JOURNAL OF CATALYSIS 150, 268–273 (1994)

Stages in the Modification of a Silver Surface for Catalysis of the Partial Oxidation of Ethylene

II. Action of the Reaction Medium

V. I. Bukhtiyarov, A. I. Boronin, I. P. Prosvirin, and V. I. Savchenko

Boreskov Institute of Catalysis, Lavrentieva Prospekt, 5, Novosibirsk 630090, Russia

Received August 16, 1991; revised April 11, 1994

The modification of clean silver foil by $C_2H_4 + O_2$ and $CO + O_2$ reaction mixtures has been studied by XPS, TPD, and TPR. It has been shown that $C_2H_4 + O_2$ treatment activates the clean silver surface for ethylene oxide formation. This is accompanied by the formation of a number of surface species (carbonates, elementary carbon and adsorbed oxygen), as well as the dissolution of oxygen and carbon atoms in the silver bulk. Displacement of ethylene in the reaction mixture by CO and comparison of composition of the silver surface after action of both mixtures indicate that the surface active centre contains two adsorbed oxygen states with different ionicity of the Ag–O bond. "Ionic" oxygen [E_b(O 1s) = 528.4 eV] produces Ag^+ ions as sites for ethylene adsorption, while "covalent" oxygen [E_b (O 1s) = 530.5 eV] seems to react with the adsorbed ethylene to form ethylene oxide. A possible mechanism of the "covalent" oxygen formation and influence of different factors (surface composition, morphology, etc.) on this process are discussed.

1. INTRODUCTION

Use of silver as a catalyst for the commercial production of ethylene oxide accounts for a large number of studies of this reaction using surface science techniques (1–6). However, it has been shown that the clean silver surface as used in surface science studies is not active in ethylene epoxidation. Indeed, adsorption of oxygen on thoroughly cleaned silver samples such as Ag(111), Ag(110), and Ag foil provides formation of only the "ionic" adsorbed oxygen state, which oxidizes the ethylene molecule to CO_2 (1–4). Moreover, treatment of these surfaces by O_2 at high pressures and temperatures leading to oxygen dissolution in the silver bulk does not appear to be enough to activate them for ethylene oxide formation (1, 5, 6). On the other hand, Grant and Lambert, who have studied this reaction on Ag(111), have demonstrated that modification of the clean silver by $C_2H_4 + O_2$ reaction mixtures produces the surface sites active for ethylene epoxidation (2, 3).

The purpose of this work is to trace the modification of Ag by $C_2H_4 + O_2$ reaction mixtures. We will show that such a modification activates the clean silver surface for ethylene oxide formation. The comparison of the surface composition after $C_2H_4 + O_2$ and $CO + O_2$ treatments will allow us to suggest the structure of the active surface centres.

2. EXPERIMENTAL

A VG ESCALAB HP electron spectrometer was used for this investigation. Basic experimental methods and procedures of cleaning a sample of Ag polycrystalline foil (99.99%) have been described earlier (1). A main feature of the experiments to be presented consists in a treatment of the sample at high pressures and temperatures in the preparation chamber, followed by its evacuation and transfer into the analyser chamber for analysis by X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption (TPD).

The use of high pressures of reaction mixtures (up to 10^3 Pa) for silver modification necessitated control of the following potential problems: (i) gas evolving from component parts of the sample holder during TPD and (ii) formation of carbonates on the silver surface. To tackle the former problem we have conducted blank experiments which have shown an absence of any gas evolving from the empty holder up to ~800 K. Carbonates were monitored by recording C 1s XP spectra and TPD profiles of CO_2 after each treatment of Ag.

3. RESULTS

3.1. Interaction of Silver with $C_2H_4 + O_2$ Reaction Mixture

Figure 1 shows (a) C 1s and (b) O 1s XP spectra, and (c) TPD profiles ("spectra") of O_2 and CO_2 recorded after treatment of the clean silver surface by $C_2H_4 + O_2$ reac-

