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Oxidation of Ethylene Catalyzed by Silver Supported on Zirconium Phosphate: Particle Size and Support Effect

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The catalytic activity of metallic silver supported on zirconium phosphate has been examined in the reaction of ethylene oxidation in terms of the average silver particle size, the surface area of the support, and the cations present in the support. The activity was found to decrease when the surface area of the support was increased. A maximum activity and selectivity was obtained with silver particles about 480 Å in average diameter supported on highly crystalline zirconium phosphate. Cations present in the ion-exchange sites of the support have a strong effect on the catalytic properties. Among the cations used, Na^+ gives the highest total conversion, K^+ gives the best selectivity for ethylene oxide formation, while Cs^+ was found to suppress the reaction completely. © 1985 Academic Press, Inc.

INTRODUCTION

Silver is unique among metals in its ability to catalyze the selective oxidation of ethylene to ethylene oxide. However, the reaction is always accompanied by CO_2 formation which is the result of either complete oxidation of ethylene or subsequent oxidation of ethylene oxide. Many types of materials have been used as supports for the silver catalyst, with those of relatively low surface area predominating. Supports with pore structures and high surface areas lengthen the retention time of the reactants and products in the cavities and result in catalysts which exhibit unsatisfactorily low selectivities (*1–3*). The most frequently used support for silver is α-alumina, though nonporous silicon carbide has also been adopted.

Studies of the effects of the support on the activity and selectivity of the silver catalysts for ethylene oxidation have been conducted by Harriott (*4*), by Riassian *et al.* (*5*) and by Verykios (*6*). Alumina and silica of moderate to high surface areas were used by Harriott. Silver supported on silica with high surface area (~300 m^2/g) was reported to be as selective as silver on low-surface-area supports, but very low selectivities were obtained for silver supported on activated alumina or dessicant-grade silica gel. Nevertheless, no tentative conclusion concerning the performance of each support can be made from this study because many variables were left uncontrolled, most importantly the size distribution of silver particles. On the other hand, Riassian *et al.* (*5*) have studied the activity patterns of silver supported on silica, alumina, and glass under more precisely controlled conditions. They observed significant changes in activity with reaction time and these changes depended on the nature of the support. Verykios (*6*) used alumina supports doped with germanium and magnesium oxides to study the influence of the support's electronic character. It was observed that when the electron population of the catalyst surface increased (or the work function decreased) both activity and selectivity decreased.

Besides the support effect, another subject of fundamental importance in using

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supported catalysts is the effect of metal particle size. Since only metal atoms exposed on the surface are effective for catalytic reaction, smaller particles, which provide a higher ratio of atoms exposed on the surface, should be more economical to use. However, several investigators indicated that catalytic activities vary with particle size (*6*, *7*). Wu and Harriott (*7*) have examined the silica in which the average particle diameter ranged from 20 to 500 Å. They reported that the specific rates for both ethylene oxide and carbon dioxide formation decreased as the average particle size increases. However, the selectivity for ethylene oxide is nearly zero for small particles and gradually increases to 60% for particles around 500 Å diameter. Verykios (*6*) has studied the particle size effect of silver supported on alumina and observed a reversed trend in selectivity for particles larger than 500 Å.

Various explanations have been given for this particle size effect. For metal clusters with diameters smaller than 50 Å, it is well known that their structural forms and electronic properties may differ markedly from those of the bulk substance (*8*). Therefore, it is understandable that very small silver particles may behave differently from larger particles. Verykios (*6*) suggested that the increase in the specific rates with increasing size is related to changes in the morphology of the silver particles. Harriott (*7*) elucidated their results in terms of changes in the proportion of steps and edges to crystal faces. However, Clayton and Norval (*9*) proposed that the size effect is due to the changes in the properties of the surface oxide layer.

In search of new catalyst materials, α-zirconium phosphate (α-ZrP), an inorganic ion-exchanger of layered structure, has been examined by a number of investigators in its applications to catalytic reactions (*10–13*). Though α-ZrP crystals contain zeolitic-type cavities in between the layers, the free volume of the cavities is so small that it is considered to be a nonporous material. Because α-ZrP can be obtained with various degrees of crystallinity and with a wide range of surface areas by changing the preparation conditions (*14*), it is a good candidate for studying the effect of the surface area of the support and that of metal particle size on catalytic reactions. In the present work, the catalytic properties of metallic silver dispersed on α-ZrP have been examined in terms of the silver particle size, the surface area of the support, and inert cations existing in the support.

EXPERIMENTAL

Support Preparation

A series of zirconium phosphate samples with different crystallinities were prepared by refluxing a zirconium phosphate gel in H_3PO_4 solution for increasing periods of time as described by Clearfield and Stynes (*15*). These samples are labeled as α-ZrP (6:48), (9:48), (12:50), and (12:336), where the first number represents the molar concentration of H_3PO_4 acid and the second number, the duration of reflux in hours. The crystallinity increases and the surface area decreases with increasing reflux time and acid concentration.

