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Promoting Effects of Re and Cs on Silver Catalyst in Ethylene Epoxidation

The study of ethylene epoxidation on promoted silver catalysts has been an active field in recent years. Alkali metals (*1–4*), boron (*5*), thallium (*6, 7*), antimony (*8*) etc., are often incorporated into practical Ag/α-Al$_2$O$_3$ catalysts in order to improve the selectivity of ethylene oxide. In recent work (*9*), it has been found that both Re and Cs added to Ag/α-Al$_2$O$_3$ can increase the selectivity greatly, but no further information about the function of promoters was given. We have recently reported that the Re-promoted electrolytic silver catalyst appears to have a higher selectivity for ethylene epoxidation (*10*), and have investigated the function of Re.

Most investigators had been concerned with the nature of promoters in ethylene epoxidation. The promoting effects of alkali and alkaline earth metal compounds were studied by Lambert and co-workers (*1–3, 11–13*) and Campbell (*4*) with surface science techniques. Most of these experiments were carried out on single Ag crystals. The present work describes the promoting effects of adding Re and Cs to electrolytic silver, on ethylene epoxidation and the adsorption of oxygen on the sample surface. The nature of Re and Cs promoters is also reported.

The silver sample (purity 99.999%) used was prepared by triple electrolytic refining. The preparation and the surface structure of electrolytic silver have been reported in detail (*14*). The catalysts shown in Table 1 were prepared by impregnating 20–40 mesh grains of electrolytic silver into the solution of Cs_2CO_3 and/or NH_4ReO_4 (the volume of solution is just enough to immerse the granules). They then were heated in a muffle furnace under forced air flow to 160°C within 1 hr, maintained for another 1 hour, and subsequently heated further up to 250°C, maintained for 3 hr, and cooled down to room temperature. The catalytic property was evaluated in a microreactor with a reaction pressure of 1.5 MPa and space time of 5000 hr^{-1}. The reactant feed consisted of 69.01% N_2, 7.19% O_2, and 23.8% C_2H_4. The catalysts were aged under reaction condition at 180°C for 30–40 hr. The products determined by gas chromatography were ethylene oxide, CO_2, and H_2O. No ethyl aldehyde was found. In the present experiments the influence of internal and external diffusion can be neglected.

The surface area was measured on a Digisorb-2600 Physisorption Analyzer with adsorbed Kr at 77 K. TDS and work-function measurements have been carried out in a UHV testing chamber which maintained vacuum pressure on the order of 10^{-7} Pa during the experiments. Attached to the system were a cylindrical mirror analyzer (CMA), an argon ion gun, a quadrupole mass spectrometer, and a low-energy electron gun for measuring the work-function change. The disk of the sample obtained by using a press was mounted on a transferable sample holder and heated radially by a tungsten filament fixed to the back of the sample. The rate of temperature change was controlled by varying the current; good linearity was obtained between 0.5 and 10 K/sec. The sample surface was cleaned by cycles of argon ion bombardment (1500 V and 25 mA) and subsequent annealing up to 850 K until the signals of the impurities carbon, sulfur,

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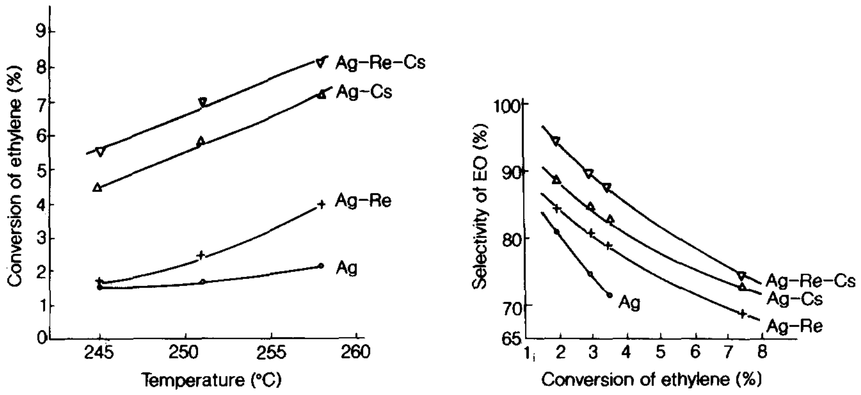

FIG. 1. Performance of various catalysts for ethylene epoxidation.

and chlorine on the surface, determined by AES, were diminished to the noise level.

The catalytic performance of the catalysts is compared in Fig. 1. It was found that the conversion of ethylene increased with the enhancement of reaction temperature, while the selectivity of ethylene oxide decreased with the enhancement of the conversion. The order of activity observed was Ag–Re–Cs > Ag–Cs > Ag–Re > Ag, and the order was the same for selectivity. Comparing the catalysts containing Re and/or Cs with electrolytic silver, it has been seen that the increase of conversion on promoted silver catalysts is faster than that on electrolytic silver, whereas the decrease of selectivity is slower. This indicates that Re and/or Cs added to silver can improve the performance of the silver catalyst, and the coexistence of Re and Cs can affect it greatly.

