Study of Cs-Promoted, α-Alumina-Supported Silver, Ethylene-Epoxidation Catalysts

IV. Model Study

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In an attempt to gain a better understanding of the structure of ethylene epoxidation catalysts and the role of the Cs promotor, a model study using Al and Ag foils was performed. Air-exposed Al and Ag foils were dipped into a 400 ppm CsOH solution, rinsed with distilled H_2O, and characterized using X-ray photoelectron spectroscopy (XPS). The data indicate that Cs readily adsorbs at the Al_2O_3 surface on the Al foil. Very little Cs adsorbs to the Ag foil which contains a thin oxide film at the surface. A sputter-cleaned Ag foil (oxide free), however, adsorbs significant quantities of CsOH indicating that the Cs bonds to a Ag metal surface but not to Ag oxide. Characterization studies were also performed on two Al foils: one which was dipped into a heated, 85% lactic acid solution containing dissolved Ag_2O and the other which was dipped into an identical solution but containing CsOH as well. XPS and ion scattering spectroscopy data show that the Al foil does not adsorb Ag from the solution unless the CsOH is present. Furthermore, the XPS data indicate that there is a chemical interaction (electronic effect) between the Al, Cs, and Ag. These results support the conclusion of the previous part of this study that one of the roles of the Cs is to act as a binder between the Ag and alumina support in ethylene epoxidation catalysts.   © 1997 Academic Press

INTRODUCTION

The epoxidation of ethylene to ethylene oxide is an important industrial process. Ethylene oxide is produced commercially through the partial oxidation of ethylene using oxygen or air over a catalyst material consisting of silver supported on low-surface area, α-alumina (1). Cs is usually added to the catalysts to improve the selectivity toward epoxidation (2–5). This selectivity enhancement apparently has not been examined systematically. Lambert and co-workers (6, 7) and Campbell (8, 9) have studied the influence of the Cs addition on the Ag(111): there is an electronic effect on the Ag by the Cs. Campbell (8) has identified a surface cesium oxide species (CsO_3) which exists in islands and decomposes at about 610 K to form gaseous Cs and O_2.

Some of the Cs migrates into the bulk Ag during reaction. Although this model system is very different than the actual industrial catalyst surfaces, it is reasonable to expect that the presence of Cs influences the electronic properties of the Ag in real catalysts also. Further support for a Cs-induced electronic effect has been provided by Monnier regarding the epoxidation of butadiene to epoxybutene (10, 11). In this case the Cs promotors significantly increase the rate of product formation. Recent studies concerning the effects of Re (12) and Cs (13) addition to $Ag/\alpha\text{-}Al_2O_3$ suggest that these promotors increase the epoxidation selectivity possibly through weakening the Ag–O bond or through the stabilization of defect regions.

Another possible cause for the selectivity enhancement due to the addition of Cs has been observed in previous parts of this study by Hoflund and co-workers (14–16). The presence of the Cs causes the Ag to completely cover the support material on the catalyst (14), and the surface characterization data indicate that the Cs is not apparent in the near-surface region until the catalyst is aged under reaction conditions (15). The Cs becomes observable as the Ag agglomerates into large crystallites leaving the $\alpha\text{-}Al_2O_3$ support with Cs at the surface exposed. Furthermore, depth profiles of the fresh Cs-promoted $Ag/\alpha\text{-}Al_2O_3$ catalyst indicate that the Cs primarily lies in the subsurface region although a small amount is present at the catalyst surface (16). This evidence indicates that the Cs also acts as a binder between the Ag and $\alpha\text{-}Al_2O_3$ support, possibly through creating or stabilizing the bond between the two phases.

This present model study was performed in an effort to gain further understanding of the role of Cs as a promotor in ethylene epoxidation catalysts. Air-exposed Al and Ag foils and a sputter-cleaned Ag foil were dipped into a CsOH solution, rinsed with distilled H_2O, and then characterized with X-ray photoelectron spectroscopy (XPS) and ion scattering spectroscopy (ISS) in order to examine the adsorption behavior of Cs onto the two constituents of the

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catalysts. Also, an Al foil was dipped into a lactic acid solution containing dissolved Ag_2O powder only and a lactic acid solution containing both CsOH and dissolved Ag_2O powder to determine the effects of Cs on the adsorption of Ag by Al_2O_3. These foils were also characterized using XPS and ISS.

EXPERIMENTAL

The high-purity Al and Ag foils were purchased from the Materials Research Corporation. The CsOH was purchased as an aqueous solution (50 wt%) from Alfa AESAR. In the first set of experiments, the as-received Al and Ag foils were dipped into separate 400-ppm-by-weight CsOH solutions at room temperature for 1 min. They were then removed and rinsed in a stream of distilled H_2O. These two samples were then inserted into an ultra-high vacuum (UHV) system (base pressure $<10^{-10}$ Torr) and characterized using XPS and ISS. The details of the characterization techniques are discussed below. The Ag foil was then sputter-cleaned using 2-keV Ar^+ for 2 h. The He^+ ISS spectrum obtained from this sample indicates that no O or C was present at the surface. This foil was then removed and quickly dipped into another 400-ppm-CsOH solution for 1 min, rinsed, reinserted into the UHV chamber, and recharacterized.

