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Ethylene Oxidation over Small Silver Crystallites

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Well-dispersed Ag/SiO_2, Ag/η-Al_2O_3, and Ag/TiO_2 catalysts were prepared and their activity and selectivity for ethylene oxide (EO) formation in the presence and absence of $C_2H_4Cl_2$ (EDC) and CO_2 were compared to those of a poorly dispersed Ag/α-Al_2O_3 catalyst. Under comparable reaction conditions, the smallest (3–4 nm) Ag crystallites had turnover frequencies (TOFs) that were over 100 times lower than those of the large crystallites on α-Al_2O_3. In the presence of 0.5 ppm EDC, selectivities over Ag/η-Al_2O_3 and Ag/TiO_2 were near 10% compared to a value near 60% over the Ag/α-Al_2O_3 catalyst, and this was attributed to the presence of secondary oxidation reactions occurring on these reactive supports. In contrast, in the absence of EDC and CO_2 at 523 K, selectivities of 17 and 55% were obtained over 4.4- and 7.6-nm Ag crystallites on SiO_2, respectively, compared to 23% from the 1-μm crystallites on α-Al_2O_3. The addition of EDC at low levels of 150–200 ppb markedly increased the selectivity to over 60% for the Ag/α-Al_2O_3 catalyst whereas the selectivity remained essentially constant at 55% over the latter 1.06% Ag/SiO_2 catalyst. The best SiO_2-supported catalyst, 1.71% Ag/SiO_2 with 13.3-nm crystallites, gave selectivities of 61–64% and a TOF for EO formation of 6.4×10^{-3} s^{-1} at 503 K in the presence of 500 ppb EDC compared to a selectivity of 61% and a TOF of 55×10^{-3} s^{-1} for the 18% Ag/α-Al_2O_3. Thus comparably high selectivities can be attained over both large and small Ag crystallites although the EDC levels for optimum values appear to differ, with larger crystallites requiring higher EDC concentrations. The lower TOF values on the Ag/SiO_2 catalysts are compensated by their much higher dispersions, and these SiO_2-supported catalysts also show much greater resistance to sintering. A comparison with literature results indicates that in the absence of moderators a 1000-fold decrease in TOF occurs as Ag crystallite size decreases to 3 nm from that in bulk samples (such as single crystals); however, structure sensitivity cannot be unequivocally claimed because of the unknown role of adsorbed oxygen on these small particles. © 1990 Academic Press, Inc.

INTRODUCTION

Silver is a unique catalyst in the ethylene oxidation reaction because of its high selectivity to ethylene oxide (EO); however, wide ranges of activity and selectivity have been reported. This is not too surprising considering the different reaction conditions employed, the various pretreatments utilized, the effects of promoters (and inhibitors), and the influence of the support which is particularly important in relation to the secondary oxidation reaction of EO to CO_2. Unfortunately, most of these investigations have not reported activity normalized to Ag surface area, such as a turnover frequency (TOF), primarily because Ag surface areas were not measured. Although Verykios *et al.* examined the influence of Ag crystallite size and morphology on catalytic behavior and reached the conclusion that structure sensitivity existed, the crystallite size range 30–740 nm was much larger than that over which such changes might be anticipated (*1*). Consequently, this conclusion has been challenged by Sajkowski and Boudart (*2*), and it appears that uncertainty remains regarding the performance of well-characterized, well-dispersed Ag catalysts in the ethylene oxidation reaction.

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Silver catalysts for this reaction have recently attracted additional attention for several reasons. First, some excellent UHV single-crystal studies have been conducted by Campbell *et al.* (*3–7*) and by Lambert and co-workers (*8–11*) which have provided not only turnover frequencies on well-defined Ag surfaces but also substantial insight into the role of inhibitors and promoters in determining catalytic behavior. In addition, Van Santen and de Groot (*12*) have provided overwhelming evidence that on Ag powder atomic oxygen existing at or below the Ag surface is involved in EO formation, rather than molecular oxygen. Thus, as stated in an excellent recent review by Van Santen and Kuipers (*13*), the previously presumed limitation of 6/7 on selectivity to EO does not exist and values approaching unity are possible, in principle. Finally, the possibility of structure sensitivity in this reaction over Ag has been addressed by Sajkowski and Boudart (*2*) in a thorough review in which they concluded that the significant variations in TOF attributed to crystallite size in the literature are more likely due to surface impurities than to structure sensitivity.

In our investigation of the adsorption and sintering behavior of Ag crystallites, a family of well-dispersed Ag catalysts was prepared (*14–17*). This provided an opportunity to examine the effect of crystallite size, especially below 10 nm, on catalytic behavior because these samples were characterized by O_2 adsorption and H_2 titration both before and after reaction and, in addition, they were routinely prepared from high purity $AgNO_3$ using well-defined pretreatments to minimize surface contamination. Finally, the dependence of TOF on the concentration of the Cl-containing "promoter," added to the feed to enhance selectivity to EO, had not been reported for supported Ag crystallites. This paper describes results related to the influence of support, crystallite size, and ethylene dichloride concentration on the catalytic behavior of Ag particles which range from 3 to 1000 nm and contain no other promoters. Finally, the influence of CO_2 in the feed was also examined because it is present under commercial processing conditions and its influence on catalytic behavior had not been reported.

EXPERIMENTAL

Catalyst preparation. The catalysts were prepared using different supports—TiO_2 (Degussa P-25, 50 m^2/g), SiO_2 (Davison, grade 57, 220 m^2/g), α-Al_2O_3 (Norton Alumdum, 0.2 m^2/g), and η-Al_2O_3 (245 m^2/g, prepared by the calcination in air of Davison β-alumina trihydrate at 863 K for 4 h) (*15*). The TiO_2- and η-Al_2O_3-supported samples were prepared by incipient wetness impregnation with an aqueous solution of $AgNO_3$ (Aldrich Co.) using doubly distilled deionized (DD) water in a N_2 atmosphere followed by drying at 368 K *in vacuo* for 2–3 h and storage in a desiccator. To vary silver crystallite size without sintering, Ag/SiO_2 catalysts were prepared by varying the silver loading, precursor salt, and silver deposition method. Some samples were prepared by the incipient wetness method using silver lactate (Pfalz & Bauer) and silver nitrate (Fisher Scientific, 99.99%), while another sample was prepared by an ion exchange technique similar to that of Benesi *et al.* (*18*). A silver–amine complex was formed by mixing $AgNO_3$ and NH_4OH in DD water, and silica was stirred in this solution overnight at a pH of 9. The catalyst was then filtered, washed with DD water, and dried in flowing air at 393 K for 2 h. To provide a comparison with large Ag crystallites, a "standard" Ag/α-Al_2O_3 catalyst, similar to a commercial EO production catalyst but without promoters, was prepared with $AgNO_3$ as described in a U.S. patent (*19*) using the low surface area α-Al_2O_3. All support materials were pretreated in a flow of dry O_2 at 723 K for 2 h prior to impregnation to remove any organic contamination. Silver loadings were determined at the Dow Chemical Co. by plasma emission spectroscopy. The catalyst compositions and prepa-

TABLE 1

Catalyst Preparation and Compositions

Catalyst	% Ag	Support	Precursor salt	Preparation method
A	1.89	η-Al_2O_3	$AgNO_3$	Incipient wetness
B	1.81	TiO_2	$AgNO_3$	Incipient wetness
C	0.70	SiO_2	$Ag(NH_3)_2^+$	Ion exchange
D	1.06	SiO_2	$AgO_3C_3H_5$	Incipient wetness
E	1.33	SiO_2	$AgNO_3$	Incipient wetness
F	1.71	SiO_2	$AgNO_3$	Incipient wetness
G	16.65	SiO_2	$AgNO_3$	Incipient wetness
H	18.0	α-Al_2O_3	$AgNO_3$	Impregnation (excess solution)

ration methods are summarized in Table 1.

