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An efficient catalyst for the production of isobutanol and methanol from syngas.
VIII: Cs- and Pd-promoted Zn/Cr spinel (excess ZnO)

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A Cs- and Pd-promoted Zn/Cr spinel (excess ZnO) higher alcohol synthesis (HAS) catalyst has been tested for the production of isobutanol and methanol. An isobutanol production rate of 170 g/(kg h) and a methanol-to-isobutanol mole ratio of 0.44 are attained at 440°C and 1000 psig. This ratio is lower than the desired value of 1.0 for MTBE production. Operating the reactor at a higher pressure of 1500 psig results in a lower isobutanol production rate of 161 g/(kg h) and an increased alcohol ratio of 0.7. A methanol-to-isobutanol mole ratio of 0.75 is also achieved under these operating conditions. These results are superior to others presented in the literature thus far. Surface characterization data indicate that the near-surface region of the catalyst consists primarily of ZnO and Cs. Pretreating the catalyst in a reductive environment similar to that given to the catalyst before reaction tests, causes an enrichment of the Cs promoter at the surface. The product stream composition does not significantly change after 5 days of testing. During this time, however, the amount of Cs relative to Zn measured by XPS at the surface decreases possibly by agglomeration. The Zn remains in a ZnO state after the reductive pretreatment and after removal from the reactor.

Keywords: higher alcohol synthesis, Cs- and Pd-promoted Zn/Cr spinel catalysts, isobutanol, methanol, synthesis gas

1. Introduction

The production of isobutanol and methanol from a syngas (CO and H_2) feedstream has received considerable attention in recent years. This research stems from the use of these two alcohol components directly as gasoline additives or in the downstream synthesis of methyl tertiary-butyl ether (MTBE), a fuel additive typically found in quantities of up to 3–5 wt% in the gasoline used today. MTBE is currently produced using C_4 petroleum feedstocks, but the development of a catalytic reactor system which produces an equimolar mixture of isobutanol and methanol with high selectivity from syngas, a coal-derived product, would lessen this dependence on petroleum.

Types of higher alcohol synthesis (HAS) catalysts include modified Fischer–Tropsch and methanol synthesis catalysts. The use of modified high-temperature, high-pressure, methanol synthesis catalysts results in the highest isobutanol-to-methanol mole ratios [1], a ratio of 1.0 being ideal for MTBE synthesis. These types of catalysts typically are composed of a Zn/Cr spinel structure which is promoted with Cs or K [1–6], with the addition of Cs usually resulting in better catalysts. Surface characterization data obtained from several HAS catalysts indicate that the near-surface region of these catalysts primarily consists of ZnO [5–8] and not a Zn/Cr spinel. The Zn/Cr spinel structures are detected using X-ray diffraction (XRD) which, however, probes bulk crystalline phases of the powder samples. These findings led to the study of HAS over a ZnO powder which simply was purchased from Aldrich Chemical Co. and promoted with potassium [9]. Although low isobutanol production rates were obtained, the BET surface area of this catalyst was quite low in comparison to the Zn/Cr spinel-based catalysts (approximately 0.2 : 1). On a surface-area basis, the 1 wt%, K-promoted ZnO powder is superior to others described in the literature in terms of isobutanol production rates. The addition of Pd to Zn/Cr HAS catalysts, as demonstrated in previous studies, also results in improved isobutanol and total alcohol production rates compared to similar catalysts which do not contain Pd [10,11]. The combination of the excess ZnO and Pd promoter, as well as Cs, on a high surface area support could result in another improvement in the production of isobutanol using HAS catalysts.

In this paper data collected using a Zn/Cr spinel-based catalyst containing excess ZnO and promoted with 3 wt% Cs and 5.9 wt% Pd is presented. The results obtained are excellent compared to HAS catalysts which have been tested in previous studies. Some surface characterization results are also shown which describe the effects of the reductive pretreatment and aging in the reactor.

