxide Synergy during Carbon Dioxide Hydrogenation to Methanol and Dimethyl Ether over $GaZrO_x$ Oxide Catalysts, Acs Catalysis, 11 (2021) 4704-4711.

[9] J.J. Wang, C.Z. Tang, G.N. Li, Z. Han, Z.L. Li, H. Liu, F. Cheng, C. Li, High-Performance M_aZrO_x (M_a = Cd, Ga) Solid-Solution Catalysts for CO_2 Hydrogenation to Methanol, ACS Catalysis, 9 (2019) 10253-10259.

[10] L. Zhang, W. Gao, F. Wang, C. Wang, J. Liang, X. Guo, Y. He, G. Yang, N. Tsubaki, Highly selective synthesis of light aromatics from CO_2 by chromium-doped ZrO_2 aerogels in tandem with HZSM-5@SiO_2

catalyst, Applied Catalysis B: Environmental, 328 (2023) 122535.
[11] Z. Li, J. Wang, Y. Qu, H. Liu, C. Tang, S. Miao, Z. Feng, H. An, C. Li, Highly Selective Conversion of Carbon Dioxide to Lower Olefins, ACS Catalysis, 7 (2017) 8544-8548.
[12] A. Ramirez, A.D. Chowdhury, M. Caglayan, A. Rodriguez-Gomez, N. Wehbe, E. Abou-Hamad, L. Gevers, S. Ould-Chikh, J. Gascon, Coated sulfated zirconia/SAPO-34 for the direct conversion of CO_2 to light olefins, Catalysis Science & Technology, 10 (2020) 1507-1517.
[13] Y. Wang, G. Wang, L.I. van der Wal, K. Cheng, Q. Zhang, K.P. de Jong, Y. Wang, Visualizing Element MigrationoverBifunctional Metal-Zeolite Catalysts and its Impact on Catalysis, Angewandte Chemie-International Edition, 60 (2021) 17735-17743.
[14] Z. Li, Y. Qu, J. Wang, H. Liu, M. Li, S. Miao, C. Li, Highly Selective Conversion of Carbon Dioxide to Aromatics over Tandem Catalysts, Joule, 3 (2019) 570-583.
[15] R.P. Ye, J. Ding, W. Gong, M.D. Argyle, Q. Zhong, Y. Wang, C.K. Russell, Z. Xu, A.G. Russell, Q. Li, M. Fan, Y.G. Yao, CO_2 hydrogenation to high-value products via heterogeneous catalysis, Nature Communications, 10 (2019) 5698.
[16] F. Zhang, K. Chen, Q. Jiang, S. He, Q. Chen, Z. Liu, J. Kang, Q. Zhang, Y. Wang, Selective Transformation of Methanol to Ethanol in the Presence of Syngas over Composite Catalysts, ACS Catalysis, 12 (2022) 8451-8461.
[17] A. Bhan, A.D. Allian, G.J. Sunley, D.J. Law, E. Iglesia, Specificity of Sites within Eight-Membered Ring Zeolite Channels for Carbonylation of Methyls to Acetyls, Journal of the American Chemical Society, 129 (2007) 4919-4924.
[18] S. Tada, H. Kinoshita, N. Ochiai, A. Chokkalingam, P. Hu, N. Yamauchi, Y. Kobayashi, K. Iyoki, Search for solid acid catalysts aiming at the development of bifunctional tandem catalysts for the one-pass synthesis of lower olefins via CO_2 hydrogenation, International Journal of Hydrogen Energy, 46 (2021) 36721-36730.
[19] S. Tada, D. Li, M. Okazaki, H. Kinoshita, M. Nishijima, N. Yamauchi, Y. Kobayashi, K. Iyoki, Influence of Si/Al ratio of MOR type zeolites for bifunctional catalysts specific to the one-pass synthesis of lower olefins via CO_2 hydrogenation, Catalysis Today, 411 (2023) 113828.
[20] N. Katada, H. Igi, J.-H. Kim, M. Niwa, Determination of the Acidic Properties of Zeolite by Theoretical Analysis of Temperature-Programmed Desorption of Ammonia Based on Adsorption Equilibrium, Journal of Physical Chemistry B, 101 (1997) 5969-5977.
[21] M. Niwa, N. Katada, New Method for the Temperature-Programmed Desorption (TPD) of Ammonia Experiment for Characterization of Zeolite Acidity: A Review, Chemical Record, 13 (2013) 432-455.