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

II. Effects of Aging

Gar B. Hoflund* and David M. Minahan†

Department of Chemical Engineering, University of Florida, Gainesville, Florida 32611; and †Union Carbide Corporation, Technical Center/P.O. Box 8361, South Charleston, West Virginia 25303

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The aging effects of an α-alumina-supported Ag, ethylene epoxidation catalyst have been examined as a function of reaction time in a Berty backmix reactor. The catalyst was prepared by impregnation of commercial α-alumina pellets (1.3 m^2/g) in a Ag_2O/lactic acid solution and contained 13.87 wt% Ag and 420 ppm Cs by weight. The fresh and used catalysts have been characterized using scanning electron microscopy (SEM), ion scattering spectroscopy, Auger electron spectroscopy, and X-ray photoelectron spectroscopy. With aging the fresh catalyst becomes more active (percentage of conversion to ethylene oxide increases), and then the activity drops with increasing reaction time. Large changes are observed in the spectra obtained from these surfaces which are due primarily to morphological changes caused by sintering as observed in the SEM micrographs. The surface Cl content is increased at the support surface by adsorption of ethyl chloride, added in small amounts to the feed gas as a moderator, from the gas phase. The surface also becomes enriched in Na due to migration of the Na binder material to the surface where it associates with the Cl to from NaCl. The SEM micrographs indicate that both the Ag and alumina crystallites grow with age and that the large Ag crystallites do not interact with the aged alumina surface suggesting that the formation of NaCl plays a role in the sintering process.

INTRODUCTION

Although $Ag/\alpha\text{–}Al_2O_3$ catalysts have been of major technological importance for over 60 years (1), characterization studies of these materials have not appeared in the scientific literature. As discussed in a review by Van Santen and Kuipers (2), many characterization studies of the interaction between Ag metal and O and many reaction studies of ethylene epoxidation over alumina-supported Ag have been published, but characterization studies of the industrial-type catalysts have not been published. This paper is the second part of a series on the preparation, characterization and catalytic behavior of $Ag/\alpha\text{–}Al_2O_3$ ethylene epoxidation catalysts. Characterization results obtained from the bare α-Al_2O_3 support and the fresh Cs-promoted $Ag/\alpha\text{–}Al_2O_3$ catalysts are discussed in the previous portion of this study (3). In this part of the study, the aging behavior of Cs-promoted $Ag/\alpha\text{–}Al_2O_3$ catalysts has been examined using X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), ion scattering spectroscopy (ISS), and scanning electron microscopy (SEM).

EXPERIMENTAL

Catalyst Preparation

The Cs-promoted, α-alumina supported Ag catalyst was prepared by impregnation based on a patent by Bhasin *et al.* (4). An 88 wt% lactic acid solution was heated to 75°C, and a CsOH solution was added while stirring. The Ag_2O powder was added to the lactic acid solution while stirring to dissolve the suspended matter. A commercial α-alumina support (1/8 in. extrudate) with a 1.3 m^2/g surface area and purity of 99.6% (the rest is a Na- and Si-containing binder material) was impregnated with the lactic acid solution at 80°C for 15 min. The solution was allowed to drain for 1 h, and the pellets were calcined at 500°C in air on a belt roaster. The resulting catalyst contains 13.87 wt% Ag and 420 ppm by weight Cs.

Characterization Details

For characterization studies the catalyst pellets were physically ground in a mortar and pestle which had been ultrasonically cleaned in soap water, distilled water, toluene, acetone, trichoroethylene, acetone, and ethanol. Previous studies have shown that these pellets fragment to expose the catalytically active surface area within the pores and that grinding does not affect the nature of the active surface. The powder was then pressed into pellet form in an Al cup. This sample was attached to a stainless steel sample holder and inserted into the ultrahigh vacuum system (base pressure $<1 \times 10^{-10}$ Torr) for surface characterization with XPS, AES, and ISS. These data were collected