TABLE 1

The Properties of Catalysts

Sample	Content of Re (ppm)	Content of Cs (ppm)	Surface area (m_2/g)
Ag	—	—	0.022
Ag–Re	4.14	—	0.020
Ag–Cs	—	6.36	0.020
Ag–Re–Cs	4.16	6.50	0.020

The fact that the selectivity is more than 6/7 indicates that the ethylene oxide may not be a product to the reaction of ethylene with adsorbed molecular oxygen, because the mechanism of adsorbed molecular oxygen predicts a maximum selectivity of 6/7 or 85.7% for the formation of ethylene oxide (*15*), but the surface atomic oxygen mechanism has no implied limit on selectivity. The fact that surface area has shown little change (as seen in Table 1) reveals that the effect on the surface area of adding Re and/or Cs is not the main reason for the improvement of the silver catalyst performance.

A series of thermal desorption spectra of oxygen were obtained by varying the exposure of oxygen as shown in Fig. 2. Three adsorbed states are observed on the surface of Ag–Re–Cs and Ag–Cs, respectively: a low-temperature peak α, a symmetric peak β, and a high-temperature dispersed peak γ. However, only two adsorbed states are noted on the surface of the Ag–Re sample: peaks α and γ. When the oxygen exposure is increased, the intensity of all peaks increases and the T_p of peak β shifts toward lower temperature, whereas peak α changes little. According to the thermal desorption theory, peak α is ascribed to first-order desorption and peak β to second-order desorption. A number of experiments (*16, 17*) have proven that CO can react with atomic oxygen on a silver surface to form CO_2 at room

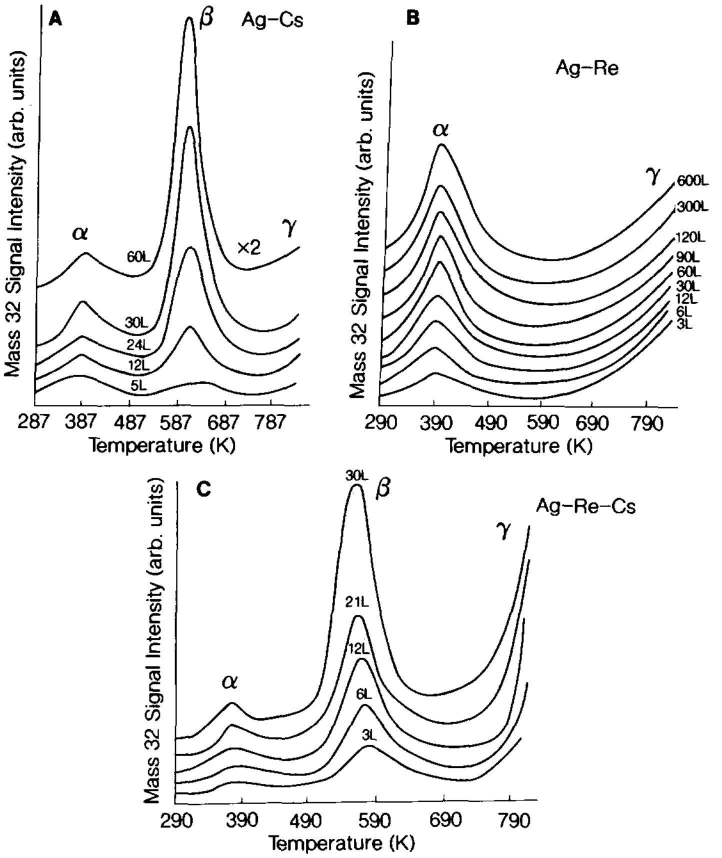

FIG. 2. TDS of oxygen on various sample surfaces: (A) Ag–Cs, (B) Ag–Re, and (C) Ag–Re–Cs Heating rate: 487 K/min.

temperature, but cannot react with molecular oxygen. In the present work, pure CO is leaked onto the surface of the sample with preadsorbed oxygen; the exposure to CO was approximately five times greater than that to oxygen. After the residual CO was pumped out, the desorption spectra of oxygen were recorded. It was found that peak β almost disappears after reaction with CO, but peak α still exists. Therefore, it may be concluded that peak α corresponds to molecular oxygen, peak β to dissociative atomic oxygen, and peak γ to subsurface oxygen, which has also been observed by other investigators (*17–19*). Since no peak β is observed for the Ag–Re sample, only that molecular and subsurface oxygen coexisted on the surface can be inferred.