In the second set of experiments, two separate Al foils were prepared in a similar manner based on a patent by Bhasin *et al.* (17). A 50-ml lactic acid solution (85 wt%) was heated to 80°C. Ag_2O powder (1.0 g) was then added to the heated solution during stirring to dissolve the powder. An Al foil was placed in this solution for 5 min, rinsed with distilled H_2O, inserted into the UHV chamber, and characterized. Another Al foil was dipped into an identical solution except that 3 ml of the 50 wt% aqueous CsOH had been added to the lactic acid with the Ag_2O powder.

XPS and ISS data were both collected using a double-pass cylindrical mirror analyzer (CMA) (Phi model 25-270AR) and pulse counting detection (18). XPS data were obtained first by operating the CMA in the retarding mode using a 50-eV pass energy for the survey spectra and a 25-eV pass energy for the high-resolution spectra. The X-rays were generated using a Mg $K\alpha$ anode X-ray source. An ISS spectrum was collected in 66 s while the CMA was operated in the nonretarding mode using a 148° scattering angle and 1-keV He^+. The 33 nA ion flux was defocused over an area of 5 mm in diameter. These conditions result in minimal damage due to the ion sputtering process.

RESULTS AND DISCUSSION

An XPS survey spectrum taken from the air-exposed Al foil after dipping in a 400-ppm CsOH solution and rinsing with distilled H_2O is shown in Fig. 1a. While the Al foil is
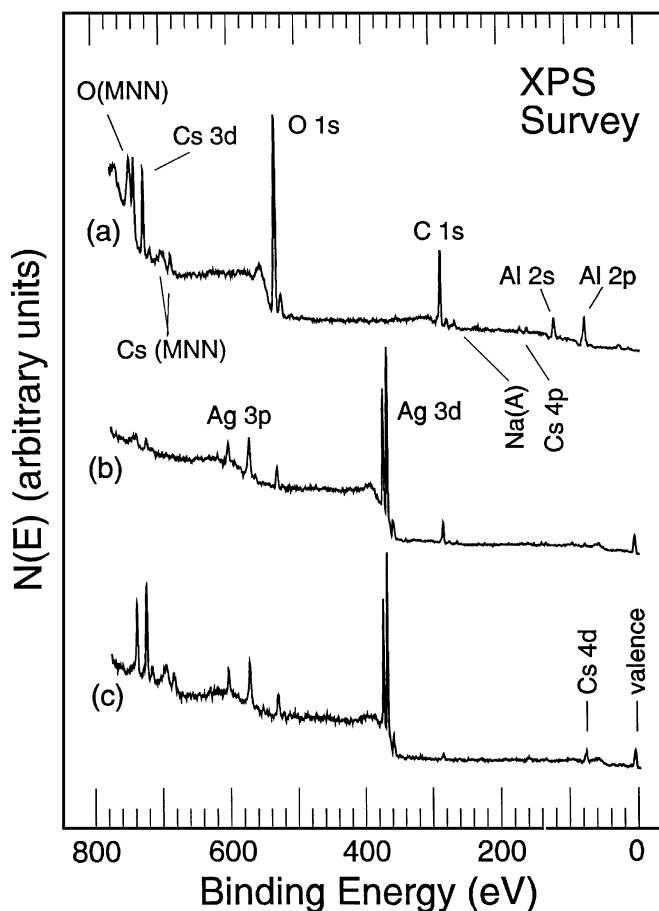

FIG. 1. XPS survey spectra obtained from (a) an air-exposed Al foil, (b) an air-exposed Ag foil, and (c) a sputter-cleaned Ag foil, all of which were dipped into a 400-ppm aqueous CsOH solution at room temperature, rinsed with distilled H_2O, and dried.

immersed in the CsOH solution, small bubbles form at the surface indicating that a reaction occurs during this process. The spectrum shown in Fig. 1a contains large C $1s$ and O $1s$ peaks which are typical of air-exposed Al foils (19, 20), as well as a small Na feature. Large Cs peaks and the Al $2p$ and Al $2s$ features are present also. These data indicate that the near-surface region of the Al foil contains significant quantities of carbon contamination, oxygen, and cesium due to the exposure to the solution. Although a substantial amount of contamination is present in the near-surface region of the Al foil, the Cs readily adsorbs to this surface. A high-resolution XPS Cs $3d$ spectrum obtained from the CsOH-dipped Al foil is shown in Fig. 2a. The predominant Cs $3d_{5/2}$ feature has a binding energy (BE) value of 724.2 eV which is near the value for CsOH (21). Features are also apparent at BE values of 722.7 and 724.9 eV, with the latter possibly corresponding to Cs_2O (22) or an Al/O/Cs interaction. No assignments for the lower BE feature could be found in the literature. However, lower BE values typically, but not always, denote a chemical state less
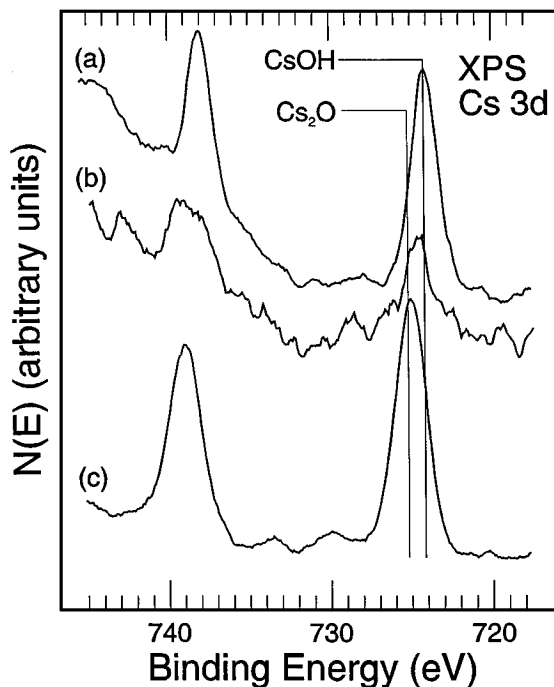
FIG. 2. XPS Cs 3*d* spectra obtained from (a) an air-exposed Al foil, (b) an air-exposed Ag foil, and (c) a sputter-cleaned Ag foil, all of which were dipped into a 400-ppm aqueous CsOH solution at room temperature, rinsed with distilled H_2O, and dried.

oxidic in nature. The possibility of Cs metal being present is very small, but the Cs may be weakly bound to the Al through O.

