Supported Silver Catalysts for the Oxidation of Ethylene: The Effects of Thermal Treatment of Alumina as Catalyst Support

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Ethylene oxidation was investigated in a flow-type reactor, using silver catalysts supported on a series of aluminas which were pretreated at different temperatures between 300 and 1800°C. Steady activity and selectivity at a set of reaction conditions were dependent upon the surface area of the catalyst which was a function of the thermal treatment of alumina.

The specific rates of ethylene oxidation, the oxidation of ethylene oxide, ethylene oxide isomerization to acetaldehyde, and acetaldehyde oxidation were investigated in a pulse reactor, using three kinds of catalysts supported on aluminas pretreated at 1150, 1200, and 1800°C. By comparing the activities of these catalysts for the above four reactions, the following were deduced: (1) A direct oxidation path of ethylene to carbon dioxide and water could be assumed for each catalyst; (2) the consecutive oxidation of ethylene via ethylene oxide was assumed to occur on each catalyst tested, and it predominated on catalysts supported on aluminas pretreated at lower temperatures, which was interpreted in terms of the complete oxidation of acetaldehyde formed in the pores of alumina by the isomerization of ethylene oxide.

INTRODUCTION

Many studies have been done on the catalytic oxidation of ethylene over silver catalysts and the results have been reviewed by several authors (1–5). Much attention has been devoted to the chemisorbed oxygen species on silver and their interaction with ethylene in connection with the mechanism of silver-catalyzed ethylene oxidation. Not only in academic studies but also in industrial practice, the silver catalysts have been used in supported form on proper carriers, alumina having been considered to be the most important one (6–14). Despite the practical importance of alumina as a supporting material, its

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characteristics and behavior in the silver catalysts are not yet well understood.

In the course of the catalytic ethylene oxidation, the following processes are assumed to occur simultaneously: (1) A part of ethylene is oxidized to ethylene oxide, and the other part to carbon dioxide and water; (2) a part of ethylene oxide which was produced by the partial oxidation of ethylene is further oxidized to carbon dioxide and water; (3) another part of ethylene oxide isomerizes to acetaldehyde; and (4) acetaldehyde is oxidized to carbon dioxide and water. The activities for these reactions and the selectivity for epoxidation of supported silver catalysts are assumed to depend not only on the catalytic properties of silver itself, but also on the

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properties of carriers. The present paper reports on the dependences of activities and selectivity of silver catalysts on some physicochemical properties of alumina as a function of thermal treatment.

EXPERIMENTAL METHODS

Aluminum isopropoxide, purified by distillation under reduced pressure, was hydrolyzed in water. The precipitated alumina hydrogel was dried at 115°C and heated at different temperatures between 300 and 1800°C. To each alumina thus obtained, 40% of its weight of Ag^I oxide, which was prepared from aqueous silver nitrate (10%) and potassium hydroxide (10%) solutions, repeatedly washed with distilled water and dried at 110°C, was mixed and triturated. The mixture was heated in a stream of hydrogen at 50–60°C for 30 hr to reduce Ag^I oxide to metallic silver. The unsupported silver catalyst was prepared by reducing the powdered Ag^I oxide in the same manner as the supported catalysts.

Argon (99.999%), ethylene (99.99%), hydrogen (99.9%), oxygen (99.8%), and helium (99.998% minimum purity) were used without further purification. Ethylene oxide was prepared from ethylene chlorohydrin (95%) and potassium hydroxide (reagent grade) and purified twice by distillation. Acetaldehyde (80%) was purified twice by distillation. Air was passed successively through a column of 20% sodium hydroxide solution and a silica gel column.

The catalytic activity for ethylene oxidation was measured using 0.875 g of each catalyst (the content of metallic silver was 0.237 g) in a Pyrex-glass reactor using a 3:97 ethylene:air flow. The gas flow rate was 1.5 liter hr^{-1} (STP), corresponding to W/F of 435 g-catal hr mol-$C_2H_4^{-1}$. The reactor of 29-mm inside diameter was heated in a stirred salt bath (KNO$_3$–NaNO$_3$–NaNO$_2$) and the catalyst bed

temperature was kept at 250 ± 0.5°C. The reaction products were analyzed by gas chromatography using a Porapak Q column at 100°C. The reaction was continued for 30 hr to get the steady activity and selectivity.

