JOURNAL OF CATALYSIS 46, 82–90 (1977)

The Catalytic Activity of Supported Silver for the Oxidation of Ethylene: Activity Patterns on Different Supports

M. RIASSIAN, D. L. TRIMM, AND P. M. WILLIAMS[1]

Department of Chemical Engineering and Chemical Technology,
Imperial College, London S.W.7, England

Received July 30, 1975; revised June 28, 1976

The catalytic activity of supported silver for the oxidation of ethylene to ethylene oxide and to carbon dioxide has been investigated as a function of support. Significant changes in activity with time of use of catalyst have been observed: these changes depend on the nature of the support. It is shown that the initial changes in activity are not connected with catalyst sintering nor with crystallite size changes. Electron spectroscopy reveals that impurities, originating from the support and from adsorption of organic material, concentrate at the surface of the silver. A tentative explanation of the changes in activity pattern is proposed in terms of the modification of the surface by these impurities.

INTRODUCTION

The activity and selectivity of a catalyst depends not only on the nature of the active components, but also upon the support and on catalyst–support interactions. The factors which dictate the choice of a support have been recently reviewed (*1*): in addition to the physical properties of the system, the effect of support on catalyst sintering and on the coordination geometry of the catalyst (*2*) are particularly important.

Previous studies (*3*) have shown that the nature of the support has a profound effect on the rate of sintering of silver under ethylene oxidation conditions. Comparisons drawn between nonporous glassy supports showed that the surface free energy of the support and impurities at the surface of the catalyst, originating from the support, played an important role in determining the rate of catalyst sintering.

The present studies were initiated to study the effect of support on the activity and selectivity of a silver catalyst used to promote the oxidation of ethylene (*4*). The experimental apparatus has been previously described (*5*), the only modification being that the reactor was operated in the pulse mode. Premixed samples of ethylene and oxygen were pulsed through a reactor containing the catalyst, using argon as a carrier. Surface areas were determined by adsorption of krypton (*6*) in a separate reactor, and the surfaces of supports were examined using a Vacuum Generators ESCA 3 electron spectrometer. The rate of sintering of the catalysts was measured under reaction conditions (*3*).

Materials used have been previously reported (*3*), except for alumina which was obtained from Corrs Ltd. at 99.5% purity. The catalyst was prepared by vacuum evaporation of silver onto the support: the thickness of the silver deposit was 1400 ±20 Å in all cases.

---

[1] Present address: V. G. Scientific Ltd., East Grinstead, Sussex, England.

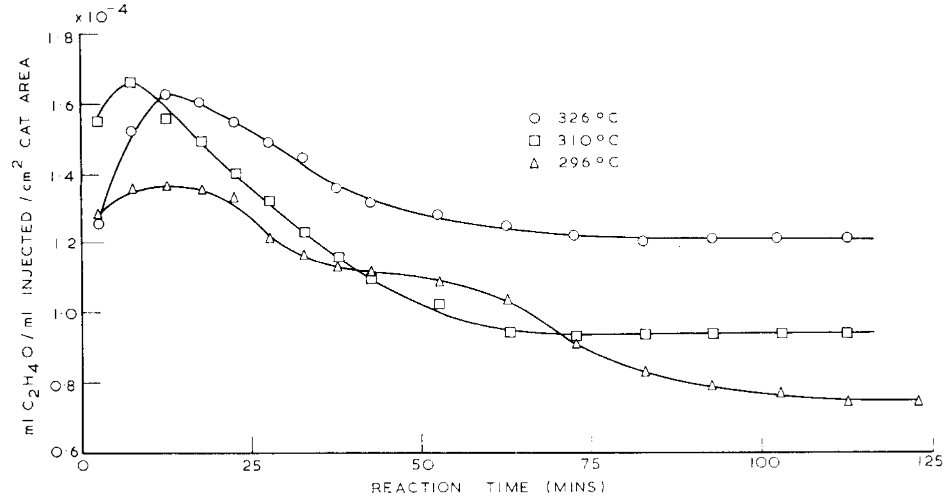

FIG. 1. Activity pattern for the oxidation of ethylene over Ag/SiO_2: ethylene oxide production.