An XPS survey spectrum taken from the air-exposed Ag foil after being dipped into a 400-ppm CsOH solution and rinsed in distilled H_2O is shown in Fig. 1b. Ag, C, O, and small Cs features are apparent. The XPS survey spectrum which was taken from a sputter-cleaned Ag foil which underwent the same CsOH treatment is shown in Fig. 1c. A smaller C 1*s* feature is present and much larger Cs 3*d* peaks are observable. Cs readily adsorbs onto the Al foil with large amounts of carbon contamination present, but does not adsorb onto the air-exposed Ag foil which contains less carbon contamination. Therefore, the carbon contamination apparently does not inhibit the adsorption of Cs. The Cs does adsorb onto the sputter-cleaned surface. As shown in Figs. 3a and 3b, no significant differences are noticeable between the Ag 3*d* XPS features obtained from these two foils. The BE values of these peaks correspond to Ag metal (23), as expected. If, however, a thin oxide layer were present (~2 Å), it would be difficult to detect using XPS because XPS probes deeply beneath the surface (~60 Å), the fact that less than 10% of the XPS signal originates from the outermost atomic layer (24), and the fact that the Ag 3*d* BEs for Ag metal and oxides are closely spaced.

An XPS O 1*s* spectrum obtained from the air-exposed Ag foil after being dipped in the CsOH solution is shown in

Fig. 4a. The feature is centered at a BE value of 532 eV. The contributions to this signal most likely arise from adsorbed H_2O at approximately 533.2 eV, OH^- groups at 531.5 eV, and carbon and oxygen-containing contamination at the foil surface. Small O 1*s* features due to oxygen bound as AgO (25) and Ag_2O (26) are evident as well. The presence of the small feature due to silver oxide verifies the assertion that an oxide resides at the foil surface. These data indicate that Cs does not readily adsorb on silver oxide at room temperature under the conditions used. An XPS O 1*s* spectrum obtained from the sputter-cleaned Ag foil after it was dipped in a CsOH solution is shown in Fig. 4b. No feature due to the presence of AgO is evident and only a small shoulder due to Ag_2O is observable. Adsorbed H_2O is present which may remain from the rinsing process. The primary peak now has a BE value of 531.3 eV which most likely is due to the presence of OH^- groups adsorbed on the Ag or associated with the CsOH. Furthermore, a small feature at approximately 527.5 eV is evident which has been assigned previously to Cs_2O (27). This small peak is not large enough to account for the large Cs 3*d* feature shown in Figs. 1c and 2c. Therefore, only a portion of the Cs which adsorbs to the sputter-cleaned Ag foil is present as Cs_2O.

High-resolution Cs 3*d* XPS spectra obtained from the two Ag foils are shown in Figs. 2b (air-exposed, CsOH dipped) and 2c (sputter-cleaned, CsOH dipped). Most of the Cs present on the air-exposed Ag foil apparently is CsOH, which may have remained at the surface because it was
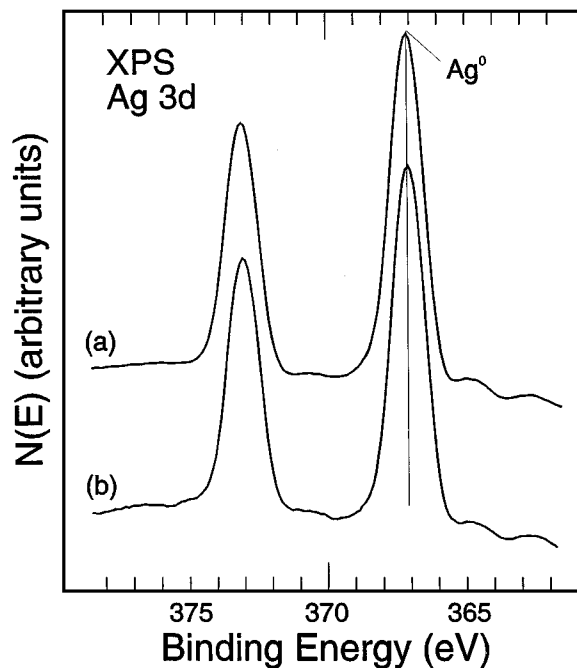