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using a double-pass cylindrical mirror analyzer (CMA, Perkin–Elmer PHI Model 25-270AR) equipped with an internal electron gun. For XPS the X-rays were generated using a PHI Model 04-151 single Mg anode Kα source with an energy of 1253.6 eV and FWHM of 0.7 eV. The CMA was operated in the retarding mode using pass energies of 25 eV to collect high-resolution spectra and 50 eV to collect survey spectra. The data were collected using a computer-interfaced digital pulse counter (5) and smoothed numerically (6). AES was performed by operating the CMA in the nonretarding mode and using a primary beam energy of 3 keV. The conventional experimental geometry (7) was used to collect the AES data. Phase-sensitive detection was used with a 0.5-V_{pp}, 10-kHz sine wave applied to the outer cylinder of the CMA. ISS data were collected using the CMA in the nonretarding mode, pulse counting detection, a scattering angle of 148° and 1 keV He^+. The 100-nA ion beam was defocused over an area of 5-mm diameter, and an ISS spectrum was collected in 90 s. The experimental conditions used for AES and ISS result in minimal sample alteration. Surface characterization studies of the thermal decomposition under vacuum conditions of AgO (8) and Ag_2O (9) have shown that Ag oxides are stable under the conditions used in this study. The SEM images were collected using a JEOL JSM-6300F field emission scanning electron microscope with a 2-kV accelerating voltage.

Reactor Experiments

In order to investigate aging, the ethylene epoxidation reaction was run for 24 days over an 80 cm^3 charge of the Cs-promoted Ag/α–Al_2O_3 catalyst in a Berty back-mixed autoclave. The feed gas consisted of 30 wt% ethylene, 8 wt% oxygen, 6 wt% carbon dioxide, 0.5 wt% ethane and 10 ppm ethyl chloride in flowing nitrogen at a GHSV of 8000 h^{-1} and pressure of 275 psia. These conditions were chosen because they result in rapid aging of the catalyst. In this study the activity is defined as the percentage conversion to ethylene oxide.

RESULTS AND DISCUSSION

The activity data, selectivity (efficiency) and reactor temperature are shown as a function of time in Fig. 1. As the reactor temperature was increased to maintain a reasonable activity, the selectivity is decreased by a few percent. The catalyst was characterized at three different points on the decay curve. These include the fresh catalyst at 0 days, the active catalyst at 4 days and the aged catalyst at 24 days. The activities of the active and aged catalysts are 0.19 and 0.13 g/gcat-h, respectively. A corresponding value is not available for the fresh catalyst because it takes about two days to bring the reactor temperature up to the operating value. The SEM micrographs obtained from the fresh, active and aged catalysts are shown in Figs. 2a, b, and c, respectively, and the corresponding ISS, AES, and XPS survey spectra are shown in Figs. 3, 4, and 5.

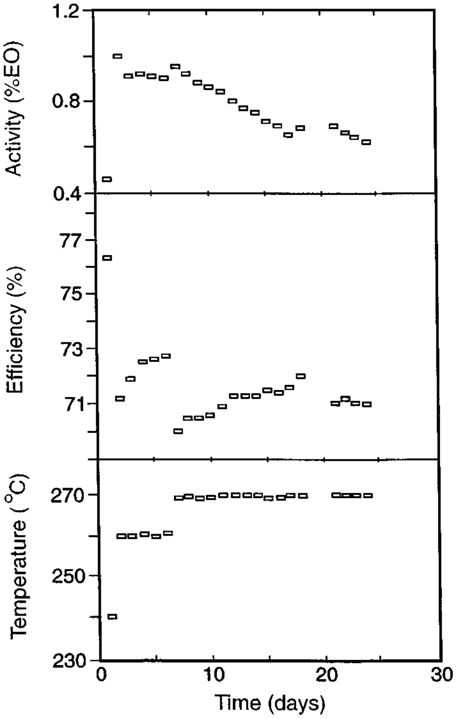

FIG. 1. Activity, selectivity (efficiency), and reactor temperature for ethylene epoxidation over the Cs-promoted Ag/α–Al_2O_3 catalyst as a function of time.

Fresh Catalyst

As discussed in the previous paper (3), the planar α-alumina surface is mostly covered by a uniform thin film of Ag on the fresh catalyst (Fig. 2a). At certain points in the micrograph, it appears that some regions of the α-alumina surface are not covered by Ag. This is confirmed by the presence of small O and Al peaks in the ISS spectrum shown in Fig. 3a. ISS is sensitive only to the outermost atomic layer, and the elemental sensitivity increases monotonically with mass. A large Ag peak and small peaks due to contamination such as S, Cl, Ca, and Ni are apparent. An estimation based on peak heights suggests that about 50% of the surface consists of O. This amount is adsorbed on a clean polycrystalline Ag surface after annealing in 75 Torr of O_2 at 250°C for 1 h (10). This observation and the fact that these catalysts were calcined in air after preparation indicates that the O coverage of about 50 wt% is associated with the Ag. This assertion is consistent with the SEM observation that the α-alumina is almost completely covered with Ag. A peak or shoulder due to Cs is not apparent on the high-E/E_0 side of the Ag indicating that a significant amount of Cs is not present in the outermost atomic layer of this catalyst.

