Design of bifunctional catalysts for the direct conversion of carbon dioxide into lower olefins and aromatics

Kang Cheng, **Xiaoliang Liu, Cheng Zhou, Qinghong Zhang, Jincan Kang and Ye Wang***
State Key Laboratory of Physical Chemistry of Solid Surfaces, Collaborative Innovation Center of Chemistry for Energy Materials, National Engineering Laboratory for Green Chemical Productions of Alcohols, Ethers and Esters, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, 361005, China
** Fax: (+86) 592-2183047, E-mail address: kangcheng@xmu.edu.cn; wangye@xmu.edu.cn*

Abstract: The direct conversion of CO_2 into lower (C_2-C_4) olefins and aromatics, which are key building-block chemicals, is highly attractive for the efficient utilization of CO_2. The current hydrogenation of CO_2 to hydrocarbons employs the modified Fischer-Tropsch (FT) catalysts, which show limited selectivity of lower olefins and almost no aromatics. Here, we report our development of new bifunctional catalysts for the direct transformations of CO_2 into lower olefins and aromatics with selectivities exceeding 80% at considerable CO_2 conversions. The bifunctional catalysts are composed of metal oxides with solid solution or spinel-compound structure and molecular sieves with a selected topology. We demonstrate that methanol/dimethyl dither (DME) are key reaction intermediates. We found that the reaction coupling can drive the CO_2 conversion and suppresses the formation of CO.

Keywords: CO_2 utilization, Bifunctional catalysis, Lower olefins, Aromatics.

1. Introduction

The transformation of CO_2 into hydrocarbon fuels or chemicals via hydrogenation is a promising route for CO_2 utilization using H_2 produced using renewable energy. Traditionally, the hydrogenation of CO_2 relies on the rich chemistry of syngas (H_2/CO) conversions. Modified FT-synthesis catalysts, which mainly produce linear hydrocarbons, have mainly been applied to the hydrogenation of CO_2 into hydrocarbons. However, the product distribution over modified FT-synthesis catalysts is broad due to the uncontrollable polymerization mechanism.[1]

We expect that the rational design of bifunctional catalysts, which can integrate the conversion of CO_2 to methanol and that of methanol to olefins and aromatics, may enable the high selective formation of lower olefins and aromatics. Actually, significant breakthroughs have been achieved in the direct conversion of syngas into C_2–C_4 olefins and aromatics with ultrahigh selectivity using the strategy of reaction coupling.[2-4] This strategy has so been used for the direct conversion of CO_2 to lower olefins in a few recent studies.[5-7] However, CO, a product from the reverse water-gas-shift (RWGS) reaction ($CO_2 + H_2 \rightarrow CO + H_2O$) dominates the product. The insights into the reaction intermediate and the reaction mechanism are not very clear. Moreover, no study on the formation of aromatics from CO_2 has been reported.

Here, we present our recent work on the design of bifunctional catalysts composed of metal oxides and molecular sieves for the direct conversions of CO_2 into lower olefins and aromatics. We will demonstrate the importance of oxygen vacancies on metal oxide surfaces for CO_2 activation and the Brønsted acid sites in molecular sieves for C-C coupling. The proximity between the two functional components will also be discussed. The surface species and reaction intermediates will also be characterized to provide insights into the reaction mechanism.

2. Experimental

The mixed oxides (in particular $ZnGa_2O_4$ with spinel structure and Zn-ZrO_2 solid solution) were prepared by either a co-precipitation or a sol-gel method. The molecular sieves including SAPO-34, SSZ-13 and ZSM-5 were synthesized by a hydrothermal method. The bifunctional catalysts were prepared by dispersion of metal oxide nanoparticles onto molecular sieves.

