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The Effect of Crystallite Size on the Activity and Selectivity of Silver Catalysts

JAMES C. WU[1] AND PETER HARRIOTT

School of Chemical Engineering, Cornell University,
Ithaca, New York 14850

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The effect of crystallite size on the activity and selectivity of silver catalysts for the oxidation of ethylene was studied in a differential reactor at 220°C, $P_{O_2} = 0.264$ atm, $P_E = 0.264$ atm. The activities per unit area for ethylene oxide formation and for carbon dioxide formation decreased with increasing crystallite size, but not at the same rate. The selectivity was nearly zero for 20 Å particles and gradually increased to 60% for 500 Å particles. Two types of active sites are believed to be formed by adsorption of oxygen at steps and faces of the silver crystals, and reaction occurs between ethylene and atomic or molecular oxygen competitively adsorbed on these sites.

INTRODUCTION

The partial oxidation of ethylene using silver catalysts has been studied for more than 40 yr, but the fundamentals of the reaction are only partly understood. Many workers now believe that chemisorbed molecular oxygen reacts with ethylene to give mainly ethylene oxide, whereas atomic oxygen reacts to give only carbon dioxide and water (*8*). However, there is evidence for more than two types of oxygen on the surface, and the contribution of each type to the kinetics is not clear. The chemisorption studies of Czanderna (*2*) and Kilty *et al.* (*7*) showed three types of oxygen adsorption, two atomic and one molecular, with activation energies of 3, 8, and 14–22 kcal/mole. Spath (*19*) suggested four types of chemisorbed oxygen, two molecular and two atomic, and Imre (*6*) proposed that molecular oxygen could be adsorbed either parallel or perpendicular to the surface. The behavior of ethylene is also complex, since ethylene adsorbs on oxygen-covered silver but not on silver itself. Marcinkowsky and Berty (*12*) found both reversibly and irreversibly adsorbed ethylene on oxygenated silver.

Most kinetic models for ethylene oxide formation are based on reaction of adsorbed molecular oxygen with either adsorbed ethylene or with gaseous ethylene. Kilty and Sachtler (*8*) favor the Rideal mechanism, which involves a molecule of ethylene from the gas phase or ethylene physically adsorbed on top of molecular oxygen. This model might fit the data for low partial pressures, where the reaction order for ethylene is between 0 and 1.0. However, studies by Klugherz and Harriott (*9*) and Metcalf and Harriott (*13*) over a wide range of concentrations showed maxima in the rates of ethylene oxide and carbon dioxide formation, indicating competitive adsorption of ethylene and molecular oxygen on a partially oxygenated silver surface. Spath and Handel (*20*) also concluded that both reactions involved dual site mechanisms, but several models based on different oxygen species were judged adequate to fit the kinetic data. To learn the details of the reaction mechanism, the steady state kinetic results must be supplemented by other techniques such as ir spectroscopy, EPR and transient ad-

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[1] Present address: E. I. du Pont de Nemours & Co., Inc., Wilmington, DE 19898.

sorption or desorption studies. Recent evidence from such techniques is discussed by Kilty and Sachtler (*8*).

The effect of crystallite size on the activity of metal catalysts has drawn much attention in recent years. Most of the studies have been done on platinum or nickel catalysts, and these studies are reviewed by Sinfelt (*17*). Some indications (*4,16*) exist that the silver crystallite size has an effect on ethylene oxidation, but the information is limited. The purpose of this study is to investigate in a systematic way the effect of crystallite size on the selectivity and activity of silver catalysts.

EXPERIMENTAL METHODS

The catalysts were prepared by depositing silver on nonporous silica supports by formaldehyde reduction of silver–ammonia complex or by hydrogen reduction of silver nitrate crystals. The catalysts were washed with deionized water, dried in an oven, and then sintered to obtain different crystallite sizes. The sintering conditions and silver contents are given in Table 1. Catalysts in the CS series were made using Cab-O-Sil M-7D as support. This fumed silica has particles about 120 Å in size, sintered together in clusters. The second support was silica Z, a nonporous silica prepared by a method similar to that used by Imelik and Carteret (*5*). The BET surface of silica Z was 172 m^2/g, and an electron micrograph showed platy particles about 1600 Å in size. The catalysts were dried in an oven, pelleted, and crushed to 30–40 mesh for kinetic tests. Further details of support and catalyst preparation are given by Wu (*22*).