RESULTS

Experiments were carried out with the objective of determining activities as a function of time-on-line. No detailed study of the reaction kinetics was carried out, the oxygen:ethylene ratio being fixed at 2:1.

The activity patterns for ethylene oxide and carbon dioxide over silver on 2 mm thick silica at 296, 310, and 326°C are shown in Figs. 1 and 2. The corresponding sintering induction period is given in Table 1. These refer to the time elapsed before holes appear in the deposited film (*3*, *12*): during this time the surface area of silver actually increases as a result of stress relief hillock formation (*3*, *12*). It can be seen that the yield of ethylene oxide passes through a maximum before falling to a steady-state value, and that this maximum appears to bear no relation to sintering.

Corresponding activity patterns for silver on alumina are shown in Figs. 3 and 4. Sintering patterns could not be measured but Fig. 5 illustrates typical metal distribution in the system. At one stage in the experiment, the reactor was cooled and reheated: the activity pattern observed is shown in Figs. 3 and 4.

Typical activity patterns for silver on glass are shown in Figs. 6 and 7, with the

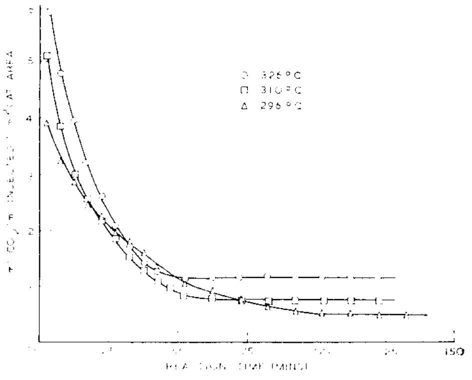

FIG. 2. Activity pattern for the oxidation of ethylene over Ag/SiO_2: carbon dioxide formation.

TABLE 1

Induction Times for 1400 Å Ag Films on 2 mm Thick Supports[a]

Temp (°C)	Induction times (min)		
	Silica	Glass	Alumina
280	21.5	26.3	Not measurable
296	13.2	15.7	
310	8.3	10.0	
326	5.0	6.0	

[a] Oxygen:ethylene = 2:1.

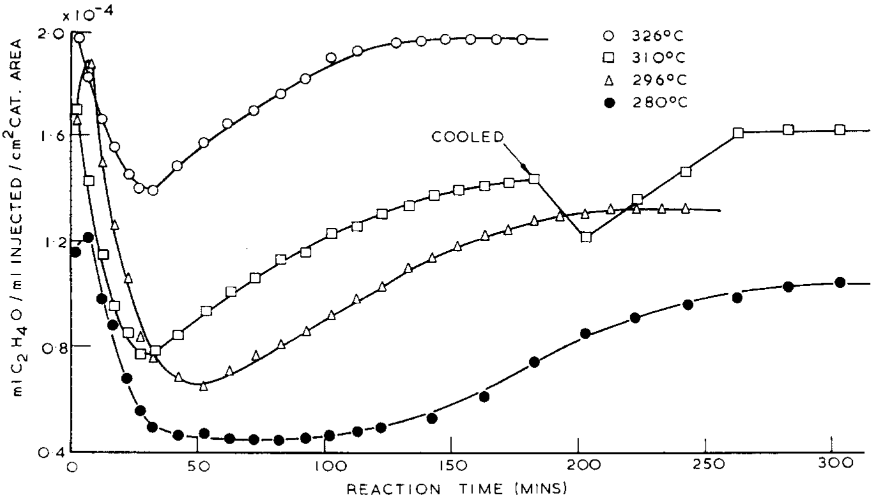

FIG. 3. Activity pattern for the oxidation of ethylene over Ag/Al_2O_3: ethylene oxide production.

corresponding sintering induction periods given in Table 1.

