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Reaction and surface characterization study of higher-alcohol synthesis catalysts XII: K- and Pd-promoted Zn/Cr/Mn spinel

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Abstract

The synthesis of higher alcohols from syngas is a potentially attractive route for the downstream production of methyl tertiary-butyl ether (MTBE), an oxygenated gasoline additive. One of the most effective types of higher alcohol synthesis (HAS) catalysts is a Zn/Cr spinel promoted with either Cs or K. Many studies have suggested that the Cr, required to form the high surface area spinel structure, is detrimental in HAS because it may enhance hydrocarbon formation. For this reason catalysts were examined in the present study in which Mn was substituted into the spinel thereby replacing some of the Cr. Two different K and Pd-promoted Zn/Cr/Mn spinel catalysts were tested for HAS using a 1:1 CO/H_2 syngas feedstream. These catalysts were promoted with 2.25 wt% K, 5.9 wt% Pd and 1.0 wt% K, 9.0 wt% Pd. The former performs better under all four reactor conditions examined (pressures of 1000 and 1500 psig and temperatures of 400°C and 440°C). At 440°C and 1500 psig the isobutanol production rate is 179 g/kg h, the total alcohol production rate is 304 g/kg h and no significant changes in the product stream composition occur over a five-day test period. The methanol-to-isobutanol mole ratio is 1.3, which is very close to the desired value of 1.0 for MTBE production. This is the most active HAS catalyst described in the literature. Surface characterization data, obtained using X-ray photoelectron spectroscopy and ion scattering spectroscopy, indicate that the Mn content in the near-surface region of the catalyst is small. The characterization data also demonstrate that the reductive pretreatments given to HAS catalysts prior to testing result in the elimination of C-containing contamination, adsorbed water and hydroxyl groups and either expose underlying K and Pd promotors or possibly induce the migration of the K and Pd to the outermost surface layers. The pretreated catalyst surface has a layered structure with an enriched K- and Pd-containing layer at the surface above the ZnO layer over the spinel support.

Keywords: Syngas; Methyl tertiary-butyl ether; Higher alcohol synthesis; Isobutanol; Methanol

1. Introduction

Most of the gasoline sold in the United States today contains methyl tertiary-butyl ether (MTBE), an oxygenated additive which raises the octane number of the fuel resulting in more complete combustion and reduced emissions. MTBE is currently produced from methanol and isobutylene precursors. The isobutylene is obtained from C_4 petroleum feedstocks so an alternative method for MTBE production would be attractive to avoid the petroleum feedstock dependence. A long-term goal of many researchers has been to discover an economical method of converting coal-

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derived syngas into an equimolar mixture of the methanol and isobutanol, which can be dehydrated easily to form isobutylene. This reaction pathway would allow for the use of more abundant supplies of coal in some countries.

Several higher alcohol synthesis (HAS) catalytic systems have been investigated in recent years. These include modified Fischer–Tropsch catalysts, alkali-promoted methanol synthesis catalysts and coprecipitated rare earth oxide materials. Of these materials, the alkali-promoted methanol synthesis catalysts, specifically those which operate at high-temperatures and high-pressures, yield more desirable product stream compositions. The high temperature, high pressure, alkali-promoted methanol synthesis catalysts are typically composed of a K- or Cs-promoted Zn/Cr spinel while the low temperature, low pressure alkali-promoted methanol synthesis catalysts are Cu/Zn based. A review of HAS catalysts by Forzatti et al. [1] details the results obtained for the different catalyst types. This study is a part of a series examining Zn/Cr-based HAS catalysts, and a summary of the results obtained from catalysts previously tested is presented in Table 1. The results shown are for catalysts which yield the largest isobutanol production rates in each study, and those cited from Refs. [2–8] yield these values at 440°C and 1500 psig unless otherwise specified. Representative literature values are also presented in Table 1. As shown, the Zn/Cr-spinel-based catalysts do result in greater isobutanol production, although the operating parameters (high temperature, high pressure) are more severe than those associated with the Cu/Zn- and rare-earth-oxide-based catalysts.

The studies in this series demonstrate that increasing the amount of Zn relative to Cr results in greater alcohol production rates [5]. In fact, pure ZnO promoted with K exhibits the highest activity on a surface area basis of all catalysts examined [4]. Furthermore, Simard et al. [15] have concluded that increased hydrocarbon production rates are obtained from a syngas feedstream using larger Cr:Zn ratios. Larger hydrocarbon byproduct rates in HAS reactions have been attributed to catalyst acidity [1] which is related to the Cr concentration. As the hydrocarbon production rate is increased, the total alcohol production rate is decreased. Hydrocarbon production is also undesirable in HAS because they must be separated from the alcohols, but they do have economic value and can be

Table 1

Summary of HAS catalyst performances from this series of studies as well as representative values obtained from the literature[a]

Catalyst (ref. number in parenthesis)	Methanol rate (g/kg h)	Isobutanol rate (g/kg h)	Total alcohol rate (g/kg h)	Hydrocarbon rate (g/kg h)	Methanol-to-isobutanol mole ratio[b]
1 wt% K/Zn/Cr Engelhard spinel [2]	49	103	167	101	1.1
3 wt% Cs/Zn/Cr Engelhard spinel [3]	48	116	214	35	0.96
1 wt% K/ZnO [4]	42	38	85	23	2.6
3 wt% K/Zn/Cr (1:1 Zn:Cr) [5]	39	90	131	47	1.0
5 wt% Cs/Zn/Cr (1:1 Zn:Cr) [5]	74	133	242	112	1.3
5 wt% K/Zn/Cr (excess ZnO) [5]	47	117	178	48	0.93
3 wt% Cs/Zn/Cr (excess ZnO) [5]	58	171	248	52	0.78
5 wt% Cs/5.9 wt% Pd/Zn/Cr (1:1 Zn:Cr) [6]	36	142	227	77	0.59
3 wt% K/5.9 wt% Pd/Zn/Cr (excess ZnO) [7]	54	136	221	111	0.92
5 wt% Cs/5.9 wt% Pd/Zn/Cr (excess ZnO)[c] [7]	32	170	228	49	0.44
1 wt% Cs/Zn/Cr/Mn (excess ZnO) [8]	50	96	153	49	1.2
Cs/Zn/Cr [9]		74.1			5.4
K/Zn/Cr [10]		25.8			
Cs/Cu/ZnO [11]		48.6			
Cs/Cu/ZnO/Al_2O_3 [12]		9.4			
Cs/Cu/Zn/Cr [13]		13.7			
K/Cu/Mg/Ce [14]		7.16			

[a] In Refs. [2–8] the catalysts were tested under identical conditions, but the conditions varied in Refs. [9–14].