The activity and selectivity of supported catalysts for ethylene oxidation together with activities for the other three reactions described in the preceding section were measured in a pulse reactor. The reactor was a Pyrex-glass U-tube with 3-mm inside diameter, which was heated in a cylindrical electric furnace. The temperature of the furnace was controlled within ±0.5°C. 0.05 g of supported catalyst (the content of metallic silver was 0.0135 g) or 0.025 g of unsupported catalyst was placed between glass wool beds which were packed in the reactor tube. One end of the reactor was connected to a four-way tap, through which the reactants were pulsed. Through another four-way tap, which was connected between the above-mentioned tap and the other end of the reactor tube, a flow of hydrogen or oxygen was introduced to the reactor for the catalyst pretreatment.

Mixtures of each hydrocarbon and oxygen (for reactions 1, 2, and 4) or helium (for reaction 3) which contained 10% by volume of hydrocarbon were prepared and stored in 3-liter flasks. The reactor and the gas reservoirs were connected to a vacuum system. For the reactions 1, 2, and 4, the catalysts were pretreated at reaction temperatures with hydrogen 1 hr, then with oxygen 5 min, and finally purged with helium 5 min. For reaction 3, the catalysts were pretreated with oxygen 1 hr, then with hydrogen 1 hr, and finally purged with helium 5 min. After a sample was pulsed through the catalyst bed, the vent gas was passed directly to a gas chromatograph. A Porapak Q column at 100°C separated He, O$_2$, CO$_2$, C$_2$H$_4$, H$_2$O, CH$_3$CHO, and C$_2$H$_4$O.

The specific surface area was determined by argon BET at −196°C. The pore-size

Conditions of Thermal Treatment of Alumina and Some Physicochemical Properties of Catalysts

Catalyst	Treatment of alumina		Crystallography of alumina	Surface area of catalyst (m² g-catal⁻¹)	Surface area of Ag (m² g-catal⁻¹)	Average pore diameter (Å)
Cat 1	300°C	5 hr	gelatinous boehmite	171.0	4.53	43[a]
Cat 2	1000	3	γ modification	73.0		101[a]
Cat 3	1100	3	γ modification	43.7	2.22	128[a]
Cat 4	1150	3	α modification	7.42	1.03	88[a]
Cat 5	1200	10	α modification	3.05	0.74	1118[b]
Cat 6	1200	20	α modification	2.66	0.81	1174[b]
Cat 7	1300	3	α modification	2.93		1354[b]
Cat 8	1500	3	α modification	1.80	0.74	1364[b]
Cat 9	1800	1	α modification	0.79	0.60	13810[b]
Cat 10	1800	3	α modification	0.37	0.49	

[a] Calculated from the total volume of pores smaller than 500 Å in width. As Cat 1–Cat 4 had no micropores which are smaller than 20 Å in width, these correspond to average mesopore diameters.

[b] Calculated from the total volume of pores smaller than 3500 Å in width. Cat 5–Cat 9 had no pores smaller than 300 Å in width.

distribution was determined by measurement with an Aminco 60,000 psi mercury-intrusion porosimeter. The surface area of silver was determined by measurement of oxygen chemisorption at 170°C. The saturation uptake was calculated from the Langmuir isotherm in a pressure range between 10 and 100 Torr (1 Torr = 133.3 N m⁻²). Reduced silver powders, which were sintered at different temperatures to prepare a series of samples of different specific surface areas, were used to draw a calibration curve. A plot of specific surface area against saturation uptake was found to be linear.

RESULTS AND DISCUSSION

The conditions of thermal treatment of alumina and physicochemical properties of catalysts used are summarized in Table 1. The specific surface area and the pore volume of a series of catalysts decreased with the rise in the temperature of alumina pretreatment. Catalysts having larger surface areas than 10 m² g⁻¹ gave ca. 100%
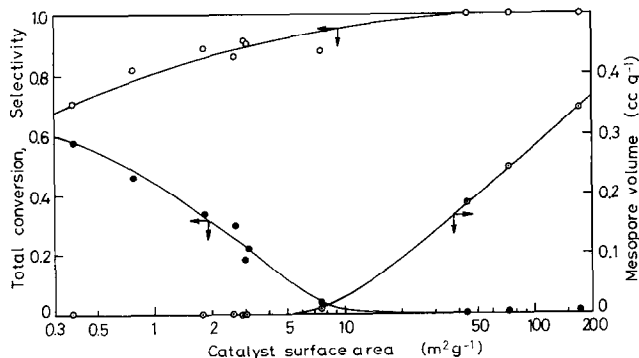

