Reaction and Surface Characterization Study of Higher Alcohol Synthesis Catalysts

VII. Cs- and Pd-Promoted 1 : 1 Zn/Cr Spinel

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A 1 : 1 Zn/Cr spinel catalyst promoted with 5.9 wt% Pd and 1, 3, or 5 wt% Cs has been tested for methanol and isobutanol synthesis using a 1 : 1 H_2 : CO syngas feedstream. The reactor was operated at two different temperatures (400 and 440°C) and two different pressures (1000 and 1500 psig). The higher temperature and pressure settings result in the highest isobutanol production rates over most of the catalysts examined. As the amount of Cs promotor is increased at 440°C and 1500 psig, the total alcohol production rate increases and the methanol-to-isobutanol ratio decreases. A maximum isobutanol production rate of 142 g/kg-h and a methanol-to-isobutanol mole ratio of 1.0 are attained using the 5.0 wt% Cs/ 5.9 wt% Pd-promoted Zn/Cr catalyst. Furthermore, the addition of 3 and 5 wt% Cs results in an increase in the selectivity to total alcohols. The addition of Pd to these catalysts enhances both the total alcohol production rate and isobutanol production rate compared to Cs-promoted Zn/Cr catalysts which do not contain Pd. Surface characterization studies using X-ray photoelectron spectroscopy (XPS) and ion scattering spectroscopy (ISS) were performed on the 5 wt% Cs/5.9 wt% Pd-promoted catalyst. The XPS and ISS data reveal that the fresh catalyst surface consists primarily of ZnO, $ZnCr_2O_4$, Cs_2O and a small amount of PdO_2. Since the catalysts are typically reduced before testing in the reactor, the catalyst sample was again characterized after a reductive pretreatment in 1×10^{-7} Torr of H_2 at 300°C for 4 h. This pretreatment results in removal of the carbon contamination, thereby exposing underlying ZnO, Cs, and Pd. Characterization studies were also performed on a 5 wt% Cs/5.9 wt% Pd-promoted catalyst which had been removed from the reactor after 5 days of testing. The XPS data indicate that the near-surface region remains enriched in Cs and Pd and that the PdO_2 present on the pretreated catalyst is converted to PdO during reaction. Apparently, the reaction process results in agglomeration of the ZnO film present on the reduced catalyst, which is the active catalytic phase in higher alcohol synthesis (HAS). © 1998 Academic Press

INTRODUCTION

Higher alcohol synthesis (HAS) has been extensively studied for direct production of fuel additives or the downstream production of methyl tertiary-butyl ether (MTBE), a common additive found in gasoline today. An ideal HAS catalyst for the downstream production of MTBE would catalyze syngas to an equimolar mixture of methanol and isobutanol with high selectivity. In previous studies the effects of K and Cs addition to a commercially available, Zn/Cr spinel, methanol synthesis catalyst have been examined (1, 2). Isobutanol production rates greater than 100 g/kg-h are obtained, and the addition of Cs proves to be more effective in lowering the methanol-to-isobutanol mole ratio and in increasing the isobutanol production rate compared to K. Surface characterization results demonstrate that the alkali promotors are bound to the Cr as chromate or dichromate species although the near-surface region of these catalysts consists primarily of ZnO. Based on these conclusions, a K-promoted ZnO powder was tested for HAS (3). Lower isobutanol production rates were obtained because the surface area of the ZnO powder is about 20% that of the spinel catalysts. Per unit of surface area, the 1 wt% K-promoted ZnO catalyst is superior to the Zn/Cr spinels for isobutanol production. In another study 1 : 1 Zn/Cr and 3 : 1 Zn/Cr spinel catalysts prepared in this laboratory were promoted with K and Cs and subsequently tested for HAS (4). When promoted with Cs, these samples result in greater isobutanol production, compared to the commercial spinel catalysts. However, the K-promoted catalysts are inferior to the K-promoted commercial Zn/Cr spinels. Furthermore, the presence of a greater amount of Cr generally leads to increased hydrocarbon production rates due to increased acidity (5). The increase in isobutanol production rate over the Cs-promoted, 1 : 1 Zn/Cr catalysts may be due to the difference in Zn : Cr weight ratio compared to the Cs-promoted Engelhard samples (3 : 1 Zn : Cr

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weight ratio) but is more likely caused by the method of preparation in which the pH of the precursor solution was carefully controlled. Of the catalysts tested, the 3 wt% Cs-promoted Zn/Cr spinel catalyst with excess ZnO yields the highest isobutanol production rate of 171 g/kg-h at 440°C and 1500 psig with a low methanol-to-isobutanol mole ratio of 1.4.

High productivities of isobutanol have been reported over a Zr/Zn/Mn/Pd/Li (30.5/8.6/15.4/0.2/1.5 wt%) catalyst by Keim and Falter (6). Based on this result, Pd (5.9 wt%) was added as a second promotor to the Cs-promoted Zn/Cr (1 : 1 Zn : Cr) spinel catalysts in this present study, and HAS reactor tests were performed. Two reactor operating pressures (1000 and 1500 psig) and two temperatures (400 and 440°C) were used, and the amount of Cs added was varied to determine the optimum Cs concentration. Surface characterization studies were also performed on the fresh, pretreated and aged catalyst which provides the best performance.

EXPERIMENTAL

The Zn/Cr support material was prepared using a mixture of Zn and Cr nitrate precursors dissolved in deionized water. 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. The remaining product was dried at 100°C in a vacuum oven, ground to 40 mesh, and analyzed to ensure that Na and K levels were below 300 ppm. X-ray diffraction (XRD) data indicate that the bulk of these samples consist of a $ZnCr_2O_4$ spinel phase. After calcining at 325°C in air, metal nitrate promotors (Pd and Cs) were added using the incipient wetness method. The reactor design and analysis of the product stream have been fully described previously (1). The reactor consists of a Cu-lined tube immersed in a fluidized sand bath. One gram of catalyst was used in each experiment, and 3 g of glass beads were added to disperse the catalyst. The feedstream was purified using an activated carbon trap, and the product stream was analyzed using a Varian 3700 gas chromatograph. Inorganic and organic products could be separated, and the organic analysis portion was calibrated to detect and quantify mixtures of C_1–C_6 normal hydrocarbons, normal and branched alcohols, and normal aldehydes. Before reaction the catalyst was given a reductive pretreatment in a 5% H_2-in-N_2 mixture at 1 atm and 300°C for 4 h. Each catalyst was tested for 5 days in the reactor, and no significant changes in the product stream composition were observed during this time period.