0021-9517/94 $6.00

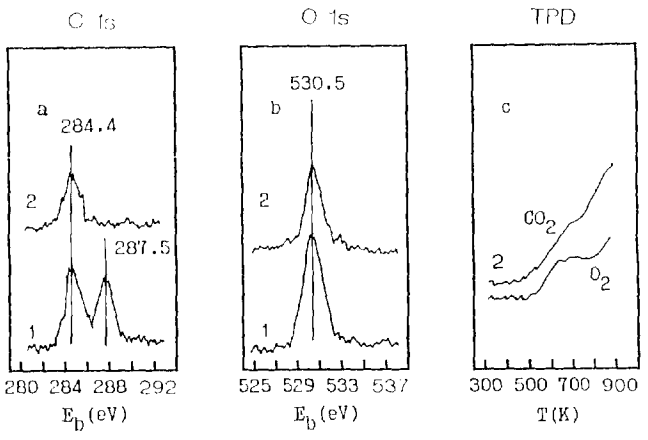

FIG. 1. (a) C 1*s* and (b) O 1*s* XP spectra, and (c) TPD profiles ("spectra") of O_2 and CO_2 for Ag surface treated by $C_2H_4 + O_2$ reaction mixture for 30 min at T = 420 K, $P(C_2H_4)$: $P(O_2)$ = 1/2, and total P = 10^3 Pa (1, 2): [1] after pumping the reaction mixture; [2] followed by flashing the sample up to 470 K in vacuum.

tion mixture for 30 min at T = 420 K, $P(C_2H_4)$: $P(O_2)$ = 1/2, and total P = 1000 Pa. The treatment conditions were chosen in accordance with the data of Grant and Lambert (2, 3). One can see the appearance of two lines with E_b = 284.4 and 287.5 eV in the C 1*s* spectrum (Fig. 1a, curve 1) and a single line with E_b = 530.5 eV in the O 1*s* spectrum (Fig. 1b, curve 1). The value of E_b(C 1*s*) = 284.4 eV is characteristic both of elementary carbon and of hydrocarbon species (7). However, the results of Nowobilski *et al.* (8) who have revealed only carbon on a silver surface in the reaction conditions allow us to assign this line to elementary carbon which seems to form due to oxidative dehydrogenation of ethylene (8, 9). The line with E_b(C 1*s*) = 287.5 eV can be assigned to the surface carbonates (10–13) which are produced due to reaction between adsorbed oxygen and CO_2 appearing as a product of total oxidation of ethylene. This assignment is confirmed by complete disappearance of this line after rapid flashing of the sample up to 470 K (Fig. 1a, curve 2). This disappearance is accompanied by a decrease in the intensity of the O 1*s* peak with E_b(O 1s) = 530.5 eV (Fig. 1b, curve 2). Absence of the line with E_b = 287.5 eV in the C 1*s* spectrum (Fig. 1a, curve 2) and the peaks with T_{max} = 450–470 K in the following TPD spectrum of CO_2 (Fig. 1c) indicates that the remaining O 1*s* peak is assigned to adsorbed oxygen, the binding energy value of which is the same as that for carbonates.

TPD results presented in Fig. 1c show that evolving CO_2 and O_2 in an amount exceeding one monolayer occurs on heating the modified sample. These peaks do not originate from the sample holder, since there has been no gas evolution in the blank experiments (see Experimental). Most probably, they are explained by mutual burning of C and O atoms dissolved in the silver bulk, and do not reflect desorption of any adsorbed species. Indeed, there is no accumulation of any additional signals in the C 1*s* or O 1*s* spectra (Figs. 1a and 1b).

Catalytic activity of the modified surface in the ethylene epoxidation was tested by temperature-programmed reaction (TPR) (Fig. 2). Details of this method were described earlier (1). As with the surface modified by pure O_2 (1), the surface containing single O_{ads} with E_b(O 1*s*) = 530.5 eV does not adsorb ethylene dosed at 300 K and P = 10 Pa. This observation is based on the absence of any additional peaks in the C 1*s* and O 1*s* spectra after ethylene adsorption. No narrow peaks appear in the TPR spectra of CO_2 and C_2H_4O under further heating of this surface (Fig. 2b). Continuous evolution of CO_2 is caused by releasing of dissolved atoms from the silver bulk. To detect small amounts of desorbed gases, we had to increase the sensitivity of recording the TPR spectra. This resulted in a sharp increase of background intensity. Therefore, only the initial parts of the TPR spectra of CO_2 are shown for convenience (Fig. 2b).