2. Experimental

The Zn/Cr catalyst support material was prepared by flowing a solution containing a 4 : 1 molar ratio of KOH : K_2CO_3 into approximately 1 ℓ of deionized water at room temperature until a pH of 10 was achieved. A mixture of Zn and Cr nitrates dissolved in deionized water was then poured into the vessel. This mixture was made to result in a 3 : 1 bulk ratio of Zn : Cr. The flows of each of the above streams were adjusted to maintain a pH of 10. The solution containing the coprecipitated product was heated to 70°C and stirred for 3 h. The product was then filtered and washed three times with 3 ℓ of deionized water. The remaining product was dried at 100°C, ground to 40 mesh and analyzed to ensure that the bulk K and Na levels were below 300 ppm. This material was then calcined in a tube furnace at 325°C for 12 h. The catalyst was impregnated with 3 wt% Cs and 5.9 wt% Pd as promoters using Cs and Pd nitrates and the incipient wetness method. The resulting catalyst has a BET surface area of about 80 m^2/g.

The reactor consisted of a 1/4 in copper-lined tube which eliminates products formed due to feedstream reactions with stainless steel tube walls at elevated temperatures. Since Cu is an active component in low-temperature HAS catalysts, blank studies were performed to ensure that HAS did not occur over the Cu. Under the conditions used in this study, a synergistic effect between ZnO and the Cu would produce hydrocarbons and not alcohols. One gram of catalyst was mixed with 3 g of glass beads for dispersion and then placed into the reactor tubes. The tubes were placed in an air-fluidized sand bath for uniform heating. The pretreatment and feedstream gases were passed through a molecular-sieve-activated carbon trap to remove water and metal carbonyl contaminants before entering the reactor tube. The catalyst was calcined in air at 325°C prior to use in order to ensure catalyst stability. The catalyst pretreatment consisted of heating the sample at 300°C for 4 h in a 5% hydrogen-in-nitrogen mixture. The reaction was run using a 1 : 1 CO : H_2 mixture at a space velocity of 12,000. The reactions were run at two different temperatures, 400 and 440°C, and two pressures, 1000 and 1500 psig. The product stream was analyzed with a Varian 3700 gas chromatograph using both thermal conductivity and flame ionization detection methods [5,6]. The focus of this study was the production of isobutanol so components produced in small quantities are neglected.

The details of the characterization experiments have been published previously [5]. The fresh catalyst samples were pressed into an Al cup and inserted into the characterization system where XPS and ISS analyses were carried out with a double-pass cylindrical-mirror analyzer (PHI model 25-255AR). This sample was then exposed to 1×10^{-7} Torr of H_2 for 4 h at 300°C and analyzed again without air exposure. The samples aged in the reactor for 5 days were exposed to air before analysis by XPS and ISS.

3. Results and discussion

A product stream composition listing is given in table 1 for the four different reactor operating conditions used in this study. Operating the reactor at the lower temperature setting of 400°C results in the higher selectivity to total alcohols due to lower hydrocarbon production rates. The greater methanol production rate at the lower temperature also contributes to the higher selectivity to total alcohols. Although lower selectivities to total alcohols are attained at the 440°C operating condition, higher isobutanol production rates are achieved. Due to the increased isobutanol production rates and lower methanol production rates at 440°C, the isobutanol-to-methanol mole ratios are also lower. A ratio of 0.44 is achieved at 1000 psig and 440°C, which is actually below the ideal ratio of 1.0 for downstream MTBE synthesis. However, a lower value can be handled more easily than the higher values which are almost always attained using HAS catalysts. Higher syngas conversions also result at 440°C. The obvious drawback is the greater hydrocarbon production rates which requires more extensive downstream separation processing. At the higher pressure condition, the molar flow rate is greater so larger quantities of products result.

The isobutanol production rate value of 170 g/(kg h) at 1000 psig and 440°C is quite significant for two reasons. In these studies [5,6,9,10] the highest values have been attained at 440°C and 1500 psig over the other catalysts examined. Therefore, less extreme reactor operating parameters (lower pressure) are possible using this catalyst. Furthermore, an isobutanol production rate of 170 g/(kg h) and an isobutanol-to-methanol mole ratio of 0.44 represent significant improvements compared to previous literature values. Beretta et al. [4] have reported isobutanol production rates of 74.1 g/(kg h) using a Cs-

Table 1
Product stream composition using a 3 wt% Cs/5.9 wt% Pd/Zn/Cr spinel catalyst containing excess ZnO. The numbers in this table are an average over a five-day operating period. The reaction was run using a 1 : 1 CO : H_2 mixture at a space velocity of 12,000