The kinetic tests were made in a differential reactor used in previous studies (*9,13*). The reactor was a 28-in. length of 0.5-in. stainless steel tubing, with a 0.125-in. stainless steel thermocouple well positioned along the center line. The annulus was packed with 1 to 11.8 g of catalyst diluted with 20 g of 20–28 mesh acid-washed Ottawa sand. The reactor and preheater were immersed in an electrically heated fluidized bed of sand. Samples were analyzed using a gas chromatograph with a Poropak Q column.

TABLE 1
SINTERING CONDITION FOR CATALYST PREPARATION

Catalysts	Reactor charge (g)	Silver (wt%)	Sintering	
			Temp[a] (°C)	Time (hr)
CS-4	4.4	7.47	240	—
CS-5	2.5	16.46	425	12
CS-6	3.5	24.92	520	24
CS-8	10.0	27.15	620	12
CS-11	5.0	26.35	550	24
CS-15	11.8	2.88	220	—
CS-16	4.0	0.548	220	—
CS-17	10.0	0.548	550	48
Z-26	4.0	9.42	240	—
Z-27	4.0	19.64	374	30 min
Z-28	3.4	28.68	360	16
Z-29	1.0	39.5	220	—
Z-30	1.5	39.5	350	30 min
Z-31	1.0	39.5	335	24

[a] The sintering temperature of catalysts CS-4, CS-15, CS-16, Z-26, and Z-29 are the highest temperatures that the catalysts were exposed to under certain reaction conditions.

The catalyst activity was quite sensitive to pretreatment conditions. After prolonged exposure to hydrogen, the catalysts showed high initial activity for ethylene oxidation, and the rates of ethylene oxide and carbon dioxide formation gradually decreased, reaching steady values in 20–30 hr. Typical results are shown in Fig. 1 for reaction at the standard conditions of 220°C, 1.32 atm, with 20% ethylene, 20% oxygen and 60% helium in the feed gas. After a catalyst (which had been exposed to air) was pretreated with ethylene, the catalyst had high initial activity for carbon dioxide formation, but little ethylene oxide was formed. However, after 30 hr, both reaction rates were constant and equal to the steady state values obtained after hy-

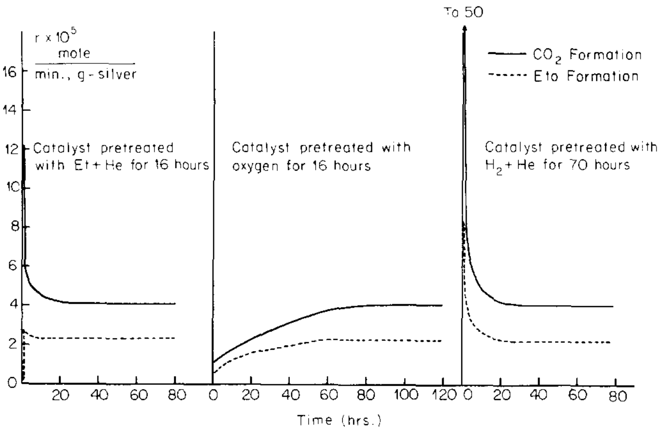

FIG. 1. The effect of pretreatment on the activity of catalyst Z-27.

drogen pretreatment. Overnight exposure of the catalyst to oxygen gave low initial activity for both reactions, and it took much longer to reach steady state than after ethylene or hydrogen pretreatment. Other investigators report similar but smaller effects of catalyst pretreatment (*15*) perhaps because their treatment times were shorter. Some of the changes in activity may be due to a change in surface area. Czanderna (*3*) has shown that exothermic reactions lead to an increase in the surface area of silver catalysts, indicating a roughening or disordering process.

For kinetic or adsorption tests, the catalysts were pretreated with hydrogen for 3 hr at 220°C and purged with helium for 2 hr. Ethylene oxidation was carried out for 30 hr using the standard feed mixture to get the steady state reaction rates and selectivity. The reaction rates were corrected to a product partial pressure of 0.01 atm using a plot of reciprocal rate against product pressure. As shown in Fig. 2, these plots are straight lines, and the corrected rates were obtained from the following equations:

$$r_{\mathrm{CO_2}}{}^0 = r_{\mathrm{CO_2}}\,(\text{meas})\,\frac{1 + aP_p}{1 + a(0.01)},$$

$$r_{\mathrm{EtO}}{}^0 = r_{\mathrm{EtO}}\,(\text{meas})\,\frac{1 + dP_p}{1 + d(0.01)}.$$

The constants *a* and *d*, which show the effect of product inhibition, are listed in Table 2. The inhibiting effect is about the same for both reactions, but the inhibition increases with increasing crystallite size. The magnitude of *a* and *d* for catalyst CS-11 (46% selectivity) is similar to that found by Metcalf and Harriott (*13*) ($a = 100$, $d = 50$ with 45% selectivity).