FIG. 3. XPS Ag 3*d* spectra obtained from (a) an air-exposed Ag foil after dipping into a 400-ppm aqueous CsOH solution at room temperature, rinsing with distilled H_2O, and drying, and (b) a sputter-cleaned Ag foil which had undergone identical treatment.
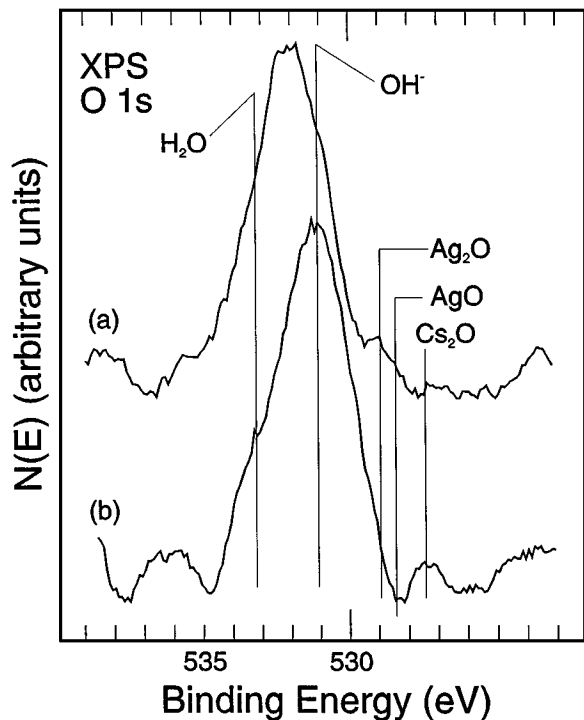
FIG. 4. XPS O 1s spectra obtained from (a) an air-exposed Ag foil after dipping into a 400-ppm aqueous CsOH solution at room temperature, rinsing with distilled H_2O, and drying, and (b) a sputter-cleaned Ag foil which had undergone identical treatment.

that the Cs plays in a promoted ethylene epoxidation catalyst. Indeed, in the comparison of two ethylene epoxidation catalysts, one made with Cs and one without, the amount of Ag on the nonpromoted catalyst was less than that on the promoted catalyst although identical preparation conditions were used (16). Furthermore, the Ag does not interact strongly with the alumina when Cs is not present. These results indicate that there is a chemical interaction between the Ag and alumina involving Cs. Since the Ag is present in the solution as Ag lactate and not as a complex involving Cs, the adsorption reactions occur at the alumina surface. In a previous part of this series of studies (15), scanning electron microscopy (SEM) data indicate that Ag covers most of the α-Al_2O_3 support when the catalyst is in its most active state. As the catalyst ages further and becomes less active, the Ag agglomerates into more spherical shapes, which interact less strongly with the support. It was concluded that the Cs promotor facilitates the interaction between the Ag and the alumina support and that with aging subsurface binder material (Na) in the support material (15) migrates to the support surface, forming NaCl which does not interact with the Ag. This results in further agglomeration of the Ag and growth of larger alumina
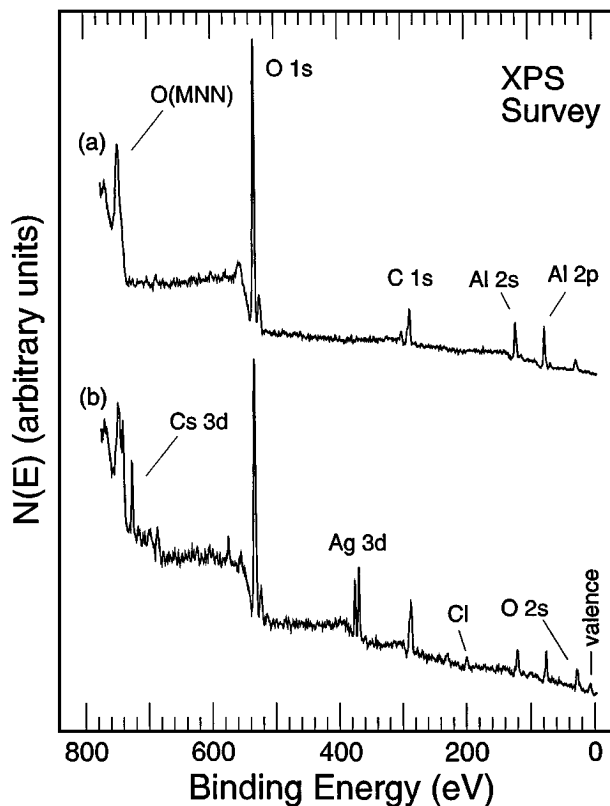
not thoroughly rinsed. A small portion of the Cs may be present as Cs_2O. A shoulder due to CsOH is noticeable in the spectrum taken from the sputter-cleaned and CsOH-dipped Ag foil also, but the primary contribution to this feature has a BE value of 725.1 eV which is close to the BE of Cs_2O. However, this feature may possibly be due to a Ag/O/Cs bonding interaction particularly since the O 1s Cs_2O feature in Fig. 4b is very small.

An XPS survey spectrum obtained from an Al foil which had been dipped into an 80°C lactic acid solution of 50 ml containing 1 g of dissolved Ag_2O powder and subsequently rinsed with distilled H_2O is shown in Fig. 5a. This spectrum contains features due to O, C, and Al. No Ag peaks are observable. The C 1s peak is smaller relative to the Al and O features in comparison to the spectrum shown in Fig. 1a obtained from the Al foil dipped in a CsOH solution. This is most likely due to the exposure of the Al foil to the lactic acid solution at 80°C, which may have removed some of the carbon contamination. An XPS survey spectrum taken from an Al foil which had been dipped into a 50-ml lactic acid solution containing both 1 g of Ag_2O and 1.5 ml of CsOH at 80°C and then rinsed with distilled H_2O is shown in Fig. 5b. Again, C, O, and Al features are apparent. However, significant Cs and Ag peaks are present as well. If the Cs promotor is not present, the Ag does not readily bond to the Al foil. This result explains one of the roles