Catalyst Preparation

The α-ZrP samples were exchanged with silver acetate solutions of various concentrations. The amount of Ag^+ taken up by the solid was calculated by difference from the amount remaining in solution as determined by EDTA titration (*16*) of the filtrate. The air-dried samples were then dehydrated at 100°C under vacuum overnight and reduced by H_2 at the same temperature in a recirculatory system. Complete reduction was indicated when the drop of hydrogen pressure ceased. The sample was characterized from its X-ray diffraction pattern and other methods described below.

The resultant silver-coated product was again exchanged with nitrate or acetate solutions of the cations of interest. They include Ag^+, Ca^{2+}, and most of the alkali metal ions—Li^+, Na^+, K^+, and Cs^+. The solid samples, after filtering, were always washed thoroughly with deionized distilled water, then air-dried.

Before each run, the catalyst was dehydrated under vacuum at 100°C overnight and at 300°C for another hour. Then, the catalyst was pretreated by flowing H_2 gas through it for about $\frac{1}{2}$ h at 300°C, followed by purging with He gas at the same temperature. Finally, the catalyst was degassed for approximately 5 min.

Gases

Ethylene gas of 99.5% purity was a product of Liquid Carbonic Corporation. Oxygen for the adsorption isotherm experiments was ultrahigh purity (99.999%) purchased from Scientific Gas Products, Inc. The oxygen was further purified by passing it through a trap containing P_2O_5 and Ascarite which absorbed moisture and carbon dioxide, respectively. Oxygen for ethylene oxidation reaction had a 99.9% purity. Hydrogen for reducing the silver samples was ultrapure gas (99.999%) and the helium carrier gas had a purity of 99.995%. These latter three gases were purchased from Airco Industrial Gases, Inc.

Apparatus and Procedures

(1) Ethylene oxidation. The ethylene oxidation reaction was carried out in a continuous flow system. The flow rates of the inlet gases—ethylene, O_2, and He (used as diluent) were controlled separately by three tubular flowmeters (Matheson Gas Inc.). The gases were passed through a mixer, the preheating zone, the catalyst bed, and finally a gas sampler to the gas chromatography (GC) analyzer. The U-shaped Pyrex glass reactor had a thermocouple well at the middle of the catalyst bed to register the temperature of the reaction zone. The reactor was heated by a tubular oven purchased from Applied Test System, Inc. (Series 3210); the heating rate and the temperature were regulated by using a Barber-Colman 520 solid-state controller. The temperature was controlled within ±0.1°C. The path after the catalyst bed was wound with heating tapes and the temperature was kept at ca. 100°C to avoid any condensation of water vapor which was one of the products. The products were analyzed by a Hewlett–Packard 5830 A gas chromatograph. A Porapak Q column was used for the separation of ethylene, carbon dioxide, O_2, and ethylene oxide. The gas sampler automatically sent 0.25 ml of the gaseous products for the GC analysis every 6 min, so that the reaction rate was recorded as a function of time.

(2) Ag-free metal surface area measurement by O_2 chemisorption. O_2 chemisorption was carried out by a volumetric method. The O_2 gas was circulated over the sample by means of an all-glass electromagnetically actuated piston pump. The change of O_2 pressure in the system was measured by a Validyne Model DM56 differential manometer accompanied by a digital readout which was able to read pressures from 0 to 1000 mm Hg at the "high" range and 0.0 to 199.9 mm Hg at the "low" range. Low pressures of the system were measured by the combination of a thermal gauge and an ionization gauge which were connected to a Granville-Phillips Series 260 gauge controller.

The O_2 chemisorption isotherm was carried out according to the method reported by Scholten *et al.* (*17*) and Kholyavenko *et al.* (*18*). They indicated that the maximum adsorption of O_2 in the temperature range of 150 to 200°C corresponds to an oxygen-to-surface silver ratio of about unity. Moreover, the oxygen in the monolayer started to desorb at 200°C, so that the 200°C isotherm had its maximum level at approximately 0.75 coverage. In the present study, the O_2 chemisorption isotherm was measured on the catalysts at a temperature ca. 180°C before use in the reactions.

(3) Instrumental. Silver particle sizes were measured by X-ray diffraction line

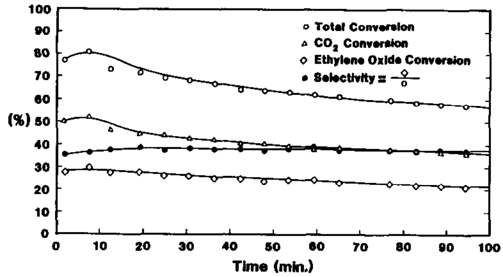

FIG. 1. Activity pattern for ethylene oxidation over silver supported on (12 : 336) $Zr(NaPO_4)_2$.

broadening. The peak for the Ag (111) reflection was chosen to calculate the average size. No changes in the average silver particle sizes were observed before and after the reactions. The powder diffraction patterns were obtained by using a Seifert Scintag Pad-II X-ray diffractometer with Cu*Kα* radiation. The dispersion of the silver particles was determined by taking electron micrographs of the samples. A JEOL electron microscope, Model JSM-35, was used for scanning electron microscopy and a Hitachi electron microscope, Model HV-11E, was used for transmission electron microscopy. A Hewlett–Packard 5950-A ESCA spectrometer was used to record the XPS spectra of various supported catalyst samples before and after the oxidation reaction. The excitation radiation was Al*Kα* ($h\nu$ = 1486.6 eV). The carbon 1*s* line was used as the reference line with binding energy of 285.0 eV (*19*).

