Higher alcohol synthesis reaction study using K-promoted ZnO catalysts. III

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Recent results indicate that modified high-temperature, high-pressure, Zn/Cr spinel methanol synthesis catalysts consist primarily of ZnO at the catalyst surfaces. Nonpromoted and K-promoted ZnO powders, therefore, were tested for methanol and isobutanol production using a 1 : 1 H_2 and CO syngas feedstream at two operating pressures (6.9 and 10.3 MPa) and two reactor bed temperatures (400 and 440°C). No isobutanol formation occurs over the nonpromoted ZnO. The highest isobutanol production is obtained using a 1 wt% K-containing ZnO catalyst while operating the reactor at 440°C and 10.3 MPa, but the greatest hydrocarbon byproduct rate also is obtained under these conditions. Although the isobutanol product rates are lower than the best values presented in the literature, the product rate of isobutanol formation is limited by a lower surface area of the promoted ZnO catalysts in comparison to the Zn/Cr spinel catalysts. The ratio of the BET surface areas of the K/ZnO catalysts to the surface area of an alkali-modified, commercial Zn/Cr spinel catalyst is approximately 0.23. Comparison of the catalysts on a surface area basis could result in the promoted ZnO samples performing better than the alkali-promoted Zn/Cr spinel catalysts. Most importantly, this study demonstrates that the promoted ZnO is the active catalyst phase for this reaction and that the spinel structure is not required for high activity.

Keywords: higher alcohol synthesis, K-promoted ZnO catalysts, isobutanol, methanol, synthesis gas

1. Introduction

There has been recent interest in the development of processes that produce higher alcohols from syngas because they can be used as fuels, fuel additives or precursors to fuel additives for reducing air pollution and increasing fuel octane ratings. Syngas produced from coal is an ideal reactant stream for higher alcohol synthesis (HAS). This reduces the need for petroleum-based additives as well as the amount of gasoline consumed.

An ideal reactant stream for the synthesis of methyl tertiary-butyl ether (MTBE), an additive present in much of the gasoline sold currently, would be a 1 : 1 molar ratio of methanol and isobutanol. Research toward the production of such a stream from syngas has been extensive. The use of modified methanol synthesis catalysts for HAS has been examined for this purpose as well as for the production of methanol–higher alcohol blends [1–5]. Beretta et al. [6] have designed a reactor which employs two types of HAS catalysts to achieve a high isobutanol product yield of 138.8 g/(kg-cat h) and a methanol-to-isobutanol mole ratio of 3. Kiem and Falter [7] also claim to have achieved high isobutanol product rates using a Zr : Mn : Zn : Pd : Li, 30.5 : 15.4 : 8.6 : 0.2 : 1.5, catalyst. In the two previous parts of this study, an alkali-promoted, commercial, methanol-synthesis catalyst has been used to achieve high isobutanol product rates and methanol-to-isobutanol mole ratios of approximately one [8,9]. For those catalysts maximum product alcohol flow rate and selectivities to total alcohols are obtained using 3 wt% Cs or K promotors and the Cs-promoted catalysts perform better than the K-promoted catalysts.

In these previous studies [8,9], XPS data indicate that ZnO is the only phase present in the near-surface region after activating pretreatments have been performed. Based on this evidence ZnO may be the active catalytic phase for HAS. This hypothesis has been tested in this study using a ZnO powder without and with K promotion as an HAS catalyst using a 1 : 1 H_2 and CO syngas feedstream.

2. Experimental

The ZnO powder was purchased from Aldrich Chemical Company. Using the incipient wetness method at a constant pH of 10, the powder samples were promoted by impregnation with 1, 3 and 5 wt% K using potassium nitrate as the precursor. Each of these catalysts was then calcined in air at 325°C and reduced with a 5% hydrogen-in-nitrogen mixture for 4 h at 300°C. Nonpromoted and promoted ZnO samples were tested for HAS catalytic activity using a 1 : 1 CO and H_2 syngas feed stream at a space velocity of 12 000 over 1 g of catalyst in a reactor that has been described previously [8]. Test measurements were taken while operating the reactor at temperatures of 400 and 440°C and pressures of 6.9 and 10.3 MPa. The catalysts were tested over a 5-day period to examine the activity as a function of time. During this period, the activity remained fairly constant. The product stream analysis was performed using a gas chromatograph.

