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The Oxidation of Ethylene Using Silver on Different Supports

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The partial oxidation of ethylene to ethylene oxide was studied using silver deposited on aluminas or silicas with moderate to high surface area. The selectivity was very low for silver on activated alumina or dessicant-grade silica gels, but selectivities of 30–60% were obtained for silver on nonporous silicas, heat treated silica gel, and heat treated aluminas. Very high activity and good selectivity were obtained with a catalyst having silver particles 30–70 Å in diameter. Even smaller particles are believed responsible for the very low selectivities observed with some catalysts.

INTRODUCTION

The partial oxidation of ethylene to ethylene oxide is carried out over silver catalysts at 200–300°C. The silver is usually deposited on a low-surface-area support, such as α-alumina (0.1–1 m^2/g), though nonporous supports such as silicon carbide have also been used. According to reviews (*1–3*), high-surface-area supports are unsatisfactory because the catalysts have low selectivity. Published studies show only traces of ethylene oxide or none at all and high conversions to carbon dioxide for silver deposited on silica gel or on high-surface-area alumina (*4*, *5*).

Supports with large surface areas have been used to prepare very active catalysts for other reactions without loss of selectivity, and there is no reason to expect low selectivity in ethylene oxidation just because the support has a large surface area. Low selectivities might have been obtained in previous studies for some of the following reasons:

1. A combination of high activity and small pore radius may have led to large concentration gradients inside the catalyst particles. The lower concentration of ethylene and the higher concentration of ethylene oxide relative to the external concentrations would increase the importance of secondary oxidation, but this can account for only a partial reduction in selectivity at a given conversion and not zero selectivity (*6*).

2. The high reaction rates and the low selectivity, which increases the average heat of reaction, may have caused hot spots inside the particles or in the catalyst bed, which would favor complete reaction to carbon dioxide.

3. The supports might have catalyzed the further oxidation of ethylene oxide. Electron micrographs have shown that silver exists as spherical particles on the surface of alumina supports, leaving most of the support surface uncovered (*7*). The ratio of silver surface area to support area tends to decrease on going to high surface-area supports, and any effect of reaction on the support itself becomes more important. The supports could also have catalyzed the isomerization to acetaldehyde, which could be rapidly oxidized over silver.

4. The nature of the support might have influenced the distribution of particle sizes of the silver, and very small particles of silver might have high activity and low selectivity. A strong effect of particle size

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has been reported for some reactions catalyzed by nickel (*8*) and by platinum (*9*).

5. Electronic interactions between the silver and the support may have changed the nature of the sites on the silver surface so that either little ethylene oxide was formed or it was rapidly oxidized to carbon dioxide.

Since none of the published data are complete enough to test these explanations, scouting tests were made with several silver catalysts prepared using alumina or silica supports with moderate to high surface areas. The activities and selectivities were measured in a small fixed bed reactor designed to minimize temperature gradients. The effects of diffusion were checked by calculation and by using different particle sizes. Electron micrographs, chemisorption tests, and X-ray diffraction measurements were used to help characterize some of the catalysts.

Support Properties

Some properties of the supports are given in Table 1. The aluminas were all prepared from alumina B, a high surface area α-monohydrate (Péchiney) in the form of 1–2-mm spheres. Lower area supports were made by heating alumina at 1000–1100°C, which greatly reduced the surface area but did not change the porosity. Complete conversion to α-Al_2O_3, as shown by X-ray diffraction, was obtained after 80 hr at 1100°C. Most catalysts in this series were prepared using support B-5, which was only about 90% converted to α-Al_2O_3 and had some theta and iota alumina. The surface area of B-5 was 17 m^2/g, about 20 times the area of typical commercial α-alumina supports.

Catalysts were prepared from a few porous silica gels with high surface areas, but they gave very low selectivity, and only two of these are listed in Table 1. Support S-3 was made by sintering a commercial silica gel in the presence of steam. The last two supports are nonporous silicas; Cab-O-Sil HS-5 consists of spherical particles about 70 Å in size, and Silica F is a material with platy particles prepared by the formic acid method of Imelik and Carteret (*10*).

