

Selective Conversion of CO₂ into *para*-Xylene over a ZnCr₂O₄-ZSM-5 Catalyst

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1. Introduction

Direct conversion of CO₂ to high value-added chemicals, particularly aromatics, has attracted wide attention in the field of CO₂ chemistry.¹⁾ It not only relieves, at least partially, the emission of CO₂ by the combustion of fossil fuels but also offers a chemical route to utilize carbon resources. Among all kinds of aromatic hydrocarbons, *para*-xylene (PX) is a significant value-added chemical, since it has an important use in producing terephthalic acid (TPA) and other chemicals.²⁾ Generally, PX is produced by the catalytic reforming of petroleum naphtha. However, the production of PX from the decreasing petroleum resources cannot meet the growing demand annually in the world. Direct and oriented catalytic conversion of CO₂ to PX, as a non-petroleum route, is still a challenge.

In this work, we presented an Oxide-Zeolite catalyst for CO₂ hydrogenation to PX, which composed of ZnCr₂O₄ and tailor-made ZSM-5 zeolite. It showed significantly high PX selectivity in total hydrocarbons to 28.6%, which is higher than those over reported Oxide-Zeolite catalysts under the same reaction conditions.

2. Experimental

ZnCr₂O₄ with a spinel structure was prepared by a precipitation method. 8.92 g Zn(NO₃)₂·6H₂O and 24.0 g Cr(NO₃)₃·9H₂O were dissolved in 90 mL deionized water, 19.2 g (NH₄)₂CO₃ was dissolved in 200 mL deionized water. These aqueous solutions were dropwise added into one beaker simultaneously, precipitated at 70 °C and pH was controlled at 7.0-8.0 under stirring. After 3 h static aging at the same temperature, the precipitate was washed by distilled water for three times and collected by filtration. The product was dried overnight at 120 °C and calcined at 500 °C for 3 h.

HZSM-5 zeolite sample was prepared by a hydrothermal method. In brief, Tetraethoxysilane (TEOS), NaAlO₂, Tetrapropylammonium Bromide (TPABr) and Butylamine were dissolved in distilled water with a molar ratio of 300 SiO₂: 1 Al₂O₃: 1 Na₂O: 13.5 TPABr: 106 Butylamine: 10160 H₂O. After magnetic stirring for 4 h, the clear solution was transferred into a Teflon-sealed autoclave and maintained at 180 °C for 48 h. After cooling down to room temperature, the resultant solid product was washed with distilled water, dried at 100 °C overnight, and calcined at

550 °C in air for 5 h to remove the organic template stored in the zeolite pores.

3. Results and discussion

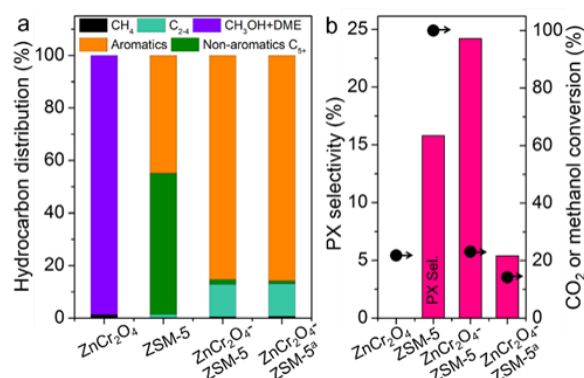


Fig. 1 (a) Catalytic performance for CO₂ to methanol, methanol to aromatics, and CO₂ to aromatics. (b) PX selectivity, CO₂ and methanol conversion. ZSM-5^a sample (SiO₂/Al₂O₃ = 300) was commercial zeolite.

As shown in Figure 1a and 1b, the ZnCr₂O₄ presented high methanol/DME selectivity of 98.6% with only 1.4% CH₄ selectivity by 21.8% CO₂ conversion at 350 °C and 4.0 MPa. No PX and other aromatics were formed over the single ZnCr₂O₄ (Figure 1b). In comparison, the tailor-made ZSM-5 zeolite was investigated in MTA under the same reaction conditions with 44.9% aromatics selectivity, including 15.8% PX in all hydrocarbons (Figure 1a and 1b). Accordingly, the ZnCr₂O₄-ZSM-5 catalyst (physical mixing, ZnCr₂O₄/ZSM-5 mass ratio as 2:1) exhibited high PX selectivity of 24.2%, with CO₂ conversion and aromatics C-mol selectivity as 23.1% and 85.3%, respectively, and the undesirable CH₄ selectivity was controlled within 1% (Figure 1a and 1b). PX selectivity is significantly higher than that of one containing commercial ZSM-5 zeolite, where PX selectivity was only 5.4%, as shown in Figure 1b. Furthermore, to the best of our knowledge, the PX selectivity was higher than those of other reported Oxide-Zeolite catalysts.

- 1) Wang, Y., Tan, L., Tan, M., Zhang, P., Fang, Y., Yoneyama, Y., Yang, G., Tsubaki, N., *ACS Catal.*, 9, 805-901 (2019).
- 2) Zhang, P., Tan, L., Yang, G., Tsubaki, N., *Chem. Sci.*, 8, 7941-7946 (2017).