[b] The methanol-to-isobutanol mole ratios in previous parts of this study have been incorrectly reported due to a software error. The values which are listed in Refs. [2–8] should be multiplied by 0.58 to obtain the correct ratio.

[c] This catalyst performed best at 1000 psig and 440°C.

used to provide energy in the process. However, Cr is required to form the spinel structure, which has a high surface area relative to a ZnO powder. Frolich et al. [16,17] examined HAS over Zn/Mn/Cr/K catalysts, and this work was extended by Forzatti et al. [18] more recently. These catalysts contain Mn as a part of the spinel structure, replacing some of the Cr. This may lower the catalyst acidity and thus lower the rate of formation of hydrocarbon byproducts. The latter study demonstrated that the Mn-containing catalyst does not perform as well as a Zn/Cr catalyst, although the authors did note that the BET surface area of the Mn-containing catalyst was much lower. Since the Zn/Cr spinel is a common support material for HAS catalysts and the presence of Cr may be detrimental to the efficiency of HAS catalysts, the substitution of Mn for some of the Cr in the spinel preparation is examined in this study. The more active catalyst was characterized using X-ray photoelectron spectroscopy (XPS) and ion scattering spectroscopy (ISS) before and at different stages during a reductive pretreatment which is typically given to the catalysts before reaction. This allows for monitoring of the changes which occur at the catalyst surface during the reductive treatment.

2. Experimental

The Zn/Cr/Mn support material was prepared using a mixture of nitrate precursors dissolved in deionized water. The weight ratios of the added precursor nitrates were 4:1:1 Zn:Cr:Mn. This mixture was poured into a basic solution (pH=10) containing KOH and K_2CO_3. The solution containing the precipitated product was heated to 70°C and stirred for 3 h. The product was filtered and rinsed three times with deionized water. It was then dried at 100°C in a vacuum oven, ground to 40 mesh and analyzed to ensure that the Na and K levels were below 300 ppm. X-ray diffraction data indicate that the bulk of these samples consists of a $ZnCr_2O_4$ spinel structure. This material was calcined in air for 12 h at 325°C and then promoted with Pd and K nitrates using the incipient wetness method. Two different catalysts were prepared and tested. One had a 2.5 wt% K and a 5.9 wt% Pd loading, and the other had a 1.0 wt% K and 9.0 wt% Pd loading. The former was chosen based on the results of a previous study of similar HAS catalysts without Mn [7], and the latter was chosen in order to examine the effects of a considerably different Pd/K ratio. Based on the excellent performance of these catalysts, a systematic study of loading will be carried out. After the addition of promotor, the product was dried in air at 100°C overnight. The catalysts have BET surface areas of approximately 80 m^2/g which remain constant during reaction. Next 1 g of catalyst was placed in the reactor tube with 3 g of glass beads to assist in catalyst dispersion. The reactor consists of a copper-lined, stainless-steel tube immersed in a fluidized sandbath for controlled heating. The copper-lined tubing eliminates reactions which occur at stainless steel walls. A reductive pretreatment was performed by flowing a 5 vol% H_2 and N_2 mixture over the catalyst bed for 4 h at 325°C. Both a 1:1 and a 1:2 CO and H_2 syngas feedstream were used in these experiments, and the catalysts were tested for five days in the reactor to examine catalyst stability. No significant changes in activity or product stream composition were noted during this period. The product stream composition was monitored using a Varian 3700 gas chromatograph. The reactor was operated at two pressures (1000 and 1500 psig) and two temperatures (400°C and 440°C). The organic products were separated using a Tenax column obtained from Alltech, and the inorganics were separated using a carbosieve S-2 column purchased from Supelco.

The surface characterization system has been described previously [2,3]. The as-prepared catalyst promoted with 2.5 wt% K and 5.9 wt% Pd was inserted into the ultrahigh vacuum (UHV) chamber, the near-surface region was characterized using XPS and the composition of the outermost surface layer was examined using ISS. When a well-defined C 1s peak due to hydrocarbons is present in the XPS spectra, its binding energy (BE) is assigned a value of 284.6 eV. For these catalysts this results in Zn 2p BEs of 1021.7 eV which corresponds to ZnO. When a significant hydrocarbon peak is not present or the C 1s peak shape is complex due to the presence of several carbon-containing species, the Zn 2p feature is used to assign the BE axis. All other features must then lie at acceptable values including the highest occupied molecular orbitals, and they do for these catalysts. This BE assignment procedure has been discussed in detail by Hoflund [19]. The as-prepared catalyst was then exposed to 1×10^{-7} Torr of H_2 at 325°C for 4 h in order to simulate the reductive pretreatment given to the catalysts in the reactor. This reductive pretreatment was accomplished in a stepwise manner in order to monitor changes occurring at the surface during the temperature ramp. During each step of this treatment, the catalysts were reexamined using XPS and ISS, and a depth profile was obtained after the 325°C treatment by sputtering with 1 keV He^+ for 5, 15 and 38 min. Calibration studies indicate that the sputter removal rate is about 0.03 nm/min under the conditions used in this study.

