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Catalytic Activity and Some Characteristics of Ag–NaCl Catalysts for Epoxidation of Ethylene

The selectivity in the first commercial process of direct epoxidation of ethylene over a silver catalyst in 1947 was 55% (*1*). Since then, a remarkable increase of 25–27% in selectivity to around 80–82% has been achieved by preparations of selective silver catalysts (*2*). The increase in selectivity has been effected by adding alkali or alkaline earth metals to silver and by the addition of traces of organic chlorides in feed gases. Kilty *et al.* (*3*) demonstrated that the effect of chlorine was to retard the dissociative adsorption of oxygen thus causing an elevation in selectivity. Other authors (*4–6*) also suggested that the addition of chlorine to silver was a factor in achieving higher selectivity. Spath *et al.* (*7*) showed that the addition of alkaline earth metals decreased the work function by covering the surface of the silver with a semiconducting film involving silver atoms as electron donors. Finally, alkali metals are known to form superoxides in the same manner as silver (*8, 9*).

Nowadays, however, when carbon-containing resources must be used more and more effectively, the selectivity level of 80–82% was not sufficient. We have recently reported that the selectivity of 85–87% was attained by the simultaneous addition of sodium and chlorine to silver (*10*). In the present work, the catalytic capability of the fresh surfaces of NaCl-doped Ag catalysts and granular NaCl-supported Ag catalysts to epoxidize C_2H_4 was examined using a pulse technique. In addition, the change of bulk composition during the preparation of the catalyst was followed by XRD, and the catalyst surface was analyzed by AES and XPS.

The dried Ag_2O, precipitated from $AgNO_3$ and KOH aqueous solutions, was mixed with an aqueous solution of NaCl. The resulting mixture was dried on a hot plate at 377–383 K, and then transferred into a U-glass tube. These operations were performed in a glove box continuously purged with N_2 gas. The mixture was exposed to a stream of H_2, and its temperature was elevated at a rate of 50 K per 20 min and finally kept at 673 K for 10 h. The reduced catalyst was powdered in the glove box to more than 150 mesh and preserved in a glass tube purged with H_2. The surface area of the NaCl-doped Ag catalysts was 0.22 to 0.40 m^2 g^{-1}. Granular NaCl-supported Ag catalysts were prepared by vaporizing C_2H_5OH from a mixture of Ag_2O, granular NaCl, and C_2H_5OH and by the subsequent reduction. The reactor was a Pylex glass U-tubing with 0.003 m i.d., in which either 0.1 g of the doped catalyst or 0.2 g of the supported catalyst was packed. A reactant mixture of $p_{C_2H_4}$ 0.03 and p_{O_2} 0.20 atm balanced by He was prepared with purified gases. Pulse size was 0.25 ml (s.t.p.) and pulse interval 14 min. Analysis of product gases was performed by a gas chromatograph equipped with DOP and Porapack Q columns in series. In the measurement of the bulk composition of the doped catalyst by XRD (Cu$K\alpha$, 35 kV, 25 mA), 0.1 g of α-alumina was mixed well with 0.4 g of sample as an internal standard. XPS spectra were measured using VG-ESCA3 (Mg$K\alpha$, 1253.6 eV) and AES was a separate instrument. Immediately before inserting the doped catalyst into the spectrometers, its surface was treated in H_2 at atmospheric pressure at 673 K overnight in

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the preparation chamber. Binding energy of photoline was calibrated by the C 1s peak at 284.6 eV.