FIG. 5. XPS survey spectra obtained from an Al foil after dipping into an 85 wt% lactic acid solution heated to 80°C and containing (a) 1 g of Ag_2O and (b) 1 g of Ag_2O and 1.5 ml of CsOH. These films were rinsed with distilled H_2O and dried.
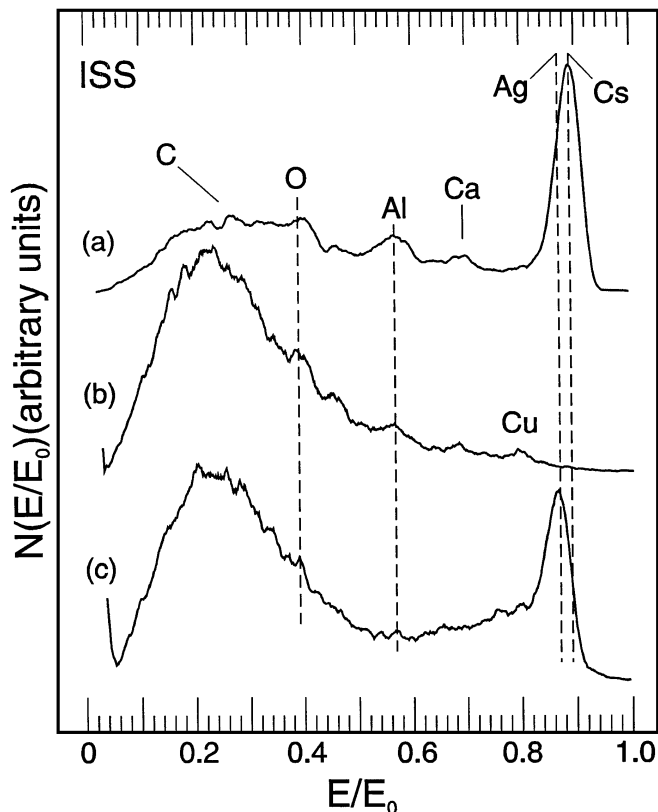
FIG. 6. ISS spectra obtained from (a) an Al foil after dipping into a 400-ppm CsOH solution, and from Al foils after dipping into an 85 wt% lactic acid solution heated to 80°C and containing (b) 1 g of Ag_2O and (c) 1 g of Ag_2O and 1.5 ml of CsOH. Each foil was rinsed with distilled H_2O after removal from the solutions and dried.

crystallites via an ionic transport mechanism. Transmission electron microscopy (TEM) data obtained from a nonpromoted 2 wt% Ag/α-Al_2O_3 sample depict small Ag crystallites lying atop the support (27). Some of these crystallites appear to interact with the support, but most are spherical in shape, indicating little interaction between the Ag and support. In a separate study of Ag/α-Al_2O_3 samples (28), the results demonstrate that the interaction between the Ag and alumina support is weak. The data presented in this present study demonstrate that the Ag does not adsorb on the Al foil without the presence of Cs under the preparative conditions used in this study. These results along with previous findings (15–17) support the assertion that the Cs promotor acts as a binder between the Ag and α-Al_2O_3 support although it most likely alters the electronic structure of the Ag as well.

ISS is a powerful surface characterization technique which yields compositional information about the outermost atomic layer of a solid. An ISS spectrum taken from the Al foil after it was dipped in a 400-ppm CsOH solution is shown in Fig. 6a. The feature due to Al is present at an E/E_0 value of approximately 0.57. C, O, and Ca peaks are

also evident. The primary peak in this spectrum is due to the presence of Cs. An ISS spectrum taken from the Al foil after dipping into the Ag_2O-containing lactic acid solution (no Cs) is shown in Fig. 6b. The Al, C, O, and Ca features are again present as is a small Cu contamination feature. The XPS data discussed above indicate that no Ag is present in the near-surface region of this Al foil. Correspondingly, the ISS spectrum contains no signal contributions due to the presence of Ag in the outermost atomic layer. The ISS spectrum obtained from the Al foil which was dipped into the lactic acid solution containing both CsOH and dissolved Ag_2O is shown in Fig. 6c. In this spectrum a distinct Al peak is not apparent. The C and O features are still present as is a large Ag peak. The presence of this feature and absence of the Al peak indicate that the Ag covers most or all of the Al which was present at the foil surface. The Cs feature is difficult to detect using He^+ due to its proximity to Ag (E/E_0 of Ag is 0.865 and that of Cs is 0.895), but some Cs may be present at the outermost atomic layer.