The catalytic activity of the supports was tested using mixtures of ethylene, oxygen, and ethylene oxide at 200–240°C. None of the supports showed a measurable rate of oxidation of ethylene, but they did catalyze oxidation of ethylene oxide. The oxidation rate was roughly first order to ethylene oxide and doubled for a 20°C rise in temperature. The measured rates were corrected to standard conditions to give the approximate values shown in Table 1. The oxidation rate on the silica supports was too small to have much effect on the catalyst performance, but the rates on the aluminas were significant.

TABLE 1
CATALYSTS SUPPORTS

Alumina	Treatment	Area (m^2/g)	V_{pore} (cm^3/g)	EO oxidation rate (mole/g, hr × 10^4)[a]
B	—	404	0.47	—
B-2	12 hr 995°C	66	—	5
B-4	11 hr 1100°C	30.1	—	2–3
B-5	30 hr 1100°C	17.3	—	0.9
B-3	80 hr 1100°C	8.2	0.48	0.7
Silica				
S-1, Davison 926	acid leached	800	0.5	—
S-2, Davison 70	—	350	1.04	0.7
S-3, Davison 70	16 hr 890°C	124	0.23	0.1
S-4, Cab-O-Sil HS-5	—	300	0.0	0.4
S-5, Silica F	—	62	0.0	0.2

[a] at 220°C, 2% EO, 30% O_2, 1 atm.

Catalyst Preparation

At first the catalysts were prepared by impregnating the particles with a large excess of aqueous silver nitrate, removing excess solution by blotting or centrifuging, drying at temperatures up to 170°C, and reducing with hydrogen at 150–200°C. However tests of this procedure using larger particles, that were easily sectioned, showed that the silver was usually not uniformly distributed within the particles (*11*). The nonuniformity was attributed to the growth of silver nitrate crystals during the relatively slow drying operation. Other techniques were tested in an attempt to get more rapid formation of a silver salt or silver itself inside the particles. Catalyst 74 was prepared from a hot saturated alcoholic solution of silver nitrate, and the particles were quenched in liquid nitrogen to precipitate the nitrate inside the pores. Catalyst 55 was made by diffusing sodium hydroxide into particles soaked in silver nitrate to precipitate silver oxide. Catalyst 72 was prepared by impregnation with aqueous silver lactate, which is much less soluble than the nitrate and should precipitate sooner on drying. These three catalysts were dried and reduced in hydrogen before analysis and catalytic tests.

Three catalysts, 71, 85, and 88, were made by direct formation of silver from aqueous solution using formaldehyde reduction of the silver–ammonia complex. This technique gives a radial gradient of silver concentration inside porous particles, but the average concentration is not far from the maximum value (*11*). Formaldehyde reduction in the presence of nonporous silica F produced a very uniform dispersion of fine silver particles, and this catalyst was the most active of any which had good selectivity. Catalysts 80 and 85 on nonporous supports were pelletized and then cut into 1–2-mm pieces for kinetic tests.

None of the catalysts were deliberately moderated by adding chlorides, as is done commercially to get higher selectivity. Some of the observed small differences in selectivity may have come from slight moderation by impurities, and only large changes in selectivity were considered significant in examining the role of the catalyst support.

Catalyst Testing

The catalyst activity was measured in one of two glass U-tube reactors which were 0.9 or 1.5 cm in diameter and 8 cm high. The reactor was immersed in an oil bath, and gas was preheated in the downflow arm of the U-tube, which had a glass rod core to increase the velocity and improve heat transfer. The bath temperature was automatically controlled, and the reactor temperature was measured with two thermocouples in radial wells formed in the side of the reactor. Except for a few early runs, the catalyst was diluted with 10–20 parts of quartz chips to minimize radial temperature gradients. Also, helium was used as a diluent gas rather than nitrogen to get a higher thermal conductivity. The bed temperature was generally within 1°C of the bath temperature except when helium was omitted to get a high oxygen concentration.