Arrhenius plots for the production of ethylene oxide and carbon dioxide were constructed in terms of the final steady rates. Energies of activation are reported in Table 2, together with energies of sintering (*3*, *12*).

Catalyst films were examined at various stages in the reaction using the AEI EM7 (1000 kV) electron microscope. No changes in crystallite sizes were detected before major reorganization occurred.

Electron spectra obtained from silica and glass supported systems have been previously reported (*3*). Alumina and silver on alumina were also examined (Figs. 8, 9, and 10), the latter both before and after the catalyst had been annealed for 45 min.

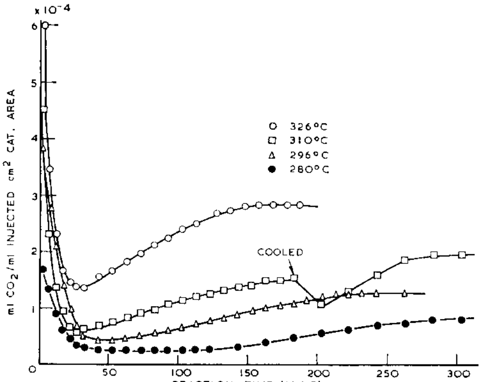

FIG. 4. Activity pattern for the oxidation of ethylene over Ag/Al_2O_3: carbon dioxide formation.

Sodium was found to have migrated to the surface on the silver during annealing, as had been previously observed with silver on float glass and on silica (*3*). Although it is difficult to make quantitative comparisons between samples using ESCA, the amount of sodium migrating to the surface [as judged by the relative peak intensities of Ag (367 eV) and Na (1070 eV)] appeared to reflect the concentration of sodium in the uncoated support. The nature of the gas passing over the surface did not appear to affect sodium migration, as the same sodium concentrations were observed on the surface of the silver when the catalysts were annealed as when they were heated at the same temperature in a mixture of ethylene and oxygen. Again, if an annealed sample was used as a catalyst (50 min reaction at 296°C), no change in the sodium concentration was observed, although the carbon peak height increased. No measurable change could be detected in the position of the silver 3*d* doublet after annealing or reaction (Fig. 11).

