One-pass Selective Conversion of Syngas to para-Xylene

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Abstract: Syngas ($CO+H_2$) is a crucial junction point bridging non-petroleum carbon resources and other basic chemicals. However, the one-pass conversion of syngas to value-added aromatics, especially para-xylene, is still in a big challenge. Here, we presented a promising hybrid catalyst Cr/Zn-Zn/Z5@S1 to effectively realize one-pass conversion of syngas to para-xylene. This hybrid catalyst exhibited enhanced activity on syngas conversion (CO conversion of 55.0%) and considerable para-xylene selectivity (27.6%). The concerted combination of two components in hybrid catalyst can effectively depress the formation of unwanted by-products and facilitate the oriented synthesis of para-xylene from syngas with unprecedented efficiency at the same time.

Keywords: Syngas, Hybrid catalyst, Zeolite, Aromatics, para-Xylene

1. Introduction

Syngas, a mixture gas of CO and H_2, can be produced from non-petroleum sources, including natural gas, coal and biomass, *etc*. To date, one-pass selective conversion of syngas into the target products, like dimethyl ether, isoparaffins/olefins and aromatics has made noticeable progress [1,2], although the catalyst activity and CO_2 formation are still in a challenge. Aromatic hydrocarbons, generally being produced through the petroleum industry, are one of the most important basic chemicals [3]. The production of aromatic hydrocarbon from syngas is a crucial alternative process [3]. Among all kinds of aromatic hydrocarbons, *para*-xylene (PX) is a significant value-added chemical. PX is produced by the catalytic reforming of petroleum naphtha as part of the BTX aromatics. And the separation of PX from aromatics mixture is a high energy-consuming process. Alternative technology for the one-pass synthesis of PX based on a non-petroleum route is required due to the growing demand for PX annually and decreasing reserves of petroleum.

In this report, we will present a hybrid catalyst. Typically, this hybrid catalyst, named Cr/Zn-Zn/Z5@S1, is composed of two components: one is Cr/Zn and the other one is core-shell-structured zeolite Zn/Z5@S1 (zinc doped H-ZSM-5 single crystal zeolite encapsulated with one Silicalite-1 zeolite shell). With this novel hybrid catalyst, we can facilely realize the one-pass selective conversion of syngas to PX with higher activity, stability and selectivity [4].

2. Experimental

2.1 Cr/Zn-Zn/Z5@S1 hybrid catalyst preparation

The Cr/Zn component was prepared through a typical co-precipitation method. The core-shell-structured Zn/Z5@S1 component with a non-acidic silicalite-1 shell is synthesized through hydrothermal synthesis. Firstly, H-ZSM-5 (Z5) zeolite was synthesized, and then the obtained Z5 (Si/Al=46) sample was modified by Zn through ion-exchange method. The epitaxial crystal growth of Zn/Z5 was performed through hydrothermal synthesis in the mother liquid used for silicalite-1 zeolite growth. Finally, the hybrid catalyst Cr/Zn-Zn/Z5@S1 was prepared by physically mixing the two components of Cr/Zn and Zn/Z5@S1 zeolite, followed by grinding and granulating into the required size in the range of 0.85-1.70 mm.

2.2 Catalytic performance evaluation

The catalyst performance evaluation of catalysts for PX direct synthesis from syngas was carried out in a fixed-bed steel reactor with internal diameter of 6 mm. All of catalysts were first reduced in the reactor for 10 h at 673 K with pure H_2. After cooling down to the room temperature, syngas with H_2/CO molar ratio of 2 was introduced into the reactor. Then, the reaction was conducted under the required conditions as follows: $H_2/CO=2$, 673 K, 5 MPa, and $W_{catalysts}/F_{syngas}= 20.7\ g\cdot h\cdot mol^{-1}$.