The flow rates of ethylene, oxygen, and helium to the reactor were measured using capillary flowmeters. The ethylene was passed through adsorbent carbon, but the other gases were used without treatment. The reactor was operated at atmospheric pressure, and the vent gases were passed directly to the sample valve of a gas chromatograph. A single column of Poropak Q at 135°C separated O_2, CO_2, C_2H_4, H_2O, and C_2H_4O, though the water peak was asymmetric.

The reactor was also connected to a gas burette and high vacuum system to permit oxygen chemisorption measurements. Most catalysts were treated to one or more cycles of outgassing, reduction by hydrogen, outgassing, and oxygen adsorption at 200°C before starting kinetic tests. The amount of oxygen chemisorbed increased slightly with pressure in the range 5–20 Torr, but the data were not very reproducible, (±20%) and usually only one measurement at about 10 Torr was made to get an estimate of the surface area. More consistent results might have been obtained by using several cycles of oxidation and reduction at a higher temperature, as was done by Czanderna (*12*), but the area would probably have been greatly reduced. Based on an area of 16.6 Å^2 per oxygen molecule, the silver areas ranged from 1 to 13 sq m^2/g-catalyst or 6 to 96 m^2/g silver.

Several catalysts were examined by X-ray diffraction to determine the average size of the silver particles by line broadening. A Phillips PW 1060 recording apparatus was used with CuK$_\alpha$ radiation. The results were similar to those of Dorling and Moss (*13*) in that some of the silver particles were too small to be detected by X-rays, and the line broadening did not give the true average size. Electron micrographs showed that most catalysts had a fairly broad distribution of silver particle size, and the particles were sometimes clustered or concentrated at edges of the support (Fig. 1a,c). However catalyst 85 had a uniform dispersion of silver on the support, and very fine particles, as shown in Fig. 1d.

Silver-Alumina Catalysts

Runs were made with several catalysts at temperatures of 180–250°C using a feed of about 25% oxygen and 2–4% ethylene. The conversions ranged from 3 to 75%, and the selectivity varied from 0 to 60%.