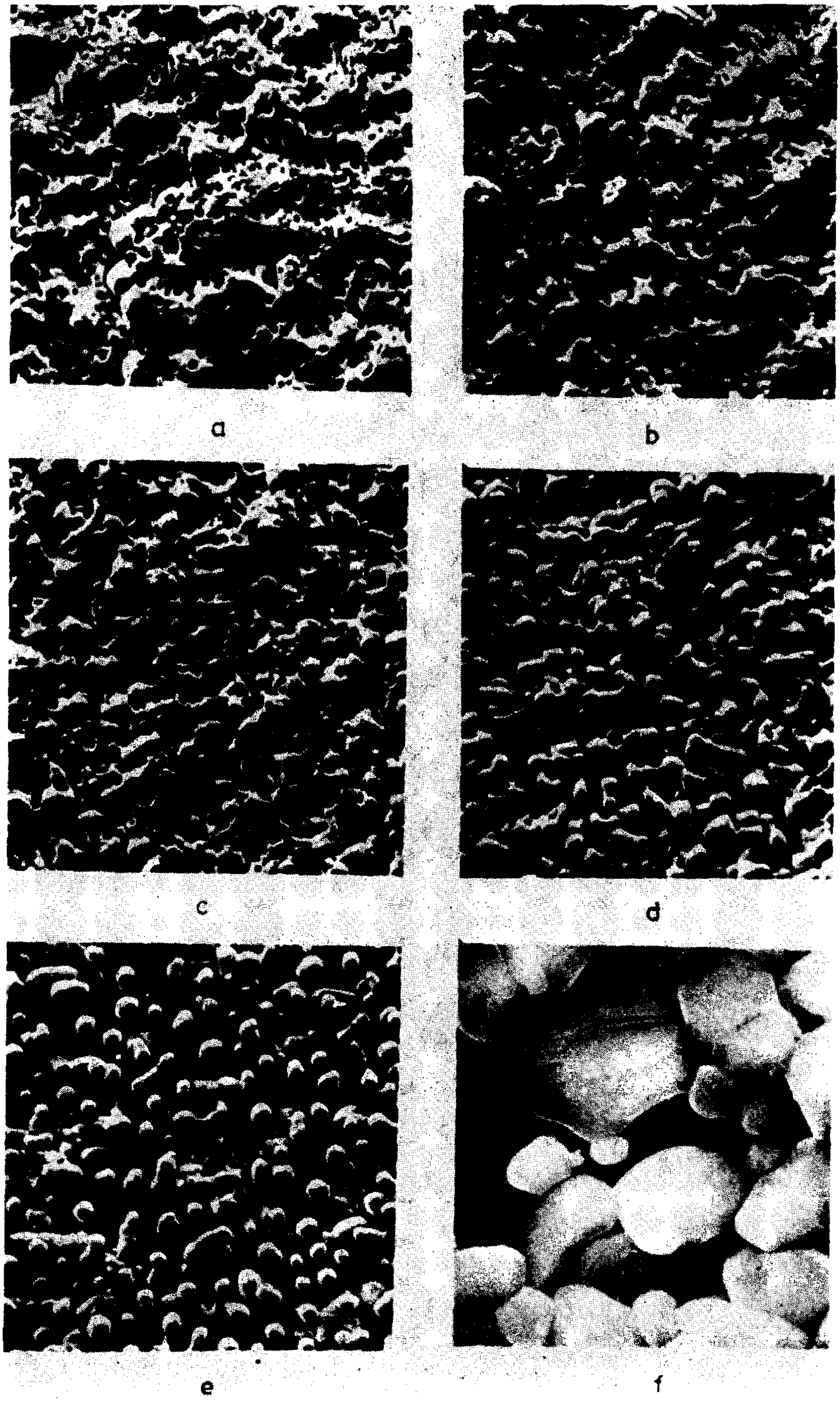

FIG. 5. Sintering of Ag/Al_2O_3 (1400 Å Ag) at 326°C. $O_2:C_2H_4 = 2:1$. (a) After 10 min, ×2500; (b) after 20 min, ×2500; (c) after 30 min, ×2500; (d) after 40 min, ×2500; (e) after 50 min, ×2500; (f) alumina surface, ×7000.

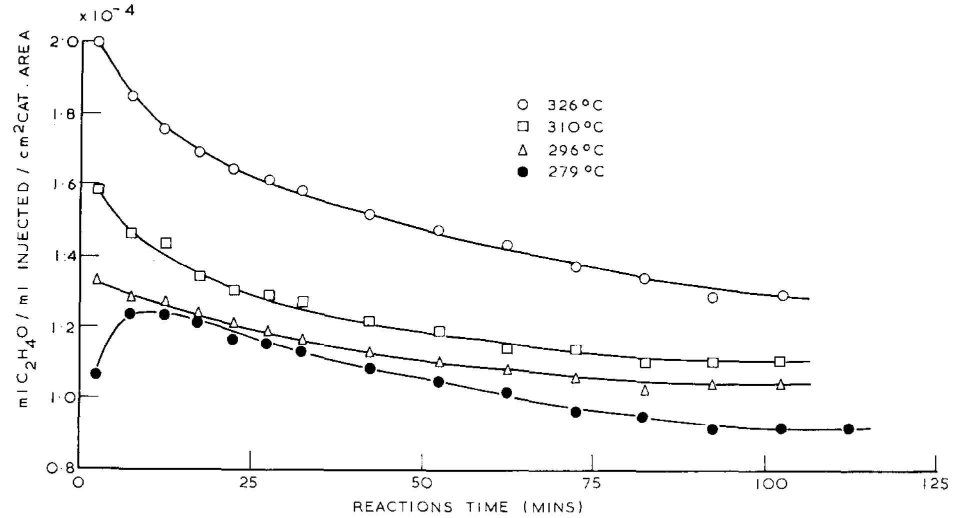

Fig. 6. Activity pattern for the oxidation of ethylene over Ag/glass: ethylene oxide production.