Catalyst characterization. Silver dispersions were measured by both oxygen chemisorption and H_2 titration of adsorbed oxygen in a grease-free, high-vacuum (2×10^{-11} kPa) system constructed primarily of stainless steel (*15*). The standard pretreatment prior to chemisorption measurements consisted of calcination in oxygen followed by: (a) reduction of samples at 573 K in flowing H_2 for 2.5 h and further evacuation; (b) flow of O_2 for 10 min at 443 K and evacuation; and (c) final reduction with H_2 for 20 min at 443 K and evacuation for 30 min at this temperature (*14*); however, the calcination step was sometimes omitted because $AgNO_3$ was used. A more recent study has shown an influence of reduction temperature (*17*); therefore, reduction at 673 K was sometimes used. The pretreatment details are listed in Table 2. All adsorption measurements (isotherms) were conducted at 443 K. The TEM measurements have been described previously (*14*). All gases used were of ultrahigh purity grade and were further purified by passage through a drying trap and/or an Oxytrap (Alltech Asso.), when appropriate.

Catalytic measurements. Each catalyst was typically reduced and characterized by chemisorption, then passivated in oxygen prior to its exposure to air and transfer to the reactor for kinetic measurements, all of which were conducted at 445 kPa (50 psig). The first series of runs, designated by (I), was conducted in an unlined stainless-steel reactor at a feed flow rate of 100 cm^3 STP, and it involved samples of 1.89% Ag/η-Al_2O_3, 1.81% Ag/TiO_2, 1.71% Ag/SiO_2, 1.33% Ag/SiO_2, and 18% Ag/α-Al_2O_3. The remaining runs (designated II) utilized a pyrex reactor placed inside a heated stainless-steel block and a feed flow rate of 40 sccm. The catalysts (ca. 0.5 g) were held in place by means of glass wool and glass beads (ca. 0.5 g). Gas flows were controlled either by mass flowmeters or rotometers. Analysis of

TABLE 2

Pretreatment Procedures and Gas Uptakes for Silver Catalysts

Catalyst code	Composition	Pretreatment				O_2/H_2 cycle at 443 K	Gas uptake (μmol/g catalyst)				Dispersion using O_2	Average particle size (nm)
		Calcination		Reduction			Fresh		Used			
		Temp (K)	Time (h)	Temp (K)	Time (h)		O_2 Ads	H_2 Titr	O_2 Ads	H_2 Titr		
A	1.89% Ag/η-Al_2O_3	—	—	573	2.5	Yes	28.0	55.8	—	—	0.32	4.2
B	1.81% Ag/TiO_2	—	—	573	2.5	Yes	36.2	72.7	—	—	0.43	3.1
C	0.70% Ag/SiO_2	773	2	673	2.5	No	10.0	20.7	10.1	20.4	0.31	4.4
D	1.06% Ag/SiO_2	773	2	673	2.5	No	8.7	18.4	10.4	23.8	0.18	7.6
E	1.33% Ag/SiO_2	—	—	673	1	Yes	8.6	17.4	—	—	0.14	9.6
F	1.71% Ag/SiO_2	—	—	573	2.5	Yes	8.0	15.3	—	—	0.10	13.3
G	16.65% Ag/SiO_2	773	2	673	2.5	No	25.3	51.5	29.3	61.8	0.033	41.0
H	18.0% Ag/α-Al_2O_3[a]	443	0.17	443	2.5	Yes	1.04	—	—	—	0.0012	1080

[a] Pretreatment *A* from Ref. (*14*) or (*15*).

the products was done using a gas chromatograph with a Porapak-Q column, and a Perkin–Elmer MGA 1200 process mass spectrometer was also used in some runs. Ethylene dichloride (EDC, CH_2ClCH_2Cl) was added to the feed by the appropriate flow rate of a mixture of 10 ppm EDC in N_2, and the levels used (0.15–0.75 ppm) gave partial pressures from 0.067 to 0.334 Pa. Nitrogen was used as the diluent gas in all runs except in runs involving unreduced 1.71% Ag/SiO_2, in which He was used. The sample pretreatment prior to the catalytic measurements and the reaction conditions were varied as noted in Tables 2–4.

To obtain an indication of the influence of Ag particle size and support on catalytic behavior and activity maintenance, long-term runs of 9 to 12 days in the absence of EDC and 14 to 27 days with EDC were conducted on the first series of catalysts. A decrease in activity occurred upon addition of EDC to the feed, and additional deactivation with time on-stream was observed in some cases. In the latter experiments, removal of EDC did not give recovery back to the original activity, so the samples were removed for chemisorption measurements because it was expected that sintering had occurred. Due to this long-term deactivation, the activation energies in Table 3 for the second series of runs were obtained from activity measurements over much shorter (1–2 h) periods on stream after each change in temperature.

RESULTS

Adsorption Measurements

Table 2 lists the O_2 chemisorption and H_2 titration results for the catalysts in this study. Corresponding silver dispersions (D) (fractions exposed) and average particle sizes (d) for silver crystallites were calcu-

TABLE 3

Catalytic Behavior of Supported Silver Catalysts (Reaction Conditions: P_{total} = 445 kPa, 0.5 g catalyst)

Catalyst	Ag dispersion	Temp (K)	TOF ($s^{-1} \times 10^3$)[a]		S^b (%)	C_2H_4 conv. (%)	E_a (kJ/mol)		P(kPa)[c]			EDC (ppm)
			(EO)	(CO_2)			EO	CO_2	C_2H_4	O_2	CO_2	
1.89% $Ag/\eta\text{-}Al_2O_3(I)^d$	0.32	547	0.065	0.95	12	0.2	—	—	73	29	9	0.50
1.81% $Ag/TiO_2(I)^d$	0.43	544	0.19	3.3	10	0.5	—	—	73	29	9	0.50
1.71% $Ag/SiO_2(I)^{d,e}$	0.10	503	6.4	7.1	64	0.7	—	—	73	29	9	0.50
1.71% $Ag/SiO_2(I)$*	0.10	503	6.9*	8.6*	61*	—	—	—	30	8	0	2*
0.70% $Ag/SiO_2(II)^f$	0.31	523	1.6	25.0	17	2.5	50	41	75	29	0	0
1.06% $Ag/SiO_2(II)^f$	0.18	523	2.9	4.9	55	0.4	43	47	81	29	0	0
1.06% $Ag/SiO_2(II)$	0.18	523	2.1	3.5	55	1.2	67	76	81	29	0	0.15
1.06% $Ag/SiO_2(II)$	0.18	523	1.7	13.7	20	1.7	90	85	84	29	9	0
1.33% $Ag/SiO_2(I)^f$	0.14	507	0.37	7.0	10	0.5	—	—	66	44	0	0
16.65% $Ag/SiO_2(II)^f$	0.033	523	1.2	5.1	31	0.9	66	—	77	29	9	0.15
16.65% $Ag/SiO_2(II)$	0.033	523	1.4	11.7	20	4.3	67	98	77	29	0	0
16.65% $Ag/SiO_2(II)$	0.033	523	0.61	7.7	14	2.2	120	110	73	29	9	0
18% $Ag/\alpha\text{-}Al_2O_3(I)^d$	0.0012	508	55	39	61	—	—	—	73	29	9	0.50
18% $Ag/\alpha\text{-}Al_2O_3(II)^f$	0.0012	523	149	1010	23	11.4	39	64	75	29	0	0
18% $Ag/\alpha\text{-}Al_2O_3(II)^f$	0.0012	523	71	94	60	2.0	80	105	75	29	0	0.15
18% $Ag/\alpha\text{-}Al_2O_3(II)^f$	0.0012	523	176	912	28	12.8	59	99	73	29	9	0
18% $Ag/\alpha\text{-}Al_2O_3(II)^f$	0.0012	523	133	160	62	5.9	95	126	73	29	9	0.15

[a] Rate of product formation.

