Highly Selective Conversion of Carbon Dioxide to Lower Olefins

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Abstract: Conversion of CO_2 to value-added chemicals has been a long-standing objective, direct hydrogenation of CO_2 to lower olefins is highly desirable, but still challenging. Herein, we report a selective conversion of CO_2 to lower olefins through CO_2 hydrogenation over a ZnZrO/SAPO tandem catalyst fabricated with a ZnO-ZrO_2 solid solution and a Zn-modified SAPO-34 zeolite, which can achieve the lower olefins selectivity as high as 80-90% among hydrocarbon products. This is realized based on the dual functions of the tandem catalyst: hydrogenation of CO_2 on the ZnO-ZrO_2 solid solution and lower olefins production on the SAPO zeolite. The thermodynamic and kinetic coupling between the tandem reactions enable the highly efficient conversion of CO_2 to lower olefins. Furthermore, this catalyst is stable toward the thermal and sulfur treatments, showing the potential industrial application.

Keywords: tandem catalysis • CO_2 hydrogenation •C-C coupling • thermodynamic coupling • solid solution oxide.

1. Introduction

Global climate change and ocean acidification caused by continuing to rise of CO_2 concentrations in atmospheric have become a worldwide problem[1-2]. From a new point of view, CO_2 can be as an abundant and sustainable carbon source, hydrogenation of CO_2 to valuable chemicals and hydrocarbon fuels based on catalysis can be promising technologies by using the CO_2-free hydrogen. Now, converting of CO_2 to methanol[3-4], hydrocarbons[5-6] and fine chemicals[7] has been paid more attention. Olefins are produced on the order of 200 Mt per year and result in 1.2-1.8 tons of CO_2 emitted per ton of olefin produced[8]. Therefore, by manufacturing these high-valued products with a CO_2 feedstock is a promising route to effectively use this C1 resource and substantially decrease the net CO_2 emissions of the process.

2. Experimental (or Theoretical)

The co-precipitation method was used to prepare the ZnO-ZrO_2 binary oxides. The tandem catalysts were prepared through physical mixing the metal oxide solid solution and SAPO-34 zeolite. The mass ratio of these two components was 1:1, unless otherwise indicated.

3. Results and discussion

In this work, we developed a ZnO-ZrO_2 mixed metal oxide catalyst which shows considerable methanol selectivity at wide temperatures, and a Zn-modified SAPO which can initiate the methanol to olefins reaction. Our proposal is to synthesize the lower olefins by taking the advantages of these two types of catalysis: CO_2 hydrogenation to methanol and selective conversion of methanol to lower olefins. Therefore, by considering these dual functional catalysis and chemical engineering factors, we fabricated a tandem catalyst by dispersing the ZnO-ZrO_2 nanoparticles on the SAPO micro-meter crystals for the CO_2 hydrogenation.

The ZnZrO/SAPO tandem catalysts can achieve the CO_2 conversion of 12.6% and the $C_2^{=}$-$C_4^{=}$ selectivity as high as 80% but the methane selectivity of only 3%. Experimental results indicate not only the synergetic activation both of H_2 and CO_2 over metal oxide but also the synergetic effect between metal oxide and zeolite for the C-C coupling over metal oxide/zeolite composite catalyst. This catalyst shows good stability and without observing obviously deactivation at least for 240 h on stream.