RESULTS

A typical activity pattern for ethylene oxidation over silver supported on zirconium phosphate is shown in Fig. 1. The activity, in terms of the percentage conversion of ethylene, decreases somewhat at the beginning and reaches a steady state after about 1.5 h. In the following sections, the data used for comparison are those obtained after the reaction had reached equilibrium. The catalyst responding to this pattern had 36.1 wt% of silver on (12 : 336) $Zr(NaPO_4)_2$. Na^+, in this case, is the cation used as described under Experimental. Initially, we tried to study the reaction of a silver catalyst supported on $Zr(HPO_4)_2$, i.e., with no cation replacing H^+ in the exchange sites. However, because of the high affinity exhibited by α-ZrP for Ag^+ ions (*20*), metallic silver was oxidized (by oxygen in the feed) to Ag^+ ions which then diffused back into the lattice of α-ZrP. As a result, the catalyst was inactivated in a few minutes. This characteristic of Ag^+ (and Cu^{2+}) of being reduced and easily reoxidized when supported on ZrP, is thought to be responsible for their behavior as catalysts in dehydrogenation reactions (*21, 22*). However, when there are cations other than H^+ present in the ion-exchange sites of ZrP, the metallic silver catalysts are stabilized because the sites for Ag^+ ions to diffuse back into are blocked. The catalysts we have used were mainly silver supported on $Zr(NaPO_4)_2$ where Na^+ was the cation blocking the ion-exchange sites of ZrP.

The Effect of Reaction Conditions

Optimization of the conversion rate was attained by varying the reaction conditions, which included the temperature of the reaction zone and the concentrations of inlet gases. Table 1 shows the influence of the concentrations of the reactants. The catalyst contained 36.1 wt% of silver on (12 : 336) $Zr(NaPO_4)_2$, and the reaction temperature was ca. 230°C. In one series of experiments, numbered 1, 2, 3, and 4, the concentration of O_2 was kept almost constant and that of ethylene was varied. The specific rates of both ethylene oxide and carbon dioxide formation were found to reach a maximum when the ratio of O_2/C_2H_4 was ca. 16. After this point, increasing the concentration of ethylene did not seem to affect the rates. Consequently, the percentage conversion of ethylene decreased as the concentration of ethylene was increased. In the other series (Experiments 3, 5, 6, and 7) the concentration of

TABLE 1

Variation of the Ethylene and Oxygen Concentrations for the Oxidation of Ethylene over Silver Supported on (12 : 336) $Zr(NaPO_4)_2$

Expt.	Feed, volume %		C.T. (s)	$R \times 10^7$ (mol/s · g Ag)		Conversion, mol% of E		S_{EO} (%)
	O_2	C_2H_4		EO + CO_2	EO	EO + CO_2	EO	
1	32.9	1.15	16.8	10.9	3.55	60.8	19.7	32.4
2	32.7	2.0	9.7	23.6	8.75	57.8	21.4	37.0
3	32.3	3.2	6.1	19.9	6.37	40.0	12.8	32.0
4	31.2	6.4	3.0	25.5	8.94	23.3	7.6	32.6
5	19.3	3.3		28.5	7.37	54.0	14.0	26.0
6	9.7	3.7		27.5	4.62	58.0	10.0	17.6
7	3.0	4.0		8.63	0	24.0	0	0

Note. Reaction conditions: 230°C, 1 atm.

ethylene was kept constant but that of O_2 was varied. Reducing the O_2/C_2H_4 concentration ratio by decreasing the pressure of O_2 seems to favor the formation of CO_2, but not ethylene oxide. Thus, the selectivity decreases as the concentration of O_2 is decreased. When the O_2/C_2H_4 ratio was less than one, there was no detectable amount of ethylene oxide formed. Table 2 shows the effect of reaction temperature in the range of 165 to 250°C. The same catalyst was used as in the previous set of experiments. The contact time was 6 s, which is slightly lower than optimum. Higher temperatures seem to favor the combustion reaction but hardly affect the formation of ethylene oxide in the temperature range from 200 to 250°C. As a result, the selectivity decreases as the temperature increases. Furthermore, by comparing the catalyst activity as a function of time, it was found that the drop in activity is somewhat faster at high temperature than at low temperature. This may result from the higher CO_2 concentration at high temperature, and implies that CO_2 inhibits both ethylene oxide and CO_2 formation. A similar inhibiting effect has also been observed by Force and Bell (*23*) using silver supported on Cab-O-Sil as catalyst. In the following studies, the reaction temperature was always kept at ca. 230°C at which temperature the maximum activity, but less than the maximum selectivity, was observed for EtO.