3. Results and discussion

3.1. Reaction studies

The product stream compositions obtained using the 2.25 wt% K- and 5.9 wt% Pd-promoted Zn/Cr/Mn catalyst at the four different reactor operating conditions are given in Table 2. The largest total alcohol rate of 407 g/kg h is obtained at 1500 psig and 400°C. However, this large rate is primarily due to the production of 248 g/kg h of methanol resulting in a large methanol-to-isobutanol mole ratio of 4.4. The lower temperature of 400°C results in the higher selectivity to total alcohols due to significantly lower hydrocarbon byproduct rates. This is a consistent trend which has been observed in all parts of this series of studies [2–8]. The higher operating temperature results in lower selectivities to the desired product due to increased hydrocarbon byproduct rates. A larger hydrocarbon byproduct rate also occurs when the pressure is increased from 1000 to 1500 psig. Although the higher pressure and temperature result in larger production of byproducts, higher isobutanol product rates are also achieved. For this catalyst an isobutanol production rate of 179 g/kg h is achieved, which is the largest value obtained in this series of studies [2–8] and is greater than any values presented previously in the literature (see Table 1). At the higher temperature, lower methanol-to-isobutanol mole ratios are obtained due to the coincident decrease in methanol production and increase in isobutanol production. At 440°C and 1500 psig, the conditions at which the most isobutanol is produced, a ratio of 1.3 is achieved. This value is close to the ideal value of 1.0 for downstream MTBE synthesis. A lower methanol-to-isobutanol mole ratio of 0.74 is obtained at 1000 psig and 440°C, the isobutanol production rate is decreased to 109 and the hydrocarbon byproduct rate achieves its largest value of 112 g/kg h. An interesting result using this catalyst is its relatively high single-pass conversion of 28%. The values presented in earlier studies have typically been under 20% although a 24% conversion was obtained using a 5 wt% Cs-promoted Zn/Cr spinel [5].

A similar 3 wt% K and 5.9 wt% Pd-promoted Zn/Cr spinel catalyst has been tested previously for HAS [6], and an isobutanol product flow rate of 136 g/kg h was attained at 1500 psig and 440°C. The catalyst contain-

Table 2
Product stream composition using a 1:1 H_2 and CO syngas feedstream and a Zn/Cr/Mn spinel-based catalyst promoted with 2.25 wt% K and 5.9 wt% Pd; 1.0 wt% K and 9.0 wt% Pd

	2.25 wt% K, 5.9 wt% Pd				1.0 wt% K, 9.0 wt% Pd	
	1000 psig, 400°C	1500 psig, 400°C	1500 psig, 440°C	1000 psig, 440°C	1000 psig, 400°C	1500 psig, 440°C
Selectivity to total alcohols (%)	84	86	64	54	69	52
Total alcohol rate (g/kg h)	233	407	304	159	164	237
Methanol rate (g/kg h)	119	248	99	35	63	65
Ethanol rate (g/kg h)	0	7	0	0	0	15
Isopropanol rate (g/kg h)	0	0	0	0	0	7
n-Propanol rate (g/kg h)	12	21	27	15	10	28
Isobutanol rate (g/kg h)	102	130	179	109	91	122
MeOH/*i*-BuOH mole ratio	2.7	4.4	1.3	0.74	1.6	1.2
Hydrocarbon rate (g/kg h)	26	37	94	112	48	145
Conversion (%)	14	24	28	28	15	22

ing Mn results in greater isobutanol production although the value may be affected somewhat by the slightly lower K loading. Furthermore, reduced hydrocarbon byproduct formation occurs at these conditions using the Mn-containing catalyst (94 vs. 111 g/kg h). This may imply that the substitution of Mn for Cr suppresses hydrocarbon formation particularly since the Mn-containing catalyst is so active. However, the results of an earlier study [5] indicate that the production of hydrocarbons may not be directly related to the amount of Cr in the catalysts. K- and Cs-promoted, 1:1 Zn/Cr spinel catalysts were compared to alkali-promoted spinel catalysts which contain excess ZnO thereby lowering the amount of Cr. The K-promoted catalysts containing excess ZnO (less Cr) produce greater amounts of hydrocarbon byproducts compared to the 1:1 Zn/Cr catalysts at all operating conditions examined. Significant hydrocarbon production rates were also obtained using a 1 wt% K-promoted ZnO powder (no Cr) [4]. The formation of hydrocarbons therefore does not depend on just the Cr concentration so other factors significantly influence the byproduct rate as well.

The product stream compositions obtained from the Zn/Cr/Mn spinel catalyst promoted with 1.0 wt% K and 9.0 wt% Pd at the two reactor conditions tested are shown in the last two columns of Table 2. The changes in the operating parameters result in the same trends as described above with the higher temperature and pressure resulting in a larger isobutanol production rate as well as a much larger hydrocarbon byproduct rate. Comparison of the product stream compositions obtained using these two catalysts indicates that the 2.25 wt% K- and 5.9 wt% Pd-promoted catalyst is superior for HAS.

The Shell gasifier produces syngas with a ratio of 1:2 H_2 and CO which therefore would be a preferred feedstream ratio for HAS. Therefore, tests were performed using this syngas ratio at 440°C and 1500 psig since these settings yield more favorable product stream compositions at the higher syngas ratio. The results are shown in Table 3. Significantly smaller amounts of the alcohols are produced, and smaller amounts of hydrocarbon byproducts form as well. Using the 2.25 wt% K- and 5.9 wt% Pd-promoted Zn/Cr/Mn spinel catalyst, a single-pass conversion of 26% and a methanol-to-isobutanol mole ratio of 0.46 are attained. However, the isobutanol production rate of 71 g/kg h is much lower than that obtained using a syngas ratio of 1:1. The use of the 1.0 wt% K- and 9.0 wt% Pd-promoted catalyst results in an even lower isobutanol production rate of 52 g/kg h, but a more ideal methanol-to-isobutanol mole ratio of 0.98.