Oxygen adsorption at T = 420 K and P = 1 Pa on the silver surface modified by the reaction mixture results in the appearance of oxygen with E_b (O 1*s*) = 528.4 eV (Fig. 2a, curve 2). This oxygen has proved to be necessary for ethylene adsorption (1). Indeed, after adsorption of C_2H_4 at T = 300 K and P = 10 Pa on the surface containing two oxygen states, narrow peaks appear in the TPR spectra both of CO_2 and of C_2H_4O (Fig. 2b, curve 2). The temperatures of the maxima of these peaks are in a good agreement with those measured by Grant and Lambert (2, 3). Therefore, the action on the clean silver of a

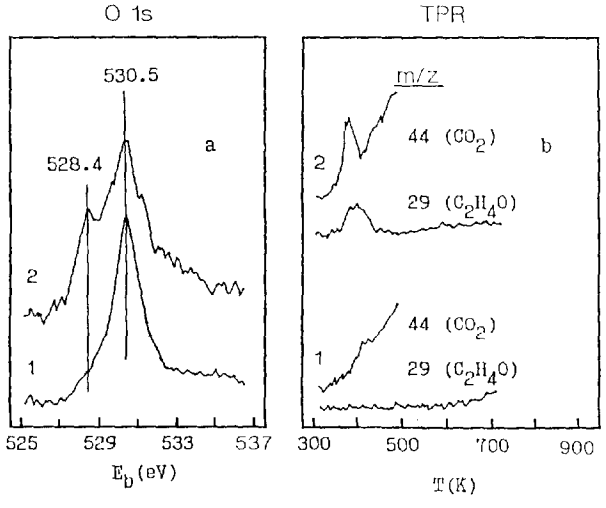

FIG. 2. (a) O 1*s* spectra before and (b) TPR spectra of CO_2 and C_2H_4O after ethylene adsorption for 10 min at T = 300 K and P = 10 Pa on silver modified by $C_2H_4 + O_2$ reaction mixture (1, 2): [1] after pumping the reaction mixture; [2] followed by O_2 adsorption for 10 min at T = 420 K and P = 10^{-2} Pa.

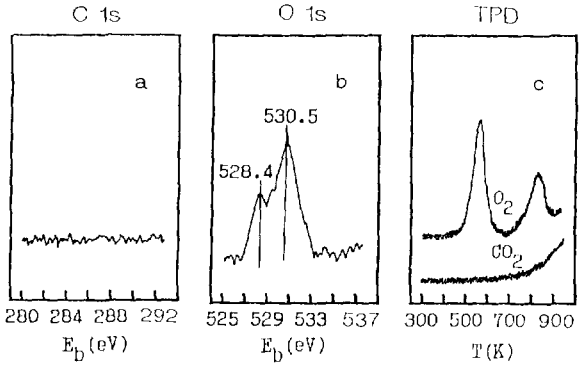

FIG. 3. (a) C 1*s* and (b) O 1s spectra, and (c) TPD spectra of O_2 and CO_2 for Ag surface treated by CO(1%) + O_2 reaction mixture for 10 h at T = 420 K and P = 1 Pa.

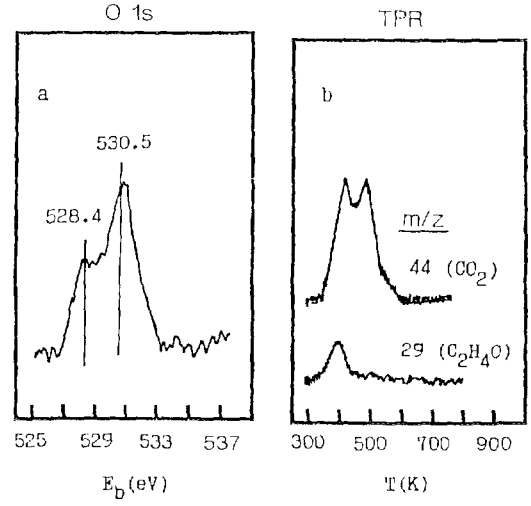

FIG. 4. (a) O 1*s* spectrum before and (b) TPR spectra of CO_2 and C_2H_4O after ethylene adsorption for 10 min at T = 300 K and P = 10 Pa on silver modified by CO + O_2 reaction mixture.

C_2H_4 + O_2 reaction mixture produces surface sites active for the ethylene epoxidation.

3.2. Interaction of Silver with CO + O_2 Reaction Mixture

The use of a CO + O_2 reaction mixture instead of C_2H_4 + O_2 is explained by an attempt to elucidate the composition of the surface sites active for ethylene oxide formation. Indeed, activation of clean silver by C_2H_4 + O_2 provided not only the appearance of adsorbed oxygen states but also the dissolution of oxygen and carbon atoms in the silver bulk.