3. Results and discussion

A detailed listing of the product stream composition under the four different reactor conditions for the four different catalysts used is shown in table 1. Using the nonpromoted sample results in relatively high production of methanol and hydrocarbon byproducts, but no higher alcohols are produced. The higher pressure and lower temperature operating condition result in increased methanol production. Contrary to results obtained from the Cs-promoted, commercial methanol-synthesis catalysts [9], at a reactor bed operating temperature of 440°C, the total alcohol rate and the selectivities to total alcohols are lower than when the reactor is operated at 400°C. This is due to a greater methanol synthesis rate at the lower temperature. Such results have not been reported in the literature previously. Very little or no isobutanol is produced at the lower operating temperature using any of the catalysts. HAS, however, occurs more readily at the higher temperature. The higher pressure condition, 10.3 MPa, enhances the total alcohol flow rate as well. Only for the 5 wt% K/ZnO catalyst does the 6.9 MPa operating pressure result in a greater isobutanol product flow rate. The higher pressure parameter also typically results in the larger syngas conversions as well. The lowest methanol-to-isobutanol mole ratios occur using the 440°C, 6.9 MPa operating parameters. The lowest ratio achieved is 2.3 using the 1 wt% K/ZnO catalyst sample. The highest isobutanol product rate in most of the data presented is obtained at these operating conditions as well.

The effects of K-promoter concentration on the product stream composition was examined, and the rate of total alcohol production as a function of K loading at a reactor bed temperature of 440°C and a pressure of 10.3 MPa is shown in figure 1a. Using the nonpromoted catalyst results in an alcohol flow rate of almost 60 g/(kg h), and the addition of K to the ZnO catalyst increases the alcohol production rate. A maximum alcohol flow rate of 100 g/(kg h) is attained using the 3 wt% K/ZnO sample while increasing the K loading to 5 wt% decreases the total alcohol flow rate. The separate methanol and isobutanol production rates as a function of potassium loading are shown in figure 1b. Promoting the catalyst with 1 wt% K increases the isobutanol flow rate from 0 to 38 g/(kg h) and yields a methanol-to-isobutanol mole ratio of 4.5. Increasing the K promoter concentration further, lowers the isobutanol product flow rate. The highest methanol flow rate is achieved using the 3 wt% K/ZnO catalyst which also corresponds to the greatest total alcohol flow rate discussed above. Further addition of K decreases the methanol product flow rate.

These results demonstrate that K-promoted ZnO is the active catalytic phase for HAS, but the synthesis rates of isobutanol over these ZnO catalysts is lower than some values presented in the literature. These results, however, are not based on surface-area considerations but on catalyst weight. The BET surface area of the ZnO catalyst is approximately 18.5 m^2/g while the BET surface areas of corresponding K-promoted, modified commercial catalysts tested in the previous studies [8,9] are approximately 80 m^2/g. Furthermore, the isobutanol production rate obtained using the 1 wt% K/ZnO catalyst is greater than the production rates obtained using Cu/ZnO catalysts [10] as well as some promoted Zn/Cr catalysts [11]. Therefore, on a surface-

Table 1
ZnO powder catalyst containing different amounts of potassium

	0% K				1% K				3% K				5% K			
P (MPa)	6.9	10.3	10.3	6.9	6.9	10.3	10.3	6.9	6.9	10.3	10.3	6.9	6.9	10.3	10.3	6.9
T (°C)	400	400	440	440	400	400	440	440	400	400	440	440	400	400	440	440
selectivity to total alcohols (%)	57	68	23	15	84	91	70	72	95	98	82	76	96	98	87	88
total alcohol rate (g/(kg h))	74	164	59	23	72	157	85	41	79	156	100	46	56	95	68	25
methanol rate (g/(kg h))	74	164	59	23	63	142	42	15	69	142	63	20	52	91	49	13
ethanol rate (g/(kg h))	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
isopropanol rate (g/(kg h))	0	0	0	0	0	0	0	0	0	0	2	1	2	0	0	0
n-propanol rate (g/(kg h))	0	0	0	0	2	6	6	0	6	0	14	5	4	4	13	3
isobutanol rate (g/(kg h))	0	0	0	0	7	8	38	26	4	14	22	20	0	0	6	9
MetOH/*i*-ButOH mole ratio	–	–	–	–	35	72	4.5	2.3	68	41	11	4.1	–	–	31	5.4
hydrocarbon rate (g/(kg h))	28	38	100	67	7	7	23	10	2	2	12	9	1	1	6	2
conversion (%)	9	10	11	8	7	8	8	7	9	10	11	9	7	7	7	7