The experimental system for the characterization studies has been described previously as well (1). XPS and ISS were used to characterize the near-surface region and outermost atomic layer respectively of the catalysts. A Mg Kα source was used to generate the X-rays and the ISS parameters were set to minimize sputter damage. After the as-prepared catalyst was examined, a reductive pretreatment was performed *in situ* (300°C in 1×10^{-7} Torr of H_2 for 4 h) before examining again with XPS and ISS. Although the pretreatment gas pressure is lower in this case, the same chemical changes would most likely occur under these conditions, but the effect of pretreatment pressure has not been studied. A depth profile of this pretreated sample was also obtained. A catalyst sample which was removed from the reactor after 5 days on stream also was characterized before and after ion sputtering.

RESULTS AND DISCUSSION

Reactor Studies

Detailed listings of the product stream compositions obtained using a nonpromoted, 1 : 1 Zn/Cr spinel and 1, 3, and 5 wt% Cs-promoted, 5.9 wt%-Pd/Zn/Cr catalysts under the four sets of reaction conditions tested are shown in Table 1. The nonpromoted sample produces a small amount of isobutanol (8 g/kg-h) at 440°C and 1500 psig but primarily produces methanol. In all cases except for the 1 wt% Cs-promoted catalyst, the highest isobutanol production rates are obtained at the higher temperature and pressure settings of 440°C and 1500 psig. These parameters, however, also result in the largest hydrocarbon production rates. The selectivity (presented on a molar basis) is lowered by this increased production of hydrocarbons, which is a stronger function of reactor temperature than pressure. This is partly due to increased methanol production at the lower operating temperature as well. The total alcohol production rate is always greater at the higher pressure operating conditions. This is also true for the syngas conversion except for the nonpromoted catalyst. Although the highest isobutanol production rates occur at 440°C and 1500 psig, the lowest methanol-to-isobutanol ratios are attained at 440°C and 1000 psig for the Cs-promoted catalyst. Values less than 1.0 are very difficult to achieve, but as these data demonstrate, a ratio as low as 0.5 can be attained using these catalysts under the appropriate reactor conditions.

Trends of the product stream composition at 440°C and 1500 psig as a function of Cs loading are shown in Figs. 1 and 2. The total alcohol rate (Fig. 1a) increases monotonically from 16 to 227 g/kg-h as the Cs loading is increased from 0 to 5 wt%. Although the nonpromoted catalyst produces 161 g/kg-h of alcohols at these settings, methanol is the primary alcohol component (153 g/kg-h as shown in Fig. 1b). Upon the addition of 1 wt% Cs, the methanol production rate decreases to 60 g/kg-h and the isobutanol production rate increases from 8 to 90 g/kg-h. Promoting the 5.9 wt% Pd/Zn/Cr catalyst further with Cs results in even better performance. The 5 wt% Cs-containing sample also

TABLE 1

Zn/Cr Spinel Promoted

	0 wt% Cs + 0 wt% Pd				1 wt% Cs + 5.9 wt% Pd				3 wt% Cs + 5.9 wt% Pd				5 wt% Cs + 5.9 wt% Pd			
P (psig)	1000	1500	1500	1000	1000	1500	1500	1000	1000	1500	1500	1000	1000	1500	1500	1000
T ($°$C)	400	400	440	440	400	400	440	440	400	400	440	440	400	400	440	440
Selectivity to total alcohols (molar basis)	73	84	56	39	45	58	36	28	70	78	59	55	79	81	68	71
Total alcohol rate (g/kg-h)	117	248	161	71	133	280	196	77	166	292	207	117	168	279	227	187
Methanol rate (g/kg-h)	116	243	153	70	62	138	60	20	56	128	39	13	58	127	36	16
Ethanol rate (g/kg-h)	0	0	0	0	0	0	5	1	0	0	0	0	0	0	0	0
Isopropanol rate (g/kg-h)	0	0	0	1	3	4	14	3	3	4	7	8	7	7	13	12
n-Propanol rate (g/kg-h)	0	0	0	0	6	19	28	12	28	41	19	9	54	69	35	33
Isobutanol rate (g/kg-h)	1	5	8	0	62	119	90	41	80	120	142	87	49	75	142	126
MeOH/i-ButOH mole ratio	332	191	78	—	4.0	4.7	2.7	2.0	2.8	4.3	1.1	0.59	4.7	6.7	1.0	0.5
Hydrocarbon rate (g/kg-h)	21	24	63	53	103	128	228	136	48	52	102	70	30	40	77	57
Conversion (%)	9	10	9	10	15	19	19	14	13	15	23	11	13	21	22	14

catalyzes the synthesis of 142 g/kg-h of isobutanol and only 36 g/kg-h of methanol. This is a methanol-to-isobutanol mole ratio of 1.0; the ideal value for downstream MTBE production. The molar selectivity to total alcohols as a func-

tion of Cs loading is shown in Fig. 2a. The catalyst containing no Cs is 56% selective toward alcohol synthesis. Upon the addition of 1 wt% Cs, this selectivity drops to 36%. This decrease in selectivity results from a sharp increase in the
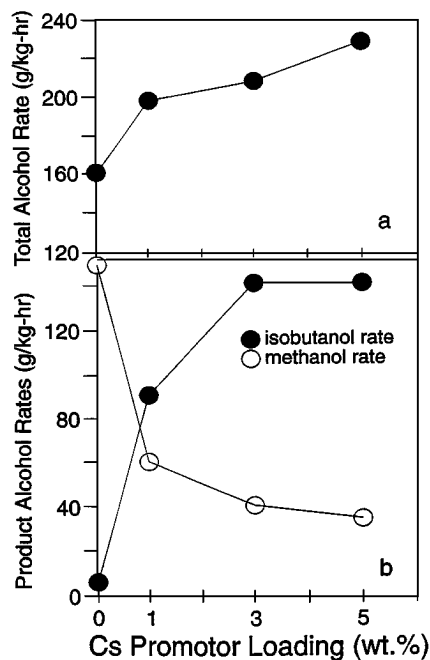