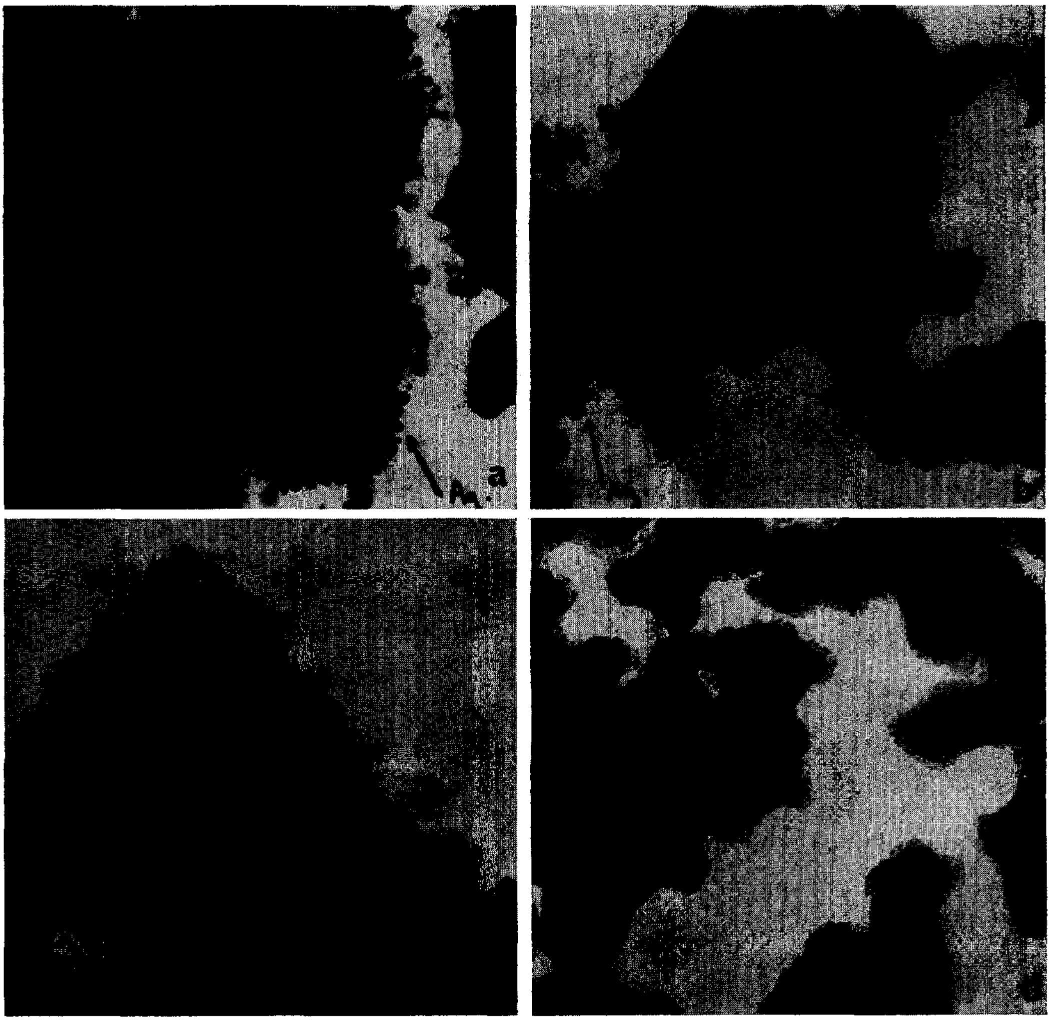

FIG. 1. Electron micrographs of silver catalysts. (a) catalyst 71, 45,000×; (b) catalyst 72, 45,000×; (c) catalyst 88, 45,000×; (d) catalyst 85, 130,000×.

Most of the catalysts showed an increase in activity during the first 1–4 hr of operation but an erratic decline in activity for overnight shutdowns or during a few days of tests. The selectivity did not change much with catalyst age but was quite a bit lower at the higher conversions. Some data for the first several hours of operation are given in Table 2, where r_{EO} is the net rate of ethylene oxide formation/g-catalyst and r_{CO_2} is the total rate of carbon dioxide formation. The compositions given are the arithmetic averages of feed and exit compositions.

Silver on untreated alumina, catalyst 20, was very active, but no ethylene oxide was found in the product. Catalyst 26 on support B-2 was less active but still unselective. (These were early runs with a small gas sample, and the selectivity might have been 5% without any ethylene oxide being detected.) The low selectivity cannot be attributed to temperature gradients, since the calculated particle temperature was only 1°C above the bulk gas temperature for the maximum rate of reaction. Also, other catalysts of the same size gave selectivities of 30% or more at comparable rates of reaction. For catalyst 20, the effectiveness factors were estimated to be between 0.3 and 0.8 based on ethylene diffusion, and allowing for product inhibition would make the values even lower. The internal concentration gradients would lower the selectivity somewhat, but the inherent selectivity for these catalysts is probably still less than 10%.

Selectivities of 15–33% were obtained with two catalysts prepared from support B-3. The higher value for catalyst 28 is attributed mainly to the lower conversion, which was 17–29% compared to 66–75% for catalyst 36. The selectivity decreases with conversion because of further oxidation on the support as well as on the silver. Based on the data in Table 1, the oxida-

TABLE 2
KINETIC DATA FOR $Ag\text{-}Al_2O_3$ CATALYSTS

Catalyst, support	Temp °C	Av composition			Rate (mole/hr·g × 10^4)		
		%E	$\%O_2$	$\%CO_2$	r_{EO}	r_{CO_2}	$S\%$
20, B	227	2.9	9	0.95	0	30.4	0
13.7% Ag	203	3.1	9	0.41	0	19.5	0
26, B-2	220	0.7	20	0.88	0	11.3	0
8.9% Ag	180	0.8	21	0.27	0	2.6	0
28, B-3	218	4.9	21	0.70	3.1	6.3	33
7.9% Ag	236	4.8	21	1.06	4.5	9.3	33
36, B-3	248	1.9	23	1.7	6.7	23	23
26% Ag	224	2.7	23	2.1	2.8	15.4	15
70, B-5	224	2.6	22	0.98	3.2	10.7	23
14.9% Ag	197	3.8	19	0.55	0.86	2.94	23
H_2	196	3.3	20	0.72	0.51	2.64	16
	225	3.0	21	0.86	3.8	9.1	29
71, B-5	180	1.9	23	0.46	2.3	7.9	22
7.9% Ag	199	1.2	24	0.70	3.7	11.5	24
HCOH	193	3.0	25	0.34	3.9	10.4	27
	193	3.1	25	0.11	6.9	9.9	41
72, B-5	222	2.6	22	0.26	8.1	10.7	43
3.5% Ag	220	3.1	23	0.05	1.1	0.96	54
lactate	220	3.2	23	0.08	0.79	0.80	49
	220	3.4	23	0.15	0.39	0.67	37
	220	3.3	96	0.15	1.78	1.32	57
74, B-5 16.3% Ag alc. sol.	222	2.6	22	0.19	1.22	4.5	21