FIG. 1. Dependences of total conversion (activity), selectivity and mesopore volume on catalyst surface area. (○) total conversion, (●) selectivity, (◎) mesopore volume.

conversion and ca. 0% selectivity in ethylene oxidation at 250°C in the flow reactor. Ethylene oxide was produced only in the case of catalysts having specific surface areas smaller than 10 m² g⁻¹. Selectivity increased with decreasing specific surface area (Fig. 1). In Fig. 1 is also plotted the relationship between specific surface area and mesopore volume, which is defined as the total volume of pores smaller than 500 Å in width (15). All the catalysts used in the present experiments had no pores smaller than 30 Å. As the activity and selectivity were functions of surface area, and the latter depended on the thermal treatment of alumina, the activity and selectivity were also functions of the thermal treatment of alumina.

In order to get a deeper understanding about the effects of the thermal treatment of alumina on catalyst performance, kinetic measurements were carried out by the pulse technique for the four reactions over three kinds of supported catalysts which were different in the thermal treatment of carriers. In contrast to the case of the flow reactor operating at steady state, ethylene oxide and acetaldehyde were not detected in the effluent gas of the pulse reactor when catalysts supported on aluminas pretreated at temperatures below 1100°C were used, since ethylene oxide and acetaldehyde were strongly adsorbed by the carriers. Accordingly, in the pulse experiments, catalysts supported on aluminas pretreated at 1150 (Cat 4), 1200 (Cat 6), and 1800°C (Cat 10) were examined. The same measurements were also carried out over an unsupported catalyst for comparison.

A small section of a catalyst column containing w g of metallic silver in a given mass of catalyst is considered (16, 17). If it is assumed that the catalyst does not adsorb the specified reactant hydrocarbon and the reaction is pseudo-first-order with respect to its partial pressure, the reaction

rate is expressed as follows:

$$r = -dn/wdt = kp, \tag{1}$$

where n is the number of moles of the hydrocarbon in the gas phase of the catalyst section, p the partial pressure of the hydrocarbon, and k the specific rate. If the volume of the gas phase per gram of silver is v,

$$p = nRT/vw.$$

Hence, from Eq. (1)

$$-dn/wdt = knRT/vw$$

or

$$-dn/n = (kRT/v)dt. \tag{2}$$

Integration of Eq. (2) gives

$$\ln N_0/N = (kRT/v)t_c, \tag{3}$$

where N_0 and N are the number of moles of the hydrocarbon fed at the inlet and exhausted from the outlet of the reactor, respectively, and t_c is the residence time. If the volume flow rate of the carrier gas is F at catalyst temperature and pressure, and W the total mass of metallic silver in the catalyst,
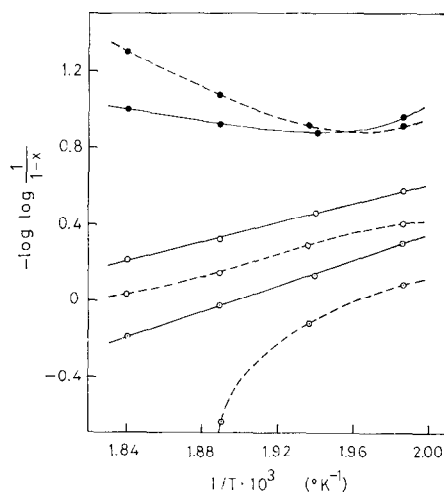
$$t_c = vW/F,$$

FIG. 2. The log log $1/(1 - x)$ versus $1/T$ plots for ethylene oxidation over Cat. 6. (– – –) reduced catalyst, (——) oxygenated catalyst; (●) ethylene oxide, (○) CO_2, (◉) total.

thus

$$\ln N_0/N = kRTW/F. \qquad (4)$$

As fractional conversion is defined as $x = (N_0 - N)/N_0$, Eq. (4) can be rewritten as

$$\ln 1/(1 - x) = kRTW/F \qquad (5)$$

or

$$k = (F/RTW) \ln 1/(1 - x). \qquad (6)$$

Since F is proportional to T at constant pressure, W is proportional to the mass of catalyst (constant), and R is the gas constant, F/RTW is also constant for a series of kinetic measurements with a given mass of catalyst. Consequently, if the pseudo-first-order kinetics holds, the specific reaction rates and the activation energy can be estimated from fractional conversions in a pulse reactor.