Table 3
Product stream composition using a 1:2 H_2 and CO syngas feedstream and a Zn/Cr/Mn spinel-based catalyst promoted with 2.25 wt% K and 5.9 wt% Pd; 1.0 wt% K and 9.0 wt% Pd

	2.25 wt% K, 5.9 wt% Pd	1.0 wt% K, 9.0 wt% Pd
	1500 psig, 440°C	1500 psig, 440°C
Selectivity to total alcohols (%)	63	47
Total alcohol rate (g/kg h)	96	92
Methanol rate (g/kg h)	14	22
Ethanol rate (g/kg h)	0	5
Isopropanol rate (g/kg h)	3	0
n-Propanol rate (g/kg h)	8	13
Isobutanol rate (g/kg h)	71	52
MeOH/*i*-BuOH mole ratio	0.46	0.98
Hydrocarbon rate (g/kg h)	41	69
Conversion (%)	26	20

3.2. Characterization studies

3.2.1. As-prepared catalyst

The 2.25 wt% K- and 5.9 wt% Pd-promoted catalyst was chosen for the surface characterization studies because it produces more isobutanol than the 1.0 wt% K- and 9.0 wt% Pd-promoted catalyst. A survey spectrum obtained from the as-prepared catalyst is quite similar to those published previously [2] so it is not shown. Zn and O features are apparent in these spectra as are small Cr and C peaks. The C contamination originates from the sample preparation process or air exposure. Based on published atomic sensitivity factors [19], peak areas and the homogeneous assumption, the calculated atomic ratio of Zn:Cr is approximately 8:1 which corresponds to a weight ratio of 10.2:1 compared to the bulk value of 4:1 indicating that the near-surface region is enriched in Zn relative to the Cr. This result is in agreement with previous results obtained from Zn/Cr spinel-based catalyst systems [2,3,6,7]. Furthermore, no Mn features are evident in the survey spectrum indicating that a detectable amount of Mn is not present in the region

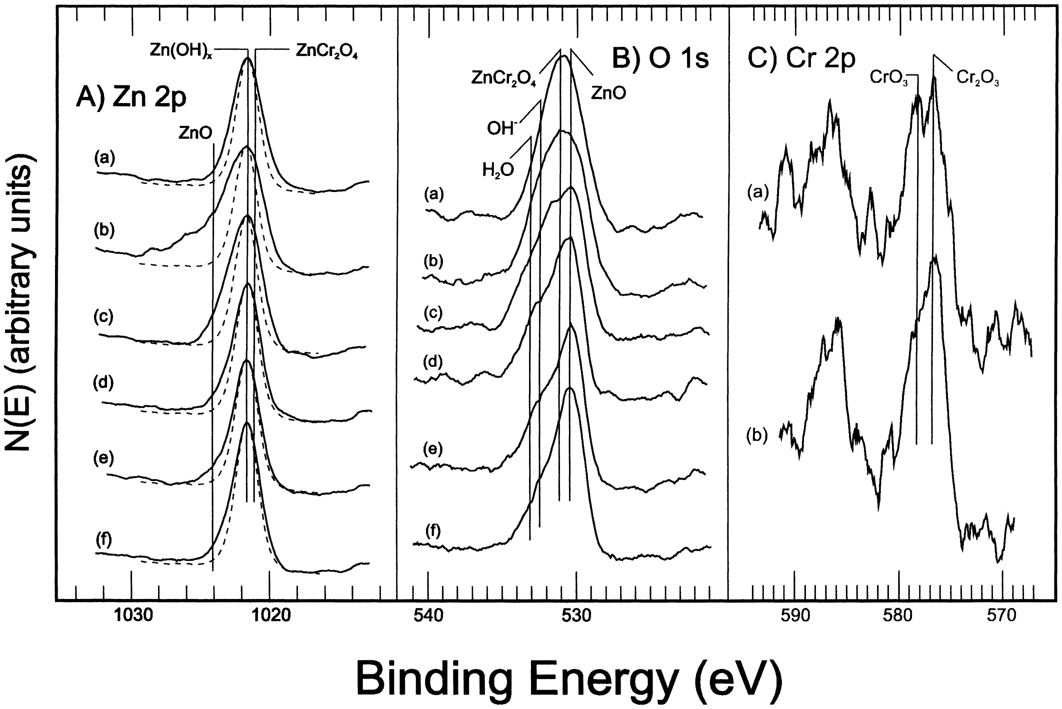

Fig. 1. XPS (A) Zn 2p and (B) O 1s spectra obtained from the as-prepared 2.25 wt% K- and 5.9 wt% Pd-promoted Zn/Cr/Mn spinel catalyst after (a) insertion into the UHV surface characterization chamber, and exposure to 1×10^{-7} Torr of H_2 at (b) 90°C, (c) 100°C, (d) 200°C, (e) 325°C, and (f) sputtering for 38 min with 1 keV He^+. The Cr 2p spectra shown in (C) were obtained: (a) after insertion into the UHV characterization chamber and exposure to 1×10^{-7} Torr of H_2 at 325°C and (b) after sputtering for 38 min with 1 keV He^+.

probed by XPS with the chosen scanning parameters implying that Mn behaves similarly to Cr in this respect. Also, no K or Pd features are apparent in the survey spectrum.