3. Results and discussion

The selectivity of xylene and PX over the hybrid catalysts is compared in Figure 1a. Both of the highest selectivities on xylene (35.7%) and PX (27.6%) were successfully realized on the Cr/Zn-Zn/Z5@S1 hybrid catalyst. The formation of meta-xylene has been completely supressed, and the major by-product in xylene isomers is only ortho-xylene. As indicated by the TEM image in Figure 1b, the Cr/Zn-Zn/Z5@S1 hybrid catalyst is composed of a Cr/Zn component and a core-shell-structured Zn/Z5@S1 zeolite component. In the reaction (as illustrated by Figure 1c), syngas is first converted into methanol on the Cr/Zn component, and then the formed methanol in situ undergoes a series of reaction steps like dehydration, C-C bonds coupling, etc., to generate PX over the core-shell-structured Zn/Z5@S1 zeolite component. The two components in this Cr/Zn-Zn/Z5@S1 hybrid catalyst contact tightly, cooperate concertedly and promote mutually. The highest PX selectivity among the products obtained by the Cr/Zn-Zn/Z5@S1 hybrid catalyst should be attributed to its zeolite component of Zn/Z5@S1 with a special core-shell structure. The ion-exchange of Z5 zeolite with Zn generates Lewis acid sites replacing the previous strong acid sites, hence the aromatics selectivity of the hybrid catalysts is clearly improved. The silicalite-1 shell can seal the exposed external acidic sites of the Zn/Z5 core zeolite, in order to depress the xylene isomerization. As a result, the Cr/Zn-Zn/Z5@S1 hybrid catalyst successfully converts syngas into PX with extremely higher selectivity.

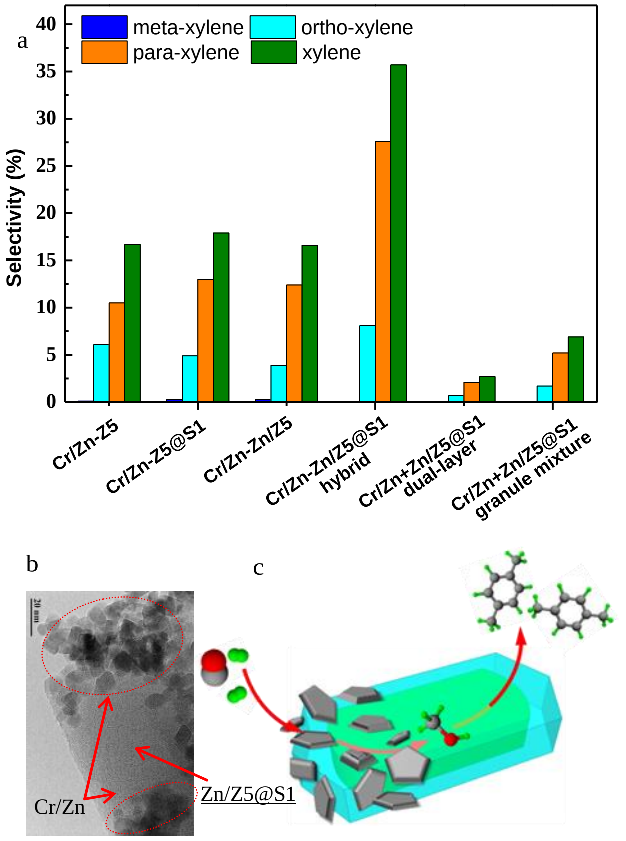

Figure 1. (a) The distribution of total xylene and isomers (OX, MX and PX) over varied catalysts; (b) the TEM image of the Cr/Zn-Zn/Z5@S1 hybrid catalyst; (c) the reaction mechanism of the one-pass selective syngas conversion to *para*-xylene over the hybrid catalyst Cr/Zn-Zn/Z5@S1.

4. Conclusions

In summary, we presented a successful hybrid catalyst Cr/Zn-Zn/Z5@S1 for the one-pass conversion of syngas to para-xylene with high activity, selectivity, stability and lower CO_2 formation. The selectivity of PX obtained by this hybrid catalyst reached up to 77.3% in the xylene isomers and accounted for 27.6% of the total hydrocarbons products at the CO conversion of 55.0%. This hybrid catalyst contained two components: one was Cr/Zn and the other one was a core-shell-structured Zn/Z5@S1 zeolite. The combination of two components in this hybrid catalyst enabled a well-organized tandem catalysis process, performing syngas to methanol and methanol to PX exclusively. The special core-shell structure of Zn/Z5@S1 could effectively seal the exposed active sites of zeolite, in order to depress the formation of unwanted xylene isomers and promote the oriented synthesis of PX. The hybrid catalyst Cr/Zn-Zn/Z5@S1 reported in this paper is extremely promising as an industrial catalyst, not only for PX synthesis, but also for the direct conversion of syngas to other value-added chemicals.

References

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