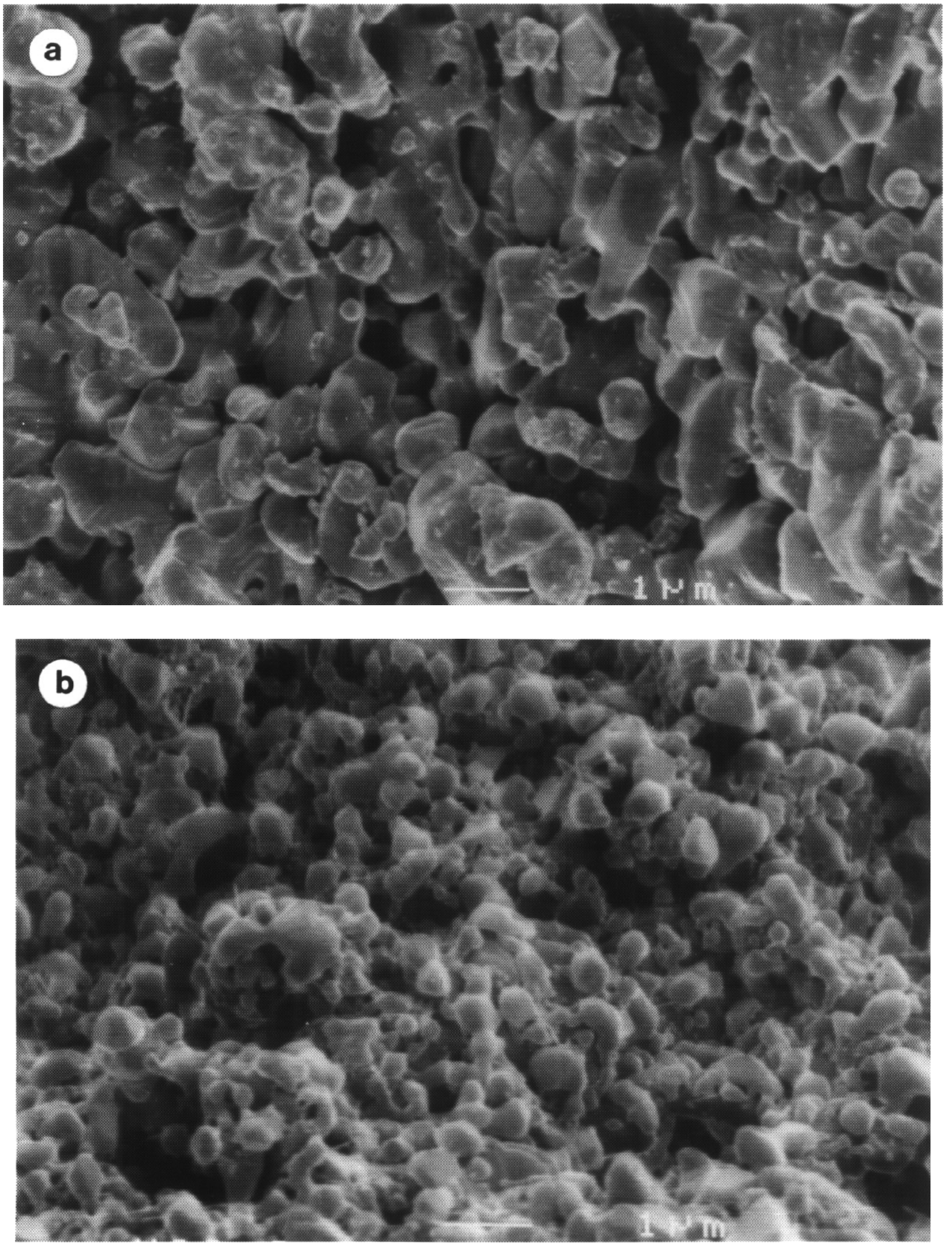

FIG. 2. SEM micrographs obtained from the (a) fresh, (b) active, and (c) aged catalysts.