FIG. 1. Effect of Cs loading on (a) the total alcohol production rate and (b) the isobutanol and methanol production rates obtained at 440$°$C and 1500 psig.
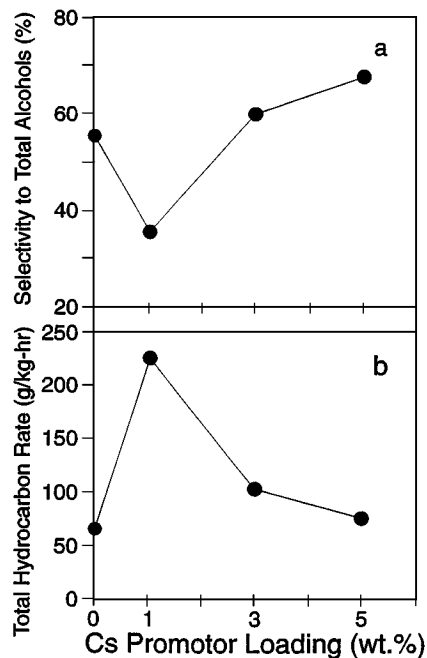

FIG. 2. Effect of Cs loading on (a) the selectivity to total alcohols and (b) the total hydrocarbon-byproduct rate obtained at 440$°$C and 1500 psig.

formation of hydrocarbon byproducts as shown in Fig. 2b. The further addition of 3 and 5 wt% Cs to the 5.9 wt% Pd/Zn/Cr catalyst causes the hydrocarbon byproduct rate to drop to 102 and 77 g/kg-h, respectively. These decreases in byproduct formation are mirrored by increases in the catalyst selectivity toward alcohol synthesis. A selectivity of 68% is achieved using the 5 wt% Cs-containing catalyst.

The addition of Pd to the Zn/Cr (1 : 1) catalysts represents an improvement over identical catalysts which do not contain Pd (4). Compared to these catalysts, the addition of Pd results in greater total alcohol production rates over all the catalysts tested except for the 5 wt% Cs-containing samples. For catalysts with and without Pd, the higher temperature and pressure operating parameters of 440°C and 1500 psig lead to the highest isobutanol production rates. At these reactor conditions higher isobutanol production rates are attained using the Pd-promoted catalysts leading to lower methanol-to-isobutanol mole ratios as well. Furthermore, except in the case of the 1 wt% Cs-containing samples, the selectivity to total alcohols is greater due to the presence of Pd. This is caused by significant differences in the hydrocarbon byproduct rates. Using the 3 wt% Cs/Zn/Cr catalyst, 77 g/kg-h more hydrocarbons are formed than over the Pd-containing catalyst, and over the 5 wt% Cs-containing catalyst, the amount of hydrocarbons formed is 35 g/kg-h greater, compared to the catalyst which contains Pd. Therefore, the addition of the Pd to Cs-promoted Zn/Cr results in improved HAS catalysts, due to the higher desired product yield and lower byproduct formation rate.

Characterization Studies

Since the highest isobutanol production rates and lowest methanol-to-isobutanol ratio are obtained using the 5 wt% Cs-containing, Pd/Zn/Cr catalyst, this sample was chosen for the surface characterization studies. An XPS survey spectrum taken from the as-prepared catalyst is shown in Fig. 3a. Features due to Zn, Cr, Cs, and O are apparent. A small peak due to the presence of C contamination is also observable. No distinct Pd 3d features are present, but the proximity of the Zn(LMM) peaks may interfere with the observation of these peaks. The catalysts are given a reductive pretreatment in order to activate the surface before the reaction feedstream is introduced. For this reason the catalyst was heated at 300°C in 1×10^{-7} Torr of H_2 for 4 h so that the effects of a reductive pretreatment could be examined. An XPS survey spectrum obtained from the pretreated catalyst is shown in Fig. 1b. The Zn 2p features are slightly decreased in height indicating that the near-surface region now contains less Zn. This is due primarily to the increase in concentration of the Cs as shown by the presence of large Cs 3d peaks. No significant changes in the peak heights associated with the Cr and O features are apparent, but a small Pd 3d feature can be observed. XPS survey spec-
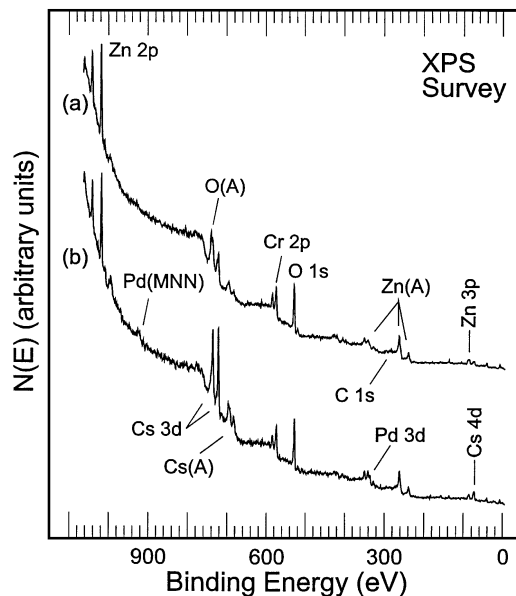

FIG. 3. XPS survey spectrum taken from the as-prepared, 5 wt% Cs/5.9 wt% Pd-promoted Zn/Cr spinel catalyst after (a) insertion into the UHV chamber and (b) pretreatment in 1×10^{-7} Torr of H_2 at 300°C for 4 h.

tra were also obtained from pretreated and sputtered, aged, and aged and sputtered samples. Only small differences in relative peak-heights are observable so these spectra are not shown.

ISS is a powerful surface characterization technique which yields compositional information about the outermost atomic layer. Although chemical state information cannot be obtained using this technique, the composition of the outermost surface layer is particularly important in catalysis since the reactions occur at the surface. Surface techniques such as XPS and Auger electron spectroscopy (AES) typically probe 30 or more atomic layers beneath the surface and less than 10% of the total signal originates from the outermost atomic layer (7, 8). Both techniques may provide chemical state identification, but it is quite difficult to separate the portion of the signal arising from the outermost surface from that which originates from beneath the surface so caution must be taken in relating XPS and AES data to catalytic reaction data. This is not the case for ISS data which usually differs from compositional results obtained from XPS and AES. Furthermore, catalyst surfaces typically are highly nonhomogeneous, and the use of the homogeneous assumption for calculating compositions from AES and XPS data usually results in unacceptably large errors (9–11).