In the first pulse reaction, total conversion of C_2H_4 was abnormally large and very much independent of the reaction temperature. Most of the product was C_2H_4O with small amounts of CO_2 and H_2O, but the discrepancy in carbon balance was remarkable (ca. 12% of C_2H_4 injected) and almost independent of catalyst composition and temperature. In the second to fourth pulses, the conversion and degree of the discrepancy (ca. 4%) were about the same. The C_2H_4 lost during the reaction would have been strongly attracted to the catalyst surface as CO_2 or its precursors, because of the effusion of CO_2 in exposing the used catalysts to a stream of H_2. This enhanced adsorption seems to arise from the presence of Na^+ or Na_2O. The formation rate of C_2H_4O, represented by the average value of the second to fourth pulses, varied with NaCl content (Fig. 1a), and the C_2H_4O concentration in the gaseous part of the product was 95–97% in all cases. Assuming that the discrepant amount of carbon balance remained on the catalyst as CO_3^{2-}, the true selectivity to C_2H_4O declines with increasing NaCl content (Fig. 1b). The higher selectivity at elevated temperatures cannot be expected from a general relationship between selectivity and temperature for complex reactions. This result could, however, be concluded by increasing the amount of the enhanced adsorption of CO_2 or its precursors with lowering temperature. Only the catalyst consisting of Ag and NaCl in the equivalent ratio of 1 : 0.001 showed a good carbon balance, normal relation of selectivity to temperature, and then 84–87% in selectivity. The selectivity agrees with those obtained over several NaCl-doped Ag catalysts using a flow reactor and the gas mixture of $p_{C_2H_4}$ 0.43 and p_{O_2} 0.12 atm (*10*). The C_2H_4O formation rate expressed in a unit per gram of Ag increased gradually with NaCl content (Fig. 1c). The results indicate that the secondary Ag particle becomes more finely dispersed on the surface and functions more effectively with increasing NaCl content. This speculation is supported by the fact that the supported catalyst showed identical activity with that of the doped catalyst with the same NaCl content (Figs. 1a and c).

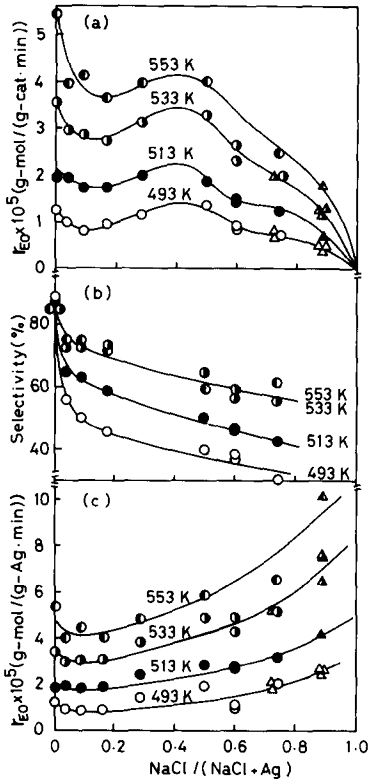

FIG. 1. Dependences of C_2H_4O formation rate (a), selectivity to C_2H_4O (b), and the C_2H_4O formation rate expressed in an unit per gram of Ag (c) on NaCl content. Circles, NaCl-doped Ag catalysts; triangles, granular NaCl-supported catalysts.

Dependences of C_2H_4O formation rate, r_{EO}, on $p_{C_2H_4}$ and p_{O_2} were measured at 493–573 K in the range of 0.015 to 0.21 atm for each partial pressure over the catalyst consisting of Ag and NaCl in the equivalent ratio of 1 : 0.04 (Cat-A). The equation obtained is as follows:

$$r_{EO} = 13.5 \exp(-43900/RT)p_{C_2H_4}^{0.74}\, p_{O_2}^{0.25} \quad \text{at } p_{O_2} \leqq 0.08 \text{ atm} \qquad (1)$$

or

$$r_{EO} = 7.5 \exp(-43900/RT)p_{C_2H_4}^{0.74} \quad \text{at } p_{O_2} \geqq 0.08 \text{ atm} \quad (2)$$

where R is gas constant (J K^{-1} mol^{-1}). Further, the Ag–NaCl catalyst was excellent in thermal stability, i.e., the activity, selectivity, and surface area for Cat-A annealed in H_2 was unchangeable below 723 K. The aggregation of Ag particles seems to be remarkably retarded by the strong interaction of Ag with Na^+ or Cl^-.

The precipitate, prepared from Ag_2O and an NaCl aqueous solution of the same equivalent weight as Ag_2O, was treated in a stream of H_2 at temperatures elevated in steps at 2-h intervals. Figure 2 shows the variation of the bulk composition of the mixture with the treatment temperature. After drying at 383 K for 2 h in He, the mixture consisted of Ag_2O, NaCl, and AgCl. XRD peaks of NaOH and metallic Ag were not detected. In this stage, the following equilibriums would have been established.

$$2\,AgCl + 2\,Na^+ + 2\,OH^- \rightleftharpoons Ag_2O + 2\,NaCl + H_2O \quad (3)$$

$$2\,AgCl + Na_2O \rightleftharpoons Ag_2O + 2\,NaCl \quad (4)$$

where it seems to be reasonable that Na other than NaCl was present in cationic form with the balanced amount of OH^-, because the mixture was not completely dehydrated and Na_2O is less stable than NaOH thermodynamically. Ag_2O in the mixture was reduced at 373 to 573 K, while above 523 K a rapid reduction of AgCl took place. The peak of Ag_2O however was not eliminated until the AgCl became completely undetectable. Consequently, AgCl can be understood to be converted to Ag_2O, which is then reduced by H_2. The mixture reduced at 673 K for 2 h comprised only bulk NaCl and metallic Ag.