TABLE 2

Effect of Reaction Temperature on the Oxidation of Ethylene over Silver Supported on (12 : 336) $Zr(NaPO_4)_2$

Expt.	Temp. (°C)	Conversion (mol%)				S_{EO} %	
		EO + CO_2		EO		50 min	90 min
		50 min	90 min	50 min	90 min		
1	165	12.3	12.2	4.6	4.6	37.4	37.7
2	200	31.3	30.5	11.2	10.6	35.8	34.8
3	225	42.5	40.0	13.6	12.8	32.0	31.2
4	250	47.7	38.5	11.0	9.0	23.1	23.3

Note. Inlet flow mixture: $P_E = 25$ Torr, $P_{O_2} = 245$ Torr, $P_{He} = 490$ Torr. Contact time = 6 s.

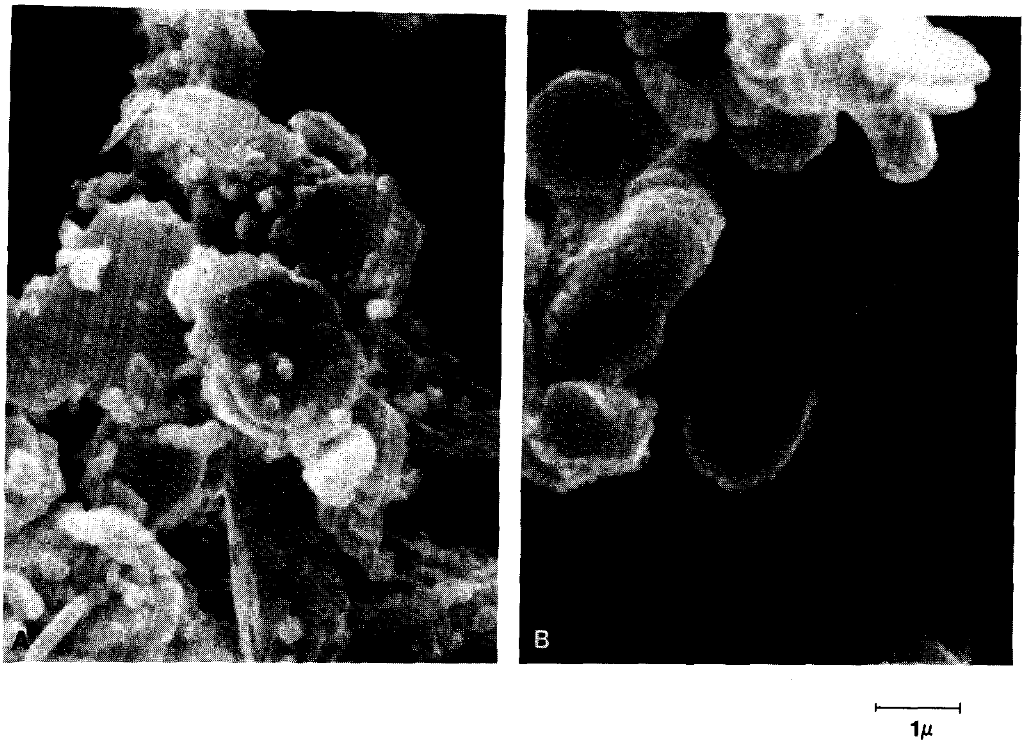

FIG. 2. SEM photos of silver supported on (12 : 336) $Zr(NaPO_4)_2$; (A) 36.1 wt% and (B) 9.1 wt% of Ag. Note the spherical metal particles on the flat platelets and larger accretions collected on the sides of the platelets.

Silver Particle Dispersion

The silver particle dispersion was examined by scanning and transmission electron microscopies (SEM and TEM). Figures 2A and B show two scanning electron micrographs of silver catalysts supported on (12 : 336) $Zr(NaPO_4)_2$, which contain 36.1 and 9.1 wt% of silver, respectively. The silver particle size increases with increasing silver loading. Sodium-exchanged zirconium phosphate crystals retain the geometry of the original α-ZrP crystals (*24*), which are hexagonal platelets. It is seen that large silver particles, in the size range of hundreds to 1000 Å, accumulate on the sides of the platelet, whereas, the base faces of the platelet (top and bottom) are mainly covered by fine silver particles which cannot be distinguished on the scanning electron micrographs. These findings are substantiated by the micrographs obtained for silver-coated α-ZrP single crystal samples with a diameter about 0.1 cm. Figures 3A and B show two kinds of particle distributions on a ZrP single crystal coated with silver particles; very thick layers of large silver particles are observed accumulated on the side surface, but a uniform distribution of fine silver particles are observed on the base surface of the platelet.