An ISS spectrum obtained from the as-prepared catalyst is shown in Fig. 4a. The primary features present are due to Cs and O at the outermost atomic layer. The large background consisting of multiply scattered ions in this spectrum is due to the electrically insulating nature of this sample
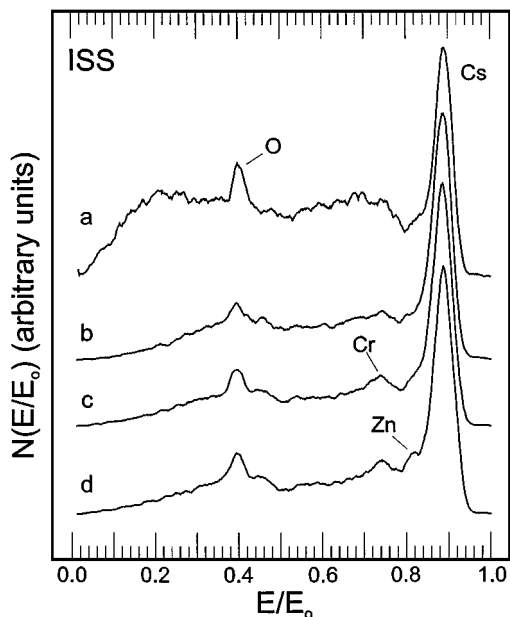
FIG. 4. ISS spectra obtained from the 5 wt% Cs/5.9 wt% Pd-promoted Zn/Cr spinel catalyst after (a) insertion into the UHV system, (b) pretreatment in 1×10^{-7} Torr of H_2 for 4 h at 300°C, (c) sputtering for 15 min with 1-keV Ar^+, and (d) sputtering for another 15 min with 1-keV Ar^+.

surface. More conductive surfaces neutalize ions more efficiently resulting in a less significant background. The cross sections in ISS increase with increasing mass so the Cs cross is considerably larger than that of O. An ISS spectrum taken from the catalyst after the reductive pretreatment is shown in Fig. 4b. The intensity of the oxygen feature is significantly diminished with respect to that of the Cs feature indicating that a considerable amount of oxygen is removed during the treatment from the outermost surface of the catalyst. Furthermore, the background is diminished indicating that the reduced surface is more electrically conductive. Small Zn and Cr features are evident as well due to the removal of some surface oxygen which was probably bound to the Zn and Cr. The ISS spectrum shown in Fig. 4c was taken after the pretreated catalyst was sputtered for 15 min with 1-keV Ar^+. The O feature is now larger and more well defined indicating that the reductive treatment discussed above produces O vacancies at the surface. The Zn and Cr features are increased relative to the Cs indicating that Cs is removed during the sputtering process. After sputtering the pretreated catalyst for an additional 15 min with 1-keV Ar^+, the ISS spectrum shown in Fig. 4d was taken. Again the Zn and Cr peaks are somewhat more pronounced as is the spectral background. These data suggest that the sputtering process removes Cs which is concentrated in the near-surface region along with O. No distinct Pd features are observable in these spectra. According to the binary elastic scattering equation, the Pd ISS peak has an E/E_o

value of approximately 0.87 while that of Cs is 0.89. Due to the closeness in spacing of the two features and the large amount of Cs at the surface according to XPS, a small Pd signal contribution may be present but impossible to discern. Also, the predominant peaks in Fig. 4 do have an E/E_o of 0.89, which corresponds to Cs, and they are quite similar in position and shape to those obtained from Cs-promoted Zn/Cr spinels which do not contain Pd (2). A close spacing of the heavier elements using He^+ as the primary ion is one of the limitations of ISS. This problem can be overcome by using Ne^+ as the primary ion although this results in greater surface damage due to the larger impacting ion mass and the decreased signal strengths thereby requiring a larger total dose to obtain an ISS spectrum.

An ISS spectrum obtained from the aged 5 wt% Cs-containing Pd/Zn/Cr catalyst after 5 days in the reactor and exposed to air is shown in Fig. 5a. The primary feature in the spectrum is Cs, and very small O and Zn peaks are apparent also. This spectrum differs from the spectrum obtained from the pretreated catalyst in that no Cr feature is evident and the intensity of the O feature is much smaller. Therefore, the reaction process alters the outermost surface layer of the catalyst. The ISS spectrum shown in Fig. 5b was taken after sputtering the sample for 15 min with 1-keV Ar^+. The Zn, Cr and O peaks are increased in size relative to the Cs feature indicating that the sputtering process removes the Cs promotor exposing the underlying Zn, Cr, and O. After an additional 15 min of sputtering with 1-keV Ar^+, the ISS spectrum shown in Fig. 5c was obtained. Both the Cr and
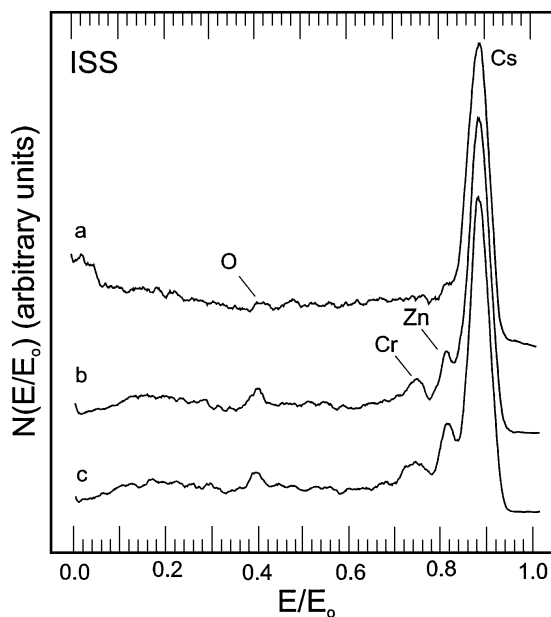

FIG. 5. ISS spectra obtained from the aged, 5 wt% Cs/5.9 wt% Pd-promoted Zn/Cr spinel catalyst after (a) insertion into the UHV system, (b) sputtering for 15 min with 1-keV Ar^+, and (c) sputtering for another 15 min with 1-keV Ar^+.

