Supplementary material

A novel BEA-type zeolite core-shell multiple catalyst for hydrogen-rich gas production from ethanol steam reforming

Ziliang Zheng, Donghua Yang, Tingting Li, Xuemei Yin, Shiyao Wang, Xu Wu, Xia An, Xianmei Xie*

College of Chemistry and Chemical Engineering, Taiyuan University of Technology, Taiyuan 030024, China.

*Corresponding author: E-mail addresses: xxmsxty@sina.com; Tel.: +86 351 6018564; fax: +86 351 6018564.

Fig. 1S (A) CH_4- and (B) CO-TPD profiles for *x*Fe*y*Cu-SB@NB and 2.5Fe2.5CuNi-Beta catalysts.

Fig. 1S(A) and (B) present CH_4- and CO-TPD profiles, respectively, obtained over the 2.5Fe2.5Cu-SB@NB, 5Cu-SB@NB, 5Fe-SB@NB and SB@NB catalysts. Studying the adsorption of CH_4 and CO molecules is very important in ESR system because it can determine if the SMR and WGS reactions of CH_4 and CO, respectively, as intermediates occur.[1] As the CH_4-TPD shown in Fig. 1S(A), all catalysts consist mainly of two peaks, one is located in the 100-200 °C range, and the other at approximately 370 °C. One peak at 300 °C in the 2.5Fe2.5Cu-SB@NB and 5Cu-SB@NB catalysts was observed, which might be due to CH_4 adsorption on the surface of metallic Cu. On the other hand, a broad peak at high temperatures above 430 °C was observed in 2.5Fe2.5Cu-SB@NB and 5Fe-SB@NB. This peak might be induced by the amount of CH_4 adsorbed on metallic Fe or Fe oxide. In addition, CH_4 adsorption increased significantly in the 2.5Fe2.5Cu-SB@NB catalyst because of the synergy effect of Cu and Fe components. In Fig. 1S(B), the profile shapes of CO adsorption in all samples were similar to those of CH_4-TPD, but the adsorption areas were different and the adsorbed CO molecules increased slightly at lower temperatures in all samples. Generally, CO desorption is accompanied by a significant production of CO_2,[2] but there is also a peak of CO at low temperatures (100-180 °C), probably due to the physically-adsorbed CO molecules. In particular, in the case of 2.5Fe2.5Cu-SB@NB had being divided in three peaks (160, 410 and 505 °C), while for the 5Cu-SB@NB, 5Fe-SB@NB and SB@NB catalysts, these peaks were recorded at 156, 317 and 410 °C, and 150, 320 and 405 °C, and °C, respectively. Significantly, two peaks in the 5Cu-SB@NB, 5Fe-SB@NB and 2.5Fe2.5Cu-SB@NB catalysts were separated at the range of 250-480 °C. This result implied that CO molecules were more easily adsorbed on the surfaces of the Cu and Fe catalysts than on the mono-metallic Ni catalyst. Moreover, the 2.5Fe2.5Cu-SB@NB catalyst could be confirmed the areas of the peak being larger if compared with other catalysts. Normally, the adsorption of reactants could increase the catalytic activity. Therefore, the SMR and WGS reactions are more efficient over 2.5Fe2.5Cu-SB@NB catalyst, attributing to the strong adsorption of CH_4 and CO molecules.

References

1 S. W. Jo, B. S. Kwak, K. M. Kim, J. Y. Do, N.K. Park, T. J. Lee, S. T. Lee and M. Kang, *Chem. Eng. J*., 2016, **288**, 858.

2 D. A. Constantinou, M. C. Álvarez-Galván, J. L. G. Fierro, A. M. Efstathiou, *Appl. Catal. B: environ*., 2012, **117**, 81.