tion of ethylene oxide on the support could account for a few percent loss in selectivity for catalyst 28. Allowing for the effect of conversion, both catalysts were more selective at higher temperatures.

Catalysts 70–74 were prepared in different ways from support B-5 and gave selectivities of 20–60%. The method of preparation influenced the surface area of the silver and the catalyst activity, but the selectivity depended mainly on gas composition. Catalyst 71, prepared by formaldehyde reduction, was about 4 times as active as catalyst 70, though it had only half as much silver. The mean particle sizes from chemisorption data were 340 Å for 70 and 150 Å for 71, which only partially accounts for the difference in activity. The electron micrographs were similar, with most particles between 50 and 200 Å in diameter.

Catalyst 72, prepared by silver lactate impregnation, was initially about as active as catalyst 71 and twice as active per gram of silver. The surface mean particle size was 80 Å, only half that for catalyst 71. The catalyst activity dropped 10-fold during overnight operations, and the last four points in Table 2 were taken at 20–25 hr, when the activity was nearly constant. These points show a decrease in selectivity from 54 to 37% as the conversion increased from 3 to 6%, which indicates an initial selectivity of over 60%. The loss of product was again greater than expected from the measured support activity, indicating a support-metal interaction or a higher than normal rate of product oxidation on the silver. The selectivity increased from 37 to 57% on going from 23 to 96% oxygen. Catalyst 74 was not very active at the start and decayed rapidly, so tests were not continued.

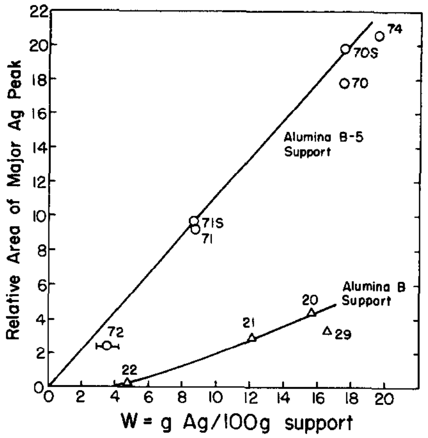

FIG. 2. X-ray diffraction results for Ag–Al_2O_3 catalysts.

The moderate selectivities obtained with catalysts on supoprts B-3 and B-5 and the low selectivity with supports B and B-2 at comparable reaction rates may result from a difference in the size distributions of the silver grains and a low selectivity for very small grains. The chemisorption data indicate mean particle sizes of 60 and 170 Å for catalysts 20 and 26, about the same as for catalysts 71 and 72. However the X-ray data show that silver is much more highly dispersed on support B than on support B-5. In Fig. 2 the area for the silver peak at 19.06° is plotted against the concentration of silver. This area is a measure of the amount of silver in particles large enough to cause appreciable diffraction. Two samples, 70S and 71S were sintered at 800°C to give large particles for calibration. These data and the data for other catalysts on support B-5 were corrected to the same sample size using the α-alumina peak as an internal standard. The catalysts on support B-5 fall slightly under the calibration line, indicating 70–95% of the particles are larger than 50 Å. However, for catalyst 20, more than two-thirds of the silver was not detected by X-rays. These very small particles could be nonselective and active enough to oxidize the ethylene oxide produced on the larger particles.