Zn features are further enhanced in size relative to the Cs feature. These sets of ISS spectra obtained from the fresh, pretreated, and aged catalyst samples form the basis for a qualitative model of the catalyst structure. The outermost atomic layer of the fresh and pretreated catalyst consists primarily of Cs and O, and this Cs layer is fairly thick. Zn and Cr along with O reside underneath this layer. The reaction process depletes the O in the outermost layer of the catalyst and spreads Cs across the surface covering the underlying Cr, Zn, and O. Identical sputtering processes were performed on both the pretreated and aged catalyst samples. However, in the spectrum obtained from the aged and sputtered catalyst (Fig. 5c) larger Zn and Cr features are present compared to those present in the ISS spectrum obtained from the pretreated and sputtered catalyst indicating that the Cs-rich surface layer is not as thick after aging in the reactor. This may be due to agglomeration of the Cs or loss of a volatile Cs species during reaction. Based on the discussion above, statements cannot be made regarding the location of the Pd.

An XPS Zn 2p spectrum taken from the as-prepared 5 wt% Cs-containing catalyst is shown in Fig. 6a. The dotted line is the Zn 2p spectrum obtained from 1 wt% K-promoted ZnO. This spectrum indicates that the Zn in the near-surface region is present mostly as ZnO, but the
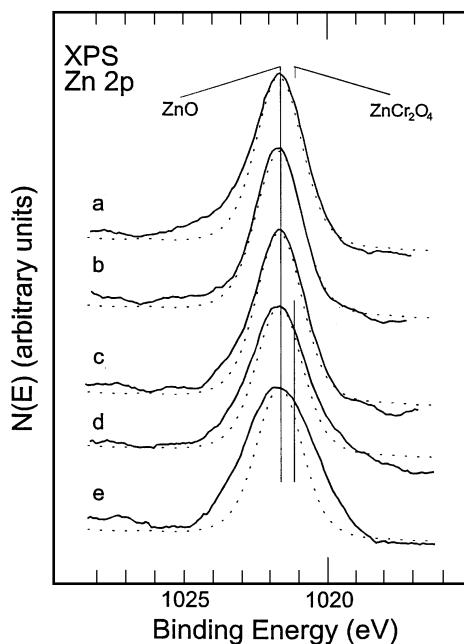
broadening on the high BE side is probably due to the presence of Zn-hydroxide. This assertion is consistent with the XPS O 1s data discussed below. The XPS spectra obtained from these surfaces are highly reproducible indicating that subtle differences between the spectra represents actual chemical-state differences. In previous studies (1, 2, 12, 13), ZnO was shown to be the only chemical state of Zn in the near-surface region of the as-prepared samples before and after a reductive pretreatment. The XPS Zn 2p spectrum shown in Fig. 6b was obtained from the catalyst after pretreatment in 1×10^{-7} Torr of H_2 at 300°C for 4 h. The widths of the peaks are diminished compared to those taken from the as-prepared sample due to a diminished influence by the Zn hydroxide feature. It has been shown that alkali-promoted ZnO is an active catalytic phase for HAS (3, 14). An XPS Zn 2p spectrum obtained after sputtering the pretreated catalyst for 30 min with 1-keV Ar$^+$ is shown in Fig. 6c. Again ZnO is the primary chemical state of Zn in the near-surface region, but the peak is broadened a little on both sides. The ion sputtering removes some of the ZnO layer. This places Zn : Cr spinel nearer the surface which results in a broadening on the low BE side of the ZnO feature. Apparently, subsurface hydroxyl groups and water are present which broadens the peak on the high BE side. The XPS Zn 2p spectrum shown in Fig. 6d was obtained from the aged catalyst. ZnO again is the primary state of Zn although the enhanced asymmetry present on the lower BE portion of the peaks indicate that $ZnCr_2O_4$ is present in the near-surface region also. This suggests that the ZnO film may agglomerate during reaction, thereby placing more of the spinel in the near-surface region where it is detected by XPS. Also, increased broadening on the high BE side indicates that more hydroxyl groups and water are present in the near-surface region. After sputtering the aged catalyst for 30 min with 1-keV Ar$^+$, the Zn 2p XPS spectrum shown in Fig. 6e was taken. A large contribution due to $ZnCr_2O_4$ is now present after sputtering much of the ZnO phase away. Both the pretreated and aged catalysts were given the same ion dose under identical sputtering conditions, but differing relative amounts of $ZnCr_2O_4$ and ZnO are evident in the near-surface regions of the two samples which lends further support to the assertion that the thickness of the ZnO-enriched layer is less on the aged catalyst.

An XPS O 1s spectrum obtained from the as-prepared catalyst is shown in Fig. 7a. As expected, a large amount of the oxygen present in the near-surface region is bound as ZnO. No O bound as Cs_2O species contributes to this spectrum, but an OH$^-$ signal and a H_2O signal are present which correspond to the presence of metal hydroxides (15) and adsorbed water. As shown in Fig. 7b, the reductive pretreatment eliminates most of the OH$^-$ and H_2O species in the near-surface region. A small Cs_2O feature is present indicating that CsOH may have decomposed to form Cs_2O and water which desorbs during the reductive treatment.