Transmission electron microscopy can better detect the small silver particles. Though the electron beam was not able to penetrate through some of the ZrP platetes because of their thickness, the silver particles situated on the sides of the ZrP crystals were detected. Figures 4A and B are the photographs of the 36.1 wt% of Ag on (12 : 336) $Zr(NaPO_4)_2$ before and after it was used as a catalyst for ethylene oxidation, respectively. The silver particle size distri-

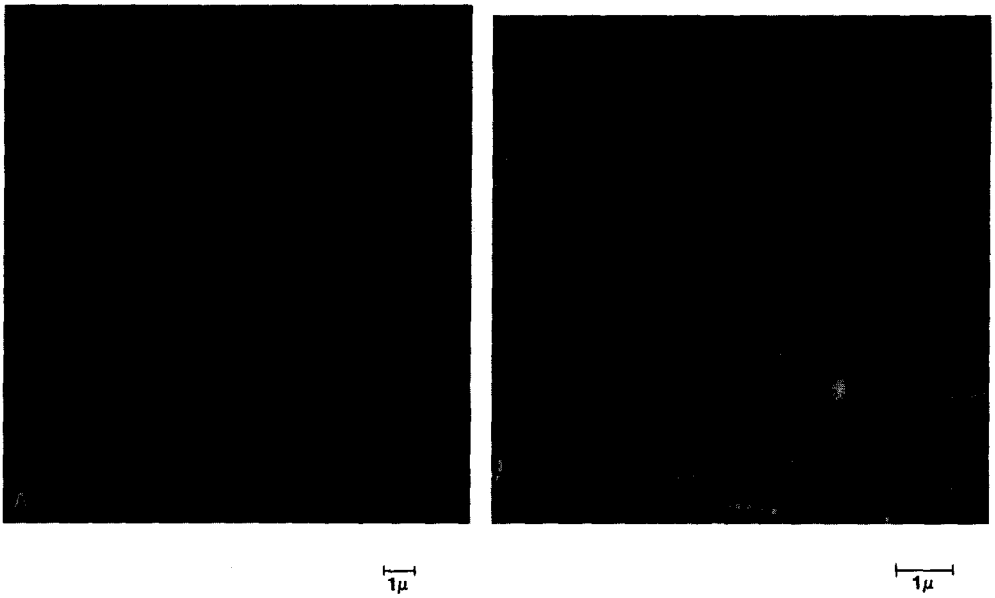

FIG. 3. SEM photos of the side (A) and the top (B) view of α-ZrP single crystal with Ag coating.

bution is not uniform. One observes large agglomerates of particles in the size range of a 1000-Å diameter which may consist of aggregates of smaller particles. Most of the larger particles have an average diameter of approximately 340 Å. In addition, there are many particles smaller than 50 Å present in these pictures. When the surface area of the

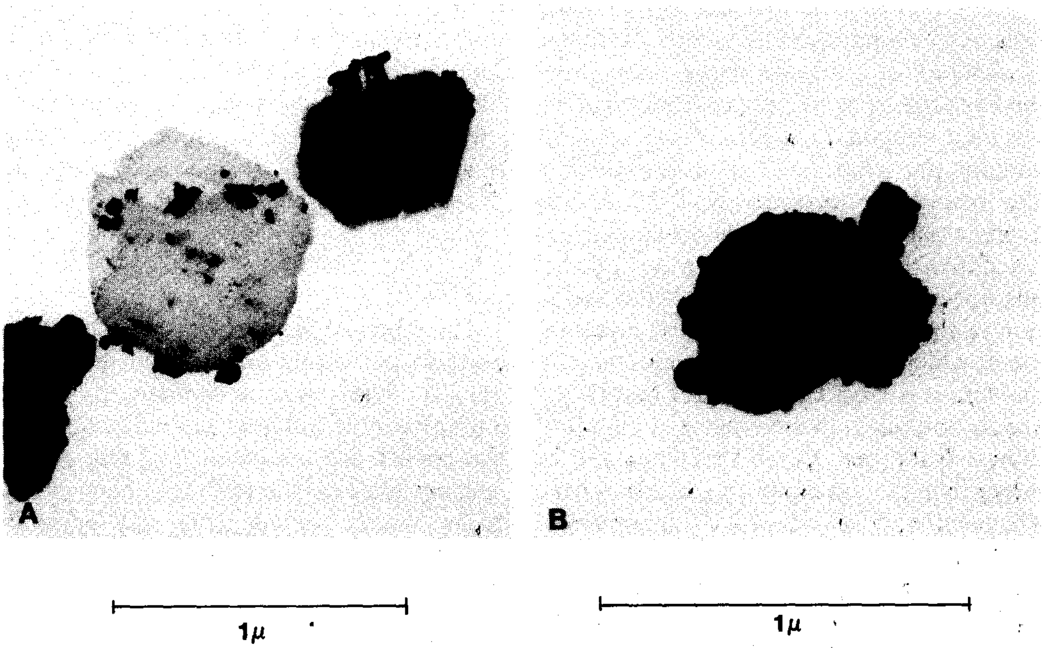

FIG. 4. TEM photos of 36.1 wt% of Ag on (12:336) $Zr(NaPO_4)_2$ before (A) and after (B) catalytic reaction.