DISCUSSION

The activity patterns for the oxidation of ethylene are seen to show a marked dependence on the nature of the support at all temperatures (Figs. 1–4, 6, 7). In addition to the rapid changes of yield with elapsed time when the catalyst is brought on line, silver on alumina also shows interesting trends in that the yields increase again after the catalyst has been used for about 2 hr (Figs. 3 and 4).

The initial drop in activity could be suggested to result from several factors, but most of these can be discounted from the present evidence. Thus, for example, studies of the sintering of glass and silica supported catalysts [Table 1, (3)] shows that the initial changes in activity are largely complete by the time that sintering has proceeded far enough to give appreciable changes in metal surface area.

Again, it has been suggested that the

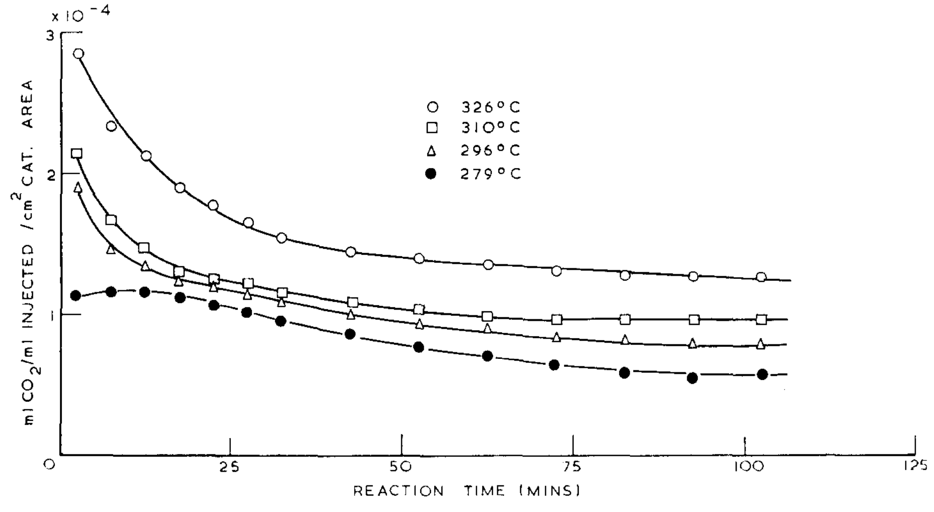

Fig. 7. Activity pattern for the oxidation of ethylene over Ag/glass: carbon dioxide formation.

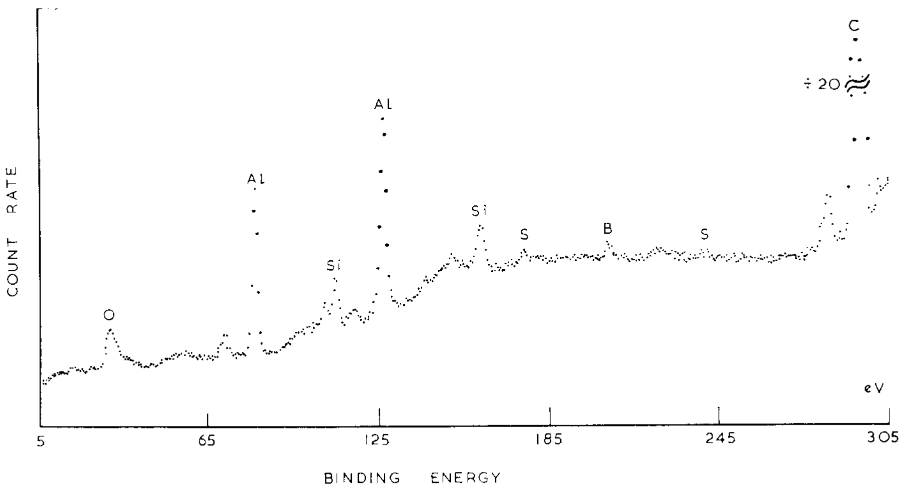

FIG. 8. ESCA spectrum of alumina.