[b] S = [mole EO formed/mole C_2^{2-} reacted].

[c] Balance composed of N_2.

[d] Feed, 100 cm^3 (STP)/min.

[e] 0.4 g catalyst.

[f] Feed, 40 cm^3 (STP)/min.

* P_{total} = 100 kPa, $C_2H_5C_l$ used.

TABLE 4

Turnover Frequencies and Selectivities for 1.71% Ag/SiO$_2$[a]

Test conditions	Temp (K)	TOF ($s^{-1} \times 10^3$)		S (%)[b]
		EO	CO$_2$	
[c]	473	0	2	0
	493	Trace	5	0
	533	3.6	28	21
[d]	473	0.5	0.33	75
	493	4.2	4.5	65
	503	6.4	7.1	64
	535	7.0	12	54

[a] Values represent averages of several measurements at each temperature when available.

[b] Selectivity = [mole EO formed/mole C_2^{2-} reacted].

[c] Initial unreduced catalyst, 5% C_2H_4, 5% O_2, 90% He, total gas flow rate = 40 cm^3/min (STP), total pressure = 445 kPa, 0.4 g catalyst. Turnover numbers are based on the dispersion of the fresh reduced catalyst.

[d] Catalyst after chemisorption measurements, 16.5% C_2H_4, 6.5% O_2, 2% CO_2, 0.50 ppm EDC, balance N_2. Total flow rate = 100 cm^3/min, total pressure = 445 kPa (50 psig), 0.4 g catalyst.

lated assuming an O_{ad}/Ag_s (or H_2/Ag_s) ratio of unity, where Ag_s is a surface atom and the equation $d = 1.3/(O_{ad}/Ag_{total})$, as discussed in Ref. (*15*). These calculated average crystallite sizes were compared with the size distributions obtained from TEM micrographs when possible. By varying the silver loading as well as the preparation method, a range of mean Ag crystallite sizes from 4 to 40 nm was obtained using the SiO$_2$ support. Well-dispersed catalysts with similar crystallite sizes of 3–4 nm were prepared on three different supports.

Kinetic Measurements

Selectivity (*S*) to ethylene oxide (EO) is defined here as the percentage ethylene reacted that is converted to EO, i.e., $S = \{\text{mole EO}/(\frac{1}{2}\text{ mole CO}_2 + \text{mole EO})\} \times 100$. Runs with carbon balances outside the range 100 ± 2% were rejected. In experiments where CO$_2$ was deliberately added to the feed gas, ΔCO_2, i.e., the amount of CO$_2$ produced during reaction, was used in the calculations. The products detected were ethylene oxide, carbon dioxide, and water except in several instances where acetaldehyde was also identified. Table 3 summarizes the results from the catalysts examined in this study.

(*a*) *1.89% Ag/η-Al$_2$O$_3$*. This catalyst, as made and with no reduction or any other pretreatment, was inactive for partial oxidation of ethylene and CO$_2$ production. The test conditions used were 5% ethylene, 5% oxygen, and 90% N$_2$ at temperatures up to 553 K. The TEM micrographs of the catalysts before and after use indicated no appreciable change in silver particle size, namely, a range of 3.5 to 8.0 nm for the fresh and 5.0 to 9.0 nm for the used catalyst. However, when fresh samples which had been reduced and characterized by O_2–H_2 chemisorption (see Table 2) were passivated in air and tested for epoxidation of ethylene, some activity for ethylene conversion was detected. Table 3 summarizes the results of catalytic measurements of this pretreated catalyst along with the reaction conditions. Under conditions employed in industrial applications, carbon dioxide and Cl-containing, gas-phase moderators such as ethylene dichloride (EDC) are present in the feed gas. The turnover frequency (TOF) values listed in Table 3 are averages of several measurements at each temperature. In some cases carbon balances were relatively poor due to very low activity; however, runs with balances outside the range of 100 ± 2% were not considered.

As shown in Table 3, even with addition of EDC as a gas-phase moderator, the selectivities to EO are very low. It should be pointed out that no significant sintering (deactivation) of this catalyst was observed when operated up to 5 days at 564 K.

(*b*) *1.81% Ag/TiO$_2$*. This sample behaved very similarly to the η-Al$_2$O$_3$-supported catalyst; i.e., in its initial unreduced state it was inactive for either partial or total oxida-