The average crystallite sizes of the catalysts were estimated using transmission electron microscopy (TEM), X-ray diffraction line broadening, and oxygen adsorp-

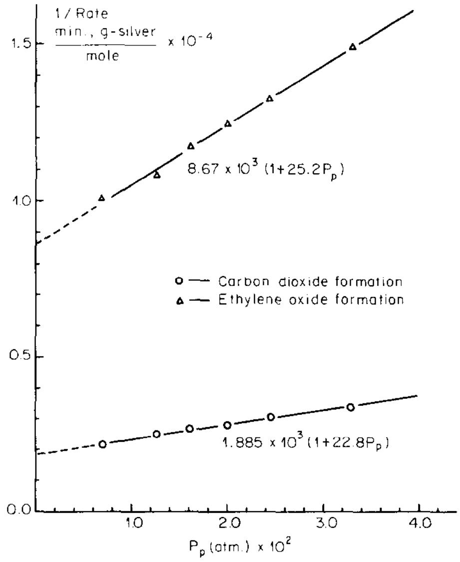

FIG. 2. The effect of product partial pressure on rate of catalyst CS-4.

TABLE 2
THE INHIBITING EFFECT OF PRODUCTS ON CARBON DIOXIDE FORMATION (*a*) AND ETHYLENE OXIDE FORMATION (*d*)

Catalysts	Inhibition constant (atm^{-1}) *a*	Inhibition constant (atm^{-1}) *d*
CS-4	22.8	25.2
CS-5	49.1	49.5
CS-6	62.2	61.5
CS-11	88.5	87
CS-8	133	127

tion. A JAM-7A electron microscope manufactured by Japan Electron Optics Laboratories Co. Ltd. was used to get electron micrographs. A Cu *Kα* irradiation with λ = 1.5405 Å was used as the X-ray source in this work. The major peak for silver was chosen to measure the apparent half-maximum intensity line breadth. A silver catalyst with silica gel Z support was sintered in the air at 900°C for 48 hr and used to get the instrumental broadening.

Chemisorption tests were performed using the flow reactor so that kinetic tests could be made afterwards without transferring the catalyst. After purging the reduced catalyst with helium, a stepchange to 1% oxygen in helium was made, and the oxygen concentration in the exit gas was measured by chromatograph at 1.5 min intervals. A blank run was made to correct for adsorption of oxygen on the reactor wall. The results for catalyst CS-11 are given in Fig. 3, where the shaded area represents the total oxygen adsorbed.

Crystallite Size and Selectivity

The average crystallite sizes calculated from X-ray line broadening agreed with the values from electron micrographs for sizes from 60 to 500 Å. However, the oxygen adsorption results assuming spherical crystallites and one oxygen atom per silver atom, gave sizes smaller by a factor of about 3. Some of the difference is due to molecular oxygen adsorption, and there may also have been some residual hydrogen left after the helium purge, which would react with oxygen and increase the apparent adsorption. Correcting the oxygen results by a factor of 3 gave fair agreement with the other methods and provided the only estimate of crystallite size for the catalyst with the smallest silver particles (see Table 3).

The selectivity for the catalyst with 500 Å crystallites was 62% after the first few

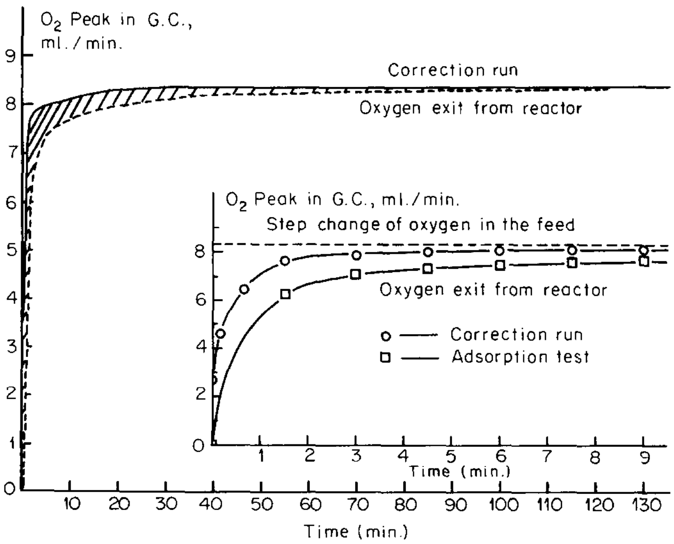

FIG. 3. Oxygen adsorption experiment.