TABLE 3

The Effect of Variation of the Silver Particle Size on the Oxidation of Ethylene

Expt.	Wt% of Ag	Ave. Ag particle size (Å)		$R \times 10^8$ (mol/s · m^2 Ag)		S_{EO} %
		X-Ray line broadening	O_2 chemisorp.	EO + CO_2	EO	
1	52.9	518	850	4.49	1.24	27.6
2	36.1	478	299	12.4	4.58	36.9
3	20.9	486	273	12.3	4.78	38.9
4	9.10	390	128	10.1	3.62	35.8
5	2.69	275	46	0	0	0

Note. Support: (12 : 336) $Zr(NaPO_4)_2$. Temperature = 230°C. Inlet flow mixture: P_E = 17.5 Torr, P_{O_2} = 250 Torr, P_{He} = 500 Torr. Contact time = 8.5 s.

support was increased (from 2.2 m^2/g for 12 : 336 to ~5 m^2/g for 12 : 50), but the sample contained the same weight percentage of Ag, a larger proportion of the particles were 50 Å or less and the large particles averaged ~200 Å.

The Effect of Silver Particle Size

The effect of silver particle size on catalytic activity and selectivity was examined in a series of catalysts which were composed of different weight percentages of silver on a nonporous sodium exchanged zirconium phosphate, (12 : 336) $Zr(NaPO_4)_2$. The results are tabulated in Table 3. The average particle size was determined by X-ray diffraction line broadening and O_2 chemisorption methods. Because of the limitation of the X-ray line broadening measurement, which cannot detect particles with diameters less than ca. 50 Å (*25*) (except by special methods) the average size as determined from the X-ray study should be larger than that obtained by gas adsorption. This was the case except for Experiment 1, Table 3. The specific rate of the reaction, which is expressed in moles per second per square meter of silver, is therefore calculated based on the surface area obtained from O_2 chemisorption experiments.

Because the electron micrographs showed that silver particles were predominantly in the size range close to that determined by O_2 chemisorption for low-silver-loaded samples, it can be concluded that silver particles with an average diameter ca. 46 Å have negligible activity for ethylene oxidation reaction as shown in Experiment 5, Table 3. Accordingly, the silver particles which are effective for catalytic oxidation of ethylene have a size close to that measured by X-ray line broadening. Therefore, the maximum activity and selectivity are obtained at ca. 480 Å diameter. For silver particles larger or smaller than this size, both activity and selectivity decrease.

The Effect of the Surface Area of the Support

The effect of the surface area of the support on the catalytic activities of the silver catalysts was examined by using $Zr(NaPO_4)_2$ of different crystallinities, and the results are tabulated in Table 4. The starting material, $Zr(HPO_4)_2$, had surface areas which varied from 2.2 m^2/g for (12 : 336) to 16.9 m^2/g for (6 : 48). The ion-exchange process disorders the crystal, somewhat increasing the surface area of the material. However, the relative surface area variation from low to high in this series would not diverge much from the initial val-

TABLE 4

The Effect of Variation of the Surface Area of the Support on the Oxidation of Ethylene

Expt.	ZrP	Wt% of Ag	Ave. Ag particle size (Å)		S.A. of the support (m^2/g)	$R \times 10^8$ ($mol/s \cdot m^2$ Ag)		S_{EO} %
			X-Ray line broadening	O_2 chemisorp.		EO + CO_2	EO	
1	12:336	36.1	478	299	2.2	12.4	4.58	36.9
2	12:336	9.10	390	128	2.2	10.1	3.62	35.8
3	12:50	36.1	415	118	5.0	1.96	0.514	26.2
4	9:48	36.1	239		7.8	0.74	0	0
5	6:48	36.1	179		16.9	0.36	0	0

Note. Temperature = 230°C. Inlet flow mixture: P_E = 17.5 Torr, P_{O_2} = 250 Torr, P_{He} = 500 Torr. Contact time = 8.5 s.

ues. When comparing samples with the same silver loading (36.1 wt% in Experiments 1, 3, 4, and 5), the activity and selectivity apparently decrease as the surface area of the support increases. However, the silver particle size also decreases concomitantly. In order to exclude the influence caused by varying silver particle sizes, a comparison is made between two samples which contain silver particles of similar average diameter but different surface areas of the support (Experiments 2 and 3). These samples contain 9.1 wt% of Ag on (12 : 336) $Zr(NaPO_4)_2$ and 36.1 wt% of Ag on (12 : 50) $Zr(NaPO_4)_2$. In this case, again, both the activity and selectivity decrease when the surface area of the support increases.

The Effect of the Cations on the Support

The cations situated at the exchange sites of zirconium phosphate are found to influence markedly the catalytic activity and selectivity. The cations which have been examined are Ca^{2+}, Ag^+, and most of the alkali metal ions including Li^+, Na^+, K^+, and Cs^+. The results are tabulated in Table 5. Among them, Na^+ ion was the one which gave the highest activity while K^+ ion produced the highest selectivity. Cs^+ ion, however, suppressed the reaction completely.