A high-resolution XPS Zn 2p spectrum obtained from the as-prepared catalyst is shown in Fig. 1(A)(a). The Zn $2p_{3/2}$ peak is centered at approximately 1021.7 eV which corresponds to the binding energy (BE) value of ZnO [20]. The dashed line also shown in this figure was obtained from a K-promoted ZnO powder sample [21]. The feature obtained from the catalyst examined in this study is broader indicating that more than one chemical state of Zn is present in the region probed by XPS. The BE of Zn in $ZnCr_2O_4$ spinel is 1021.1 eV [22] which explains the broadening on the lower BE side of the feature. The signal contribution at the higher BE portion originates from the presence of Zn hydroxide species in the near-surface region based on results of previous studies [2,3,6] of these types of catalysts and the discussion below. Although other studies [15,16] have identified the presence of the $ZnCr_2O_4$ spinel phase using X-ray diffraction (XRD) (a bulk-sensitive technique), the primary chemical state of the Zn in the near-surface region of this as-prepared HAS catalyst is ZnO. The Zn/Cr spinel phase only functions as a stable, high-surface-area support for the catalytically active promoted ZnO [2,3,6,7,23].

A high-resolution XPS O 1s spectrum taken from the as-prepared catalyst is shown in Fig. 1(B)(a). The peak is quite broad and consists of signal contributions from multiple oxygen-containing species in the near-surface region. These species include, but may not be limited to ZnO, $ZnCr_2O_4$, hydroxyl groups, adsorbed water and C-containing species. The predominant O-containing species are ZnO and hydroxyl groups, and their contributions add together to make it appear that $ZnCr_2O_4$ predominates. However, this is not the case since it would be inconsistent with the Zn 2p data shown in Fig. 1(A)(a). The XPS C 1s spectrum obtained from the as-prepared catalyst (not shown) contains features due to O-containing species includ-

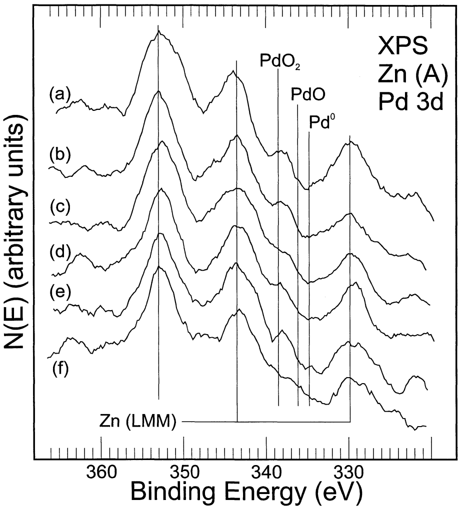

Fig. 2. XPS Pd 3d spectra obtained from the as-prepared 2.25 wt% K- and 5.9 wt% Pd-promoted Zn/Cr/Mn spinel catalyst after (a) insertion into the UHV surface characterization chamber, and exposure to 1×10^{-7} Torr of H_2 at (b) 90°C, (c) 100°C, (d) 200°C, (e) 325°C, and (f) sputtering for 38 min with 1 keV He^+.

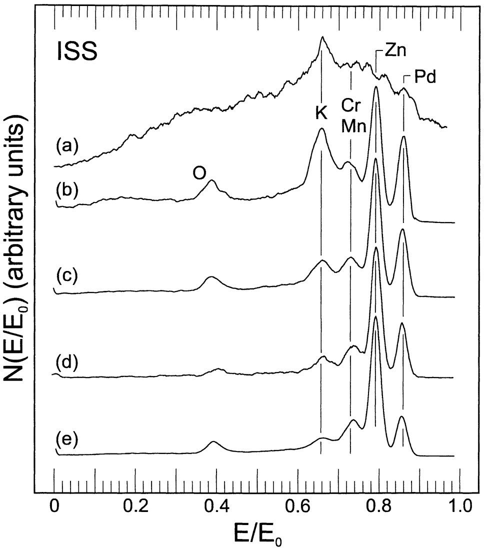

Fig. 3. ISS spectra obtained from the as-prepared 2.25 wt% K- and 5.9 wt% Pd-promoted Zn/Cr/Mn spinel catalyst after (a) insertion into the UHV surface characterization chamber, (b) exposure to 1×10^{-7} Torr of H_2 at 325°C, and sputtering with 1 keV He^+ for (c) 5, (d) 15 and (e) 38 min.

ing $CO_3^=$ and alcohols [19]. Hydrocarbon species are also present at the surface and contribute to the intensity of the peak centered at 285.0 eV. Due to the presence of several species, the C 1s peak shape is complex. Pd features have BE values which are near those of the Zn Auger (LMM) peaks as shown in Fig. 2(a). The Zn Auger features are labeled and lie at BE values of approximately 330, 343 and 353 eV. A Pd 3d feature is evident at 338.8 eV which corresponds to the presence of PdO_2 [20]. A very small feature at 336.4 eV due to PdO also may be present, but a detectable amount of metallic Pd is not present. The corresponding XPS K 2p spectrum does not exhibit any features attributable to K. The above results demonstrate that the as-entered catalyst consists predominantly of ZnO and small amounts of Zn hydroxide, $ZnCr_2O_4$, adsorbed water, PdO_2, PdO, Cr and some C contamination.

ISS is a powerful surface characterization technique for studying catalysts because it provides compositional information about the outermost atomic layer [19]. This is important because catalytic reactions occur at the outermost atomic layer. An ISS spectrum obtained from the as-prepared catalyst is shown in Fig. 3(a). The signal-to-noise ratio of this spectrum is relatively low and few distinct features are apparent. This is typical of an ISS spectrum obtained from a surface that is highly oxidized. The features which are evident are due to the presence of K and Pd, even though the Pd is not prominent and the K is not visible in the XPS data obtained from this sample. This seemingly contrary result is due to the differences in probing depths and sensitivity factors of these two techniques. ISS is sensitive only to the outermost atomic layer while XPS typically probes approximately 60 Å beneath the surface. Furthermore, the XPS signal contribution arising from the outermost layer is normally less than 10% of the total signal [19]. Therefore, the fractional monolayers observed using ISS may be below the detection limits in XPS for a given set of data collection parameters particularly if significant quantities of the same elements are not present in the subsurface region. The low, broad feature ranging from an E/E_0 of 0.20–0.40 is due to both C and O. These elements have very small ISS cross sections compared to the other elements present because their masses are relatively small [25]. This spectrum indicates that the outermost atomic layer of the as-prepared catalyst predominantly consists of O, K and Pd.