The corresponding AES and XPS survey spectra are shown in Figs. 4a and 5a, respectively. In the Auger spectrum features due to Ag, Al, O, Cl, Si, and Cs are apparent. The large Ag/O and Ag/Al peak-height ratios of 2.6 and 7.7, respectively, are consistent with the thin film morphology found with SEM. Silver has a higher Auger sensitivity factor (11) than either Al or O (0.95, 0.5, and 0.23, respectively), and so the fact that most of the alumina surface is covered with a Ag film is responsible for the large Ag/O peak–height ratio. This is primarily a matrix effect derived from the spatial distribution of Ag, Al, and O in the near-surface region. Due to the highly nonhomogeneous nature of these catalysts, it would be incorrect to calculate a composition based on the Auger spectra using the homogeneous assumption.

Features apparent in the XPS survey spectrum include the O 1s, Ag 3d, and the Ag and O Auger peaks. The Ag 3d peaks are nearly as large as the O 1s peak, and peaks due to species in the support such as Al and Na are barely discernible. This spectrum is consistent with the corresponding Auger spectrum and thin Ag film morphology observed in the SEM micrograph. The XPS sensitivity factors are 2.25 for Ag, 0.11 for Al, and 0.63 for O (12). As with the Auger data, the thin film morphology coupled with the relative sizes of the sensitivity factors is responsible for the relative

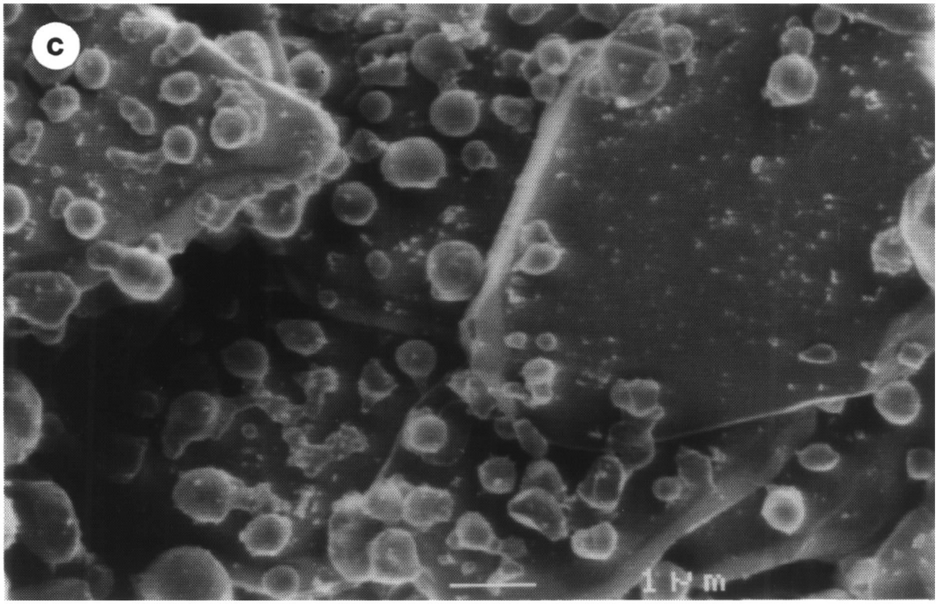

FIG. 2—*Continued*

peak heights in Fig. 5a so the compositions cannot be calculated using the homogeneous assumption.

Active Catalyst

As observed in Fig. 2b, the morphology of the active catalyst is quite different than that of the fresh catalyst. The thin film becomes globular in nature during the first four days of reaction, but it appears to maintain a significant interaction with the α-alumina. The Ag globules are mostly about 0.2 to 0.3 μm in diameter, and a large fraction of the support is exposed. The formation of the globules is the early stage of the sintering process. The fact that this surface is catalytically active suggests that the interaction of the Ag with the α-alumina support may provide a beneficial effect. At a constant temperature (days 2–6), the selectivity increases during the initial stages of sintering. Initially, the

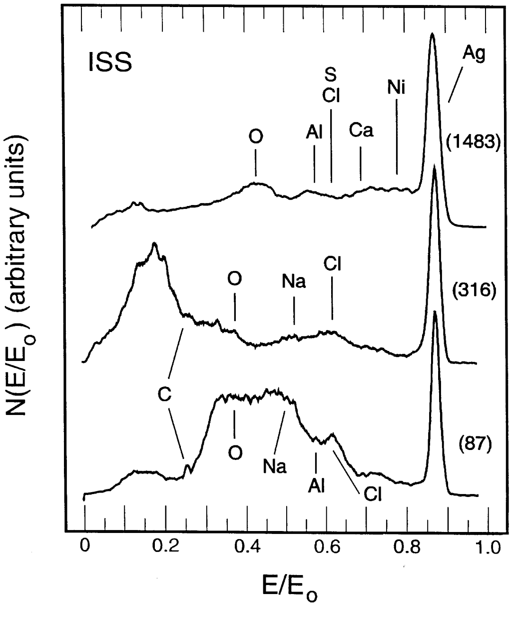

FIG. 3. ISS spectra obtained from the (a) fresh, (b) active, and (c) aged catalysts. These spectra are normalized based on the height of the Ag peak. The actual Ag peak heights are listed in parentheses.