TABLE 5

The Effect of Cations in the Support on the Oxidation of Ethylene

Expt.	Cations	$R \times 10^7$ ($mol/s \cdot g$ Ag)		Conversion, mol% of E		S_{EO} %
		EO + CO_2	EO	EO + CO_2	EO	
1	Li^+	11.6	1.93	18.6	3.0	16.0
2	Na^+	25.7	9.80	34.3	13.1	38.2
3	K^+	7.21	3.73	9.6	5.1	53.2
4	Cs^+	0	0	0	0	0
5	Ca^{2+}	5.33	0	7.3	0	0
6	Ag^+	18.1	2.74	20.9	3.2	15.3
7	Ca^{2+}/Na^+	33.8	11.3	42.1	14.1	33.5

Note. Reaction condition: temperature = 230°C. P_E = 17.5 Torr, P_{O_2} = 250 Torr, P_{He} = 500 Torr. Contact time of E = 8.5 s.

Furthermore, Experiments 2, 5, and 7 show that the catalytic activity and selectivity vary with mixed cations present at the exchange sites. In Experiment 7, the catalyst contained both Ca^{2+} and Na^+ ions with the Ca^{2+}/Na^+ ratio $\frac{1}{9}$. While the overall reactivity increased, the selectivity of ethylene oxide formation decreased as compared with that of the catalyst containing only Na^+ ions. However, when most of the Na^+ ions were replaced by Ca^{2+} ions as in Experiment 5, only a small amount of carbon dioxide and no detectable amount of ethylene oxide was formed.

DISCUSSION

The activity patterns for ethylene oxidation over silver supported on zirconium phosphate always showed an initial drop in activity. Similar activity patterns were observed by Riassian *et al.* (*5*) and Giordano and co-workers (*26*) for different supports which included SiO_2, Al_2O_3, and glass. Possible reasons for this initial decrease, which have been proposed in Riassian's system, are as follows: (1) modification of the silver surface by impurities from the supports and from carbon species deposited during the reaction, (2) silver particle sintering, (3) the formation of some oxidized form of silver, and (4) hillock formation on the silver surface, or the reorganization of the silver surface.

Factors (2) and (4) can be eliminated in our system because the activity of the catalyst can be regenerated with a H_2 gas flow at 300°C.

The deposition of organic residues on the surface was examined by taking ESCA spectra and carbon analysis on the catalyst samples before and after the reactions. The results indicated that no significant amount of carbon was deposited on the catalyst during the reaction. Wachs and Kelemen (*27*), who studied the oxidation of ethylene by atomic oxygen on silver (110) planes, found that carbon deposited on the silver surface was oxidized by additional oxygen. Since our reactant mix always contained excess oxygen, it is likely that any deposited carbon was reoxidized to CO_2.

The explanation for the initial changes in activity must then rest with (1) and (3). That a silver surface can adsorb oxygen and form a subsurface oxygen species was proved by Backx and co-workers (*28*). It is also generally accepted that these species are essential for the ethylene oxidation reaction (*9, 29*). Our studies of the catalytic activity of silver supported on the proton form of ZrP, $Zr(HPO_4)_2$ revealed that silver could be oxidized to Ag^+ ions. Therefore, it is proposed that the silver surface reacts with oxygen to form some kind of oxidized species which then exchanges Ag^+ ions with the cations present in the support; the initial drop in activity may be due to this ion-exchange process by which the surface properties of the silver particles are changed and the catalytic activity decreases. However, the amount of silver participating in this reaction must be very small because the X-ray powder diffraction patterns of the used catalysts did not show the presence of Ag^+ exchanged phases of zirconium phosphate.

This hypothesis is further strengthened by the observation that the rate of the initial drop in activity is a function of the reaction temperature and the type of cations situated at the exchange sites of ZrP. For example, the catalytic activity decreases more rapidly at high temperatures than at low temperatures because the ion-exchange process is faster at higher temperatures. On the other hand, silver supported on $Zr(KPO_4)_2$ was found to lose its activity much faster than on $Zr(NaPO_4)_2$ at all temperatures. According to our hypothesis, the surface properties of these two catalysts are varied because of the substitution of Ag^+ in the subsurface oxide layer with K^+ and Na^+ ions in the support. Ion-exchange isotherms show that the affinity of α-ZrP to the concerned ions is in the order of $Ag^+ > Na^+ > K^+$ (*20, 30*). Therefore, K^+ in $Zr(KPO_4)_2$ is easier to replace by Ag^+ than Na^+ in $Zr(NaPO_4)_2$. Consequently, the drop in the activity is faster for silver supported on $Zr(KPO_4)_2$ than on $Zr(NaPO_4)_2$.