3. Results and discussion

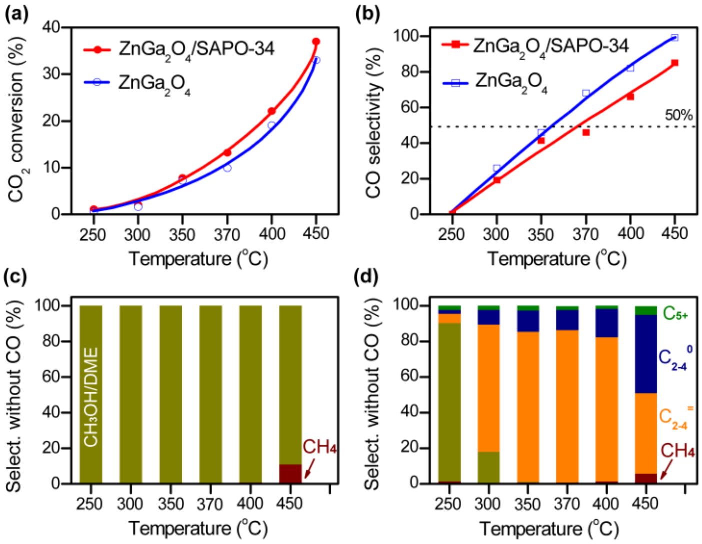

Figure 1. Effect of reaction temperature on hydrogenation of CO_2 over $ZnGa_2O_4$ and $ZnGa_2O_4$/SAPO-34 catalysts. (a) CO_2 conversion. (b) CO selectivity by the RWGS reaction. (c) Selectivity without CO over $ZnGa_2O_4$. (d) Selectivity without CO over $ZnGa_2O_4$/SAPO-34.

We discovered that the combination of $ZnGa_2O_4$ with a spinel structure and SAPO-34 catalyzed the direct conversion of CO_2 into C_2–C_4 olefins. At 370 ℃, the conversion of CO_2 was 13% and the selectivity of C_2–C_4 olefins reached 86% with only 1% CH_4 in hydrocarbons (Figure 1), breaking the limitation observed for the modified FT catalysts. The bifunctional catalyst was stable during a 100 h reaction. CH_3OH and DME were the major products on $ZnGa_2O_4$ under the same reaction conditions. As compared to $ZnGa_2O_4$, CO_2 conversion became higher over the bifunctional catalyst possibly owing to the thermodynamic driving force. Moreover, the selectivity of CO, which is formed by the RWGS reaction, decreased from 68% to 46% at 370 ℃ by using the bifunctional catalyst instead of $ZnGa_2O_4$. Thus, the push of CH_3OH into C_2–C_4 olefins also suppressed the formation of CO.

The bifunctional catalyst composed of Zn−ZrO_2 solid solution nanoparticles and H-ZSM-5 was found to catalyze the direct conversion of CO_2 into aromatics. The selectivity of aromatics reached ~80% at a CO_2 conversion of 15%. There exist optimum Zn/Zr ratio and density of Brønsted acid sites for selective formation of aromatics. The closer proximity between the two components favors the aromatic formation.

Our characterizations using EPR and FT-IR reveal that the oxygen vacancy on $ZnGa_2O_4$ and Zn−ZrO_2 surfaces works for the activation of CO_2 to methanol via formate and methoxide species. The correlation of the rates of CH_3OH/DME and CO formations with the density of oxygen vacancies suggests that the CO_2-to-methanol and RWGS reactions occur on different sites and are competitive on $ZnGa_2O_4$ and Zn−ZrO_2 catalysts.

4. Conclusions

We have succeeded in synthesizing lower olefins and aromatics directly from CO_2 with selectivity of >80% by designing bifunctional catalysts composed of metal oxides and molecular sieves such as SAPO-34 or H-ZSM-5. The metal oxides with oxygen vacancies are responsible for the hydrogenation of CO_2 to methanol, while molecular sieves account for the subsequent C-C coupling. Compared with conventional modified FT catalysts, on which CO_2 activation and C-C chain growth occur on the same metal surface, our bifunctional catalyst separates these two processes using different active sites, and thus can achieve precise control over C-C coupling. This work demonstrates that the reaction coupling is a promising strategy not only in syngas chemistry but also in the transformation of CO_2 into high value-added chemicals.

References

1. K. Cheng, J. Kang, D. L. King, V. Subramanian, C. Zhou, Q. Zhang, Y. Wang, Adv. Catal. 60 (2017) 125.
2. F. Jiao, J. Li, X. Pan, J. Xiao, H. Li, H. Ma, M. Wei, Y. Pan, Z. Zhou, Q. Fu, X. Bao, et al., Science 351 (2016) 1065.
3. K. Cheng, B. Gu, X. Liu, J. Kang, Q. Zhang, Y. Wang, Angew. Chem. Int. Ed. 55 (2016) 4725.
4. K. Cheng, W. Zhou, J. Kang, S. He, S. Shi, Q. Zhang, Y. Pan, W. Wen, Y. Wang, Chem 3 (2017) 334.
5. Z. Li, J. Wang, Y. Qu, H. Liu, C. Tang, S. Miao, Z. Feng, H. An, C. Li, ACS Catal. 7 (2017) 8544.
6. X. Liu, M. Wang, C. Zhou, W. Zhou, K. Cheng, J. Kang, Q. Zhang, W. Deng, Y. Wang, Chem. Commun. 54 (2018) 140.
7. P. Gao, S. Dang, S. Li, X. Bu, Z. Liu, M. Qiu, C. Yang, H. Wang, L. Zhong, Y. Sun, et al., ACS Catal. 8 (2018) 571.