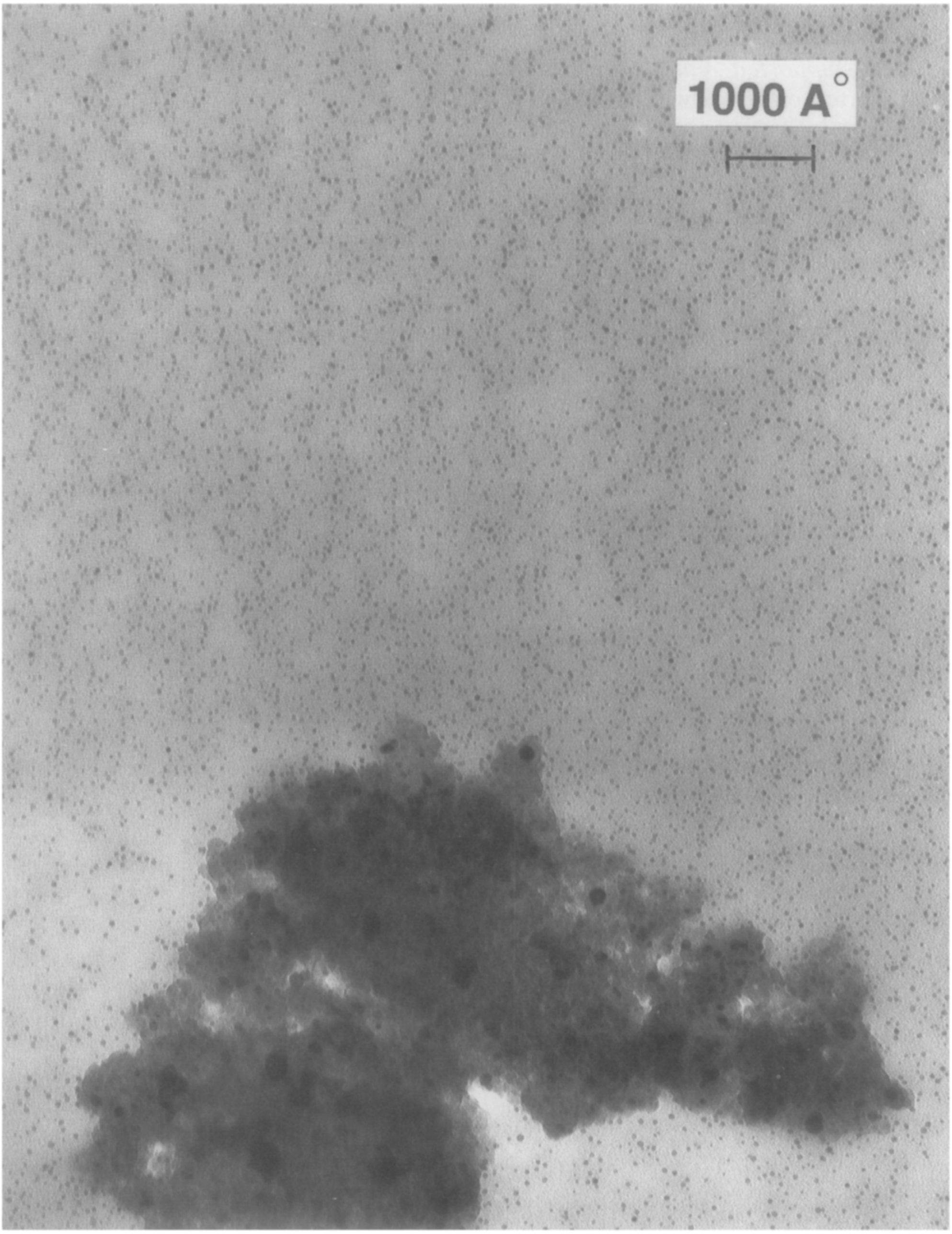

FIG. 1. TEM micrograph of 1.71% Ag/SiO_2 (magnification, 170,000×; 1 mm = 5.9 nm).

tion of ethylene when tested under the same conditions (5% C_2H_4, 5% O_2, 90% N_2) at temperatures up to 515 K. However, as with the Ag/η-Al_2O_3 catalyst, following reduction and characterization by chemisorption (see Table 2) it showed activity for ethylene oxidation but with low selectivities. The results are shown also in Table 3. The average crystallite size of the used Ag/TiO_2 catalyst remained stable in the 3.5- to 7.0-

nm range, as analyzed from TEM micrographs.

(*c*) *SiO_2-supported catalysts.* Several SiO_2-supported catalysts with different silver loadings were prepared (see Table 2) and tested for epoxidation of ethylene. These catalysts were more active and selective than those prepared with η-Al_2O_3 or TiO_2 but unlike the latter two catalysts, the 1.71% Ag/SiO_2 catalyst, with no reduction or any other pretreatment, was active for oxidation of ethylene but had very low selectivity, as shown in Table 4. The activity and, in particular, the selectivity of this catalyst increased after reduction prior to catalytic measurements (see Table 4). Figure 1 shows a TEM micrograph of the 1.71% Ag/SiO_2 catalyst as made and without any reduction. As seen, the silver precursor particles are very uniformly dispersed as small crystallites (4–10 nm).

The catalyst with the lowest silver content was 0.70% Ag/SiO_2. Figure 2 shows representative Arrhenius plots for both C_2H_4O and CO_2 as the reaction temperature was increased. These results were obtained in the absence of EDC or CO_2 in the feed gas.

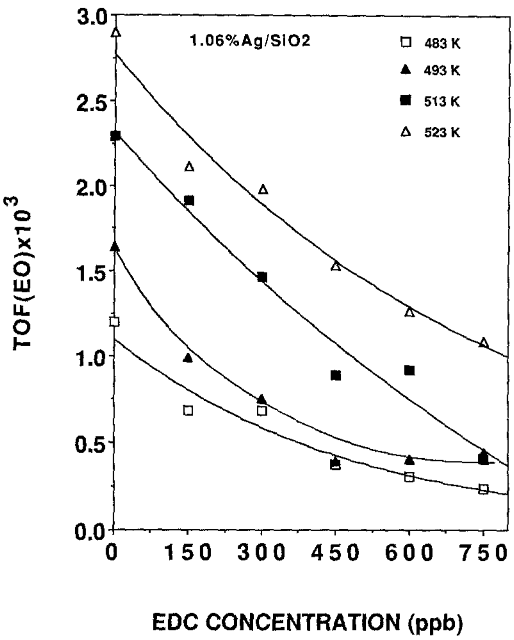

FIG. 3. Effect of EDC ($C_2H_4Cl_2$) feed concentration on ethylene oxide formation at different temperatures over 1.06% Ag on silica; feed composition: 16.5% C_2H_4, 6.5% O_2, 77.0% N_2, P_{Total} = 445 kPa.

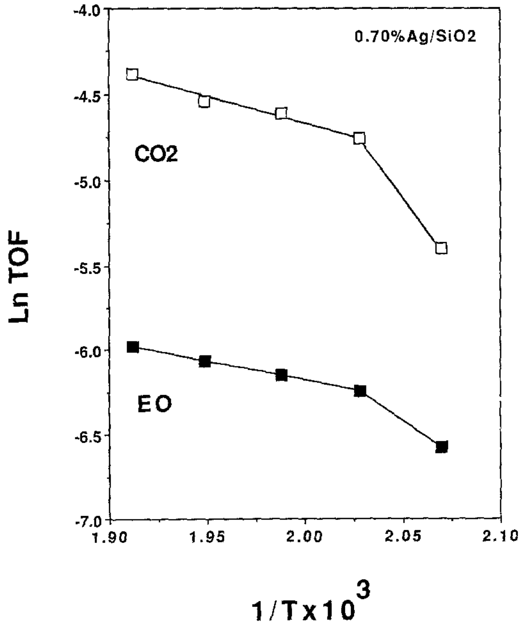

FIG. 2. Turnover frequency (molecule · s^{-1} · $site^{-1}$) of ethylene oxide and carbon dioxide formation over 0.70% Ag on silica versus reciprocal temperature; feed composition: 16.5% C_2H_4, 6.5% O_2, 2.0% CO_2, 75.0% N_2, P_{Total} = 445 kPa.

The 1.06% Ag/SiO_2 catalyst was tested much more extensively at different temperatures over a range of EDC concentrations, as well as with the addition of CO_2 to the feed stream. The dependence of EO and CO_2 turnover frequencies on EDC concentration in the absence of CO_2 in the feed is represented in Figs. 3 and 4, while the effect on selectivity is plotted in Figure 5. The TOFs decreased with increasing EDC levels at all temperatures; however, the most notable change occurred after the addition of the first 150 ppb of EDC. The selectivity versus EDC concentration exhibited little variation and it decreased several percent as the temperature increased from 493 to 523 K. The addition of CO_2 to the feed gas in the absence of EDC caused a

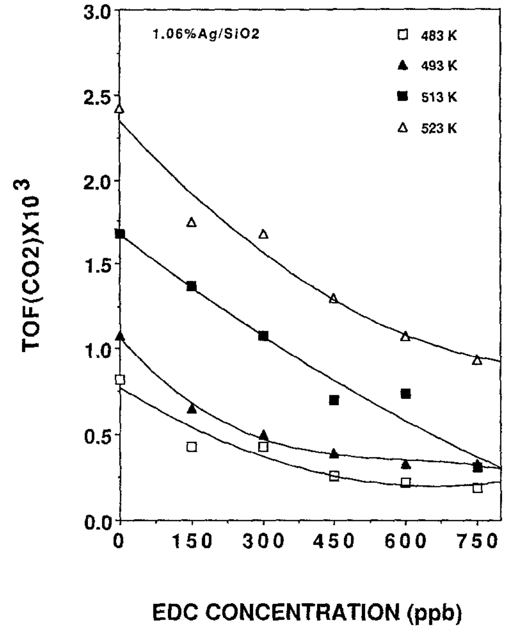

FIG. 4. Effect of EDC ($C_2H_4Cl_2$) feed concentration on carbon dioxide production over 1.06% Ag on silica; see Fig. 3 for run conditions.

