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Optimal mixing method of ZnZrO_x and MOR-type zeolite to prepare a bifunctional catalyst for CO₂ hydrogenation to lower olefins

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Carbon dioxide hydrogenation, Mordenite, Bifunctional catalyst, Physical mixing

Abstract

In recent years, the issue of global warming caused by CO₂ emissions has become a critical problem and poses a worldwide challenge. To address this issue, we have developed a bifunctional catalyst that can convert CO₂ to lower olefins in a single stage. Our bifunctional catalysts are a combination of two catalysts, a CO₂-to-methanol hydrogenation catalyst (Zn-doped ZrO₂, 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 ($\text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$), 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 $\text{Cu/ZnO/Al}_2\text{O}_3$ and Cu/ZnO/ZrO_2 , operate at around 250 °C. [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 ZrO₂ [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 ZrO₂, for example, H₂ and CO₂ are activated on Zn²⁺ and Zr⁴⁺ sites, respectively. [6] At the interfacial sites, Zn²⁺-O-Zr⁴⁺, CO₂ 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 ZrO₂ and HZSM-5. [10] Li et al. developed bifunctional catalysts with ZnO-ZrO₂ 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 Cr₂O₃/HZSM-5 and ZrO₂/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 ZrO₂ and HZSM-5 were investigated by Li et al. to determine how they affect product distribution in the CO₂ hydrogenation reaction. [14] Their results show that when both catalysts were thoroughly mixed, aromatic hydrocarbons were selectively synthesized, while C₅+ 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 CO₂ 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 $t\text{-ZrO}_2$ and a weak peak attributed to ZnO. According to our previous research [6], Zn species can be wholly incorporated into the $t\text{-ZrO}_2$ 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 $t\text{-ZrO}_2$ 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 microscopy 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 ZnZrO_x particles in the STEM image of $\text{ZnZrO}_x + \text{MOR104}$.

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 $42 \text{ m}^2 \text{ g}^{-1}$, which was lower than the specific surface areas of MOR104 ($603 \text{ m}^2 \text{ g}^{-1}$), as shown in **Table S1**. The isotherm of MOR104 was classified as type I, indicating the presence of micropores ($< 2 \text{ nm}$). 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 $270 \text{ m}^2 \text{ g}^{-1}$. Remarkably, this estimated value closely approximates the actual measured value of $280 \text{ m}^2 \text{ g}^{-1}$ (**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 $^\circ\text{C}$) and the other on the high-temperature side (350-550 $^\circ\text{C}$). 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 $^\circ\text{C}$, which means that MOR104 possessed a small number of strong acid sites. [21]

The oxidation states of Zn species in ZnZrO_x and $\text{ZnZrO}_x + \text{MOR104}$ 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.