TABLE 3
THE EFFECT OF CRYSTALLITE SIZE ON ACTIVITY AND SELECTIVITY

Catalysts	Crystallite size (Å) TEM	X-Ray	O_2-ads	Standard rate (mole/min, g Ag) $r^0_{CO_2} \times 10^5$	$r^0_{EtO} \times 10^5$	Surf. area[a] (m^2/g Ag)	Specific rate (mole/min, m^2 Ag) $\bar{r}^*_{CO_2} \times 10^6$	$\bar{r}^*_{EtO} \times 10^6$	Selectivity (%)
CS-4	60	58.3	65.67	38.47	9.77	95.23	4.04	1.03	20
CS-5	100	97	103.77	5.59	4.06	57.14	1.67	0.71	29.5
CS-6	190	170	192.72	2.00	1.15	30.07	0.66	0.37	36.5
CS-8	500	526	509.28	0.139	0.228	11.43	0.12	0.20	62
Cs-11	290	276	302.34	0.501	0.435	19.70	0.25	0.22	46.5
CS-15	120	123	118.28	28.73	11.38	47.62	6.03	2.39	28.5
CS-16	—	—	18.5	—	—	—	—	—	<0.7
CS-17	30	—	26.57	—	—	—	—	—	12
Z-26	60	58	63.93	10.78	2.76	95.23	1.13	0.29	20
Z-27	180	140	180.15	4.17	2.32	31.74	1.31	0.73	36
Z-28	400	387	389.16	0.610	0.715	14.29	0.43	0.50	54
Z-29	55	76	68.31	36.10	8.97	103.89	3.48	0.86	20
Z-30	90	—	—	—	—	—	—	—	26
Z-31	80	120	86.97	14.80	5.13	71.43	2.08	0.72	25
Z-27[b]		140		4.17	2.32	40.81	1.02	0.57	

[a] Calculated from TEM data.
[b] Calculated from X-ray data.

hours. As shown in Fig. 4, the selectivity became constant several hours before the individual reaction rates reached steady state. All other catalysts tested had a lower selectivity, and the selectivity correlates very well with crystallite size, as Fig. 5 shows. The smallest crystallites gave almost zero selectivity, but the most surprising result was the large change in selectivity in the size range 100–500 Å. In studies of supported platinum and nickel catalysts, size effects have generally been found only for crystallites smaller than 100 Å.

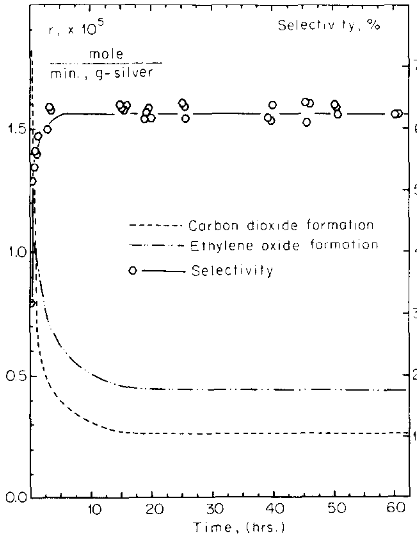

FIG. 4. The activity and selectivity change of catalyst CS-8 during reaction.

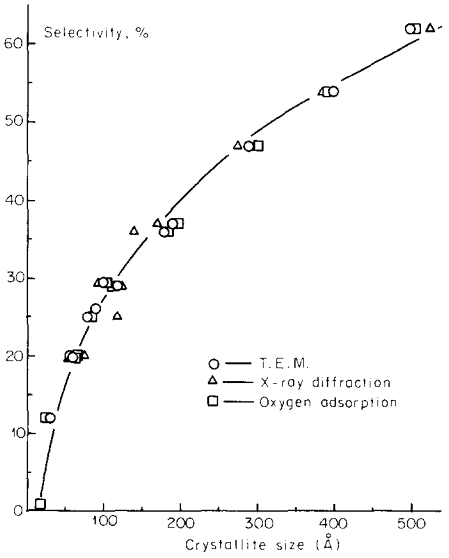

FIG. 5. The effect of crystallite size on selectivity.