initial changes in activity are related to the formation of some oxidized form of silver (*13*). However, the lack of movement of the silver doublet peak (Fig. 11) would indicate that no significant change in the surface silver was occurring during the initial drop in activity.

It is also known that crystallite size can have a large effect on the activity of these catalysts (*14*). As reported above, high voltage transmission electron microscopy shows that no change in crystallite size occurs during the initial deactivation.

The most obvious remaining explanation of the initial patterns of activity is that they result from hillock formation on the silver, which is known to occur within the induction period in order to relieve thermal stress (*3*). This, however, seems very unlikely, in that ethylene oxidation on silver has been reported to be a facile reaction which has little dependence on catalyst geometry (*7*, *8*). Surface rearrangements are known to occur under reaction conditions (*9*, *10*), but the fact that the oxidation of ethylene on silver proceeds at

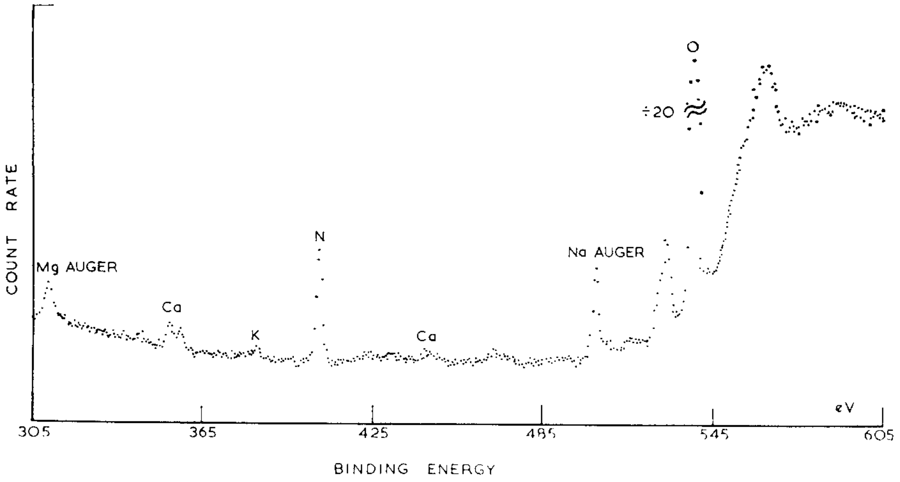

FIG. 9. ESCA spectrum of alumina.