3.2.2. Effects of a reductive pretreatment

Since these catalysts are reduced in a 5% H_2 and N_2 mixture at 325°C prior to testing for HAS in the reactor, the as-prepared catalyst was given a reductive treatment and characterized. This process consisted of exposing the sample to a flowing H_2 stream at 1×10^{-7} Torr while heating the sample stepwise to 325°C and then maintaining this temperature for 4 h. The heating was done in steps in order to observe the changes which occur at the surface during the reduction. The step sizes were determined by monitoring the pressure in the UHV system during the temperature ramp. Since a pressure increase indicates the desorption of species from the catalyst surface, the surface was characterized after each desorption peak. The first desorption feature was observed at approximately 90°C. The XPS Zn 2p spectrum obtained after this treatment is shown in Fig. 1(A)(b). A significant increase in the signal is apparent at the high-BE portion of the spectrum. This is caused by an increase in the Zn hydroxide concentration in the near-surface region of the catalyst sample. Furthermore, the feature is slightly broader on the low-BE side due to an increase in the $ZnCr_2O_4$ species relative to the ZnO possibly because the thickness of the ZnO layer is decreased due to loss of water. The changes in the corresponding O 1s spectrum shown in Fig. 1(B)(b) are consistent with those of the Zn 2p feature. Increased signal contributions due to the presence of OH^- groups and $ZnCr_2O_4$ are evident as is a shoulder due to adsorbed water. A strong signal from the presence of ZnO remains. The increased surface concentrations of hydroxyl and adsorbed water species indicates that migration of these species from the subsurface region occurs more rapidly than desorption. A significant decrease in the near-surface carbon concentration occurs during this reductive treatment (not shown). According to the Pd 3d spectrum shown in Fig. 2(b), the chemical nature of the Pd is not significantly affected by the 90°C reductive treatment, but the Pd signal may be slightly decreased in intensity suggesting that it is covered by other species or agglomerates. The corresponding K 2p spectrum (not shown) contains no K or Na Auger features. Based on these data the species which desorb at 90°C from the surface of the catalyst most likely consists of C-containing contamination.

The next large increase in the background pressure occurred when the sample temperature reached 100°C. As shown in Fig. 1(A)(c), the amount of Zn hydroxide species is now significantly reduced although some is still present. A small decrease in the Zn/Cr spinel concentration also occurs during the treatment possibly through a redistribution of the ZnO film. The O 1s spectrum obtained after heating at 100°C is shown in Fig. 1(B)(c). The portion of the signal due to the presence of adsorbed water and hydroxyl species is significantly lower indicating that they desorb most likely as H_2O. Due to these decreases the peak position shifts towards the BE value of Zn in ZnO which remains as the predominant species in the near-surface region. As shown in Fig. 2(c), the amount of PdO_2 in the near-surface region is also decreased during the 100°C reductive treatment probably due to coverage by other species or agglomeration. Furthermore, the amount of carbon contamination is lowered again, and no K is present in the near-surface region after this step according to XPS.

The next desorption of species occurs at about 200°C, but the associated pressure increase is much smaller than those of the previous two desorption peaks. The Zn 2p spectrum obtained after the 200°C treatment is shown in Fig. 1(A)(d). Again, this reductive treatment removes more of the Zn hydroxide species from the near-surface region, and the near-surface $ZnCr_2O_4$ concentration is diminished further as well. Results from previous studies indicate that a layered structure exists at Zn/Cr catalyst surfaces after a reductive pretreatment is performed [6,7,24]. This structure consists of an alkali overlayer residing above an enriched ZnO layer which covers the Zn/Cr spinel support material. The XPS data presented in this study are consistent with these earlier results. The signal due to the presence of $ZnCr_2O_4$ is diminished which indicates that either the near-surface spinel is converted to ZnO by the reductive treatment or that it becomes more uniformly covered by ZnO. The O 1s spectrum obtained after the 200°C treatment in hydrogen is shown in Fig. 1(B)(d). Again, the near-surface hydroxyl group and adsorbed water concentrations are decreased. The amount of oxygen associated with the spinel is also diminished, which is consistent with the Zn 2p data discussed above. The corresponding Pd 3d spectrum shown in Fig. 2(d) contains a slightly increased Pd signal present as PdO_2. Although the lower temperature reductive treatments cause the near-surface XPS Pd signal to decrease, the 200°C treatment either induces migration of the Pd towards the surface or causes a redispersion of the Pd species across the surface or uncovers underlying Pd. The PdO_2 phase may be dispersed over the surface as discussed below. C is not present after this treatment. Similarly, the K 2p spectrum remains unchanged (not shown) in that no XPS signal due to the presence of K is apparent.