Other catalysts prepared from alumina B were not tested in the reactor, because the selectivity was presumed small, but the X-ray results are included in Fig. 2. With decreasing silver content, the fraction of silver in small particles increases, and this trend is similar to the increase in the fraction of silver nitrate adsorbed during impregnation *(11)*. Silver nitrate is strongly adsorbed on alumina, and for catalyst 20, two-thirds of the silver came from adsorbed silver nitrate and one-third from the pore solution. The adsorbed salt probably leads to very small grains of silver, though some of these would disappear by sintering during reduction. A low reduction temperature was used for catalyst 29 and this catalyst had less silver in large particles than catalyst 20.

Silver-Silica Catalysts

Catalysts prepared using a commercial fine-pore silica gel and a similar gel prepared from specially purified reagents gave zero selectivity. As shown in Table 3, a little ethylene oxide was obtained with catalyst 55, made from a moderate pore-size gel. Catalyst 88 on the heat treated support S-3 gave selectivities of 34–47%. Heating the support reduced the total surface but slightly decreased the average pore size, so the improved selectivity is not a mass transfer effect. The higher selectivity is believed to come from a change in the size of the silver particles, brought about by a change in the nature of the silica surface. A simple adsorption test showed that the surface was altered by sintering; the water adsorbed per unit area on exposure to room air was only half as great as for the original material.

More extensive tests were carried out with the catalysts made using nonporous silicas. Catalyst 80 gave selectivities of 51 and 66%, increasing with decreasing conversion or increasing oxygen concentration. The total reaction rate per gram of silver

TABLE 3

KINETIC DATA FOR Ag–SiO_2 CATALYSTS

Catalyst, support	Temp (°C)	Av. composition			Rate (mole/hr·g × 10^4)		
		%E	%O_2	%CO_2	r_{EO}	r_{CO_2}	$S\%$
60, S-1 11.5% Ag	229	4.4	32	0.37	0	1.18	0
55, S-2 4.9% Ag	238	2.9	48	0.11	0.07	0.46	13
88, S-3	223	2.6	23	0.54	0.44	0.84	34
5.2% Ag	223	2.0	22	0.36	0.34	0.56	38
(HCOH)	223	3.8	25	0.46	0.43	0.76	36
	223	3.6	47	0.35	0.60	0.69	47
80, S-4	220	2.5	25	0.19	3.28	2.07	61
9.5% Ag	220	2.3	25	0.40	2.33	1.81	56
H_2	220	2.6	97	0.18	7.27	3.75	66
	220	3.1	11	0.21	2.21	2.13	51
85a, S-5	201	2.6	21	0.38	14.2	25.0	36
29% Ag	200	2.3	21	0.72	8.7	12.7	41
(HCOH)	200	2.4	22	1.17	4.9	7.0	41
1–2 mm	200	2.5	96	0.70	17.4	11.4	60
	181	2.6	96	0.39	9.2	7.0	57
	181	2.8	97	0.27	13.5	12.2	52
	181	3.8	96	0.31	15.8	14.6	52
	201	2.7	21	0.70	9.7	12.0	45
	219	1.4	21	0.82	11.6	14.1	45
	219	1.6	20	0.55	22.7	28.7	44
	219	1.5	48	0.50	30.3	26.7	53
	219	1.6	97	0.50	31.1	23.8	57
	219	2.3	22	0.87	12.1	15.1	45
	243	2.3	20	1.20	28.8	40.8	41
85b	202	2.0	20	1.09	8.9	14.2	39
2.7 × 6.2 mm	203	2.1	20	0.76	15.0	24.7	38
pellets	203	2.0	43	0.75	21.8	23.8	48
	202	2.3	96	0.71	30.1	21.3	59

was about twice that for catalyst 88, though both electron micrographs showed particles 200–300 Å in size. Catalyst 85 was about 12 times as active as catalyst 80 and 4 times as active per gram of silver. The electron micrograph, Fig. 1d, shows a fairly narrow distribution of particle sizes with an average size of about 50 Å, 5 times smaller than for catalyst 80. The selectivities were slightly less than for catalyst 80, though still in the normal range for unpromoted catalysts. If there is an effect of particle size on selectivity, the major change must come for particles less than about 30 Å in diameter.