Figure 3 shows (a) C 1*s* and (b) O 1*s* spectra, and (c) TPD spectra of O_2 and CO_2 recorded after treatment of the clean silver surface by CO (1%) + O_2 reaction mixture for 10 h at T = 420 K and P = 1 Pa. One can see that in this case two peaks appear in the O 1*s* spectrum, with E_b = 528.4 eV and 530.5 eV (Fig. 3b), but there are no peaks in the C 1*s* spectrum (Fig. 3a) or in the TPD spectrum of CO_2 (Fig. 3c). Thus, unlike the C_2H_4 + O_2 action, the CO + O_2 reaction mixture produces two different adsorbed oxygen states without modification of the silver bulk by dissolved atoms of carbon and oxygen.

The absence of dissolved oxygen giving background intensity in the TPD spectra of O_2 (Fig. 1c) allows us to define the TPD characteristics of O_{ads} with E_b(O 1*s*) = 530.5 eV. From Fig. 3c, it is seen that the T_{des}^{max} of this oxygen is about 820 K. The first TPD peak at 580 K shows desorption of O_{ads} with E_b(O 1*s*) = 528.4 eV.

Data on catalytic testing of the surface modified by the CO + O_2 reaction mixture are shown in Fig. 4. As for the surface modified by C_2H_4 + O_2, both CO_2 and C_2H_4O peaks are observed on heating this surface after ethylene adsorption (Fig. 4b). These data indicate that the two oxygen states are necessary for the ethylene oxide formation.

*3.3. Reactivity of O_{ads} with E_b(O 1*s*) = 530.5 eV towards C_2H_4 and Its Location with Respect to the Silver Surface*

Figure 5 shows a titration curve of oxygen with E_b(O 1*s*) = 530.5 eV by a C_2H_4 + O_2 reaction mixture. The use of the reaction mixture for titration as opposed to pure ethylene is explained by the necessity of O_{ads} with E_b (O 1*s*) = 528.4 eV for ethylene adsorption. Indeed, input of pure ethylene does not change the O 1*s* intensity, whereas a rather fast decrease in this signal is observed in the opposite case (Fig. 5). This result reflects a high reactivity of O_{ads} with E_b(O 1*s*) = 530.5 eV towards ethylene. The efficiency of this interaction estimated from the data of Fig. 5 is about 10^{-5}.

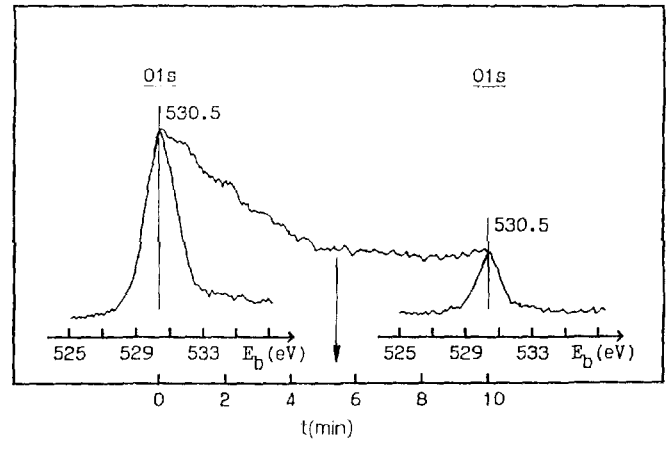

FIG. 5. Variation in intensity of oxygen (E_b(O 1*s*) = 530.5 eV) with time under its titration by C_2H_4 + O_2 at T = 420 K, $P(C_2H_4)$: $P(O_2)$ = 1/2, and total P = 1 Pa.

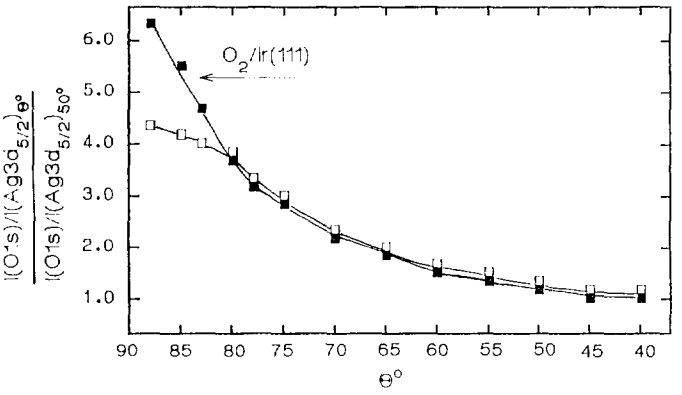

FIG. 6. Variation in O 1*s* and Ag $3d_{5/2}$ intensity ratio (□) with take-off photoelectron angle (Θ) for O_{ads} with E_b(O 1*s*) = 530.5 eV. Angular dependence for O_2/Ir(111) (■) is also shown for comparison (14).