P (psig) *T* (°C)	1000 400	1500 400	1500 440	1000 440
selectivity to total alcohols (%)	85	84	67	71
total alcohol rate (g/(kg h))	193	282	238	228
methanol rate (g/(kg h))	71	150	48	32
ethanol rate (g/(kg h))	1	3	0	0
isopropanol rate (g/(kg h))	1	2	7	4
n-propanol rate (g/(kg h))	15	22	22	23
isobutanol rate (g/(kg h))	105	105	161	170
MeOH/*i*-ButOH mole ratio	1.6	3.3	0.70	0.44
hydrocarbon rate (g/(kg h))	22	31	84	49
conversion (%)	17	18	20	19

promoted Zn/Cr catalyst with a high methanol-to-isobutanol mole ratio of approximately 5.4. Tronconi et al. obtained an isobutanol production rate of 25.8 g/(kg h) using a K-promoted Zn/Cr catalyst [12] and 18.9 g/(kg h) using a Cs-promoted Zn/Cr catalyst [13] while Nunan and coworkers [14] have tested a Cs-promoted, low-temperature, low-pressure methanol synthesis catalyst (Cu/ZnO) and observed an isobutanol production rate of 48.6 g/(kg h). A similar catalyst, but supported on Al_2O_3, results in an even lower isobutanol production rate of 9.4 g/(kg h) [15]. A separate study by Boz et al. [16] was performed using the alumina-supported samples, but promoted with K, and these authors observed catalyst deactivation within the first 10 h of reaction. No change in the product stream composition occurred during the experiments performed in the present study over a five-day test period. Stiles et al. [17] examined a Cu/Mn/Zn/Cr/K catalyst and obtained an isobutanol production rate of only 20.2 g/(kg h) while in another study Campos-Martin et al. [7] obtained a value of 13.7 g/(kg h) using a Cs-promoted Cu/Zn/Cr catalyst. Furthermore, other types of catalysts do not yield higher isobutanol production rates. An Fe-containing Cu/Mo catalyst results in a total alcohol production rate of 51.9 g/(kg h) with 57% of the alcohol products composed of methanol [18]. A recent report [19] has shown that the use of a K/Cu/Mg/Ce sample catalyzes the synthesis of isobutanol and methanol, but again the isobutanol production rate is quite low, with only 7.16 g/(kg h) formed over the best of these catalysts tested. Keim and Falter [11] have reportedly obtained excellent isobutanol synthesis rates, although Forzatti et al. [1] state that these values are similar to those obtained using their catalysts which are listed in the discussion above [1,12,13]. As indicated from comparison of the values presented above and those shown in table 1, the Pd- and Cs-promoted, excess ZnO-containing Zn/Cr spinel catalyst described here performs better than those described in the literature. Furthermore, the production rates presented here represent significant improvements over others obtained using the same reactor system [5,6,9,10].

XPS and ISS surface characterization techniques were both used in order to gain a better understanding of this catalyst. An XPS survey spectrum obtained from the as-prepared sample is shown in figure 1. Features due to the presence of Zn, Cs and O are readily apparent in this spectrum as is a small Cr peak at about 580 eV. No Pd is observable due to interference by the Zn(LMM) peaks and the fact that only a small amount is present. Although the sample was prepared using a 3 : 1 Zn : Cr weight ratio, the near-surface region consists of a substantially greater amount of Zn relative to Cr. The effects of a catalyst pretreatment and aging under reaction conditions also were examined using XPS and ISS. A Zn 2p spectrum obtained from the as-entered HAS catalyst is shown in figure 2a. As expected, the only state of Zn present in the near-surface region is ZnO [20]. ZnO is the only state of Zn which has been observed on several HAS catalysts which have been characterized in these studies [5,6,21]. These results indicate that the Zn/Cr spinel structure acts as a high-surface area support for the ZnO phase and does not play a role in the catalysis. After treating the catalyst material in 1×10^{-7} Torr of H_2 for 4 h at 300°C, the Zn 2p spectrum shown in figure 2b was taken. No differences are noticeable between the spectra shown in figure 2a and figure 2b which indicates that the reductive treatment does not change the state of the ZnO in the region examined by XPS. Furthermore, according to the data shown in figure 2c, which was taken from the catalyst after aging under reaction conditions for 5 days, the chemical state of the Zn remains unaltered. This same trend has been observed in previous characterization studies of HAS catalysts as well [5–8,21]. The alkali-promoted ZnO apparently is the active phase in HAS [9].