Ethylene oxidation was carried out over Cat 6 which was pretreated in a flow of hydrogen at reaction temperatures. The results are shown in Fig. 2 (broken lines). Neither epoxidation nor complete oxidation obeyed pseudo-first-order kinetics with respect to ethylene. When the catalyst was pretreated in a flow of oxygen at reaction temperatures, the complete oxida-
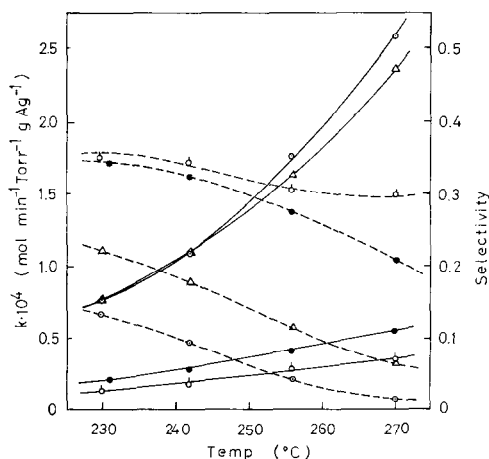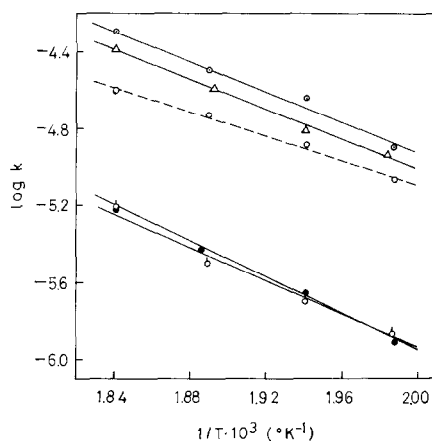

FIG. 4. Arrhenius plots for ethylene oxide isomerization. (○) Cat 4, (△) Cat 6, (⦶) Cat 10, (●) unsupported, (◯) alumina support of Cat 4.

tion and the total consumption of ethylene obeyed quite closely pseudo-first-order kinetics (solid lines in Fig. 2). But epoxidation did not obey pseudo-first-order kinetics even over the oxygenated catalyst. Over any other oxygenated catalyst pseudo-first-order kinetics were found to hold both for the complete oxidation and for the total consumption of ethylene.

Similarly, the oxidation of ethylene oxide and acetaldehyde over oxygenated catalysts followed pseudo-first-order rate law with respect to ethylene oxide and acetaldehyde, respectively. Isomerization of ethylene oxide, when it was carried out over reduced catalysts, was also of pseudo-first-order with respect to ethylene oxide.

Kinetic measurements were carried out over four different catalysts at several temperatures between 230 and 270°C, and the relationships between specific rate (activity) and temperature were estimated. It is seen from Fig. 3, which represents the relationships of activity and selectivity versus temperature for ethylene oxidation, that a silver catalyst supported on alumina pretreated at a lower temperature is more active than the one supported on alumina pretreated at a higher temperature, whereas the reverse holds for selectivity. The

FIG. 3. Temperature dependences of specific rates and selectivity for ethylene oxidation. (——) k, (– – –) selectivity; (○) Cat 4, (△) Cat 6, (⦶) Cat 10, (●) unsupported.

TABLE 2

Activation Energies for Four Reactions over Three Kinds of Alumina-Supported
and Unsupported Ag Catalysts

Catalyst	Activation energy, E (kcal mol^{-1})[a] for			
	Total consumption of ethylene	Ethylene oxide oxidation	Ethylene oxide isomerization	Acetaldehyde oxidation
Cat 4	16.7	17.3	18.2	25.2
Cat 6	15.1	11.6	17.9	32.3
Cat 10	11.1	9.6	20.1	14.6
Unsupported	13.6	17.2	21.4	17.7

[a] 1 kcal = 4.185 × 10^3 J.

activation energies of the total consumption of ethylene were calculated from the Arrhenius plots and are tabulated in Table 2. In Table 2, the activation energies of the other three reactions are also tabulated, estimated from the corresponding Arrhenius plots, of which only those for ethylene oxide to acetaldehyde isomerization are shown in Fig. 4.