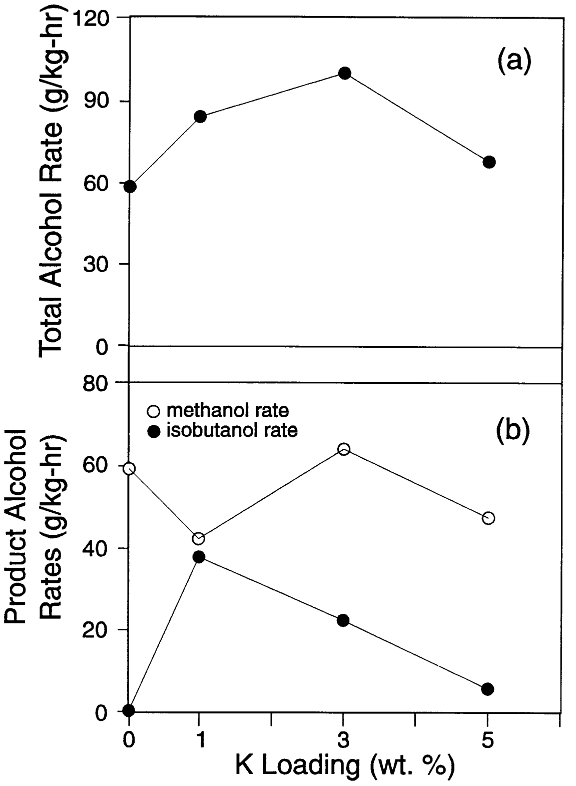

Figure 1. The effect of K loading on the (a) total alcohol product rate and (b) isobutanol and methanol product rates obtained by operating the reactor at 440°C and 10.3 MPa.

area basis, the K-promoted ZnO catalyst would be superior in performance compared to the activities of other catalysts presented in the literature. This will be demonstrated in future studies by supporting the ZnO on high surface area supports. The Zn/Cr catalysts that have been investigated previously contain underlying Zn/Cr spinel structures which apparently behave only as a high surface area support for the promoted ZnO at the surface. Both low-temperature and high-temperature methanol synthesis catalysts typically contain Zn as one of the components. The data presented above suggests the other components are not necessary for HAS. Campos-Martin et al. [12] and Forzatti et al. [13] have also examined Zn-containing catalysts for HAS. In both studies a ZnO phase was found using XRD. This is consistent with the assertion that ZnO is the active catalyst phase for HAS.

The selectivity to total alcohols as a function of promotor loading is shown in figure 2a. The addition of 1 wt% K to the ZnO powder causes an increase in the alcohol product selectivity. Promoting the sample further results in even greater selectivities, but the rate of enhancement decreases. An alcohol selectivity of 87% is achieved using a 5 wt% K/ZnO catalyst under the reaction conditions employed. This is a high value compared to the results typically obtained in HAS [2]. The use of the modified methanol synthesis catalysts results in hydrocarbon production which causes a decrease in the catalyst selectivity. As shown in figure 2b the increase in alcohol selectivity is due to a decrease in the hydrocarbon byproduct rate upon addition of the promotor. The data shown in figures 2a and b are related directly and the figures are mirror images of each other. The product hydrocarbon rate using the nonpromoted catalyst is 100 g/(kg h) while that of the 5 wt% K/ZnO catalyst is 6 g/(kg h).

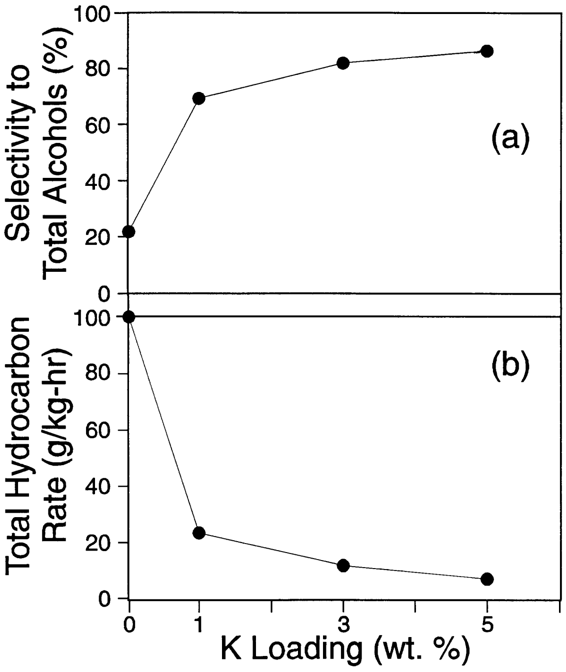

Figure 2. The effect of K loading on the (a) selectivity to total alcohols and (b) hydrocarbon byproduct rate obtained by operating the reactor at 440°C and 10.3 MPa.

4. Summary

Nonpromoted and K-promoted ZnO powders were tested for higher alcohol synthesis using a 1 : 1 CO and H_2 syngas feedstream. Two pressure settings (6.9 and 10.3 MPa) and two reactor bed temperature settings (400 and 440°C) were used. The highest isobutanol rates are obtained at 440°C and 10.3 MPa using the 1 and 3 wt% K-containing catalysts and at 440°C and 6.9 MPa using the 5 wt% K-containing catalyst. No isobutanol is formed over the nonpromoted ZnO sample. The highest hydrocarbon byproduct rates occur at the 440°C and 10.3 MPa operating parameters. The addition of K to the ZnO decreases the hydrocarbon rate resulting in an increase in the alcohol selectivity. A maximum in the rate of isobutanol production as a function of K-promotion is obtained using a 1 wt% K/ZnO catalyst. At 440°C and 10.3 MPa, the use of this catalyst results in a methanol-to-isobutanol mole ratio of 4.5.

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