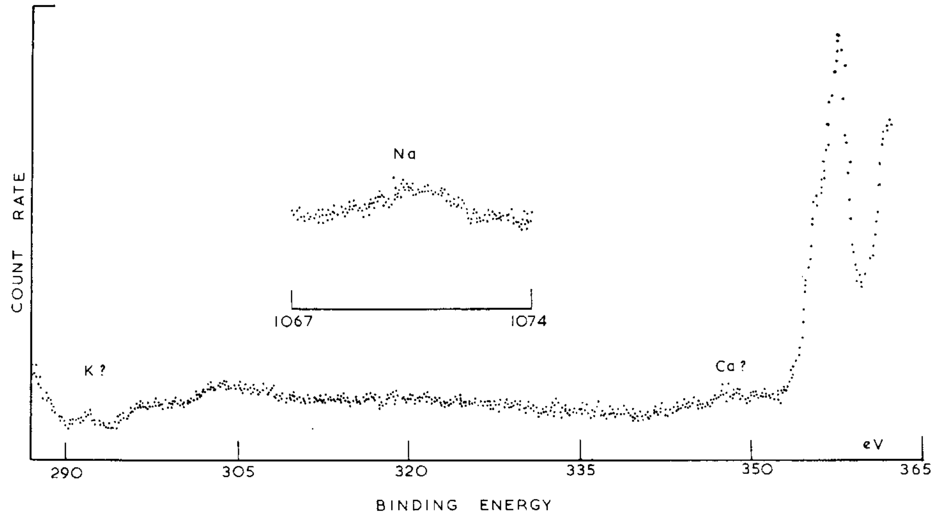

Fig. 10. ESCA spectrum of 1400 Å Ag on Al_2O_3. Pretreated in argon for 45 min at 296°C.

approximately the same rate and selectivity on different crystal faces (*7–9*) suggests that the activity pattern observed does not result from this rearrangement.

The most probable explanation of the initial changes in activity would seem to involve the effect of impurities concentrated at the surface of the silver. Electron spectroscopy shows that migration of sodium to the surface of the silver is facile and that, as a result of the chemical composition of the support, the concentration of sodium at the silver surface decreases in the order [(*3*), Fig. 10]:

glass > alumina > silica ~ 0.

TABLE 2

The Effect of Support on the Energies of Activation of Sintering and of Ethylene Oxidation[a]

Catalyst	E_A (kcal $mole^{-1}$ ± 0.1 kcal $mole^{-1}$)		
	Sintering	CO_2 formation	C_2H_4O formation
Ag/SiO_2	21.1	19.9	11.2
Ag/glass	25.0	10.7	4.6
Ag/Al_2O_3	—	18.1	9.1

[a] 1400 Å Ag. O_2:C_2H_4 = 2:1.

Comparisons of Figs. 1, 2, 3, 4, 6, and 7 show that this sodium does appear to affect the selectivity of the reaction, higher sodium concentrations leading to increased yields of ethylene oxide (*11*). However, the similarity of activity patterns before (no sodium on the surface) and after (sodium on the surface) annealing makes this conclusion dubious, and shows that initial changes in activity are not connected with sodium.

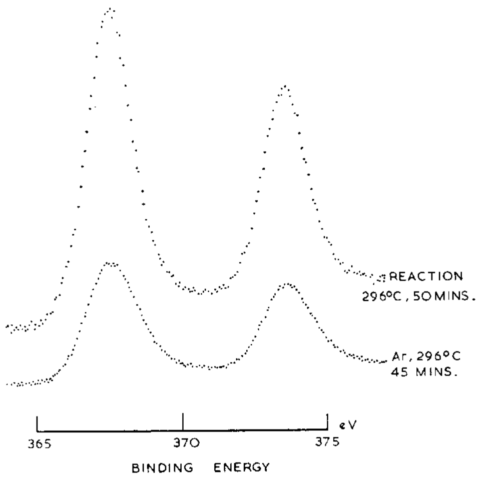

Fig. 11. ESCA spectrum of 1400 Å Ag on Al_2O_3 Ag 3*d* doublet.