Like the "ionic" oxygen (1), the location of O_{ads} with E_b(O 1*s*) = 530.5 eV was determined using angle-resolved (AR) XPS. Figure 6 shows the variation in O 1*s* and Ag $3d_{5/2}$ intensity ratio with the take-off angle of photoelectrons (Θ) measured for this oxygen formed by C_2H_4 + O_2 reaction mixture (Fig. 1b). The angular dependence of relative O 1*s* and Ir $4f_{7/2}$ intensities obtained after oxygen adsorption at an Ir(111) surface (14) is also shown for comparison. Rather good coincidence of the two curves indicates a similar structure for the adsorbed layers. Since oxygen on Ir(111) is located at the surface without reconstruction of this close-packed plane (15), it is clear that oxygen adsorbed on silver also has a surface location. Deviation of the two curves observed at $\theta > 80°$ seems to be caused by a higher roughness for polycrystalline silver compared with the smooth plane of the Ir(111) single crystal.

4. DISCUSSION

The treatment of clean silver by a C_2H_4 + O_2 reaction mixture produces surface centres active for ethylene oxide formation (Fig. 2). This activation results in the formation of a number of surface species such as carbonates [E_b(C 1*s*) = 287.5 eV and E_b(O 1*s*) = 530.5 eV], elementary carbon [E_b(C 1*s*) = 284.4 eV], and adsorbed oxygen [E_b(O 1*s*) = 530.5 eV], as well as dissolution of carbon and oxygen atoms in the silver bulk (Fig. 1). To elucidate which species are included in the active centre, we have applied CO + O_2 reaction mixture for activation of the clean surface. Indeed, displacement of ethylene by CO allowed us to avoid both the formation of elementary carbon and the dissolution of C and O in the metal bulk (Fig. 3). Such a modified sample containing two adsorbed oxygen states is also active in the ethylene epoxidation (Fig. 4). Since O_{ads} with E_b(O 1*s*) = 528.4 eV or "ionic" oxygen is formed as an initial step of O_2 adsorption (1, 10–12), it is clear that the main feature of activation of the clean silver surface by reaction mixtures is formation of the other oxygen state with E_b(O 1*s*) = 530.5 eV.

The appearance of this oxygen changes neither the E_b (O 1*s*) (528.4 eV) nor the T_{des}^{max} (580 K) of the "ionic" oxygen (1). The catalytic properties of the "ionic" oxygen as total oxidant of ethylene, therefore, is not very likely to change. On the other hand, O_{ads} with E_b = 530.5 eV has a high reactivity towards ethylene, with the efficiency of 10^{-5} being close to that for ethylene epoxidation on silver catalysts. Thus, although additional experiments using oxygen isotopes to label different O_{ads} are necessary, the data obtained allow us to suggest that it is O_{ads} with E_b (O 1*s*) = 530.5 eV which incorporates into the ethylene molecule producing ethylene oxide.

We have obtained the O_{ads} with E_b(O 1*s*) = 530.5 eV using high temperature treatment of silver by pure O_2 (1). It has been shown that it has a more covalent character for the Ag–O bond than oxygen as surface oxide [E_b (O 1*s*) = 528.4 eV]. Based on simultaneous analysis of XPS and TPD data, we have suggested that this state is the adsorbed oxygen, as opposed to Bao *et al.* (16), who have assigned it to subsurface oxygen. ARXPS data measured in this work confirm our previous suggestion. Indeed, unlike the "ionic" oxygen (1), the "covalent" oxygen has a constant increase in the (O 1*s*)/(Ag $3d_{5/2}$) intensity ratio with increasing photoelectron take-off angle (Fig. 5). A dependence of this type is characteristic of surface location of adsorbate (14). Thus, O_{ads} with E_b(O 1*s*) = 530.5 eV represents atomic oxygen adsorbed at the silver surface with a more covalent character of the Ag–O bond than the oxygen of surface oxide.