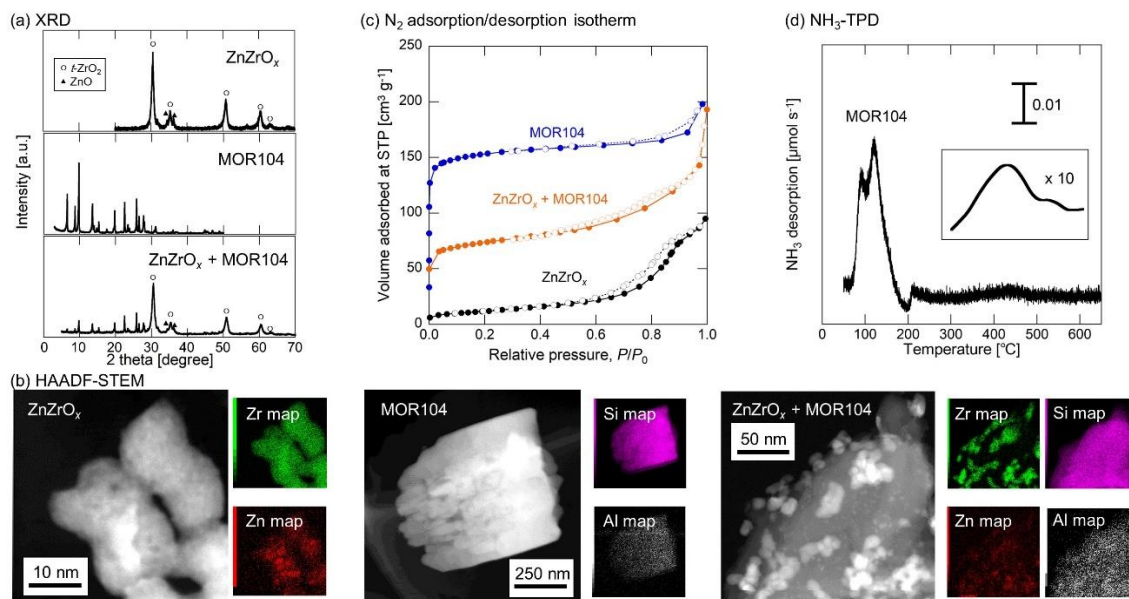


Figure 1 (a) XRD patterns of ZnZrO_x , MOR104, and $\text{ZnZrO}_x + \text{MOR104}$, (b) STEM image of ZnZrO_x , MOR104, and $\text{ZnZrO}_x + \text{MOR104}$ with elemental mapping, (c) N_2 adsorption/desorption isotherms of ZnZrO_x , MOR104, and $\text{ZnZrO}_x + \text{MOR104}$ at -196°C, and (d) NH_3 -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 olefins (C₂=-C₄=) 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 C₂-C₄ hydrocarbons was low, with methanol and CH₄ being the main products. Conditions such as (c) were expected to produce mainly the products produced by ZnZrO_x because MOR104 is inactive in CO₂ hydrogenation. Although the yields of C₅₊ and C₂=-C₄= 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 C₂=-C₄= 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 CO₂ in a one-pass process significantly increases CO₂ 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 CO₂ 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 CO₂-to-methanol hydrogenation.

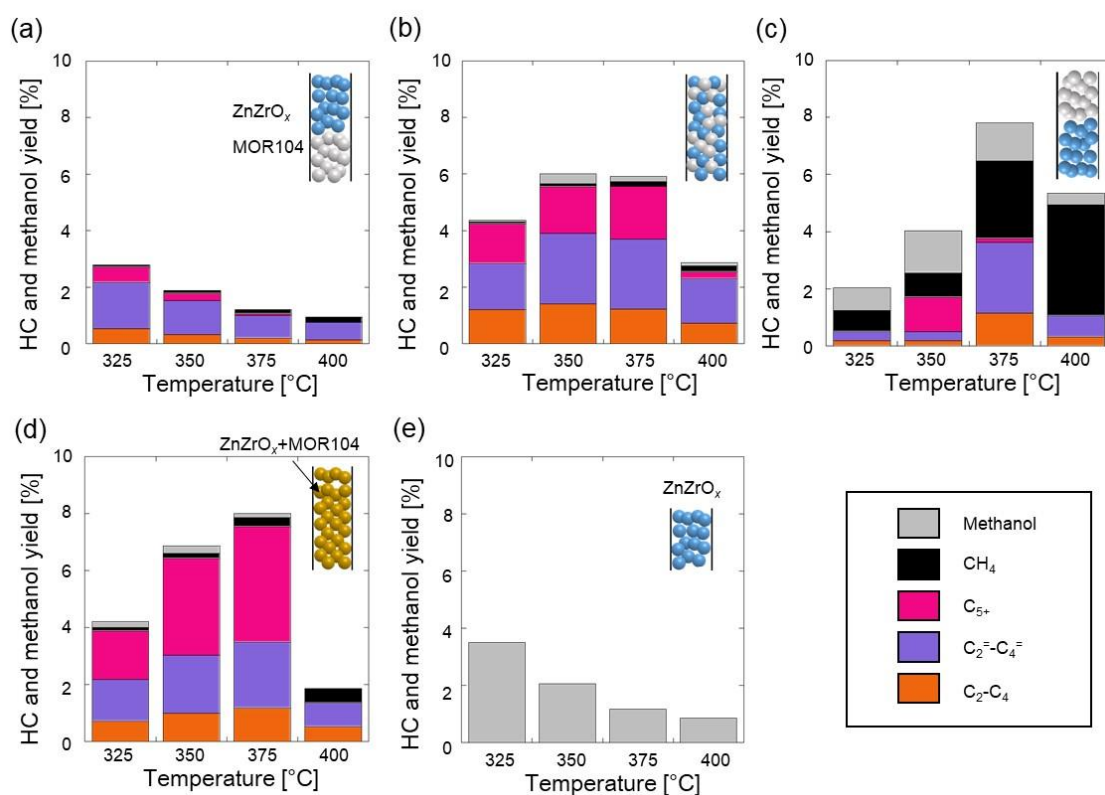


Figure 2 Yields of hydrocarbons and methanol over (a-d) ZnZrO_x-MOR104 bifunctional catalysts and (e) a ZnZrO_x catalyst at 1.0 MPa.

4. Conclusion

The present study examined a bifunctional catalyst that facilitates the production of hydrocarbons through CO₂ 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.

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