FIG. 6. High-resolution XPS Zn 2p spectra taken from the 5 wt% Cs/5.9 wt% Pd-promoted Zn/Cr spinel catalyst after (a) insertion into the UHV chamber, (b) pretreatment in 1×10^{-7} Torr of H_2 at 300°C for 4 h, (c) sputtering the pretreated sample for 30 min with 1-keV Ar$^+$, (d) insertion of the aged 5 wt% Cs/5.9 wt% Pd-promoted Zn/Cr spinel catalyst into the UHV chamber, and (e) sputtering the aged catalyst for 30 min with 1-keV Ar$^+$. The dotted Zn 2p spectrum, shown for comparison, was obtained from a 1 wt% K-promoted ZnO catalyst.
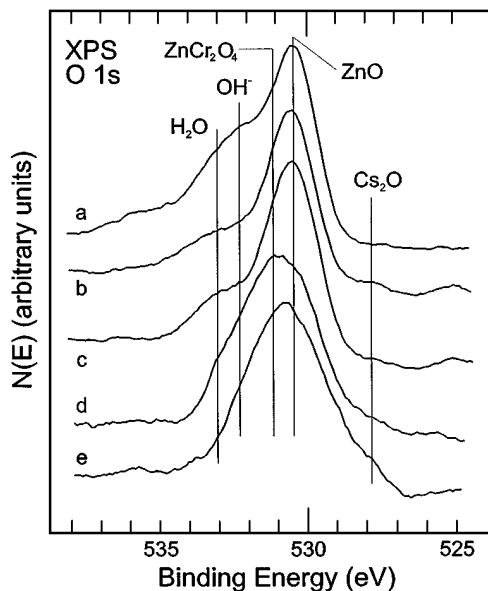
FIG. 7. High-resolution XPS O 1s spectra taken from the 5 wt% Cs/ 5.9 wt% Pd-promoted Zn/Cr spinel catalyst after (a) insertion into the UHV chamber, (b) pretreatment in 1×10^{-7} Torr of H_2 at 300°C for 4 h, (c) sputtering the pretreated sample for 30 min with 1-keV Ar^+, (d) insertion of the aged 5 wt% Cs/5.9 wt% Pd-promoted Zn/Cr spinel catalyst into the UHV chamber, and (e) sputtering the aged catalyst for 30 min with 1-keV Ar^+.

Cs_2O is typically not considered to be a stable species under a reductive environment but may be stabilized at the surface by the ZnO. The XPS O 1s spectrum shown in Fig. 7c was taken after sputtering the pretreated catalyst for 30 min with 1-keV Ar^+. The OH^- signal and H_2O signal are increased in intensity indicating that the reductive pretreatment does not completely eliminate OH^- or H_2O from the subsurface region, although most of the oxygen is still bound as ZnO. An XPS O 1s spectrum obtained from the aged catalyst sample after 5 days of use in the reactor is shown in Fig. 7d. Although much of the oxygen is bound as ZnO, the O 1s peak is broadened indicating the presence of additional chemical states of oxygen. The O 1s feature of $ZnCr_2O_4$ has a BE of 531.2 eV (16) which is consistent with the interpretation of the Zn 2p spectra in that O in spinel contributes to this spectrum. A greater concentration of OH^- groups and H_2O are present as well as Cs_2O. During the reaction process, OH groups accumulate at the surface as expected since alcohols are the reaction products. Water may accumulate since it is a product of the water–gas shift reaction which occurs simultaneously during the reaction process as well. After sputtering the aged catalyst for 30 min with 1-keV Ar^+, the relative amounts of OH^- and H_2O are decreased as shown in Fig. 7e. A larger signal arises from Cs_2O indicating that this Cs state resides in the subsurface region of the aged catalyst which may explain its presence or that it forms during ion sputtering. O in a spinel state is still prominent as expected, and the shift toward ZnO suggests that ion

sputtering the spinel may cause decomposition to ZnO and possibly $Cr(OH)_x$ as discussed below. No O 1s features due to Cs_2CrO_4 and $Cs_2Cr_2O_7$ are apparent in Fig. 10. K_2CrO_4 and $K_2Cr_2O_7$ have O 1s BEs of 530.3 and 530.5 eV, respectively (17, 18), and the O 1s values for the corresponding Cs compounds are most likely similar. These values are close to that of ZnO so these smaller features cannot be discerned.

A high-resolution Cr 2p XPS spectrum obtained from the as-prepared 5 wt% Cs-containing catalyst is shown in Fig. 8a. A mixture of Cr chemical states is present which is primarily comprised of $ZnCr_2O_4$ (16) and possibly some Cr_2O_3 (19). $Cs_2Cr_2O_7$ (20) and possibly CrO_3 species are present as well. Cs_2CrO_4 has a BE value very similar to that of $Cs_2Cr_2O_7$ and may be present also. Chromium hydroxide is also evident which contributes to the OH^- signal present in the corresponding O 1s spectrum (Fig. 7a). After the catalyst was pretreated in 1×10^{-7} Torr of H_2 at 300°C for 4 h, the Cr 2p XPS spectrum shown in Fig. 8b was taken. Less $ZnCr_2O_4$ is now present in the near-surface region which coincides with the decreased $ZnCr_2O_4$ signal in the corresponding Zn 2p spectrum (Fig. 6b). Cr is now bound predominantly as $Cr(OH)_x$, and an increased contribution by Cs_2CrO_4 or $Cs_2Cr_2O_7$ is evident. Although a reductive treatment from a thermodynamic standpoint would tend to decrease the possibility of the formation or presence of the chromate species, these states apparently are stabilized in this catalyst either by the alkali promotor or the ZnO
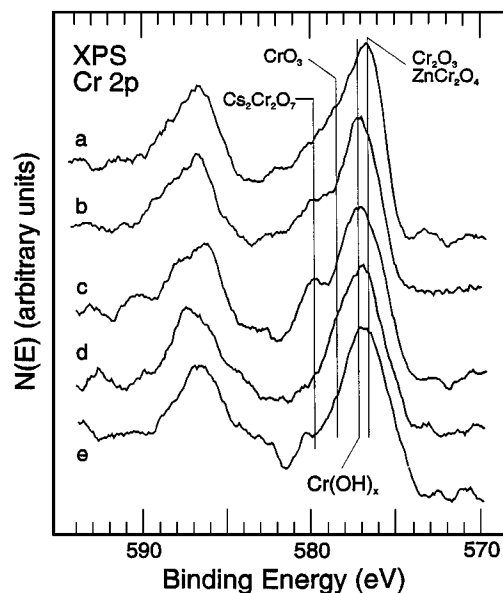