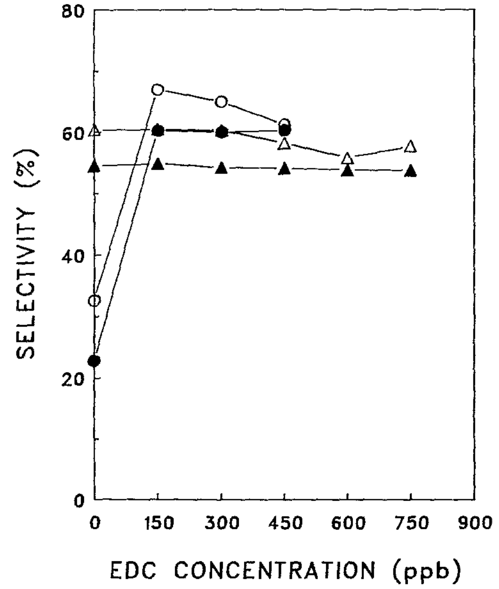

FIG. 5. Effect of EDC feed concentration on overall selectivity to EO (mole EO formed/mole C_2H_4 reacted) over 1.06% Ag on silica and 18% Ag on α-Al_2O_3 at different temperatures (no CO_2 added); see Fig. 3 for run conditions. (○, ●) 18% Ag/α-Al_2O_3; (△, ▲) 1.06% Ag/SiO_2. T = 493 K, open symbols; T = 523 K, solid symbols.

decrease in both the TOF for EO formation and the selectivity, as indicated in Table 3.

The Ag/SiO_2 catalyst with the largest crystallite size (40 nm) contained 16.65% Ag. It was tested under conditions similar to those described for the 1.06% Ag/SiO_2 catalyst, and results in the presence of CO_2 in the feed are shown in Figs. 6–8. The effect of temperature on TOFs was similar to that described previously for the 1.06% Ag/SiO_2 catalyst, but the EDC produced a small increase in TOF up to 300 ppb before it declined. Therefore, the selectivity patterns at various temperatures were more similar to the 18% Ag/α-Al_2O_3 catalyst although the maxima were attained at higher EDC concentrations, as shown in Fig. 8.

(*d*) *18.0% Ag/α-Al_2O_3 catalyst.* As mentioned earlier, this catalyst was prepared according to the procedure described in a U.S. patent (*19*), which is typical for catalysts used in the industrial epoxidation of ethylene, and it was tested under the same conditions described for the Ag/SiO_2 cata-

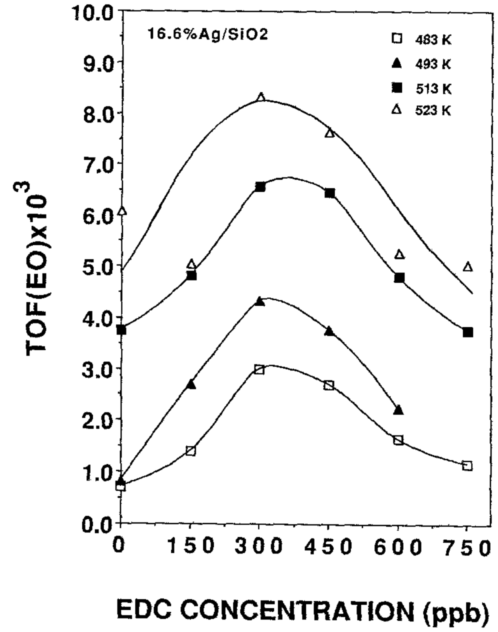

FIG. 6. Effect of EDC ($C_2H_4Cl_2$) feed concentration on ethylene oxide formation at different temperatures over 16.65% Ag on silica; feed composition: 16.5% C_2H_4, 6.5% O_2, 2.0% CO_2, 75.0% N_2, P_{total} = 445 kPa.

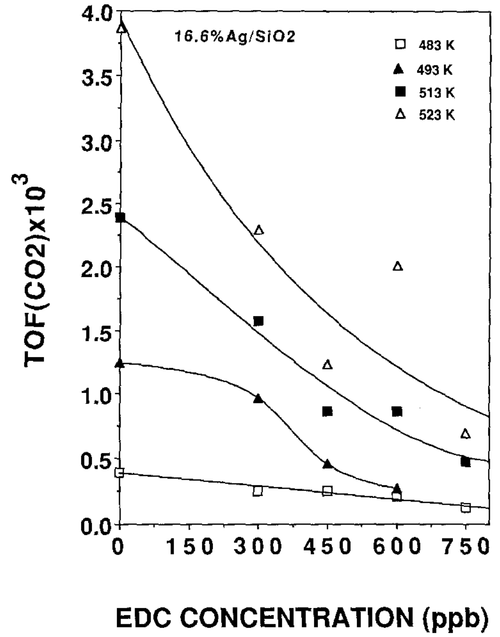

FIG. 7. Effect of EDC ($C_2H_4Cl_2$) feed concentration on carbon dioxide formation over 16.65% Ag on silica; see Fig. 6 for reaction conditions.

lysts. The variation of TOFs with EDC concentrations was similar to that observed for the Ag/SiO_2 catalysts, as indicated in Figs. 9 and 10 (no CO_2 present), but the TOFs changed more drastically with temperature in the absence of any EDC regardless of whether CO_2 was present or not in the feed. The most pronounced change in selectivity occurred after adding the first 150 ppb of EDC, as shown in Fig. 5, after which selectivities varied little up to 450 ppb. The greatest decrease in activity was also produced by the first level of EDC added, as illustrated by Figs. 9 and 10. The addition of 2% CO_2 to the feed gave a maximum in selectivity at 150 ppb EDC that ranged from 75% at 493 K to 62% at 523 K; thus the presence of CO_2 over this catalyst further increases the maximum selectivity.

DISCUSSION

As mentioned in the Introduction, the influence of Ag crystallite size on specific activity and selectivity in the ethylene oxida-

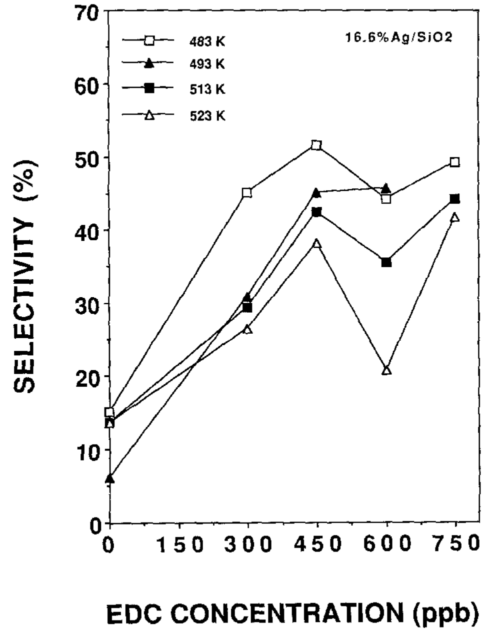

FIG. 8. Effect of EDC ($C_2H_4Cl_2$) feed concentration on selectivity (mole EO formed/mole C_2H_4 reacted) at different temperatures over 16.65% Ag on silica; see Fig. 6 for reaction conditions.