No significant increase in the pressure was observed between 200°C and 325°C so the corresponding XPS Zn 2p spectra shown in Fig. 1(A)(d) and (e) are quite similar as expected. A smaller amount of Zn hydroxide species may be present, but this is difficult to assess by these spectra. However, the corresponding O 1s spectrum does exhibit a smaller contribution at 532.5 eV due to a reduced amount of hydroxyl groups in the near-surface region. The spinel contribution at 531.1 eV is also reduced, but this may be influenced by the smaller hydroxyl feature and related matrix effects. No C 1s signal is apparent after this treatment. The Pd 3d spectrum obtained after the 325°C reductive treatment shown in Fig. 2(e) indicates that more PdO_2 is present in the near-surface region due to a rearrangement of the surface species and that a small amount of Pd metal is also present. A K 2p feature with a BE value of 293.5 eV is evident (not shown) after the 325°C reductive treatment. K_2CrO_4 and $K_2Cr_2O_7$ species have been observed previously in HAS catalyst studies [2], but K in these compounds have BE values of 292.6 [25] and 292.8 eV [26], respectively. Although a small amount of K may be bound as chromate or dichromate species, most is present in some other form possibly associated with the Zn or Pd. High-resolution Mn spectra were also obtained but no features are observed in these spectra. This result indicates that the amount of Mn contained in the near-surface region is below the XPS detection limits for the experimental parameters used. Mn was added to the catalyst formulation to determine if the hydrocarbon production rate would be lowered. This did occur to a small extent as noted above, but the increase in activity is more significant. Since the Mn is not observed in the near-surface region of these catalysts, the catalytic effect must be a long-range electronic field. The Cr 2p spectrum obtained from the pretreated catalyst is shown in Fig. 1(C)(a). A feature is evident with a BE of approximately 576.8 eV indicating the presence of Cr_2O_3 in the near-surface region [27]. Another feature is apparent at 578.1 eV which may be due to CrO_3 and/or chromate or dichromate species. Previous XPS results demonstrate that the amount of K in the near-surface region increases during the reductive pretreatment. Such an increase in the near-surface region K concentration is also observed in this study. The ISS spectrum obtained from the pretreated catalyst (Fig. 3(b)) contains a large feature due to the presence of K at the outermost atomic layer of the sample, and features due to O, Cr, Zn and Pd are evident also. The small Cr feature may contain a contribution from Mn since their masses are similar. Compared to spectrum a, the features in spectrum b are much better defined and the signal-to-noise ratio is significantly increased indicating that the reductive treatment produces a more electrically conductive surface [19].

3.2.3. *Depth profile*

A compositional depth profile was obtained from the pretreated catalyst by sputtering the sample with He^+ and taking ISS spectra at various intervals. The spectrum shown in Fig. 3(c) was obtained after sputtering with 1 keV He^+ for 5 min. The amount of K at the surface is significantly reduced relative to the other components indicating that the outermost surface region is enriched in this promotor. The Pd signal is also smaller relative to the Zn feature indicating that the Pd preferentially resides at or near the surface as well. Further sputtering results in further decreases in the Pd and K signal intensities as shown in Fig. 3(d) and (e) which were obtained after 15 and 38 min of sputtering with 1 keV He^+, respectively. The Zn:Cr ratio remains relatively constant indicating that they are uniformly distributed throughout the depth examined. The O signal also does not change significantly as expected. An XPS Zn 2p spectrum obtained after 38 min of He^+ sputtering is shown in Fig. 1(A)(f), and the corresponding O 1s spectrum is shown in Fig. 1(B)(f). They indicate a small loss in intensity of hydroxide signal, but no other differences are evident. The fact that the spinel feature is not enhanced indicates that the ZnO layer which covers the spinel is relatively thick or possibly that the sputtering process converts the spinel to ZnO and Cr oxides. The Pd 3d spectrum shown in Fig. 2(f) exhibits no signal due to Pd. This supports the assertion that the Pd lies at the surface after the reductive treatment. The K 2p spectrum obtained after the sputtering process contains no K signal again indicating that the small amount of K present lies near the surface. The corresponding Cr 2p spectrum is shown in Fig. 1(C)(f). The signal is now significantly increased in size and indicates that most of the Cr in the near-surface region is present as Cr_2O_3 and that less CrO_3 is present. Possibly the CrO_3 is reduced to Cr_2O_3 during the sputtering process or perhaps more CrO_3 resides near the surface with Cr_2O_3 beneath.

In a recent study [7] both K-promoted and Cs-promoted Zn/Cr spinel catalysts containing excess ZnO and 5.9 wt% Pd were tested for HAS. The K and Cs loadings were varied from 0 to 7 wt%. The catalyst with 5 wt% K and 5.9 wt% Pd but no Mn yields a total alcohol production rate of 190 g/kg h, an isobutanol production rate of 134 g/kg h, a methanol-to-isobutanol production rate of 0.71 and a conversion of 17% at 440°C and 1500 psig. This catalyst does not perform nearly as well as the similar catalyst in which some of the Cr has been replaced with Mn. Both of these catalysts have been characterized using XPS and ISS, and comparing the resulting data indicates that the presence of Mn results in differences in the chemical make-up of these surfaces. However, no significant differences are apparent in the XPS survey spectra. Comparison of the O 1s spectra indicates that the pretreated surface of the catalyst without Mn contains a very small hydroxyl group concentration relative to the pretreated catalyst surface with Mn. The Pd 3d features relative to the Zn Auger features are much smaller for the catalyst with Mn, but the Pd chemical-state distribution is similar for both catalysts both before and after pretreatment. A potentially significant difference is that the K and Cr are bound primarily as $K_2Cr_2O_7$ and K_2CrO_4 at the surface of the catalyst without Mn. Apparently, these compounds are not present in significant quantities of the catalyst containing Mn where most of the Cr is present as Cr_2O_3 and CrO_3. The corresponding ISS spectra also provide some interesting differences. No charging occurs for the catalysts containing Mn whereas significant charging occurs for the catalyst without Mn. This indicates that the electrical properties of these two surfaces are quite different due to the presence of Mn. The K feature from the catalyst without Mn is larger as expected as is the Pd feature. The latter is consistent with the XPS data. A well-defined O feature is present in the spectra from the catalyst with Mn, but it is not apparent in the spectra obtained from the catalyst without Mn. A Na contaminant feature is present in the previous study which is not present in this present study.