The activity and selectivity for the ethylene oxidation reaction was found to depend on the silver particle size of the supported catalyst. Moreover, the activity and selectivity always varied in a parallel manner with the change in average silver particle diameter. They were both nearly zero for silver particles of average diameter 46 Å and generally increased to a maximum at 480-Å particles. For larger particles, both the activity and selectivity were found to decrease. This observed size effect on the selectivity is quite consistent with the results obtained by Verykios *et al.* (*6*) and Wu and Harriott (*7*).

However, the reverse trend was found by these authors for the reaction rate. Wu and Harriott (*7*) explained their results in terms of changes in the proportion of steps and edges to crystal forces. Although such effects are well known for hydrocarbon reactions over platinum and other metals (*31*), they are usually not applicable to particles larger than 50 Å (*8*, *32*).

Verykios *et al.* introduced the importance of morphology to explain the performance of their catalysts. By using scanning electron microscopy, they found that the silver crystallites were spherical in shape when 350–600 Å in size and began to lose their sphericity and develop a dendritic structure for particles larger than 600 Å. Perhaps a more accurate determination would have resulted from the use of transmission electron micrographs. Our photographs obtained by the latter technique (Fig. 4) showed that most of the silver particles are not perfectly spherical even for diameters of ~100 Å.

Geometric and structural factors are generally thought to be important for chemical and catalytic activities of metallic particles of diameters smaller than 50 Å (*8*). The structural form of small clusters of metal atoms may differ markedly from that of the crystal lattice of the bulk substance. By comparing the static potential energy of the cluster, Hoare and Pal (*33*) and Hoare and McInnes (*34*) pointed out that in the size range below 50 atoms, the most stable clusters are never lattice crystallites of fcc or hcp type but are polytetrahedral structures consisting of face-to-face combinations of four-atom tetrahedra, distorted as necessary for closure. Even though the structural variation is not necessary, crystallites of diameter smaller than ca. 50 Å can have tremendously different chemical properties from the bulk substance because the degree of coordination of surface atoms is a function of crystallite size. Poltorak and Boronin (*32*) have studied the fcc octahedra model as representative of finely divided platinum catalysts, and found that the mean coordination number of the surface atoms increases from 4 to 8.64 over the size range from 6 to 3894 atoms (5.5- to 49.5-Å edge length). They indicated that the crystal size range over which most of the change occurs is between 8 and 40 Å linear dimension. Moreover, atoms located at corners, edges, and other surface singularities have a larger number of unsaturated bonds, they are the ones with lower coordination number and usually thought to be particularly active sites for adsorption and catalysis.

In view of the above discussion, the surface of the silver crystallites of diameter smaller than ca. 46 Å is probably so active toward absorbed oxygen that the surface tends more toward the composition Ag_2O than metallic silver. It is known that silver(I) oxide is not a selective catalyst for ethylene oxide (*35*). Another possibility is that the fine particles are saturated with respect to adsorbed oxygen atoms. It has been shown recently that Ag_2O does not form but that levels of adsorbed atomic oxygen greater than one-half the surface sites retards the formation of ethylene oxide (*37*). As the average silver particle diameter increases, the selectivity and activity increase because the population of fine particles with diameters smaller than ca. 46 Å is reduced and the larger particles yield a higher proportion of the desired surface oxygen species. However, other morphological influences become important when the particles grow to larger sizes. The TEM photo in Fig. 4 shows that silver particles with diameters larger than ca. 480 Å have polyhedral or dendritic shapes. These irregularly shaped particles apparently include a large number of dislocations. Accordingly, the dislocations contain atoms of low coordination number which can form strong bonds with oxygen to give oxide species, e.g., Ag_2O. Therefore, the selectivity decreases as the average silver particle diameter gets larger than 480 Å.

The size effect on the catalytic activity in the present study showed a reverse trend as compared with those observed in other studies (*6*, *7*). This discrepancy is probably due to the different materials used as supports and to the different conditions used to prepare the catalysts. Wu and Harriott (*7*) obtained catalysts with different crystallite sizes by varying the nature and surface area of the support, the preparative variables, and by sintering at different but relatively low temperatures. Consequently, their results may have involved complicated influences from the different supports and different preparation conditions. Verykios and co-workers (*6*) varied the crystallite size by sintering the catalysts at different temperatures and for different periods of time. In the present study, the silver particle size was varied simply by changing the silver loading on the same support material. However, the silver particle size distribution was still very broad.

It is clear from the data in Table 4 that increasing the surface area of the support decreases the activity of the silver catalyst. Although it is almost impossible to eliminate the effect of different silver particle sizes from consideration, it appears that not all of the reduction in activity can be ascribed to diminished particle size. However, a greater proportion of the silver contacts the surface when the support surface area is increased. This would provide a better opportunity for interaction between the cations in the support and the Ag_2O layer which forms during reaction. Apparently, the Na_2O produced by the exchange process may strongly influence the sorption characteristics of oxygen on the affected silver surface. Since different cations in the support affected the reaction differently, a systematic study of this effect should yield information on the relative importance of electronic interactions, surface oxide formation, and basicity on activity and selectivity in the oxidation reaction.

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