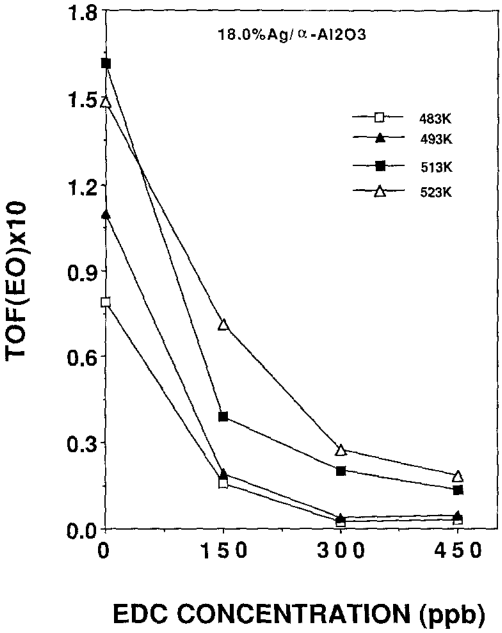

FIG. 9. Effect of EDC ($C_2H_4Cl_2$) feed concentration on ethylene oxide formation at different temperatures over 18% Ag on α-alumina; feed composition: 16.5% C_2H_4, 6.5% O_2, 77.0% N_2, P_{total} = 445 kPa.

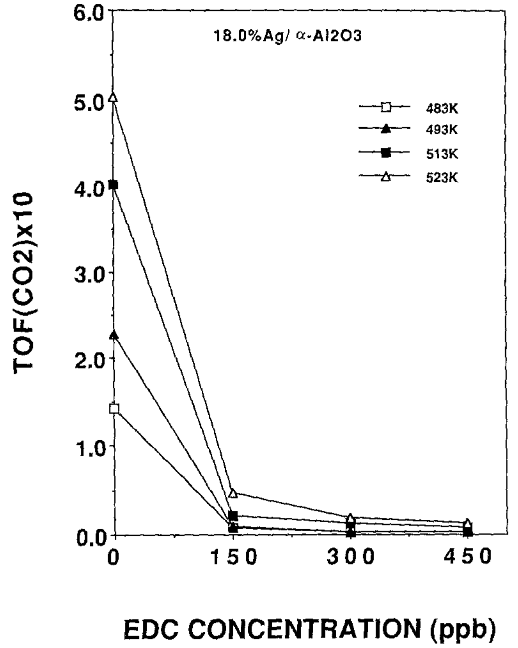

FIG. 10. Effect of EDC ($C_2H_4Cl_2$) feed concentration on carbon dioxide formation at different temperatures over 18% Ag on α-alumina; see Fig. 9 for reaction conditions.

tion reaction has not been resolved. Conventional wisdom in both the open and the patent literature has taught that high selectivity can be acquired only with extremely large Ag crystallites on inert, nonacidic, low-surface-area supports (*20, 21*). In addition, moderators such as Cl-containing compounds and Group IA and IIA elements are required for high selectivities (*20, 21*). The emphasis in this study was to determine the catalytic behavior of very small Ag crystallites on SiO_2, to compare it to that of very large Ag crystallites on α-Al_2O_3, and to examine the effect of ethylene dichloride (EDC) feed concentration on both large and small Ag particles. In all cases, no chemical promoters were present in the catalysts, and the only moderator was EDC in the feed.

Most of the Ag catalysts used in this investigation had been prepared and thoroughly characterized in previous studies in which both O_2 adsorption and the H_2 titration reaction of adsorbed oxygen was used to measure Ag surface area and calculate average crystallite sizes (*14–17*). These values for the fresh reduced catalysts are shown in Table 2 along with values obtained on the used Ag/SiO_2 catalysts from series II. It is clear that a wide range of Ag crystallite size was attained as mean values varied from 3 to 1100 nm. Perhaps the most important result in the table is the fact that the three Ag/SiO_2 catalysts that exhibited deactivation during the long-term runs of 36 to 48 days did not lose Ag surface area. *Therefore, this decrease in activity was not due to sintering, which is the principal reason for deactivation in commercial processes, and it indicates one advantage of stable, well-dispersed Ag catalysts.* This behavior is consistent with that found in a previous study in which well-dispersed, SiO_2-supported Ag could not be sintered when we purposely tried to do so (*15*). This result also introduces the possibility that at least a portion of the deactivation observed commercially may be due to the presence of poisons, i.e., surface contamination. If so, the pretreatment used here is capable of completely removing these poisons.

It is well known that one of the reasons for poor selectivity can be the presence of active sites on the support which catalyze the complete oxidation of ethylene, presumably by a secondary reaction in which EO is oxidized, and thereby produce very low selectivities. This trend is readily demonstrated by the 1.89% Ag/η-Al_2O_3, 1.81% Ag/TiO_2, and 0.70% Ag/SiO_2 catalysts in Table 3. The first two utilize supports with relatively high concentrations of surface acid sites and, even with 0.5 ppm EDC in the feed, selectivities are only 10–12%. Under identical conditions, the 18% Ag/α-Al_2O_3 catalyst gives *S* values of 61%. It is also apparent that the TOFs over these two well-dispersed catalysts are extremely low compared to that on the large particles on α-Al_2O_3. In comparison, the 0.70% Ag/SiO_2 catalyst gives a higher selectivity of 17%, even in the absence of EDC, and the TOF is an order of magnitude higher than the values for the Ag/η-Al_2O_3 and Ag/TiO_2 catalysts. This may be due, at least partially, to an interaction with the support surface which affects the oxidation state of the Ag. As mentioned under Results, neither of the latter two samples was active if no reduction step was used whereas the 1.71% Ag/SiO_2 catalyst did exhibit some activity, as shown in Table 4. This implies that the $AgNO_3$ decomposed more readily on SiO_2 to give metallic Ag particles compared to the two acidic supports.

The most surprising result is that relatively small 13-nm Ag crystallites give selectivities comparable to the 1100-nm particles on α-Al_2O_3 (64 vs 61%), although the TOF is still substantially lower. At lower temperatures, S values as high as 75% were obtained (Table 4.) The performance of this 1.71% Ag/SiO_2 catalyst was verified in another laboratory under comparable, but different, reaction conditions, and at lower pressures of C_2H_4 and O_2 in the absence of CO_2, a selectivity of 61% was obtained and the TOF value was reproduced, as shown in Table 3. This result dispels the belief that high selectivities can be acquired only over large (very poorly dispersed) Ag crystallites, particularly since this high-surface-area SiO_2 might be expected to have a very small concentration of active (i.e., acid) sites which give some degradation of selectivity. Selective poisoning of these sites on the SiO_2 consequently could result in even higher S values. Finally, it should be emphasized that none of these catalysts contained any moderators such as Group IA or IIA metals.