FIG. 8. High-resolution XPS Cr 2p spectra taken from the 5 wt% Cs/5.9 wt% Pd-promoted Zn/Cr spinel after (a) insertion into the UHV chamber, (b) pretreatment in 1×10^{-7} Torr of H_2 at 300°C for 4 h, (c) sputtering the pretreated sample for 30 min with 1-keV Ar^+, (d) insertion of the aged 5 wt% Cs/5.9 wt% Pd-promoted Zn/Cr spinel catalyst into the UHV chamber, and (e) sputtering the aged catalyst for 30 min with 1-keV Ar^+.
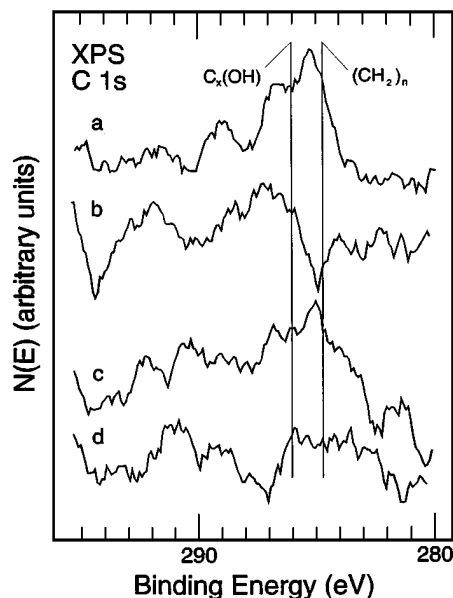
FIG. 9. High-resolution XPS C 1s spectra taken from the 5 wt% Cs/5.9 wt% Pd-promoted Zn/Cr spinel catalyst after (a) insertion into the UHV chamber, (b) pretreatment in 1×10^{-7} Torr of H_2 at 300°C for 4 h, (c) insertion of the aged 5 wt% Cs/5.9 wt% Pd-promoted Zn/Cr spinel catalyst into the UHV chamber, and (d) sputtering the aged catalyst for 30 min with 1-keV Ar^+.

phase. Significantly more Cs_2CrO_4 or $Cs_2Cr_2O_7$ is present in the subsurface region of the pretreated catalyst as shown in Fig. 8c which was obtained after a 30-min sputter treatment with 1-keV Ar^+. Furthermore, the sputtering process exposes some underlying $ZnCr_2O_4$. In a previous study of the Cs-promoted, commercially available Zn/Cr spinel catalyst (2), most of the near-surface Cr is bonded to the Cs promotor. The catalyst used in this study, however, contains a larger amount of Cr (1 : 1 Zn : Cr vs 3 : 1 Zn : Cr) so an excess of Cr relative to the Cs is present in the near-surface region, resulting in the presence of other chemical states of Cr. A Cr 2p spectrum obtained from the aged catalyst is shown in Fig. 8d. Much less chromate or dichromate is present indicating that the reaction process eliminates this state of Cr. Furthermore, the amount of CrO_3 is increased after 5 days in the reactor. After sputtering the aged catalyst for 30 min with 1-keV Ar^+, the Cr 2p XPS spectrum shown in Fig. 8e was taken. The amount of CrO_3 is diminished somewhat, and the shoulder due to $ZnCr_2O_4$ is more prominent as expected. Other changes are not apparent indicating that the Cr species distribution in the near-surface and subsurface regions of the aged catalyst material are similar. Changes in the chemical states of Cr may occur after the catalyst is removed from the reactor, exposed to air, and transferred to the analysis chamber. The somewhat homogeneous distribution of the Cr states as a function of depth, however, indicate that the Cr states identified are present in the catalyst after 5 days in the reactor.

An XPS C 1s spectrum obtained from the as-prepared 5 wt% Cs/5.9 wt% Pd-promoted Zn/Cr catalyst using the same scanning parameters as the other elements is shown in Fig. 9a. Very little C contamination is evident, although small signals from hydrocarbon and alcohol contamination are observable. This indicates that this catalyst surface is relatively inert to the adsorption of carbon-containing compounds from air at room temperature. The reductive pretreatment eliminates this contamination as shown in Fig. 9b exposing more of the active catalyst surface. According to the C 1s XPS spectrum obtained from the aged catalyst surface (Fig. 9c), very little C buildup occurs during the reaction process. The C 1s spectrum obtained from the aged catalyst material after 30 min of sputtering with 1-keV Ar^+ and shown in Fig. 9d indicates that the small amount of carbon present at the surface of the aged catalyst is removed by this treatment. The fresh K-promoted Zn/Cr spinel catalysts also exhibit low C levels. However, these catalysts have high levels after aging. This may provide insight as to why Cs is a better promotor than K for these catalysts.

A high-resolution XPS Cs 3d spectrum obtained from the as-prepared catalyst is shown in Fig. 10a. Cs_2CrO_4 and CsOH and/or $Cs_2Cr_2O_7$ species contribute to this spectrum (15, 20). The feature with a BE of 727.9 eV is a Cr(LMV) peak, and the feature with a BE of about 742 eV is an O(MNN) peak (15). After pretreating the catalyst in 1×10^{-7} Torr of H_2 at 300°C for 4 h, the Cs 3d spectrum
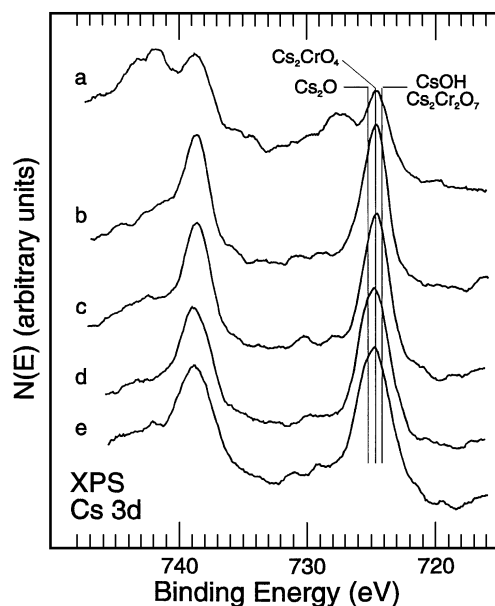

FIG. 10. High-resolution XPS Cs 3d spectra taken from the 5 wt% Cs/5.9 wt% Pd-promoted Zn/Cr spinel after (a) insertion into the UHV chamber, (b) pretreatment in 1×10^{-7} Torr of H_2 at 300°C for 4 h, (c) sputtering the pretreated sample for 30 min with 1-keV Ar^+, (d) insertion of the aged 5 wt% Cs/5.9 wt% Pd-promoted Zn/Cr spinel catalyst into the UHV chamber, and (e) sputtering the aged catalyst for 30 min with 1-keV Ar^+.