The kinetic tests of catalyst 85 were carried out with a large excess of oxygen and at moderate conversions of ethylene. There was no catalyst decay and check runs gave reproducible results. The effects of product inhibition and temperature on the rate of ethylene oxide formation are shown in Fig. 3. The data were corrected to 2.5% ethylene using an effective order of 0.7, obtained from data for other catalsyts in this range of pressures (*16*). The rate varied nearly inversely with product concentration in the range 0.5–1.0% CO_2, but no attempt was made to fit these results to a kinetic equation. The relative importance of CO_2, H_2O and EO on the rate was not measured.

The data for small particles at 181–219°C indicate a 2- to 2.5-fold increase in rate per 20°C, or an apparent activation energy of 17–22 kcal, which is in the range of published values. However the rate at 243°C was higher than expected, and pellets of catalyst gave a higher rate than small particles. Both these effects can be explained by temperature gradients caused by the very high activity of catalyst 85. Based on an estimated thermal conductivity of 0.5×10^{-3} cal/sec·cm·°C and an external Nusselt number of 5, the 1–2-mm particles would be on the average about 2°C above the gas temperature at 219°, with the internal and external gradients of about equal importance. The temperature differences would be about twice as great at the start of the bed where the product concentration is low. The differences would increase with bed temperature and give too high an activation energy.

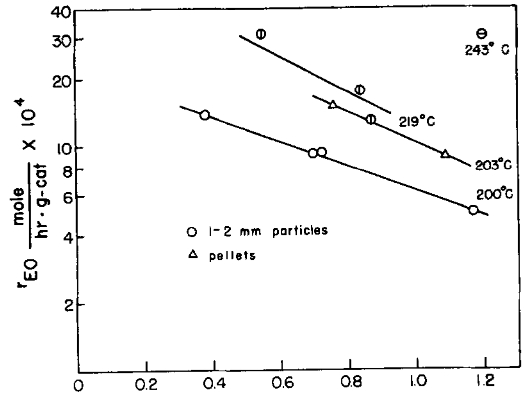

FIG. 3. Kinetic data for catalyst 85, for 2.5% E, 21% O_2.

The pellets, which were 2.7 × 6.2 mm, were estimated to be 10–20°C hotter than the gas in the bed. Although the concentration gradients in the pellet must be significant at these rates, they only partly offset the higher temperatures, and the effectiveness factor is greater than one. It should be pointed out that a catalyst this active would give extreme radial temperature gradients or a runaway reaction if used in a tubular reactor under normal conditions for ethylene oxide synthesis. The gradients were minimized in this study by use of a small diameter bed, dilution with quartz, and use of helium as a carrier gas. Of course the activity would be reduced by the poisoning agents used to improve selectivity, and with such an active catalyst, a greater concentration of poison might be feasible.

The effect of oxygen on reaction rate is shown in Fig. 4. The rate of formation of ethylene oxide increases with oxygen pressure, and the rate of carbon dioxide formation slightly decreases, suggesting a maximum in the rate at 20% oxygen or less. A maximum in reaction rate is predicted with competitive adsorption models; other studies (*16*) show maxima with changing ethylene pressure, though not with oxygen pressure over the same pressure range. The general model and form of the kinetic equations may be the same for different

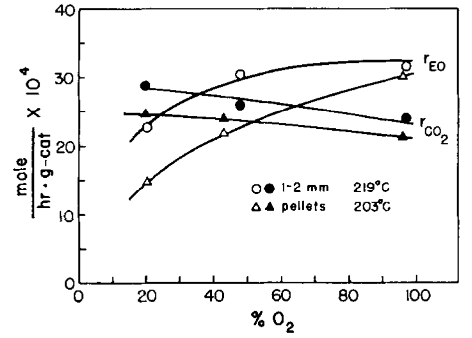

FIG. 4. Effect of oxygen concentration on reaction rates for catalyst 85.

silver catalysts, but the parameters probably depend on the particle size distribution and purity of the catalyst.

