The Role of Potassium Promoter for Isobutanol Synthesis on Zn-Cr Based Catalysts

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Experimental section of Temperature Programmed Desorption of CO

The Temperature Programmed Desorption of CO (CO-TPD) was recorded on TP-5050 automatic chemical adsorption instrument in the range from 50 °C to 450 °C. For the sake of accuracy, pure standard mixtures [zeolite + activated carbon] were used during preliminary TPD measurements. The catalysts were saturated with CO flow at 50 °C after pretreatment at 400 °C for 180 min in reducing gas which contains 10% H_2 in Ar. Then pure Ar flowed for 120 min at the same temperature to eliminate the adsorption of physically adsorbed water and impurities. Finally, the temperature was increased at a constant rate of 5 °C min^{-1} under an appropriate amount of Ar flow. The desorbed species were analyzed by thermal conductivity measurements.

Analysis of the results of Temperature Programmed Desorption of CO

The CO adsorption characterization of reduced catalysts is estimated by Temperature Programmed Desorption of CO analyses (CO-TPD) and the results are reported in Fig. 1S. Nearly similar changing trends of desorption peaks for CO is observed. All of these CO-TPD patterns have three peaks, namely, weak CO adsorption at 120.0 °C (label as peak α) moderate CO adsorption at 280.5 °C (label as peak β) and strong CO adsorption at 380.0 °C (label as peak γ).

When the specific uptakes are compared, it is evident that moderate CO uptakes (peak β) are increased obviously with increasing K loading and get the maximum when the K loading reaches to 3%, while the weak CO adsorption (peak α) and strong CO adsorption (peak γ) keep almost the same. In general, in a heterogeneous catalytic reaction, there are 3 necessary steps for the reactants to become products, namely reactant adsorption on catalyst surface, surface reaction and products desorption from catalyst surface. Appropriate adsorption strength is essential for our reaction; weak adsorption cannot induce surface

reaction and strong adsorptionwill form by product (mainly CH_x species). On the basis of above observations, it seems that the K promoter could enhance the moderate CO adsorption, which may play an essential role in alcohol synthesis. That may be another non-ignorable factor for better performance when K loading gets to the optimal value on catalyst.

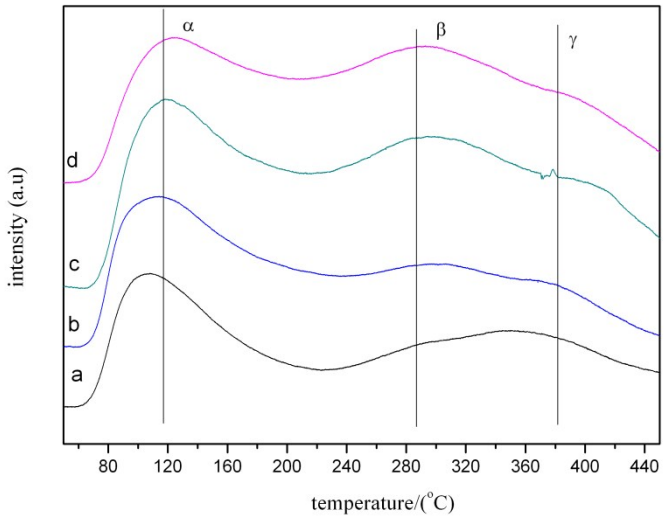

Fig-1S: CO-TPD of catalysts with different contents of potassium, (a) 0K-ZnCr, (b) 1K-ZnCr, (c) 3K-ZnCr and (d) 6K-ZnCr.

Catalytic activity measurements

As a complement, the catalytic activities of the samples with 4% and 5% K loading for the synthesis of isobutanol and MeOH are shown in Table 1S. The change tendency of CO conversion, alcohol selectivity, and alcohol distribution are almost the same as the results in our original paper.

Tab. 1S. Typical catalytic performance of Zn-Cr based catalysts

catalysts	CO conversion (%)	Alcohol selectivity (%)	Total alcohol rate (g/ml h)	Alcohol distribution /wt%				
				Methanol	Ethanol	Propanol	Isobutanol	C_{5+} alcohol
0K-ZnCr	12.96	40.84	0.066	87.67	0.92	0.43	9.09	0.27
1K-ZnCr	17.96	42.84	0.079	79.01	0.81	1.93	15.82	0.92
3K-ZnCr	26.09	46.71	0.093	76.58	2.51	1.33	18.55	1.03
4K-ZnCr	23.53	46.86	0.092	77.46	2.56	3.65	16.54	0.99
5K-ZnCr	19.45	46.21	0.088	79.20	2.54	5.21	14.23	1.02
6K-ZnCr	18.16	45.51	0.086	78.53	2.58	6.33	11.04	1.03

Reaction conditions: Temperature=400°C, Pressure=10 Mpa, GHSV=3000h^{-1}