The influence of the ionicity of different oxygen states on the routes of the ethylene oxidation has been the subject of a number of papers (2, 3, 17–19). It has been shown that the high ionicity of the surface oxide oxygen determines the cleavage of the C–H bond in the ethylene molecule which is the first stage of total ethylene oxidation (19). In accordance with this conclusion, no ethylene oxide formation has been observed under the oxidation of ethylene by the "ionic" oxygen which is formed after oxygen adsorption (1, 4). Grant and Lambert (2, 3) and van Santen and co-workers (17, 18) have suggested that modification of clean silver surfaces by a reaction mixture decreases the ionicity of adsorbed oxygen and provides for its participation in the ethylene epoxidation. Our data confirm this suggestion experimentally. Indeed, the formation of the "covalent" oxygen provides the appearance of ethylene oxide amongst the reaction products (Figs. 2 and 4). Although the "ionic" oxygen is not active in ethylene oxide formation (1), it is of great importance for ethylene epoxidation. This is explained by its producing Ag^+ ions which are necessary for ethylene adsorption. Only

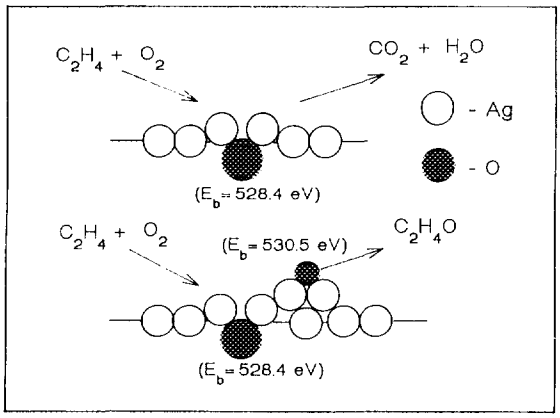

FIG. 7. Possible structures of surface centres active in total and partial oxidation of ethylene.

then can the adsorbed ethylene react with the "covalent" O_{ads}. Thus, the surface centre active in the ethylene epoxidation must contain two adsorbed oxygen states with different ionicities for the Ag–O bond (Fig. 6): the "ionic" oxygen is responsible for ethylene adsorption, the "covalent" are for ethylene oxide formation.

Figure 7 shows a possible structure for such an active centre containing two oxygen states. To provide the interaction of adsorbed ethylene with "covalent" oxygen both the O_{ads} should be close to each other. Indeed, if adsorbed ethylene has only "ionic" oxygen in its nearest environment, the latter will oxidize the ethylene molecule to CO_2 with high efficiency. It is clear that the number of active centres is determined by that of the neighboring pairs of different O_{ads}. The necessity of such a neighborhood seems to explain our failure to produce an active silver surface under the action of pure O_2 despite the formation of the "covalent" oxygen (1). Apparently, high temperature action of O_2 produces large islands of individual oxygen states (20). The amount of the neighboring pairs with different O_{ads} which will be present only along the borders of these islands is small in this case. Therefore, such a surface has a very low efficiency in the ethylene oxide formation (1).

From the suggested structure of the active surface centre (Fig. 7) and conditions of its creation, it is clear that the efficiency of different silver samples in the ethylene epoxidation should be determined by features of the "covalent" oxygen formation. For such samples as single crystals or Ag foil this process seems to include creation of defective sites on the silver surface due to repeating cycles of formation and decomposition of surface silver oxide: $Ag + \frac{1}{2}O_2 \rightleftharpoons Ag_2O$ (1). This mechanism suggested by us after studying the action of pure O_2 is confirmed by the data presented and, above all, by the decrease in the temperature at which the "covalent" oxygen appears. Indeed, removal of the "ionic" oxygen due to reaction with C_2H_4 or CO will proceed at a lower temperature than that due to desorption in the case of pure O_2 action.

For more defective samples such as Ag wire or Ag powder, defective sites responsible for the "covalent" oxygen formation can exist on the initial surface. This suggestion is confirmed by the data of Bowker *et al.* (21), who have shown that O_2 adsorption on Ag powder results in an oxygen with the high desorption temperature of $\approx$860 K. This result seems to indicate easier formation of the "covalent" oxygen on the rough surface of Ag powder compared with Ag foil. The influence of initial silver morphology is most likely to explain why for a long time attempts to register ethylene epoxidation on single crystals have failed (5, 6, 9).