The role of the silica surface in determining the particle size and selectivity of the silver catalyst has not been established. Cab-O-Sil, which is formed at 1100°C, and the sintered silica gel have fewer hydroxyl groups on the surface than an untreated silica gel. However Silica F has twice as many hydroxyl groups as a typical xerogel (*17*). Perhaps the method of deposition of silver is more important than the nature of the support surface.

CONCLUSIONS

Silicas with high surface area can be used to prepare silver catalysts which are much more active and about as selective as silver on low-surface-area supports. Good yields of ethylene oxide were obtained for silver on two nonporous silicas and a heat treated silica gel with areas of 60–300 m^2/g. The very low selectivity for silver on dessicant-grade silica gel was not caused by heat or mass transfer effects or by direct oxidation of ethylene oxide on the support. The low selectivity may have been caused by a greater dispersion of the silver, with the smallest particles having high activity for further oxidation of ethylene oxide. Since nearly normal selectivity was obtained for one catalyst with an average particle size of only 50 Å, any major change in activity with size must occur for even smaller particles.

Moderate selectivities were obtained for silver on heat treated aluminas of intermediate surface area, but the selectivity decreased quite rapidly with increasing conversion, indicating further oxidation of ethylene oxide. These aluminas had greater catalytic activity than the silicas, but the support activity alone was not enough to account for the lower yields. A support–metal interaction might have been responsible, or the increased reaction rate of ethylene oxide could be attributed to the very small grains of silver. A significant fraction of the silver was in particles too small to be detected by X-rays, and for silver on activated alumina, which had zero selectivity, most of the silver was in such very small particles.

The particle size of the silver is determined both by the nature of the support and the conditions used in preparing the catalyst. Strong adsorption of the impregnating salt on a porous support tends to give very small particles, but crystal growth during drying and reduction give some large particles and a broad distribution. The most uniform catalyst and the one with the smallest average grain size was obtained by rapid reduction to form silver on a nonporous silica. This technique could probably be used to prepare similar catalysts with different average grain sizes to check the effect of size on activity and selectivity.

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REFERENCES

1. SHERWOOD, P. W., *Ind. Chem.* **35**, 126 (1959).
2. DIXON, J. K., AND LONGFIELD, J. E. "Catalysis" (P. H. Emmett, ed.), Vol. 7, p. 248. Reinhold, New York. 1960.
3. VOGE, H. H., AND ADAMS, C. R., *Advan. Catal. Relat. Subj.* **17**, 151 (1967).
4. REYERSON, L. H., AND OPPENHEIMER, H., *J. Phys. Chem.* **48**, 290 (1944).
5. WOLF, F., AND GOTZE, H., *Chem. Tech. Leipzig* **14**, 600 (1962).

6. Wheeler, A., *in* "Catalysis" (P. H. Emmett, ed.), Vol. 2. Reinhold, New York, 1955.

7. Vasilevich, L. A., Boreskov, G. K., Gur'yanova, R. N., Ryzhak, I. A., Filippova, A. G., and Frolkina, I. T., *Kinet. Katal.* **7**, 525 (1966).

8. Taylor, W. F., Sinfelt, J. H., and Yates, D. J. C., *J. Phys. Chem.* **69**, 3857 (1965).

9. Boudart, M., Aldag, A. W., Ptak, L. D., and Benson, J. E., *J. Catal.* **11**, 35 (1968).

10. Imelik, B., and Carteret, Y., *Bull. Soc. Chim. Fr.* **18**, 864 (1951).

11. Harriott, P., *J. Catal.* **14**, 43 (1969).

12. Czanderna, A. W., *J. Phys. Chem.* **70**, 2120 (1966).

13. Dorling, T. A., and Moss, R. L., *J. Catal.* **7**, 378 (1967).

14. Kurilenko, A. I., Kul'kova, N. V., Baranova, L. P., and Temkin, M. I., *Kinet. Katal.* **3**, 208 (1962).

15. Orzechowski, A., and MacCormack, K. E., *Can. J. Chem.* **32**, 388 (1954).

16. Klugherz, P., PhD Thesis, Cornell University, 1969.

17. Dalmai, G., Frachon de Pradel, A., and Imelik, B., *Congr. Catal. 2nd Paris,* 865 (1960).