By comparing the initial desorbed temperature of peak γ at the same exposure of oxygen, an order has been discovered, which is Ag–Cs(790 K) > Ag–Re–Cs(700 K) > Ag–Re(620 K). Similarly, the peak temperature of β also displays an order: Ag–Cs(600–640 K) > Ag–Re–Cs(550–580 K). This demonstrates that adding Re can (1) weaken the interaction between atomic oxygen and silver, which is confirmed by the desorption activation energy (E_d) of atomic oxygen (peak β), 148.0 and 79.9 KJ/mol for Ag–Cs and Ag–Re–Cs, respectively; (2) reduce the potential energy between surface and subsurface oxygen (*20*), which promotes the transfer of oxygen between surface and subsurface. XPS and IR results (*10*) show that the species of Re on the sample

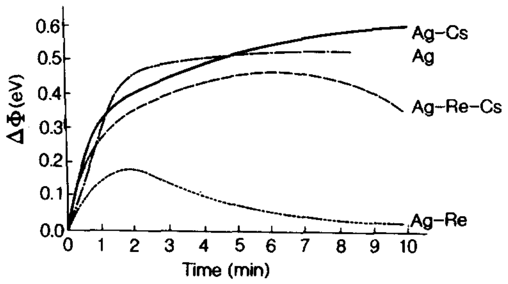

FIG. 3. Variation of the work function with exposure of oxygen at room temperature. $P_{O_2} = 6.7 \times 10^{-4}$ Pa.

surface is a type of Re oxyanion, which has a binding energy of 45.1 eV from the $\mathrm{Re}_{4f2/7}$ level. It is near the binding energy of Re_2O_7 (46.0 eV). Therefore, it can be inferred that the electrons transfer from silver to Re_2O_7 to make a type of Re oxyanion in which Re has a valence of $7 - \delta$, meanwhile making silver electron-deficient. This may lead to the results mentioned above.

During adsorption of gas on the metal surface, the work-function change could be related to the electron transfer between adsorbate and metal. The changes of the work function on Ag, Ag–Re–Cs, Ag–Cs, and Ag–Re as a function of oxygen exposure are shown in Fig. 3. It has been seen that the adsorption of oxygen on all sample surfaces results in an increase of the work function, and the effect of oxygen exposure on the work-function change is different for different samples. The maximum value of the work-function change is 0.50 eV for Ag, 0.60 eV for Ag–Cs, 0.47 eV for Ag–Re–Cs, and 0.18 eV for Ag–Re, indicating that the electron transfers from Ag to adsorbed oxygen. This is in accord with the conclusion by Bao *et al.* (*21*) who used UPS and work-function measurement to study the adsorption of oxygen on electrolytic silver, and observed that Ag donates electrons to adsorbed oxygen. Since the value of the work-function change is related to the magnitude of electron transported from Ag to adsorbed oxygen species, the electron density of adsorbed oxygen should exhibit the same order as the work-function change, as follows: Ag–Cs > Ag > Ag–Re–Cs > Ag–Re. This demonstrates that the electron density of adsorbed oxygen on the Ag–Cs surface is more than that on Ag, whereas the density on the surface with Re is less than that on Ag; that is to say, adding Cs can increase the electron density of surface oxygen species, while adding Re can decrease it.

Grant and Lambert (*1*) have proposed that the pivotal factor in selective ethylene oxidation is the effective charge state of O(a). If this is not too high, electrophilic attack on ethylene is possible, leading eventually to ethylene oxide formation. If the charge state of O(a) increases, the chance of ethylene combustion is enhanced. In a silver sample with Re added, the small change of work function induced by oxygen adsorption shows the lower electron density of adsorbed oxygen due to Re oxyanions competing with adsorbed oxygen for silver lattice electrons; the combustion of ethylene is thus suppressed, and the selectivity is improved. This is contrary to the sample with Cs added, where the increased electron density of adsorbed oxygen due to the interaction of Ag with Cs oxyanion benefits the total oxidation of ethylene. It may be suggested that the enhancement of the selectivity be ascribed to the oxidation of ethylene oxide being suppressed. This is consistent with the observation by Grant and Lambert (*1*), who investigated the oxidation of ethylene and ethylene oxide on Cs/Ag(111), and proposed that Cs acts to suppress the further oxidaton of ethylene oxide while at the same time promoting direct combustion. From our results, it can be inferred that enhancement of selectivity by suppressing the oxidation of ethylene oxide is greater than reduction of selectivity by increasing the electron density of surface oxygen on the Ag–Cs sample; thus the selectivity is increased. In the sample with both Re and Cs added, the common action of Re and Cs increased the selectivity: adding Cs suppressed the oxidation of ethylene oxide, while increasing the electron density of adsorbed oxygen species which was, however, reduced by adding Re. To a certain extent, this overcomes the negative effect of adding Cs to promote the complete oxidation. Therefore the selectivity of the Ag–Re–Cs catalyst is the highest.

ACKNOWLEDGMENT

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