The ratios of activities of each catalyst for different reactions are tabulated in Table 3. From the results in Table 3, the followings can be deduced:

1. In a temperature range of about 230 to 270°C, $k_2/(k_1)_{CO_2}$ was smaller than unity for any catalyst, suggesting that a path other than the consecutive oxidation of ethylene via ethylene oxide cannot be excluded in the complete oxidation of ethylene. This direct path is more preferred over Cat 10 and unsupported catalyst than over Cat 4 and Cat 6. We suggest that the intermediate occurring in this direct path may be an adsorbed radical formed from an ethylene molecule and oxygen adatom (18, 19).

2. The fact that the larger values of $k_2/(k_1)_{CO_2}$ were estimated for Cat 4 and Cat 6 compared with Cat 10, suggests that the combustion of ethylene oxide including the combustion of acetaldehyde formed by the isomerization of ethylene oxide predominates in the former catalysts. This can be ascribed in one part to the ease for isomerization of ethylene oxide to acetaldehyde over the carriers of the former catalysts. The broken line in Fig. 4, which represents the Arrhenius plot for ethylene

TABLE 3

Ratios of Specific Rates for Cat 4, Cat 6, Cat 10, and Unsupported Catalyst[a]

	$k_2/(k_1)_{CO_2}$[b]				k_3/k_2[b]				k_4/k_3[b]			
	230[c]	242	256	270	230	242	256	270	230	242	256	270
Cat 4	0.64	0.66	0.68	0.70	0.41	0.41	0.42	0.43	2.89	3.40	4.13	4.83
Cat 6	0.61	0.62	0.62	0.62	0.43	0.50	0.61	0.69	1.09	1.52	2.15	3.14
Cat 10	0.21	0.20	0.19	0.19	0.68	0.87	1.18	1.47	2.41	2.12	1.77	1.61
Unsupported	0.17	0.19	0.23	0.26	0.73	0.79	0.88	0.97	1.31	1.21	1.10	1.01

[a] The specific surface area of unsupported catalyst was 0.50 m^2 g^{-1}.

[b] $(k_1)_{CO_2}$, k_2, k_3, and k_4 are the specific rates (mol min^{-1} Torr^{-1} g-Ag^{-1}) for complete oxidation of ethylene, oxidation of ethylene oxide, isomerization of ethylene oxide, and oxidation of acetaldehyde, respectively.

[c] Temperature (°C).

oxide isomerization over alumina pretreated at 1150°C, shows that ethylene oxide isomerizes not only over silver alone but also over alumina. But the fact that k_3/k_2 was 0.4 to 0.7 even for these catalysts having high activity for isomerization suggests that there may be another route for the oxidation of ethylene oxide, as we suggested elsewhere (18, 19).

3. As described above, a part of ethylene oxide is assumed to be oxidized via isomerization to acetaldehyde. The ratio k_3/k_2, which can be regarded as a measure of the participation of isomerization in ethylene oxide oxidation, was larger for the unsupported catalyst and Cat 10 than for Cat 4 and Cat 6. It must be reminded, however, that ethylene oxide isomerization was investigated over reduced surfaces in a helium atmosphere, whereas the oxidation of ethylene and ethylene oxide were investigated over oxygenated surfaces in oxygen atmospheres. In the presence of oxygen, a larger fraction of the sites on silver would be occupied by adsorbed oxygen species, so that the actual rate of isomerization must be lower than the rate in the helium atmosphere.

4. Over any catalyst examined, acetaldehyde was oxidized to carbon dioxide and water at a rate larger than the rate of its formation, in agreement with the fact that only a trace amount of acetaldehyde is usually detected in the reaction mixture at ordinary conditions of ethylene oxidation.