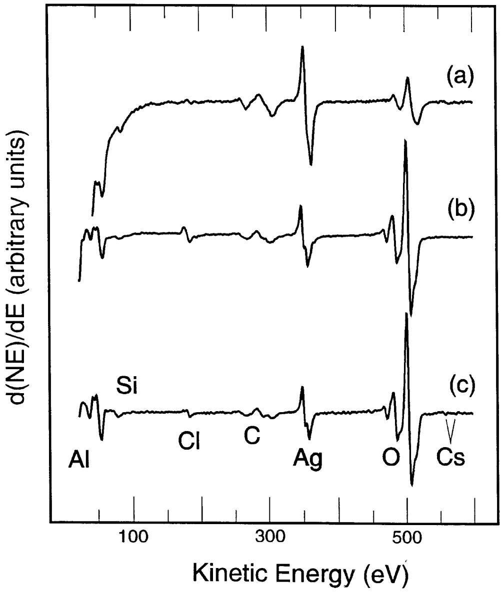

FIG. 4. AES spectra obtained from the (a) fresh, (b) active, and (c) aged catalysts.

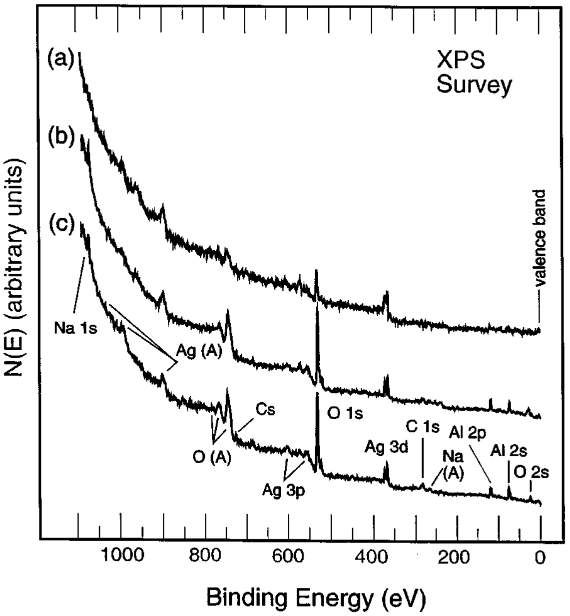

FIG. 5. XPS spectra obtained from the (a) fresh, (b) active, and (c) aged catalysts.

activity is low but increases rapidly as the temperature is increased. It drops and goes through a maximum at 4 days before beginning a long-term decay.

The ISS spectrum obtained from the active catalyst (Fig. 3b) contains small peaks due to C, O, Na, and Cl and a predominant peak due to Ag. The ISS spectra shown in Fig. 3 are all normalized to the height of the Ag peak. However, using the same data collection parameters, the Ag peak is reduced from 1483 counts for the fresh catalyst to 316 for the active catalyst. This is indicative of sintering, but changes in the ion neutralization factor, charging or surface roughness could also influence these values. The Cl peak is due to adsorption of ethyl chloride from the gaseous reaction mixture. The Na peak is due to migration of the Na binder to the surface under the influence of Cl. High-resolution XPS data yield a Na 1s binding energy of 1071.5 eV and a Cl 2p binding energy of 198.0 eV indicating that the Na and Cl from NaCl during reaction. The lack of a significant Al feature indicates that Al is not present in the outermost atomic layer due to coverage by NaCl, O, and Ag.

The corresponding Auger spectrum shown in Fig. 4b is quite different from that obtained from the fresh catalyst. The Ag-to-O and Ag-to-Al peak–height ratios are greatly reduced to 0.36 and 2.0, respectively. This is characteristic of sintering in which the Ag agglomerates to from the globules and simultaneously places more alumina near the surface. The O-to-Al peak–height ratio is 3.5 which is equal to that obtained from Al_2O_3 Auger data (11). This suggests that the O responsible for the large Auger peak in Fig. 4b is associated with the Al. Since the total amounts of Ag, O, and Al near the surface are probably similar for the fresh and active catalyst surfaces, the spectral differences are due to a matrix effect; i.e., a redistribution of the near-surface elements as observed in the SEM micrographs.