shown in Fig. 10b was taken. Consistent with the survey spectra shown in Fig. 3, the reductive pretreatment results in an increase in the near-surface concentration of Cs which accounts for the enhanced signal-to-noise ratio of this spectrum in Fig. 10. The primary chemical state of the Cs is Cs_2CrO_4. $Cs_2Cr_2O_7$ is present according to the corresponding Cr 2p spectrum shown in Fig. 8b, and some CsOH may be present also. The Cs 3d spectrum shown in Fig. 10c was obtained after sputtering the pretreated sample for 30 min with 1-keV Ar^+. The peaks are not changed indicating that the Cs in the near-surface and subsurface regions are of similar chemical states. The Cs 3d spectrum obtained from the aged catalyst (Fig. 10d) closely resembles that taken from the pretreated catalyst except that a larger contribution due to CsOH is present. This is consistent with the corresponding O 1s spectrum. According to the corresponding Cr 2p spectrum, less $Cs_2Cr_2O_7$ is present. Another unidentified state of Cs with a BE of 723.0 eV also is present. After sputtering the aged sample for 30 min with 1-keV Ar^+, the XPS Cs 3d spectrum shown in Fig. 10e was taken. A larger contribution from Cs_2O is again evident which corresponds to the increased Cs_2O signal in the O 1s spectrum as well (Fig. 7e). Compared to the pretreated catalyst, these spectra and those in Figs. 7 and 8 indicate that the near-surface region of the aged catalyst contains a significant enrichment of Cs(OH) and Cs_2O relative to $Cs_2Cr_2O_7$.

A high-resolution XPS spectrum of the Pd 3d BE region obtained from the as-prepared catalyst is shown in Fig. 11a.
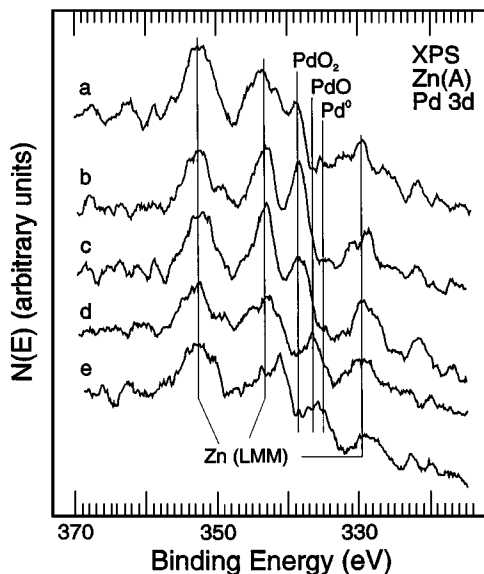

FIG. 11. High resolution XPS Zn (A) and Pd 3d spectra taken from the 5 wt% Cs/5.9 wt% Pd-promoted Zn/Cr spinel after (a) insertion into the UHV chamber, (b) pretreatment in 1×10^{-7} Torr of H_2 at 300°C for 4 h, (c) sputtering the pretreated sample for 30 min with 1-keV Ar^+, (d) insertion of the aged 5 wt% Cs/5.9 wt% Pd-promoted Zn/Cr spinel catalyst into the UHV chamber, and (e) sputtering the aged catalyst for 30 min with 1-keV Ar^+.

Zn(LMM) features are observed in this spectrum as well. The chemical state of the Pd in the near-surface region of the fresh catalyst is PdO_2 (15), and no PdO or Pd metal features are apparent. After pretreating the fresh catalyst in 1×10^{-7} Torr of H_2 at 300°C for 4 h, the XPS spectrum shown in Fig. 11b was taken. The PdO_2 feature is increased in size relative to the Zn(LMM) peaks, and a small shoulder due to PdO is present as well. Previous research on Pd-supported catalysts (21, 22) has demonstrated that a room-temperature reductive treatment can reduce certain Pd oxide structures to Pd metal when supported on alumina while another PdO-type species is more stable. This does not occur in the present study during the reductive pretreatment suggesting that PdO_2 is stabilized by ZnO and/or Cs. Sputtering the pretreated catalyst material results in a relative decrease in the size of the Pd feature as shown in Fig. 11c. These data indicate that the reductive pretreatment causes an enrichment of Pd in the near-surface region. Furthermore, this enriched Pd region is at or very near the catalyst surface since a smaller amount is present after sputtering. The Pd 3d XPS spectrum obtained from the aged catalyst is shown in Fig. 11d. Compared to the spectrum taken from the pretreated catalyst (Fig. 11b), the amount of Pd relative to the Zn apparently is somewhat diminished. This may be due to agglomeration of the Pd. Also, the chemical state of the Pd is changed from PdO_2 to PdO. After sputtering the aged catalyst for 30 min with 1-keV Ar^+, the amount of Pd is decreased further again indicating that the near-surface region is enriched in Pd relative to the subsurface region of the catalyst. The extent of decrease is smaller in this case supporting the assertion that the PdO forms and agglomerates during reaction.

CONCLUSIONS

A 1 : 1 Zn : Cr spinel promoted with 5.9 wt% Pd and various amounts of Cs ranging from 0 to 5 wt% have been tested for higher alcohol synthesis. The best reactor operating conditions of those examined for the 3 and 5 wt% Cs-containing catalysts are 440°C and 1500 psig. The total alcohol production rate increases with increasing Cs loading while the methanol-to-isobutanol mole ratio decreases. A methanol-to-isobutanol mole ratio of 1.0, which is ideal for downstream MTBE synthesis, is obtained using the 5 wt% Cs catalyst, and 142 g/kg-h of isobutanol is produced. Surface characterization studies demonstrate that the near-surface region of the fresh catalyst material is composed of a complex mixture of ZnO, $ZnCr_2O_4$, Cs_2CrO_4, $Cs_2Cr_2O_7$ and small amounts of PdO_2 and carbon contamination. A reductive pretreatment eliminates the carbon, reduces the O content of the outermost atomic layer, and significantly increases the near-surface Cs and Pd contents. This pretreated catalyst contains a Cs_2CrO_4, PdO_2, and ZnO enriched layer over a Pd-depleted layer which contains greater amounts

of $ZnCr_2O_4$ spinel material. The thickness of the promotor-enriched layer decreases during the reaction process, and the chemical state of the Pd changes from PdO_2 to PdO. However, the catalyst activity does not change during the 5-day period tested.

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