A high-resolution XPS Cs $3d$ spectrum obtained from the Al foil which was dipped into the lactic acid solution containing both dissolved Ag_2O and CsOH is shown in Fig. 7a, and the Cs $3d$ XPS spectrum taken from the Al
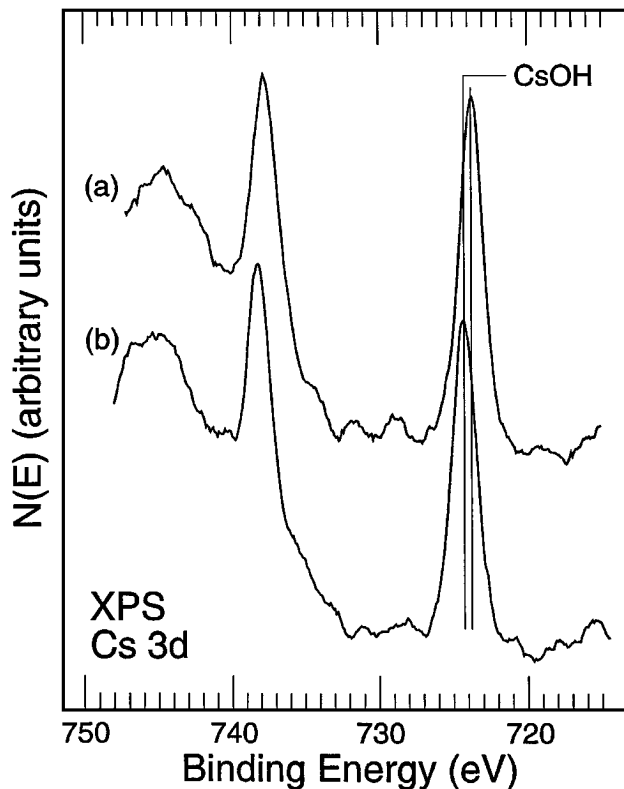

FIG. 7. XPS Cs $3d$ spectra obtained from (a) an Al foil after dipping into an 85 wt% lactic acid solution heated to 80°C and containing 1 g of Ag_2O and 1.5 ml of CsOH and (b) an Al foil after dipping into a 400 ppm CsOH solution. Each foil was rinsed with distilled H_2O after removal from the solutions and dried.
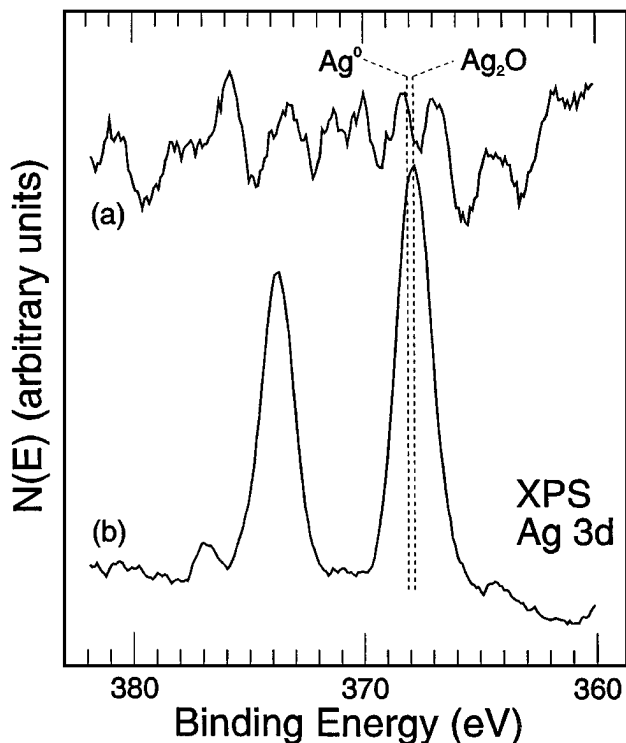
FIG. 8. XPS Ag $3d$ spectra obtained from an Al foil after dipping into an 85 wt% lactic acid solution heated to 80°C and containing (a) 1 g of Ag_2O and (b) 1 g of Ag_2O and 1.5 ml of CsOH. Each foil was rinsed with distilled H_2O after removal from the solutions and dried.

dominant feature is broadened and exhibits a shoulder at a BE of about 73.9 eV due to some type of chemical interaction with the adsorbed Cs. The XPS Al $2p$ spectra obtained from the Al foils after they were dipped in the lactic acid solution containing only Ag_2O and both Ag_2O and CsOH are shown in Figs. 9b and 9c, respectively. Again the predominant state of the Al is Al_2O_3. The O $1s$ spectra obtained from the same three Al foil samples (shown in Fig. 10) are very similar and indicate that the O is primarily bound as Al_2O_3. As expected, the spectrum shown in Fig. 9b does not contain either the Cs $4d$ contribution or the shoulder on the Al $2p$ feature, so the predominant peak due to Al_2O_3 is narrow and well defined. The peak due to Al metal is now smaller with respect to the peak due to Al_2O_3, indicating that the thickness of the alumina film increased during the hot (80°C) lactic acid treatment. With Cs present in the lactic acid solution, both the Cs $4d$ and the shoulder are apparent in the Al $2p$ spectrum (Fig. 9c). The Al metal peak is nearly eliminated by this treatment because this surface adsorbs a film of Ag, placing the Al metal so far beneath the surface that it is barely detectable. There is a BE difference between the Cs $4d$ features in Figs. 9a
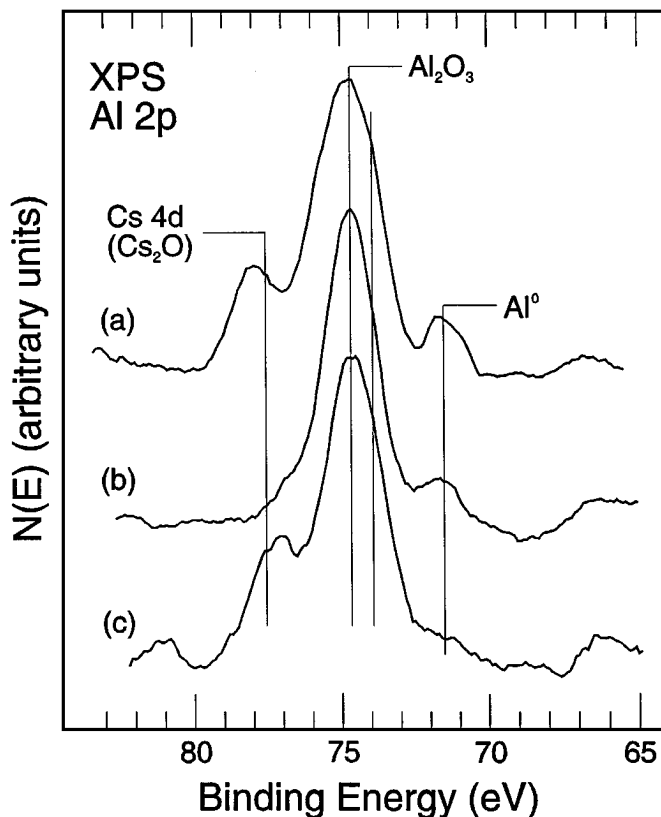
foil which was dipped in the CsOH solution (no Ag_2O) is redisplayed in Fig. 7b to facilitate comparison. The Cs $3d_{5/2}$ peak in Fig. 7a is slightly shifted to a lower BE (723.8 eV). Furthermore, the peak is slightly asymmetric on the higher BE side which indicates that some CsOH may be present. The shift to a lower BE does indicate that the Cs is in a less oxidic state. This shift could be caused by an enhanced interaction of the Cs with the Ag and Al.