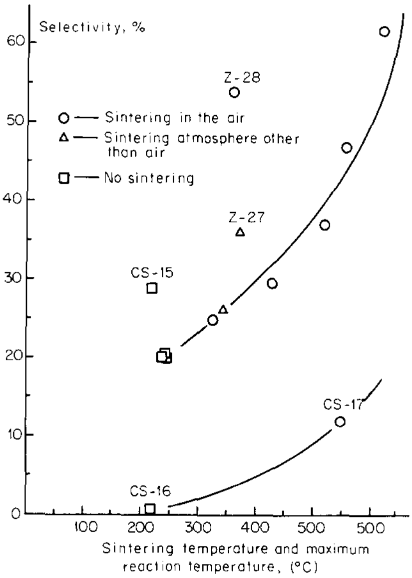

FIG. 6. The effect of sintering temperature and maximum reaction temperature on selectivity.

Since the largest crystallites were made by sintering, it might be thought that annealing produced the changes in selectivity. To check this, the selectivities were plotted against the sintering temperature or the maximum reactor temperature in Fig. 6. A correlation is evident for all catalysts prepared under identical conditions before sintering, but points for other catalysts do not fit the correlation. Catalyst CS-16 (0.54% Ag, 20 Å) had almost zero selectivity, and sintering this material to make Catalyst CS-17 increased the crystallite size to 30 Å and the selectivity to 12%. Catalysts CS-15 and Z-28 were prepared by different techniques to give larger crystallite sizes before sintering, and they fall above the other points in Fig. 6. Catalyst Z-27 was sintered in the reactor during a temperature excursion to 374°C, but the catalyst temperature may have been still higher. Sintering may change the number of defects, but the effect is apparently small compared to the effect of crystallite size.

The selectivity of 62% for the largest crystallite is comparable to the higher values reported by other workers who used unmoderated silver catalyst. Klugherz and Harriott (*9*) found a selectivity of about 60% for silver on α-alumina; electron micrographs indicated an average crystallite size of about 1000 Å. Cambron and Alexander (*1*) got 60% selectivity with porous silver, and the sharp X-ray diffraction peaks indicated crystallites at least 1000 Å in size. Studies of silver films or powders, which should behave like large particles, have not given consistent results. Imre (*6*) and Spath *et al.* (*21*) found selectivities of 60–68%, but MacDonald and Hays (*10*) and Moss and Thomas (*14*) got selectivities of only 10–30%. Manara and Parravano (*11*) reported 72% selectivity for a Ag–Ba catalyst (0.5% Ba) with 3000–5000 Å crystallites but zero selectivity for 100 Å crystallites. However, their 100 Å crystallites were supported on γ-alumina, which may be catalytically active, and the catalyst was tested at 140°C, perhaps too low for significant adsorption of molecular oxygen which is needed for ethylene oxide formation.

Specific Activity

The catalysts with the smallest crystallites were the most active per gram of silver and were also more active per unit area, as shown in Figs. 7 and 8. Both reaction rates decreased with increasing crystallite size, but the decrease was more pronounced for carbon dioxide formation, giving an increase in selectivity. With silver on silica Z support, the activity for carbon dioxide formation varied approximately with the −1 power of the crystallite size, while the ethylene oxide activity decreased only slightly and may have reached a limiting value for large sizes. The activity of CS-catalysts decreased more rapidly as the size increased, which may be due to some type of metal–support interaction. The different preparation methods for the silica supports would lead to differences in surface structure, such as the concentration of hydroxyl groups.

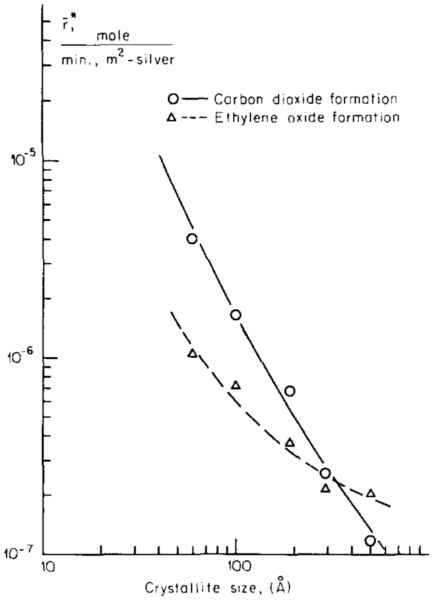

FIG. 7. The effect of crystallite size on the specific activity of CS-catalysts.