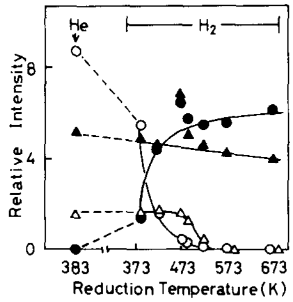

FIG. 2. Variation of the XRD bulk composition with the treatment temperature when the precipitate prepared from Ag_2O and NaCl in the equivalent ratio of 1 : 1 was treated in steps in a stream of H_2 at 2-h intervals. The relative intensity means the ratio of the intensity of a given XRD peak to that at 35.2° (2θ) for α-Al_2O_3. ○, Ag_2O 32.7°; ▲, NaCl 31.7°; △, AgCl 32.2°; ●, Ag 44.3°.

In AES and XPS measurements, the doped catalyst including Ag and NaCl in the equivalent ratio of 1 : 0.5 was used. In the AES spectrum, O peak at 503 eV and a very small C peak at 272 eV were observed. The binding energy and FWHM of the Ag $3d_{5/2}$ XPS peak having a shoulder at 369.5 eV were 368.3 and 1.3 eV, respectively. These measurements are slightly larger than 368.2 and 1.1 eV for pure Ag powder. Also, the Ag 4d doublet peak broadened at the high binding energy side. Zatko and Prather (*11*) reported that Ag^{3+} of diamagnetic ethylenebis(biguanide) silver(III) persulfate caused an Ag $3d_{5/2}$ peak at 371.4 eV. Romand *et al.* (*12*) indicated that the difference in binding energy of Ag 3d between Ag and Ag_2O was only +0.1 eV and FWHM for Ag_2O was larger than Ag. According to these results, the peak at 369.5 eV corresponds to higher oxidation states of Ag than Ag^+, and the 368.3 eV peak may include an effect of the presence of Ag^+ because of spreading of +0.2 eV in its FWHM. The Na 1s spectrum was split into two peaks at 1073.0 and 1075.8 eV and the intensity of the latter was larger. Also, the Cl $2p_{3/2}$ spectrum was a broad one showing a 201.9 eV peak with a shoulder at 198.9 eV. Comparing these peaks with those for pure NaCl powder, it was found that the Na 1s peak at 1073.0 eV and the Cl $2p_{3/2}$ peak at 198.9 eV were their original peaks and the Na 1s-Cl $2p_{3/2}$ peak separation 874.1 eV agreed with that for pure

NaCl. So, the Na 1s and Cl $2p_{3/2}$ peaks of higher binding energy are quite new peaks, which seems to be related to the occurrence of the 369.5 eV peak of Ag $3d_{5/2}$. The fact that the values of FWHM for Ag $3d_{5/2}$, Na 1s, and Cl $2p_{3/2}$ spectra for the Ag–NaCl catalyst are larger than those of pure Ag and NaCl reflects distortions of their band structures.

The XPS spectrum of O 1s possessed three peaks of 532.0, 533.3, and 534.5 eV, and the FWHM was very large. The largest O 1s peak at 532.0 eV was assigned to subsurface oxygen, and the peak at 533.3 eV to oxygen admolecule (*13–15*). The small peak at 534.5 eV seems to be related to the Ag $3d_{5/2}$ peak at 369.5 eV, but this is not certain. The XPS spectrum of O 1s and the AES peak of O were not eliminated even after several repetitions of overnight reduction and outgassing at 673 K. Small amounts of oxygen are speculated to have been confined in the surface layers by strong ionic interactions with Ag, Na, and Cl or to have bonded with some of their atoms. Such an oxygen atom would function as an active site in the subsequent oxygen adsorption and epoxidation of C_2H_4. From the results mentioned above, each atom in the Ag–NaCl catalyst is estimated to form a spread band structure and then a high oxidation state, which are promoted by the presence of oxygen contaminants.

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