A high-resolution Ag $3d$ XPS spectrum taken from the Al foil after it was dipped in the Ag_2O-containing lactic acid solution is shown in Fig. 8a. No Ag $3d$ peaks are evident above the noise level. The spectrum shown in Fig. 8b was taken from the Al foil after it was dipped in the Ag_2O and CsOH-containing lactic acid solution. The large Ag $3d_{5/2}$ peak is centered at a BE of 367.8 eV and is asymmetrical on the lower BE portion. Ag_2O has a BE of 367.7 eV (25) and Ag^0 has a BE of 368.1 eV (26). The state of the Ag adsorbed on the Al foil apparently is a mixture of Ag^0 and Ag_2O but another state of Ag may be present which consists of Ag interacting with both Cs and alumina.

The high-resolution Al $2p$ XPS spectrum obtained from the Al foil after it was dipped in the aqueous 400 ppm CsOH solution is shown in Fig. 9a. Both Al metal and Al_2O_3 are present in the near-surface region of this sample (22, 29) with the alumina forming a film over the metal. The pre-

FIG. 9. XPS Al $2p$ spectra obtained from (a) an Al foil after dipping into a 400-ppm CsOH solution, and from an Al foil after being dipped into an 85 wt% lactic acid solution heated to 80°C and containing (b) 1 g of Ag_2O and (c) 1 g of Ag_2O and 1.5 ml of CsOH. Each foil was rinsed with distilled H_2O after removal from the solutions and dried.
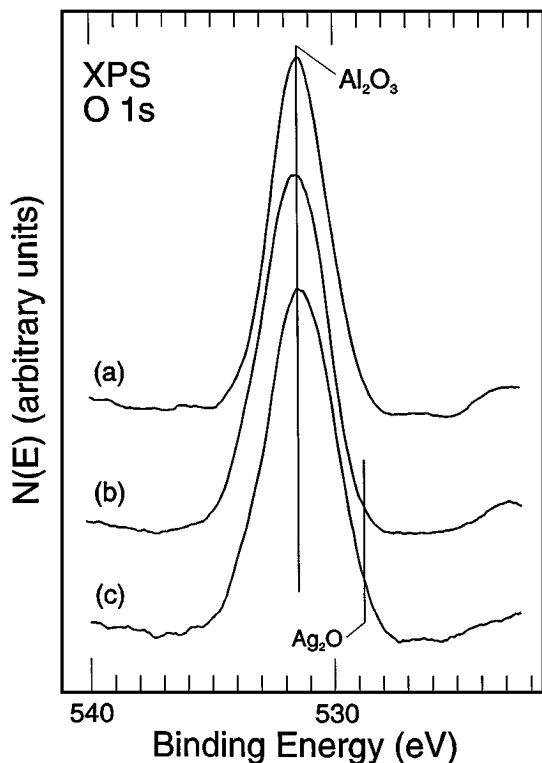
FIG. 10. XPS O 1s spectra obtained from (a) an Al foil after dipping into a 400-ppm CsOH solution, and from an Al foil after dipping into an 85 wt% lactic acid solution heated to 80°C and containing (b) 1 g of Ag_2O and (c) 1 g of Ag_2O and 1.5 ml of CsOH. Each foil was rinsed with distilled H_2O after removal from the solutions and dried.

and 9c. This fact is consistent with the XPS Cs 3d BE differences observed in Fig. 7 for these same two surfaces, indicating that the Cs is chemically altered by the presence of the Ag.

The O 1s XPS spectrum obtained from the Al foil dipped in the 400 ppm CsOH solution is shown in Fig. 10a. As stated above, most of the oxygen is bound to the Al as Al_2O_3 (22, 29). The peak is slightly asymmetric on the low BE side which denotes the presence of other oxygen-containing chemical states. These states may be O which is bonded to both Al and Cs. This asymmetry is not present in the spectrum shown in Fig. 10b, which was obtained from the Al foil dipped in the Ag_2O-containing lactic acid solution. The asymmetry is enhanced, however, in the spectrum obtained from the Al foil dipped in the CsOH and Ag_2O-containing lactic acid solution. The spectrum shown in Fig. 10c clearly exhibits a low-BE shoulder which may be due either to the presence of Ag_2O or to O associated with Al, Cs, and Ag interaction or to both types of O.