Another factor affecting the formation of the "covalent" oxygen is the composition of the silver surface. Our data show that much easier formation of the "covalent" oxygen occurs in the case of carbon-containing Ag foil (13) or the real catalysts such as Ag powders with impurities of C, O and promoted by Ba or Cs. The results obtained for these systems will be published elsewhere.

In conclusion, it should be noted that modification of silver foil by reaction mixtures activates the clean surface for ethylene oxide formation. Displacement of ethylene by CO in the reaction mixture has allowed us to define that the catalytic surface centre active in ethylene epoxidation must contain two adsorbed oxygen states with different ionicities of the Ag–O bond. The "ionic" oxygen [E_b(O 1s) = 528.4 eV] produces the sites (Ag^-) for ethylene adsorption, while the "covalent" oxygen [E_b(O 1s) = 530.5 eV] incorporates in the ethylene molecule, forming ethylene oxide. Various factors increasing the covalency of adsorbed oxygen should influence the efficiency of the ethylene oxide formation.

REFERENCES

1. Bukhtiyarov, V. I., Boronin, A. I., and Savchenko, V. I., *J. Catal.*, **150,** 262 (1994).
2. Grant, R. B., and Lambert, R. M., *J. Chem. Soc. Chem. Commun.* **112,** 662 (1983).
3. Grant, R. B., and Lambert, R. M., *J. Catal.* **92,** 364 (1985).
4. Campbell, C. T., *Surf. Sci.* **139,** 396 (1984).
5. Rovida, G., and Pratesi, F., *Surf. Sci.* **52,** 542 (1975).
6. Rovida, G., Pratesi, F., and Ferroni, E., *Appl. Surf. Sci.* **5,** 121 (1980).
7. Wagner, C. D., Riggs, W. M., Davis, L. E., *et al.*, "Handbook of X-ray Photoelectron Spectroscopy." Perkin–Elmer Corporation, Eden Prairie, MN, 1979.
8. Nowobilski, P. J., Wilke, T., Davis, J. R., Patterson, M., Weaver, M. J., and Takoudis, C. G., *in* "Proceedings, 9th International Congress on Catalysis, Calgary, 1988" (M. J. Phillips and M. Ternan, Eds.), Vol. 3, p. 1159. Chem. Institute of Canada, Ottawa, 1988.
9. Wachs, I. E., and Kelemen, S. R., *in* "Proceedings, 7th International Congress on Catalysis, Tokyo, 1980" (T. Seiyama and K. Tanabe, Eds.), p. 682. Elsevier/Kodansha, Amsterdam/Tokyo, 1981.

10. Felter, T. E., Weinberg, W. H., Lastushkina, G. Ya., Boronin, A. I., Zhdan, P. A., Boreskov, G. K., and Hrbek, J., *Surf. Sci.* **118,** 369 (1982).
11. Bowker, M., Barteau, M. A., and Madix, R. J., *Surf. Sci.* **92,** 528 (1980).
12. Campbell, C. T., and Paffett, M. T., *Surf. Sci.* **143,** 517 (1984).
13. Boronin, A. I., Bukhtiyarov, V. I., Vishnevskii, A. L., Boreskov, G. K., and Savchenko, V. I., *Surf. Sci.* **201,** 195 (1988).
14. Baschenko, O. A., Bukhtiyarov, V. I., and Boronin, A. I., *Surf. Sci.* **271,** 493 (1992).
15. Hagen, D. I., Nieuwenhuys, B. E., Rovida, G., and Somorjai, G. A., *Surf. Sci.* **57,** 632 (1976).
16. Bao, X., Muhler, M., Pettinger, B., Schlögl, R., and Ertl, G., *Catal. Lett.* **22,** 215 (1993).
17. Backx, C., Moolhuysen, J., Geenen, P., and van Santen, R. A., *J. Catal.* **72,** 364 (1981).
18. van Santen, R. A., and de Groot, C. P. M., *J. Catal.* **98,** 530 (1986).
19. van Santen, R. A., Moolhuysen, S., and Sachtler, W. M. H., *J. Catal.* **65,** 478 (1980).
20. Bukhtiyarov, V. I., Boronin, A. I., and Savchenko, V. I., *Surf. Sci.* **232,** L205 (1990).
21. Bowker, M., Pudney, P., and Roberts, G., *J. Chem. Soc. Faraday Trans. I* **85,** 2635 (1989).