After this series of experiments, a family of Ag/SiO_2 catalysts with different dispersions was prepared to further examine the influence of crystallite size and to determine the effect of EDC concentration on TOF and S values. Three catalysts—0.70% Ag/SiO_2, 1.06% Ag/SiO_2, and 16.65% Ag/SiO_2—were prepared with mean crystallite sizes of 4.4, 7.6, and 41 nm, respectively, and the oxidation reaction was conducted over the latter two along with the 18% Ag/α-Al_2O_3 catalyst in the presence of various concentrations of EDC up to 750 ppb EDC in the feed. The effect of CO_2 was also examined for these three catalysts by adding 2% CO_2 in the feed. For all catalysts except 16.65% Ag/SiO_2, TOF values at all temperatures for both EO and CO_2 dropped markedly upon addition of EDC, and examples are provided in Figs. 3, 4, 6, 7, 9, and 10. For all but the 16.65% Ag/SiO_2 catalyst, which showed an initial increase in EO activity before it declined, the sharpest decrease came with the addition of the first 150 ppb EDC, and the CO_2 rate was inhibited more sharply than that for EO. This pattern is very consistent with older studies of this reaction (*2*, *20–22*), and it is in agreement with the more recent UHV studies of Campbell *et al.* and Lambert *et al.* on the effect of Cl on the catalytic behavior of Ag single crystals in this reaction. Both groups reported that the TOF for EO on Ag(111) increased slightly as Cl coverages increased up to ~0.3; then it dropped markedly at higher Cl coverages (*6*, *10*). On the Ag(110) surface, the EO TOF declined monotonically (*5*). The TOF for CO_2 showed a continual, more rapid decline over both surfaces thus producing significant increases in selectivity. For the 18% Ag/α-Al_2O_3 catalyst, S values at all temperatures increased sharply after the addition of 150 ppb, then remained relatively constant at concentrations up to 450 ppb, as indicated in Fig. 5. In contrast, the enhancement over the small Ag crystallites was much smaller and sometimes did not occur at all over well-dispersed Ag, as shown in Fig. 5. When present, it appeared to go through a maximum around 150 ppb. Thus higher EDC concentrations are detrimental for the well-dispersed Ag/SiO_2 catalysts and this pattern offers another possible benefit of well-dispersed Ag catalysts—a much lower Cl-containing moderator concentration is required for optimum performance. The behavior of the 16.65% Ag/SiO_2 sample is less well-defined, but it also indicates a possible maximum at 150 ppb (Fig. 8). Another interesting difference between the 7.6-nm Ag crystallites in the 1.06% Ag/SiO_2 catalyst and the 1100-nm crystallites on α-Al_2O_3 is the dependence of TOF on EDC concentration. The addition of 150 ppb EDC decreased the EO TOF by about 25% on the small particles whereas it dropped by over 50% on the 18% Ag/α-Al_2O_3 catalyst (Table 3). The reason for this difference is not known at this time, but it may be due to differences in O and Cl bond strengths on small silver particles coupled with the absence (or reduced amounts) of subsurface oxygen, which has been shown to play an integral role in the epoxidation reaction (*10–13*).

In the absence of EDC and CO_2 in the feed, the activation energies for EO formation varied from 39 to 67 kJ/mol, which is well within the range reported in the literature, as indicated in Table 5. The introduction of EDC usually increased these values, which is consistent with the behavior for Ag(111) and Ag(110) single crystals as Cl coverages increased up to $\theta_{Cl} = 0.1$–0.3 (*5, 10*); however, we observe an increase in E_{act} values for CO_2 formation whereas they declined continuously over these two Ag surfaces (*5,10*). This again indicates the possibility that interactions between O, Cl, and Ag atoms differ on small Ag particles compared to those on large crystallites. The addition of 2% CO_2 also increased the activation energy for EO formation, which is in agreement with the results of Tan *et al.* for a Ag(111) crystal plane (*11*).

At the time of our study, the only other examination of activity and selectivity as a function of the Cl-containing moderator concentration was that of Petrov *et al.*, who used a 20% Ag/Al_2O_3 catalyst promoted with calcium (*22*). However, the EDC concentrations reported for selectivity variations were much higher—4 to 24 ppm (0.4–2.4 Pa)—and S values varied only from 48 to 61% over this range. Unfortunately, the EDC level used in their activity comparison to an unpromoted sample was unspecified; regardless, the EDC caused a notable decrease in activity which was dependent upon the ethylene partial pressure. Similar behavior has also been reported in a very recent paper by Yong and Cant, who studied the effect of EDC concentration over a range of 0.8–5.4 ppm (0.08–0.54 Pa) (*23*).

TABLE 5

Turnover Frequencies and Reaction Conditions for Ethylene Oxide Formation in the Absence of Promoters

Catalyst	TOF_{EO} (s^{-1})	Dispersion (Ag_s/Ag_{total})	T (K)	$P_{C_2^{2-}}$ (kPa)	P_{O_2} (kPa)	S[a] (%)	$E_{a_{EO}}$ (kJ/mol)	Ref.
Ag(110)	2.5	$\sim 10^{-8}$	490	2.7	20	36–50	22–94	4
Ag(111)	1.9	$\sim 10^{-8}$	490	2.7	20	36–46	~43	4
Ag(111)	0.1	10^{-8}	500	33	33	18–37	43–51	8
Ag(111)	0.7	10^{-8}	550	0.27	0.27	11	25	11
Ag(polycrst.)	0.34	$\sim 10^{-8}$	483	7.3	15	—	—	25
Red. Ag_2O	0.3	1×10^{-3}	513	3.0	20	0–60[b]	45–70[c]	26
Ag film	0.27	2×10^{-3}	543	1	10	82–84	—	27
Ag/Al_2O_3	0.12	1×10^{-3}	513	85	15	71	28	28
Ag/SiO_2–Al_2O_3	0.06	3×10^{-3}	488	85	15	47	72	28
$Ag/Zr(NaPO_4)_2$	$(0.6–2.2) \times 10^{-3}$	0.014–0.094	503	2.3	33	43–56	—	29
Ag/α-Al_2O_3	$(1–7) \times 10^{-3}$	0.009–0.026	513	45	224	40–67	—	1
Ag/SiO_2	$(0.7–1.8) \times 10^{-3}$	0.09–0.19	493	263	263	34–77	—	30
Ag/SiO_2	0.06–0.18	0.03–0.22	473	22	13	76–86	60	31

[a] S = [(mole EO formed)/(mole C_2H_4 reacted)].

[b] Pulse reactor, S not defined.

[c] Total C_2^{2-} consumption.

[d] Unsintered samples only.

Under their reaction conditions and an EDC pressure of 0.08 Pa, the approximate 12-fold decrease in activity for overall ethylene conversion over a Ag sponge is comparable to the nearly 6-fold decrease we observed for the large crystallites in the 18% Ag/α-Al_2O_3 catalyst under 0.067 Pa EDC (See Table 3). Thus it appears that the greatest influence of EDC is incurred at concentrations well below 1 ppm, with our results indicating that levels of only 150–200 ppb (<0.1 Pa) are required to give optimum selectivities. This optimum is expected to depend on reactions conditions, however.

The addition of CO_2 to the feed increased the activation energies for both EO and CO_2 formation from ethylene, as shown in Table 3. Over the smaller Ag crystallites the TOF for EO decreased by about one-half while the TOF for CO_2 formation was less affected; thus significant decreases in selectivity occurred. This behavior did not occur with the large Ag crystallites on α-Al_2O_3 and, in contrast, the selectivity increased somewhat. The increase in E_{act} values and selectivity is consistent with the results of Tan *et al.*, which were obtained with a Ag(111) single crystal, although their activation energies of 47 kJ/mol were significantly lower (*11*). This could be due in the latter study to the lower CO_2 pressures, which were near 100 Pa, and the different reaction conditions. An even more recent study of Ag powder by Bulushev and Khasin (*24*) has also shown that the presence of CO_2 (13 Pa) in the reactant gases causes a decrease in ethylene oxidation with a greater increase in selectivity (3 to 20%) than that reported by Tan *et al.*

Addressing the topic of a possible Ag crystallite size effect, it is overwhelmingly clear from Table 3 that TOFs for either EO or CO_2 formation are markedly higher on large Ag crystallites. For example, at 523 K in the absence of EDC and CO_2 in the feed, TOF values are 100 times lower on the 4.4-nm crystallites and 50 times lower on the 7.6-nm crystallites compared to the 1100-nm crystallites; however, in the presence of 150 ppb EDC the TOF is only 34 times lower on the 1.06% Ag/SiO_2 catalyst. If these TOF values on *unpromoted* Ag are compared to those in Table 5, which were obtained from the limited number of papers either reporting such values or allowing their estimation (*1, 4, 8, 11, 25–31*), a general trend does appear to emerge despite rather wide ranges of temperature and partial pressures. In this table we have excluded all Ag catalysts which had been sintered because of the strong possibility of surface contamination, as discussed by Sajkowski and Boudart (*2*). To perceive this trend more easily, these reported TOF values as well as our own are plotted versus fraction Ag exposed (dispersion) in Fig. 11 with all dispersions of 0.001 or lower placed on a single line. There are obviously large uncertainties associated with many of these values not only because of the variation in