SUMMARY

Surface characterization studies have been performed on chemically treated Ag and Al foils in an effort to further understand the structure of ethylene epoxidation catalysts. XPS data indicate that Cs readily chemisorbs on Al_2O_3 and Ag metal surfaces but does not interact with a Ag oxide surface. Furthermore, the Cs chemisorbs on the Al foil surface even though a substantial amount of carbon contamination is present. High-resolution XPS data suggest that an interaction occurs between the Cs and Al foil probably through O. Additional studies were performed by dipping one Al foil into a lactic acid solution containing dissolved Ag_2O and another into a lactic acid solution containing both dissolved Ag_2O and CsOH. Ag does not chemisorb onto the alumina surface from the solution without CsOH. The Al foil which was dipped into the solution with CsOH adsorbs a large amount of Ag which covers the Al foil surface. These results support the assertion that one function of the Cs promotor used in ethylene epoxidation catalysts is to act as a binder between the Ag and α-Al_2O_3 support material, resulting in the selectivity enhancement observed upon Cs addition. The fact that Ag covers the alumina in the presence of Cs reduces the possibility that ethylene or ethylene oxide is converted to CO_2 and H_2O on the alumina surface. The XPS data indicate that there is a chemical interaction between the Al, Cs, and Ag which may be responsible for an alteration of the electronic properties of the Ag in these catalysts. This also may modify the catalytic behavior of this system.

REFERENCES

1. Lefort, T. E., French Patent No. 729,952, March 27, 1931 [to Societe Francaise de Catalyse Generalisee].
2. Nielsen, R. P., and LaRochelle, J. H., U.S. Patent No. 3 962 136, 1976; and U.S. Patent No. 4 012 425, 1977.
3. Berty, J. M., in "Applied Industrial Catalysis" (B. E. Leach, Ed.), Vol. 1, p. 207, Academic Press, New York, 1983/1984.
4. Satterfield, C. N., "Heterogeneous Catalysis in Industrial Practice," 2nd ed., McGraw–Hill, New York, 1991.
5. Van Santen, R. A., and Kuipers, H. P. C. E., *Adv. Catal.* **35**, 265 (1987).
6. Grant, R. B., and Lambert, R. M., *J. Catal.* **93**, 92 (1985).
7. Tan, S. A., Grant, R. B., and Lambert, R. M., *J. Catal.* **106**, 54 (1987).
8. Campbell, C. T., *J. Phys. Chem.* **89**, 5789 (1985).
9. Campbell, C. T., and Daube, K. A., *J. Catal.* **106**, 301 (1987).
10. Monnier, J. R., U.S. Patent No. 4 897 498, 1990.
11. Monnier, J. R., U.S. Patent No. 4 950 773, 1990.
12. Jun, Y., Jingfa, D., Xiaohong, Y., and Shi, Z., *Appl. Catal. A* **92**, 73 (1992).
13. Goncharova, S. N., Paukshtis, E. A., and Bal'zhinimaev, B. S., *Appl. Catal. A* **126**, 67 (1995).
14. Minahan, D. M., and Hoflund, G. B., *J. Catal.* **158**, 109 (1996).
15. Hoflund, G. B., and Minahan, D. M., *J. Catal.* **162**, 48 (1996).
16. Minahan, D. M., Hoflund, G. B., Epling, W. S., and Schoenfeld, D. W., *J. Catal.* **168**, 393 (1997).
17. Bhasin, M. M., Ellgen, P. C., and Hendrix, C. D., U.S. Patent No. 4 916 243, 1990.
18. Gilbert, R. E., Cox, D. F., and Hoflund, G. B., *Rev. Sci. Instrum.* **53**, 1281 (1982).
19. Tripathi, K. C., and Clark, D. T., *Nature Phys. Sci.* **241**, 162 (1973).

20. Epling, W. S., Mount, C. K., Hoflund, G. B., and Young, V. Y., to be published.
21. Wagner, C. D., Riggs, W. M., Davis, L. E., Moulder, J. F., and Muilenberg, G. E. (Eds.), "Handbook of X-Ray Photoelectron Spectroscopy," Physical Electronics Division, Perkin–Elmer Corp., Eden Prairie, MN, 1979.
22. Yang, S. J., and Bates, C. W., *Appl. Phys. Lett.* **36**, 675 (1980).
23. Hoflund, G. B., Weaver, J. F., and Epling, W. S., *Surf. Sci. Spec.* **3**, 151 (1995).
24. Davidson, M. R., Hoflund, G. B., and Outlaw, R. A., *J. Vac. Sci. Technol. A* **9**, 1344 (1991).
25. Hoflund, G. B., Weaver, J. F., and Epling, W. S., *Surf. Sci. Spec.* **3**, 163 (1995).
26. Hoflund, G. B., Weaver, J. F., and Epling, W. S., *Surf. Sci. Spec.* **3**, 157 (1995).
27. Lee, J. K., Verykios, X. E., and Pitchai, R., *Appl. Catal.* **50**, 171 (1989).
28. Gavriilidis, A., Sinno, B., and Varma, A., *J. Catal.* **139**, 41 (1993).
29. Strohmeier, B. R., *Surf. Sci. Spec.* **3**, 135 (1995).