It has become apparent in the present experiments that the catalytic activities of silver were higher when it was supported on aluminas pretreated at lower temperatures. It has been shown in Table 1 that silver had larger specific surface areas when it was supported on aluminas pretreated at lower temperatures, e.g., the specific surface area of silver in Cat 1 was 4, 6, and 9 times that of Cat 4, Cat 6, and Cat 10, respectively. Consequently, higher activities of silver catalysts supported on aluminas

pretreated at lower temperatures may be attributed to the larger surface area of metallic silver.

As the catalysts used in the present experiments were prepared in a relatively high silver concentration ($Ag:Al_2O_3 = 0.3723:1$), the percentage exposed, or metal dispersion, calculated on the basis of 1.31×10^{19} Ag atoms/m^2 (20), was only 3.92% even in Cat 1. The average metal crystallite size was 350 Å. The percentage exposed of Cat 4, Cat 6, and Cat 10 were 0.89, 0.70, and 0.42%, respectively. The average crystallite sizes were 1500, 1900, and 3200 Å, respectively. Accordingly, the crystallite size effect should be of no significance in the catalyses by such catalysts with large metal crystallites.

As shown in Fig. 4, the ethylene oxide isomerization was catalyzed not only by silver but also by alumina itself. A possible mechanism is that the oxide ions on alumina surfaces abstract hydrogen ions of ethylene oxide molecules to form carbanion intermediates, thus forming acetaldehyde molecules on desorption. As described above, the catalysts which were poor in selectivity had relatively narrow pores (ca. 40–130 Å in average diameter) compared to the larger metal crystallite size of silver (ca. 350–1500 Å), so that a limited number of smaller metal particles may be found in such narrow pores, and hence, both ethylene and ethylene oxide which was formed from ethylene can rarely be oxidized in the catalyst pores. The only reaction accelerated in the pores should be the isomerization of ethylene oxide on the internal surface sites of alumina to acetaldehyde, which can easily be oxidized to carbon dioxide and water, thus decreasing the selectivity for epoxidation.

REFERENCES

1. Margolis, L. Ya., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 14, p. 429. Academic Press, New York, 1963.

2. Voge, H. H., and Adams, C. R., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 17, p. 151. Academic Press, New York, 1967.

3. Sachtler, W. M. H., *in* "Catalysis Reviews" (H. Heinemann, Ed.), Vol. 4, p. 27. Dekker, New York, 1971.

4. Kilty, P. A., and Sachtler, W. M. H., *in* "Catalysis Reviews" (H. Heinemann and J. J. Carberry, Eds.), Vol. 10, p. 1. Dekker, New York, 1974.

5. Hacknall, D. J., "Selective Oxidation of Hydrocarbons," Chap. 2. Academic Press, New York, 1974.

6. Harriott, P., *J. Catal.* 21, 56 (1971).

7. Klugherz, P. D., and Harriott, P., *AIChE J.* 17, 856 (1971).

8. Presland, A. E. B., Price, G. L., and Trimm, D. L., *J. Catal.* 26, 313 (1972).

9. Mikami, J., Satoh, S., and Kobayashi, H., *J. Catal.* 18, 265 (1970).

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

11. Riassian, M., Trimm, D. L., and Williams, P. M., *J. Chem. Soc., Faraday Trans. I* 72, 925 (1976).

12. Riassian, M., Trimm, D. L., and Williams, P. M., *J. Catal.* 46, 82 (1977).

13. Kenson, R. E., and Lapkin, M., *J. Phys. Chem.* 74, 1493 (1970).

14. Inui, T., and Tanabe, Y., *J. Catal.* 52, 375 (1978).

15. Burwell, R. L., *in* "Advances in Catalysis" (D. D. Eley, H. Pines and P. B. Weisz, Eds.), Vol. 26, p. 351. Academic Press, New York, 1977.

16. Bassett, D. W., and Habgood, H. W., *J. Phys. Chem.* 64, 769 (1960).

17. Schwab, G. M., and Watson, A. M., *J. Catal.* 4, 570 (1965).

18. Ayame, A., Kanoh, H., Kanazuka, T., and Baba, H., *Bull. Japan Petrol. Inst.* 15, 150 (1973).

19. Ayame, A., Harano, Y., Imoto, T., and Kanoh, H., *Nippon Kagaku Kaishi* 1974, 1189.

20. Scholten, J. J. F., Konvalinka, J. A., and Beekman, F. W., *J. Catal.* 28, 209 (1973).