4. Summary

A 2.25 wt% K- and 5.9 wt% Pd-promoted Zn/Cr/Mn spinel catalyst and a 1.0 wt% K- and 9.0 wt% Pd-promoted Zn/Cr/Mn spinel catalyst were tested for HAS using a 1:1 and a 1:2 $CO:H_2$ syngas feedstream at two temperatures (400°C and 440°C) and two pressures (1000 and 1500 psig). This catalyst type was compared to similar catalysts studied previously which did not contain Mn. A motivation for this study was that the presence of Mn may lower the surface acidity and therefore result in smaller hydrocarbon byproduct rates. Of the reactor conditions tested, the higher temperature, 440°C, and higher pressure, 1500 psig, result in the largest isobutanol production rate. For the 2.25 wt% K- and 5.9 wt% Pd-promoted catalyst, 179 g/kg h of isobutanol are produced, but the largest amounts of hydrocarbon byproducts are also formed. Compared to similar catalysts tested previously, the addition of Mn results in a somewhat reduced hydrocarbon byproduct rate, but other factors also influence this rate. This catalyst with a total alcohol production rate of 304 g/kg h and a methanol-to-isobutanol mole ratio of 1.3 is the most active of all those tested previously and reported in the literature. The replacement of Cr with Mn clearly improves catalyst performance but this may be due to an increase in activity rather than a change in selectivity.

Surface characterization data indicate that the as-prepared catalyst contains primarily ZnO in the near-surface region, although some C-containing contamination and significant amounts of water and adsorbed hydroxyl groups are present. Pretreating the catalyst in 1×10^{-7} Torr of hydrogen in stages to 325°C results in the elimination of most of the carbon contamination at 90°C and most of the adsorbed water and hydroxyl groups at 100°C. The Pd and K XPS signal strengths are increased after the 325°C treatment. This could be due to the migration of these species to the surface, removal of species which cover the Pd and K or redistribution of the K- and Pd-containing species across the surface. A depth profile indicates that a layered structure exists after the reductive pretreatment consisting of an enriched K and Pd layer at the surface above a ZnO layer over the spinel support. CrO_3 and Cr_2O_3 states are also present, but spinel or K chromate or dichromate species are not observed. No Mn is apparent in the data indicating that the influence of the Mn on the catalyst performance does not simply involve replacement of surface Cr with Mn but may involve long-range electronic effects from subsurface Mn or a lessening of these effects from subsurface Cr.

References

[1] P. Forzatti, E. Tronconi, I. Pasquon, Catal. Rev.-Sci. Eng. 33 (1991) 109.
[2] W.S. Epling, G.B. Hoflund, D.M. Minahan, J. Catal. 169 (1997) 438.
[3] W.S. Epling, G.B. Hoflund, D.M. Minahan, J. Catal. 172 (1997) 13.
[4] G.B. Hoflund, W.S. Epling, D.M. Minahan, Catal. Lett. 45 (1997) 135.
[5] D.M. Minahan, W.S. Epling, G.B. Hoflund, Appl. Catal. A 166 (1998) 375.
[6] W.S. Epling, G.B. Hoflund, D.M. Minahan, J. Catal. 175 (1998) 175.
[7] D.M. Minahan, W.S. Epling, G.B. Hoflund, J. Catal. 179 (1998) 241.
[8] W.S. Epling, G.B. Hoflund, D.M. Minahan, Appl. Catal. A (1999) submitted for publication.
[9] A. Beretta, L. Lietti, E. Tronconi, P. Forzatti, I. Pasquon, Ind. Eng. Chem. Res. 35 (1996) 2154.
[10] E. Tronconi, N. Ferlazzo, P. Forzatti, I. Pasquon, Ind. Eng. Chem. Res. 26 (1987) 2122.
[11] J.G. Nunan, C.E. Bogdan, K. Klier, K.J. Smith, C.-W. Young, R.G. Herman, J. Catal. 116 (1989) 195.
[12] J.G. Nunan, R.G. Herman, K. Klier, J. Catal. 116 (1989) 222.
[13] J.M. Campos-Martin, J.L.G. Fierro, A. Guerrero-Ruiz, R.G. Herman, K. Klier, J. Catal. 163 (1996) 418.
[14] C.R. Apesteguia, B. DeRites, S. Miseo, S. Soled, Catal. Lett. 44 (1997) 1.
[15] F. Simard, U.A. Sedran, J. Sepulveda, N.S. Figoli, H.I. deLasa, Appl. Catal. 125 (1995) 81.
[16] P.K. Frolich, W.K. Lewis, Ind. Eng. Chem. 20 (1928) 354.
[17] P.K. Frolich, D.S. Cryder, Ind. Eng. Chem. 22 (1930) 1051.
[18] P. Forzatti, C. Cristiani, N. Ferlazzo, L. Lietti, E. Tronconi, P.L. Villa, I. Pasquon, J. Catal. 111 (1988) 120.
[19] G.B. Hoflund, in: J.C. Rivière, S. Myhra (Eds.), Handbook of Surface and Interface Analysis: Methods in Problem Solving, Dekker, NY, 1998, p. 57.
[20] C.D. Wagner, W.M. Riggs, L.E. Davis, J.F. Moulder, G.E. Muilenberg, Handbook of X-Ray Photoelectron Spectroscopy, Perkin-Elmer, Eden Prairie, MN, 1979.
[21] G.B. Hoflund, D.M. Minahan, W.S. Epling, J. Elect. Spectrosc. Rel. Phenom. 95 (1998) 289.
[22] C. Battistoni, J.L. Dormann, D. Fiorani, E. Paparazzo, S. Viticoli, Sol. State Commun. 39 (1981) 581.
[23] E. Tronconi, L. Lietti, P. Forzatti, I. Pasquon, Appl. Catal. 47 (1989) 317.
[24] W. Moser, K.E. Connoly, Chem. Eng. J. 64 (1996) 239.
[25] W.S. Epling, G.B. Hoflund, D.M. Minahan, Surf. Sci. Spect. 4 (1997) 161.
[26] W.S. Epling, G.B. Hoflund, D.M. Minahan, Surf. Sci. Spect. 4 (1997) 168.
[27] G.B. Hoflund, W.S. Epling, Thin Solid Films 307 (1997) 126.