The activity data were more scattered than the selectivity results, and not all the data are included in Figs. 7 and 8. The steady state rates for catalysts CS-16 and CS-17 were too low for accurate results, and catalyst Z-30 was studied for only 3 hr, long enough to get the selectivity but not the steady state activity. The activity of catalysts Z-26 and CS-15 were respectively one-third and three times the expected values, and the reasons are not known.

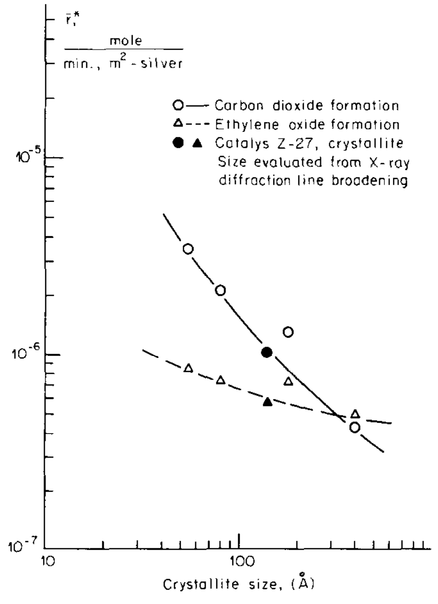

FIG. 8. The effect of crystallite size on the specific activity of Z-catalysts.

DISCUSSION

The changes in activity and selectivity suggest that there are different types of reaction sites and that the proportions of these sites change with crystallite size. There may be sites of different activity on a single crystal face, and various faces such as the (100), (110) or (111) planes might have different types of sites. However, the proportions of sites of these types or sites at defects would not be expected to change very much with particle size. The sites associated with atoms at edges or corners where crystal faces meet would become a smaller fraction of the total sites as the crystallite size increased. Sites at steps on the surface of a nearly spherical crystallite would also be less numerous for large crystallites, and the changing proportions of edge or step sites relative to sites on low index planes might be the reason for the observed changes in selectivity and activity.

The evidence for stepped surfaces, which have special characteristics, is reviewed by Somorjai (*18*). High index surfaces of platinum, copper and other materials, prepared by cutting crystals at a small angle, have been shown to consist of regular terraces of low index planes separated by steps of monatomic height. Adsorption on these surfaces can give surface structures different from those produced by chemisorption on low index planes. For example, oxygen was chemisorbed on stepped surfaces of platinum at pressures too low for measurable adsorption on normal low index faces. Silver has the same face-centered cubic structure as platinum, and step sites on silver should also chemisorb oxygen more strongly than normal sites. There is no direct evidence for steps on the surface of tiny silver crystallites, but it seems likely that they would exist. The particles of silver on supported catalysts appear spherical in electron micrographs, and cubo-octahedral models that are almost spherical can be made with fixed numbers of atoms. However, a particle in a real catalyst will not have exactly the number of atoms for a perfect crystal, and the excess atoms will probably form a cluster or partially completed layer over part of the surface. Step sites would be found at the periphery of the clusters, and the fraction of surface atoms at such sites would vary inversely with the size of the crystallite, if the number of atoms in the cluster is proportional to crystallite size.

Kinetic models based on various types of sites can be developed to fit the observed changes in specific activity and selectivity. The simplest model has two types of sites, with Type I, which may be edge, corner, or step sites, producing mainly carbon dioxide and a little ethylene oxide. Type II sites, which may be on low index faces, would produce mainly ethylene oxide. The data in Fig. 8 for Z-catalysts can be fitted assuming Type I sites are 30 times as active as Type II and comprise one-fourth of the total sites for 50 Å crystallites, this fraction varying inversely with crystallite size. The data in Fig. 7 for CS-catalysts are not fitted as easily, since the specific activity for carbon dioxide production decreases more rapidly with size than an inverse relationship predicts. There might be a metal–support interaction which would be less important for large crystallites, and more data on other types of supports is needed to test this possibility.

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