The XPS survey spectrum obtained from the active catalyst (Fig. 5b) provides complimentary information to the corresponding Auger spectrum. The Ag 3d-to-O 1s peak–height ratio is greatly reduced, and distinct Al 2p and 2s and Na 1s peaks are now observable. Again, the changes in this XPS spectrum are consistent with the assertion of sintering as observed in the SEM micrographs. These spectra illustrate the fact that the homogeneous assumption cannot be used to calculate the near-surface composition of highly nonhomogeneous catalysts since the matrix effect determines the relative peak heights.

Aged Catalyst

After six days of reaction, the temperature was increased from 260 to 270°C. This results in a decrease in selectivity due to an increased combustion rate at higher reaction temperatures and a small increase in conversion to ethylene oxide. Although the activity decrease is not monotonic, the minimum activity of about 0.6% conversion of ethylene to ethylene oxide was obtained after 24 days of reaction. The reaction study was ended at this point even though further decay in activity would have occurred.

The SEM micrograph obtained from the aged catalyst (Fig. 2c) exhibits dramatic differences compared to those obtained from the fresh and active catalysts. The Ag crystallites are increased in size to an average diameter of about 0.5 μm, and some are larger than 1 μm. Furthermore, the Ag crystallites do not interact very strongly with the α-alumina based on the nearly spherical shape of the crystallites, the large contact angle and the small contact area. The structure of the α-alumina support is also changed quite significantly. The average crystallite diameter is increased by a factor of about 10. Therefore, the morphological change of the α-alumina support is larger than that of the Ag crystallites, and a small fraction of the alumina is covered by Ag. Alumina is structurally stable to a much higher temperature than those used to run the reaction so the morphological changes must be associated with the chemical changes which occur during reaction.

The corresponding ISS spectrum is shown in Fig. 3c. Consistent with the SEM micrograph, the Ag peak is reduced in size compared to the support species which include C, O, Na, Al, and Cl, and its absolute value is now decreased to 87 counts from 316 counts for the active catalyst. With continued aging more Cl is adsorbed and a correspondingly larger Na peak is apparent. The Al peak is quite small probably due to coverage by oxygen. Although the C peak is small, a significant amount is present in the outermost atomic layer because the C neutralization factor is large.

The corresponding AES and XPS spectra are shown in Figs. 4c and 5c, respectively. In both cases O-to-Ag and

Al-to-Ag peak–height ratios are decreased, and features due to Cs are apparent. The relative peak–height changes are consistent with further sintering of the Ag indicating that the extent of sintering correlates well with changes in the XPS and AES data.

SUMMARY

A Cs-promoted, Ag/α–Al_2O_3 catalyst has been prepared and was utilized in a Berty backmix reactor for ethylene epoxidation. The activity initially increases and then steadily decays while the selectivity drops as the reaction temperature is increased but increases slowly at a given temperature until leveling off at about 71% for the fully aged catalyst.

The fresh, active, and aged catalysts have been characterized using SEM, ISS, AES, and XPS. The SEM micrographs provide a visual image of the large morphological changes which occur during aging. Corresponding large changes occur in the ISS, AES, and XPS spectra which can be related to the observed morphological changes. The AES and XPS relative peak sizes are determined by the elemental sensitivity factors and the elemental spatial distribution (matrix effects). The changes in relative peak sizes can be understood by considering morphological changes. It would be incorrect to use the homogeneous assumption to calculate the near-surface compositions of these highly nonhomogeneous catalysts.

The fresh catalyst consists of a thin Ag film uniformly covering the α-alumina. Globules of Ag form during the initial stages of sintering, and these grow to form large Ag crystallites, which do not interact with the support surface, during continued aging. The α-alumina crystallites also sinter during aging to form very large crystallites. Ethyl chloride, added to the feed gas as a moderator, is adsorbed on the support surface during reaction. The Na added to the α-alumina as a binder material migrates to the surface where it reacts with the Cl to form NaCl according to XPS data. The presence of the NaCl may be responsible for the weak metal–support interaction on the aged catalyst and may play a role in the sintering and aging processes.

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