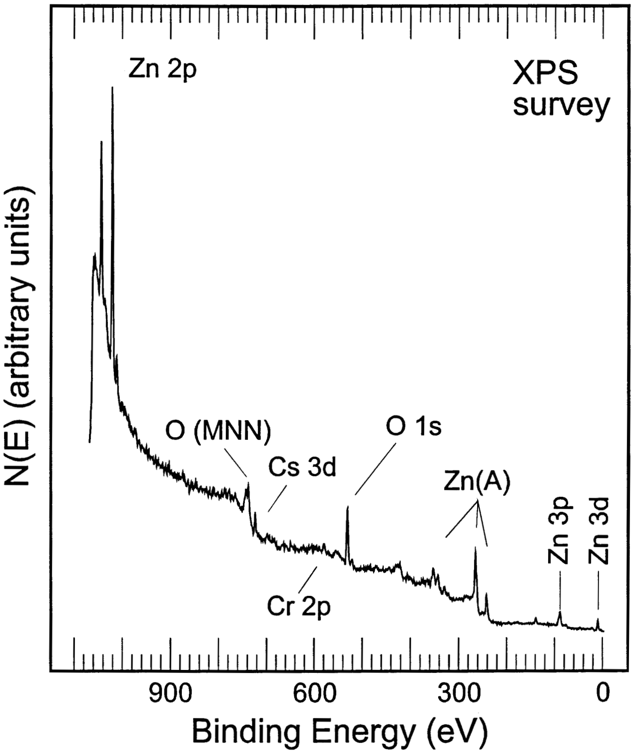

Figure 1. XPS survey spectrum obtained from the 3 wt% Cs/5.9 wt% Pd/Zn/Cr catalyst containing excess ZnO after insertion into the UHV characterization chamber. The Zn(A) features are the Zn(LMM) Auger peaks.

An ISS spectrum obtained from the as-prepared catalyst is shown in figure 3a. A large feature due to sample charging is present below an E/E_0 value of approximately 0.4. Due to this charging feature, it is difficult to obtain information regarding the amounts of carbon or oxygen at the surface. The features which lie at higher E/E_0 values, however, are less affected by charging and do provide compositional information concerning the

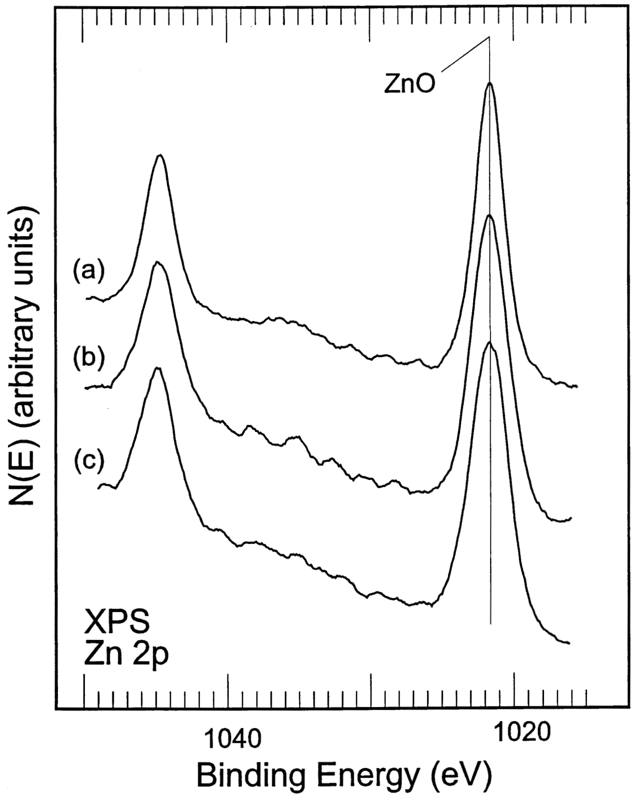

Figure 2. XPS Zn 2p spectra obtained from the 3 wt% Cs/5.9 wt% Pd/Zn/Cr catalyst containing excess ZnO after (a) insertion into the UHV surface characterization chamber, (b) treatment in 1 × 10^{-7} Torr of H_2 for 4 h at 300°C and (c) removal from the reactor after 5 days of exposure to reaction conditions.