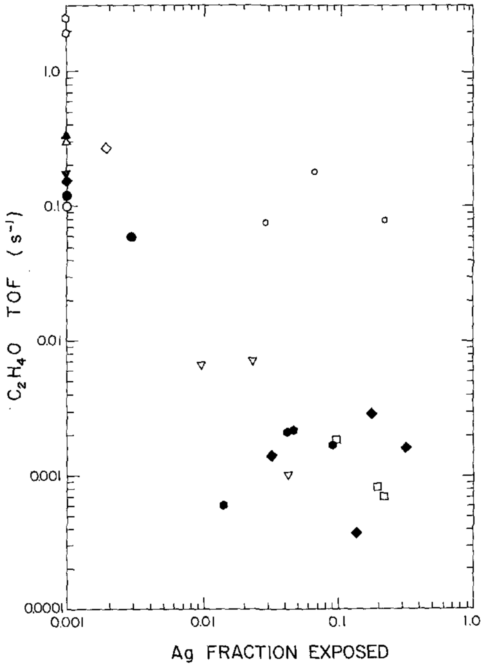

FIG. 11. Correlation of turnover frequency for C_2H_4O formation vs silver dispersion in the absence of promoters. Reaction conditions are listed in Table 5. Results from Ref. (*1*), ▽; Ref. (*4*), ○ ; Ref. (*8*), O; Ref. (*11*), ▼; Ref. (*25*), △; Ref. (*26*), ▲; Ref. (*27*), ◇; Ref. (*28*), ●; Ref. (*29*), ⬢; Ref. (*30*), □; Ref. (*31*), ○; this study, ◆.

reaction parameters but also because of the method used to determine Ag surface area (a site density of 1.3×10^{15} Ag_s cm^{-2} was used when necessary to obtain TOF values). Regardless, more than three orders of magnitude exist between TOFs reported for large Ag crystallites and those obtained on the smallest Ag particles, and the values obtained in the present study are very consistent with previous results. There is one clear exception—the TOFs reported by Jarjoui *et al.* are unexpectedly higher than all other values on well-dispersed Ag. For this we have no explanation. It should be noted that our TOFs are in good agreement with the values from the well-dispersed Ag/SiO_2 catalysts studied by Wu and Harriott (*30*); however, the selectivities on their most highly dispersed Ag catalysts approached zero and on 6.4- to 6.8-nm crystallites *S* values were only 3.3%, using our definition of selectivity. The 7.6-nm Ag particles in our 1.06% Ag/SiO_2 catalyst gave a selectivity of 55%, as shown in Table 3, although a lower value of 17% was obtained with the most highly dispersed 0.70% Ag/SiO_2 catalyst. Therefore, on the smallest Ag crystallites, selectivities indeed appear to be significantly lower. It should be noted, though, that any support contribution to decrease selectivity would be amplified in these catalysts because of the low Ag loadings and the relatively high support surface areas.

In their review article, Sajkowski and Boudart pointed out the need to prepare supported Ag catalysts which are free of impurities and contain Ag crystallites smaller than 5 nm in size (*2*). We believe the 0.70% Ag/SiO_2 catalyst studied in this paper satisfies these requirements and the 1.06% Ag/SiO_2 approaches the 5-nm stipulation. The TOFs obtained, when combined with previous reported values in Fig. 11, exhibit a trend that strongly implies a crystallite size effect. However, we concur at this time with the above authors that ethylene oxide formation may not unequivocally be termed a structure-sensitive reaction. There are four reasons to support this opinion. The first is the similarity in behavior between the Ag(111) and (110) planes, as reported by Campbell (*4, 6*). These TOF values vary by less than a factor of 2 and the distribution of these two planes could account for the small variations over 13- to 100-nm supported Ag crystallites, as recently reported by Lee *et al.* (*32*). The definition of structure sensitivity requires a larger variation than this (*2*). The second is the relative insensitivity of TOF to the presence of modifiers such as Cl (*2, 4*). Our results verify this, as only modest decreases of 25–50% were observed upon addition of EDC. The third is that the principal increase in TOF occurs as the crystallite size increases from 40 nm to even *larger* particles and does not change markedly as particle size decreases below 10 nm. The last reason relates to the role of subsurface oxygen coupled with the oxidation state of Ag in small particles (*2*). It is possible that these variations in TOF and selectivity as dispersion increases may be due to changes in the adsorbed state of oxygen, in the extent of subsurface oxygen formation, and in the oxidation state of the Ag atoms in very small clusters. Evidence has already been provided that alterations in oxygen adsorption behavior occur in ultrahighly dispersed Ag catalysts (*33*). One reviewer suggested the possibility that the support could provide impurities which migrate to the silver surface, and this cannot be discounted. However, all three supports decreased TOFs on small Ag crystallites and their impurity levels were low, especially for the SiO_2. Thus an obvious explanation for this behavior does not appear to exist at this time. Future studies related to O–Ag_s and Cl–Ag_s bond strengths, adsorbed oxygen species, and Ag oxidation states, and surface analyses of small, dispersed Ag particles are required to resolve this issue.

SUMMARY

Clean, highly dispersed Ag catalysts were prepared using three different supports—TiO_2, η-Al_2O_3, and SiO_2—and TOFs and selectivities in the presence and absence of EDC were obtained and compared to those for a poorly dispersed Ag/α-Al_2O_3 catalyst. Very small 3- to 4-nm Ag crystallites had TOF values for EO formation ranging from less than 10^{-4} s^{-1} to near 2×10^{-3} s^{-1}, which are two to three orders of magnitude lower than those (0.15 s^{-1}) on large Ag particles. However, the much higher Ag dispersions provide partial compensation to give activities per gram catalyst that are less divergent. Selectivities from these small crystallites on reactive supports like TiO_2 and η-Al_2O_3, in the presence of 0.5 ppm EDC, were much lower than those of the large particles (~11 vs 60%). However, in the absence of EDC, the selectivity of 17% from the 4.4-nm crystallites on SiO_2 was comparable to the value of 23% over the 1-μm crystallites on α-Al_2O_3, and the selectivity from the 7.6-nm crystallites was much higher at 55%. The addition of EDC at low levels of 150–200 ppb increased S values to greater than 65% over the 18% Ag/α-Al_2O_3 catalyst whereas selectivity over the 1.06% Ag/SiO_2 remained constant at 60%, and higher EDC concentrations up to 750 ppb produced no additional benefits in selectivity while TOFs were markedly decreased. An optimum concentration near 200 ppb or lower seems to exist, at which level only small decreases in TOF occur for the well-dispersed Ag/SiO_2 catalysts. The addition of CO_2 increases the activation energies for both EO and CO_2 formation, and the TOF values for EO decrease by half on smaller Ag crystallites with a commitant drop in selectivity. On large Ag crystallites, however, TOF values are less affected and selectivity increases slightly.

A comparison of these results with TOF values in the literature indicates that a Ag crystallite size effect does exist, as a 1000-fold decrease in ethylene oxide TOF occurs as Ag crystallite sizes decrease to 3 nm. However, it is not possible at this time to unequivocally conclude that EO formation is a structure-sensitive reaction because of the marked alterations in oxygen adsorption and subsurface oxygen formation which appear to occur on very small Ag clusters and may be responsible for this trend. Regardless, high selectivity to EO can still be obtained over small Ag crystallites, which have the advantage of being resistant to sintering.

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