Iso-butanol synthesis from syngas over the alkali metals modified Cr/ZnO catalysts

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Abstract: The Cr/ZnO catalysts prepared by co-precipitation method were modified by some alkali metals like Li, Na, K and Cs. The effects of alkali metals modification to Cr/ZnO catalysts were investigated in the reaction of iso-butanal direct synthesis from syngas. Among the used alkali metals, the catalytic ability of the K modified catalyst Cr/ZnO-K was better than that of others. Reaction results showed that the CO conversion of Cr/ZnO-K catalyst was 27.39%, with the highest iso-butanol selectivity of 15.58%. The properties of all catalysts were further characterized by BET, XRD, H2-TPR, TG and SEM-EDS.

Keywords: iso-butanol synthesis; syngas; non-stoichiometric spinel ZnₓCr₂/₃(1-x)O

1. Introduction:

Iso-butanol is an important basic chemical and widely utilized for producing antioxidants, paint solvents, flavors, synthetic rubber, etc. Besides, it can also be used as additives of petroleum-derived fuels in order to enhance fuel quality [1]. Iso-butanol is a petroleum-derived chemical. Until now, it is obtained mainly through propylene carbonylation. But the productivity of this process can not meet the increasing market demand in the future.

In order to expand iso-butanol production, many new processes have been developed, such as bio-fermentation and coal-based iso-butanol synthesis technology. Previous researchers in Germany develop a coal based methanol and iso-butanol synthesis technology, to which high reaction temperature and pressure are necessary [2]. And the commonly used catalysts for this process are Cr-based catalysts with some other metals as promoter. Iso-butanol production by
using the Cr-based catalysts is relatively simple, but the selectivity of iso-butanol is low. In order to promote iso-butanol selectivity, generally more harsh reaction conditions must be adopted.

In this report, we prepare a Cr/ZnO catalyst by co-precipitation method. In order to further enhance iso-butanol selectivity, we select some alkali metals, like Li, Na, K and Cs, as promoters to modify Cr/ZnO catalyst (Fig.1). In addition, the physical properties of the prepared alkali metals modified Cr/ZnO catalysts are characterized by BET, XRD, H₂-TPR and SEM in detail, by which to further uncover the real active phase of Cr/ZnO catalyst for iso-butanol formation.

2. Experimental:

The Cr/ZnO catalyst was prepared through co-precipitation method by mixing the aqueous solution of Zn(NO₃)₂·6H₂O and Cr(NO₃)₃·9H₂O (Zn:Cr=1:1 in molar) with (NH₄)₂CO₃ as precipitant. The prepared Cr/ZnO catalyst was impregnated with the aqueous solution of K₂CO₃, Cs₂CO₃, Na₂CO₃ or Li₂CO₃. The modified Cr/ZnO catalysts were denoted as Cr/ZnO-Li, Cr/ZnO-Na, Cr/ZnO-K and Cr/ZnO-Cs.

The catalytic reactions were carried out by using a stainless steel fixed-bed reactor loaded with 5 ml catalysts for each test. The catalysts were first reduced using 20% H₂ in Ar at 400 °C for 6 h. After the reduction process, syngas was introduced into the reactor to react. The reaction conditions are as follows: H₂/CO=2.3, 10 MPa, GHSV=3000 h⁻¹ and reaction temperature of 400 °C.

3. Results and discussion:

All the reaction results, obtained on the pure Cr/ZnO catalyst and alkali metals modified catalysts Cr/ZnO-Li, -Na, -K and -Cs, are given in Table 1. Three alkali metals of Na, K and Cs, rather than Li, can obviously improve the iso-butanol selectivity, as well as the catalyst activity on CO conversion. Among the tested catalysts, the K modified catalyst Cr/ZnO-K shows a better CO conversion (27.39%) and the highest iso-butanol selectivity (15.58%) [3].

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>CO Conv. (%)</th>
<th>Products distribution (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>MeOH</td>
</tr>
<tr>
<td>Cr/ZnO</td>
<td>12.61</td>
<td>83.06</td>
</tr>
<tr>
<td>Cr/ZnO-Li</td>
<td>11.81</td>
<td>91.83</td>
</tr>
<tr>
<td>Cr/ZnO-Na</td>
<td>28.62</td>
<td>77.62</td>
</tr>
<tr>
<td>Cr/ZnO-K</td>
<td>27.39</td>
<td>77.31</td>
</tr>
<tr>
<td>Cr/ZnO-Cs</td>
<td>31.93</td>
<td>85.88</td>
</tr>
</tbody>
</table>

* Reaction conditions: H₂/CO=2.3, 10 MPa, GHSV=3000 h⁻¹ and 400 °C; The alkali metals loading amount for each catalyst was 3 wt%. † n-PrOH means normal propanol and i-BuOH stands for iso-butanol.

4. Conclusion

Combining with the catalysts characterization, the results suggest that the non-stoichiometric spinel of Zn₅Cr₂(Si,Al)₃O₁₀ in Cr/ZnO catalyst should be the active phase for iso-butanol synthesis from syngas. Some alkali metals modification to the Cr/ZnO catalyst, as presented in this report, can promote the activation of CO and H₂ under the used reaction conditions, whereby to improve catalyst performance on CO conversion and iso-butanol synthesis.

References
[3] Li Tan, Guohui Yang, Yoshihuru Yoneyama, Yongli Kou, Yisheng Tan, Tharapong Vitidsantc, Noritatsu Tsubaki, Applied Catalysis A: General, 2015, 505, 141 - 149