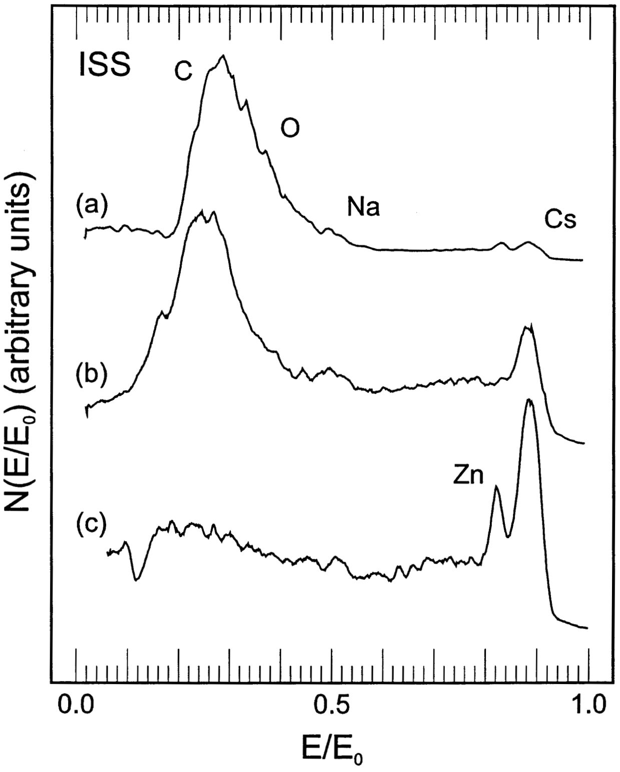

Figure 3. ISS spectra obtained from the 3 wt% Cs/5.9 wt% Pd/Zn/Cr catalyst containing excess ZnO after (a) insertion into the UHV surface characterization chamber, (b) treatment in 1 × 10^{-7} Torr of H_2 for 4 h at 300°C and (c) removal from the reactor after 5 days of exposure to reaction conditions.

outermost layer. Cs and Zn peaks are present in this spectrum as well as a Na feature. A Cr feature would have an E/E_0 of 0.76. The presence of this contaminant should not negatively affect the performance of this sample since Na itself can act as promoter in HAS [9,21]. The ISS spectrum shown in figure 3b was obtained after the reductive pretreatment. The charging feature has slightly decreased in size and shifted to a lower E/E_0 value. An oxygen feature is now noticeable, the Na feature is still apparent and the Cs feature is increased in intensity. The Zn peak is now barely observable above the noise level of the spectrum. The increased intensity of the Cs relative to the other primary component of the near-surface region, Zn, indicates that the pretreatment causes an enrichment of the promoter at the outermost atomic layer. The presence of the alkali promoter is required for HAS over ZnO powder [9]. Also, this same effect has been observed upon pretreating other Cs-promoted HAS catalysts [6,21]. An ISS spectrum was obtained from the catalyst after it was removed from the reactor where it had been tested for 5 days under the syngas feedstream. This spectrum is shown in figure 3c. The intensity of the Zn peak relative to the Cs peak increases during the reaction process suggesting that the promoter agglomerates exposing ZnO during reaction. Furthermore, although the spectral background is large, the charging feature is absent. This result may be due to a decrease in surface oxygen content. As the surface becomes less oxidized, the surface conductivity increases so sample charging decreases. The presence of the large background, however, does indicate that the surface is not very conductive even though no oxygen peak is observed. As the sample becomes more conductive, the ion neutralization efficiency of the sample increases which results in a smaller background signal due to a smaller amount of escaping ions which have undergone multiple collisions with atoms in the near-surface region. These results seem to indicate that less surface O is present after the reaction process although the amount lost cannot be quantified.

4. Summary

A 3 wt% Cs/5.9 wt% Pd/Zn/Cr catalyst which contains excess ZnO was tested for HAS. The reaction data indicate that this catalyst is quite efficient in the production of isobutanol with a production rate of 170 g/(kg h) at 440°C and 1000 psig. This value is greater than those found in the literature for HAS catalysts. Furthermore, a methanol-to-isobutanol of 0.44 is attained at these operating conditions which is considerably lower than values thus far presented in the literature. XPS and ISS data reveal that the as-prepared sample consists primarily of ZnO and Cs. A reductive pretreatment, similar to that given to the catalysts before the reaction, causes an enrichment of the outermost layer in Cs. After 5 days of catalyst testing under reaction conditions, less Cs is present relative to Zn at the outermost layer. The near-surface Zn remains in a ZnO state during the entire process.

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