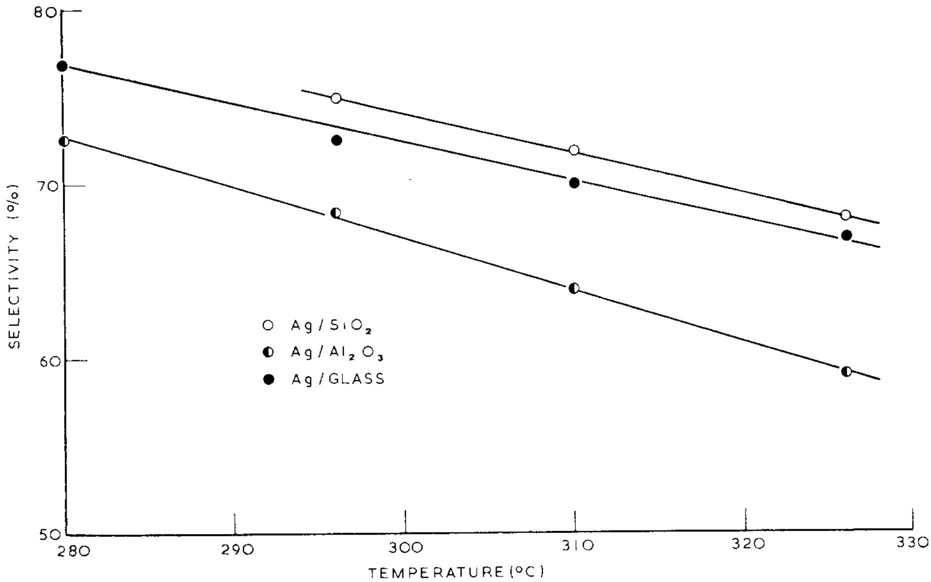

FIG. 12. Final selectivity of reorganized catalysts vs temperature.

What would seem more probable is that the initial drop in activity is due to doping effects arising from the deposition of organic residues on the surface (*15*). ESCA does show that the carbon 1*s* signal increases during reaction, although not to such an extent as to encapsulate the surface (*14*). Although tenuous, and difficult to prove absolutely, elimination of other possible modes of deactivation would seem to leave surface doping by organic residues as the most likely cause of the initial drop in activity. In the absence of other evidence, the formation of silver glyoxide from ethylene oxide (*15*) would fit all of the observations.

In these terms, the increase in catalytic activity of silver on alumina (observed after some 2 hr of reaction) probably results from a reaction involving alumina and these organic residues. The particular advantages of alumina may result from facile migration of organic residues on this support, but this is far from certain.

One interesting feature of the experiments is the high selectivity that can be obtained on these nonporous catalysts. As shown in Fig. 12, the selectivity of the catalyst in its final steady state form reaches 70–80%, even in the absence of a moderating additive.

ACKNOWLEDGMENT

The authors thank Pilkington Brothers for valuable financial assistance.

REFERENCES

1. Dowden, D. A., *Ind. Chem. Eng. Symp. Ser.* **27**, 18 (1968).
2. Kazanski, V. B., *Kinet. Catal.* **11**, 378 (1970).
3. Riassian, M., Trimm, D. L., and Williams, P. M., *Faraday Trans. I*, **72**, 925 (1976).
4. Twigg, G. H., *Proc. Roy. Soc. A* **188**, 92 (1946).
5. Presland, A. E. B., Price, G. L., and Trimm, D. L., *J. Catal.* **26**, 313 (1972).
6. Aylmore, D. W., and Jepson, W. B., *J. Sci. Instrum.* **38**, 156 (1961).
7. Woodward, J. M., Lindgren, R. G., and Corcoran, W. H., *J. Catal.* **25**, 292 (1972).
8. Kummer, J. T., *J. Phys. Chem.* **60**, 666 (1956).
9. Wilson, J. N., Voge, H. H., Stevenson, D. P.,

Smith, A. E., and Atkins, L. T., *J. Phys. Chem.* **63,** 463 (1959).

10. Czanderna, A. W., *J. Colloid Interface Sci.* **24,** 500 (1967).

11. Spath, H. T., Tomazic, G. S., Wurm, H., and Torkar, K., *J. Catal.* **26,** 18 (1972).

12. Presland, A. E. B., Price, G. L., and Trimm, D. L., *Progr. Surface Sci.* **3,** 63 (1973).

13. Seiyama, T., Kagawa, S., and Kurama, K., *J. Chem. Soc. Japan* (*Ind. Chem.*) **70,** 1137 (1967).

14. Wu, J. C., and Harriott, P., *J. Catal.* **39,** 395 (1975).

15. Ayame, A., Numabe, A., Kanazuka, T., and Kano, H., *Bull. Japan. Petrol. Inst.* **15,** 142 (1973).