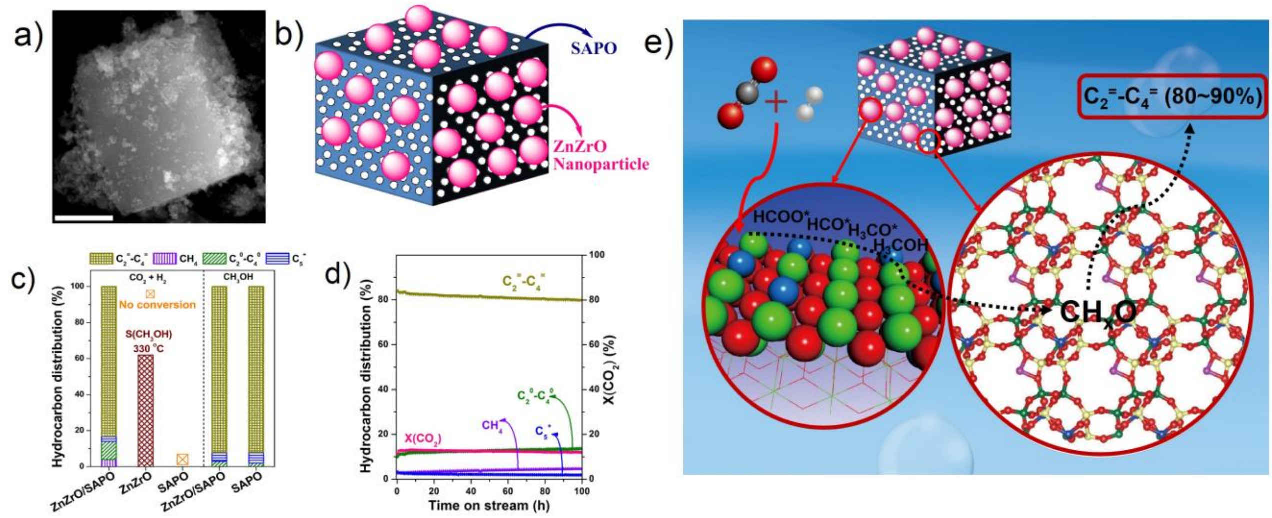

Figure 1. a) SEM image of ZnZrO/SAPO; b) Schematic description of ZnZrO/SAPO; c) CO_2 hydrogenation on ZnZrO/SAPO, ZnZrO and SAPO and methanol conversion on ZnZrO/SAPO and SAPO; d) Stability test for ZnZrO/SAPO. Reaction condition for ZnZrO/SAPO: 380 °C, 2 MPa, 3600 mL/g_{cat}/h; ZnZrO: 330 °C, 2 MPa, 3600 mL/g_{cat}/h (different from 380 °C, the reaction temperature for lower olefins production, where the methanol selectivity is about 2%); SAPO: 380 °C, 3mL/g_{cat}/h, all catalysts were tested in a tubular fixed bed reactor, with catalyst 0.2 g; e) Schematic for the proposed reaction mechanism of CO_2 hydrogenation on the tandem catalyst, ZnZrO/SAPO.

4. Conclusions

In summary, the direct hydrogenation of CO_2 to lower olefins with outstanding selectivity was realized by constructed tandem catalyst, ZnZrO/SAPO, which CO_2 and H_2 were activated on ZnZrO and the C-C bond formation was performed on SAPO. The selectivity of lower olefins can reach to 80% while only 3% methane among hydrocarbon products at a CO_2 of 12.6%. Tandem catalysis facilitates the thermodynamics and kinetics coupling through the transferring and migrating of CHxO intermediate species that not only included methanol, which enable the high efficient conversion of CO_2 to lower olefins. Tandem catalyst showed the resistance to thermal and sulfur treatments (H_2S and SO_2), suggesting the promising potential application in industry.

References

1. Xie, S.; Zhang, Q.; Liu, G.; Wang, Y., *Chem. Commun.* **2016,** *52* (1), 35-59.
2. Wang, W.; Wang, S.; Ma, X.; Gong, J., . *Chem. Soc. Rev.* **2011,** *40* (7), 3703-3727.
3. Martin, O.; Martín, A. J.; Mondelli, C.; Mitchell, S.; Segawa, T. F.; Hauert, R.; Drouilly, C.; Curulla-Ferré, D.; Pérez-Ramírez, J., *Angew. Chem. Int. Ed.* **2016**, *55*, 6261-6265.
4. Kattel, S.; Ramírez, P. J.; Chen, J. G.; Rodriguez, J. A.; Liu, P., . *Science* **2017,** *355* (6331), 1296-1299.
5. Wang, J.; You, Z.; Zhang, Q.; Deng, W.; Wang, Y., . *Catal. Today* **2013,** *215*, 186-193.
6. Zhang, J.; Lu, S.; Su, X.; Fan, S.; Ma, Q.; Zhao, T., . *Journal of CO_2 Utilization* **2015,** *12*, 95-100.
7. Ren, X.; Zheng, Z.; Zhang, L.; Wang, Z.; Xia, C.; Ding, K., *Angew. Chem. Int. Ed.* **2016**, 56, 310-313.
8. Porosoff, M. D.; Yan, B.; Chen, J. G., *Energ. Environ. Sci.* **2016,** *9* (1), 62-73.