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

Li Tan[1], Yoshiharu Yoneyama[1], Guohui Yang[1, 2], Yisheng Tan[2], Noritatsu Tsubaki[1*]

[1]. Department of Applied Chemistry, School of Engineering, University of Toyama, Gofuku 3190, Toyama 930-8555, Japan. *E-mail: tsubaki@eng.u-toyama.ac.jp. Tel./Fax: +81-76-4456846
[2]. State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, 030001, China

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, H_2-TPR, TG and SEM-EDS.
Keywords: iso-butanol synthesis; syngas; non-stoicheiometric spinel $Zn_xCr_{2/3(1-x)}O$

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.

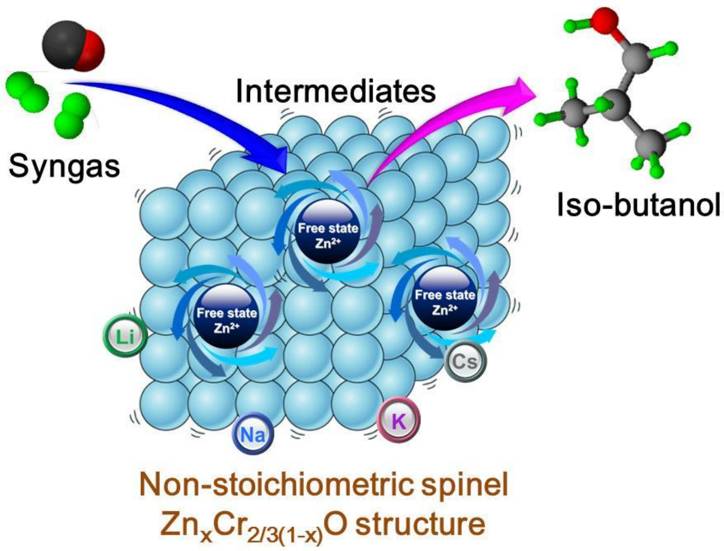

Fig. 1 Direct synthesis of iso-butanol from syngas on the Cr/ZnO-based catalyst

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, H_2-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 $Zn(NO_3)_2 \cdot 6H_2O$ and $Cr(NO_3)_3 \cdot 9H_2O$ (Zn:Cr=1:1 in molar) with $(NH_4)_2CO_3$ as precipitant. The prepared Cr/ZnO catalyst was impregnated with the aqueous solution of K_2CO_3, Cs_2CO_3, Na_2CO_3 or Li_2CO_3. 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% H_2 in Ar at 400 ^oC for 6 h. After the reduction process, syngas was introduced into the reactor to react. The reaction conditions are as follows: H_2/CO=2.3, 10 MPa, GHSV=3000 h^{-1} and reaction temperature of 400 ^oC.

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 1 Iso-butanol synthesis on the alkali metals modified Cr/ZnO catalysts [a]

Catalysts	CO Conv. (%)	Products distribution (wt%)				
		MeOH	EtOH	n-PrOH [b]	i-BuOH [b]	C_5-OH
Cr/ZnO	12.61	83.06	4.46	4.94	6.01	1.53
Cr/ZnO-Li	11.81	91.83	1.41	0.94	5.63	0.19
Cr/ZnO-Na	28.62	77.62	6.58	4.00	11.09	0.71
Cr/ZnO-K	27.39	77.31	4.17	2.24	15.58	0.7
Cr/ZnO-Cs	31.93	85.88	1.45	0.88	11.43	0.36

[a] Reaction conditions: H_2/CO=2.3, 10 MPa, GHSV=3000 h^{-1} and 400 ^oC; The alkali metals loading amount for each catalyst was 3 wt%. [b] 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-stoichimetric spinel of $Zn_xCr_{2/3(1-x)}O$ 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 H_2 under the used reaction conditions, whereby to improve catalyst performance on CO conversion and iso-butanol synthesis.

References

[1]Cheng Jia, Jiang Chun-bo. Chemical Industry .2007, 25(10): 28-31
[2]Marschner F, Moertel H. G. Hydrocarbon Processing, 1986, 1:65-70
[3]Li Tan, Guohui Yang, Yoshiharu Yoneyama, Yongli Kou, Yisheng Tan,TharapongVitidsantc, NoritatsuTsubaki, Applied Catalysis A: General,2015,505, 141 – 149