Study on Nickel Oxide-Silica-Alumina Catalyst for Ethylene Polymerization. I. Catalyst Activity for Ethylene Polymerization and Selectivity in the Formation of Butene-Isomers

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A number of papers[1-7] have dealt with the catalytic polymerization of olefins over nickel oxide-silica-alumina catalysts, but the catalyst selectivity from the view point of isomer formation has not been described at all. In this paper both the catalyst activity for ethylene polymerization and the selectivity in butene-isomer formation are presented on a series of catalysts with a progressively increasing aluminum content and with a fixed amount of nickel oxide.

Experimental

Catalyst. — Coprecipitated catalysts comprising silica, alumina, and nickel oxide were used in this study. The catalysts contained a fixed amount of nickel oxide, 0.03[8] in terms of the atom ratio Ni/(Ni+Al+Si), while the aluminum content, given by the atom ratio Al/(Al+Si), varied from 0 to 0.5. The precipitation was made by vigorously mixing a sodium silicate solution containing 5 wt. % of silica with another solution of nitrates of aluminum and nickel. Caution was exercised to keep the pH of the resulting hydrogel solution within the small range of 8±0.5. This was achieved either by adding, prior to the mixing, an amount of caustic soda to the sodium silicate solution or an amount of nitric acid to the solution of nitrates, according to whether a greater amount of silica or of alumina was to be contained in the finished catalyst. Moreover, the product concentration[9] was maintained at 0.03 g./cc. The solution was then subjected to a treatment similar to that of Holm et al.[7]: after filtration on a Buchner funnel, the hydrogel was broken up, placed in evaporating dishes under heat lamps, and allowed to dry in this manner for a day, after which it was dried for several hours in an oven at 110°C. The dried catalyst was treated with successive portions of a 5% hot ammonium nitrate solution and then with hot water in order to remove the sodium. After drying, it was heated at 350°C for 4 hr. The compositions of the catalysts prepared in this way (hereafter designated as catalysts A) are shown in Table I.

Besides the catalysts A, two other catalysts, designated as calalyst AI-4 and AII-4, of the same composition as catalyst A-4 but prepared by different methods, were used. In the preparation of

TABLE I. CATALYSTS COMPOSITION

Catalyst[a]	A-1	A-2	A-3	A-4	A-5	A-6
Al/(Al+Si) (atom)	0	0.03	0.05	0.11	0.30	0.50

a) Throughout all the catalysts the nickel oxide content is kept at a fixed Ni/(Ni+Al+Si) ratio of 0.03.

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[1] Y. Konaka, *J. Soc. Chem. Ind., Japan* (*Kôgyô Kwagaku Zassi*), **39**, 906 (1936).

[2] K. Morikawa, ibid., **41**, 694 (1938).

[3] M. Koizumi et al., *J. Chem. Soc. Japan* (*Nippon Kwagaku Kwaisi*), **64**, 257, 263, 794 (1943).

[4] T. Shiba and A. Ozaki, ibid., **74**, 295 (1953); A. Ozaki, ibid., **75**, 1, 4, 6 (1954); **77**, 888 (1956); *Catalyst* (*Shokubai*), **14**, 65 (1957).

[5] S. Kawaguchi and K. Kihara, ibid., **75**, 15 (1954); S. Kawaguchi, *J. Phys. Chem.*, **61**, 394 (1957).

[6] J. P. Hogan, R. L. Banks et al., *Ind. End. Chem.*, **47**, 752 (1955).

[7] V. C. F. Holm, G. C. Bailey and A. Clark, ibid., **49**, 250 (1957).

[8] According to the statement by Holm et al.[7], the catalyst activity for ethylene polymerization was highest in the catalyst with this nickel content.

[9] The product concentration was defined by g. $NiO+Al_2O_3+SiO_2$ contained in 1 cc. of the hydrogel (refer to 10).

[10] C. J. Plank and L. C. Drake, *J. Colloid Sci.*, **2**, 389 (1947).

catalyst AI-4, the hydrogel was washed before the drying, while catalyst AII-4 was a sample of aerogel prepared by means of the method of Kistler[11] from the washed hydrogel of catalyst A-4.

The catalyst samples were crushed into granules 1~2 mm. in size and heated at 500°C for 15 hr. in a stream of air, atter which they ware evacuated at the same temperature for 3 hr. under a reduced pressure of 1×10^{-4} mmHg and were used for the polymerization.

Ethylene.—Ethylene was produced by the dehydration of ethanol over an alumina catalyst. It was purified by successive passages through 30% caustic soda solution, 87% sulfuric acid, and finally a trap placed in a bath of dry ice and methanol. After the purification, it was frozen in a trap cooled with a liquid nitrogen bath. The solid ethylene was distilled in vacuo into another trap by replacting the liquid nitrogen bath with a dry ice bath. The distillation was repeated four times to get rid of the last traces of inert gas, and then the gaseous ethylene was introduced into a gas reservoir.

Catalyst Activity.—The apparatus was a circulatory flow system with a total volume of 2.1 l. and a catalyst cell containing 5 cc. of the catalyst. The flow rate throughout was 70 l./hr. at N. T. P., and the initial ethylene pressure was 350 mmHg. Immediately after the catalyst cell there was placed a U-trap which had been cooled in a bath of dry ice and methanol. Since butene at −78°C retains a vapor pressure of 10 mmHg, all the butene produced was circulated throughout the system until the butene formation had proceeded so far as to attain the pressure of 10 mmHg (an earlier stage of the polymerization) ; as soon as butene attained this pressure, a part of the circulating butene began to condense in the trap in an amount corresponding to the amount produced (a subsequent stage). The pressure decrease in the system within time of polymerization was measured by means of a mercury manometer attached to the system ; the decrease at the subsequent stage gave a measure of the catalyst activity.

After the polymerization had proceeded to such an extent that the total pressure of the system was as low as 0.57 times the initial pressure, the catalyst cell was removed by sealing off the glass tube on both sides of the cell. Part of the condensation product in the trap was then evaporated into the system by replacing the dry ice bath with an ice bath. After the evaporation the gaseous product comprised ethylene and butene, while the liquid product comprised hydrocarbons higher than hexene. The liquid product remaining in the trap was weighed. The experiments made in this manner will be denoted as in series A.

On the other hand, another series of experiments (series B) was made with a few modifications in the experimental procedure, using the same apparatus with a smaller catalyst bed of 1 cc. The modifications were that the trap was cooled with ice and that small portions of the exit gas from the cell were withdrawn at frequent intervals. The change in the composition of butene isomers with time was followed by a gas chromatographic analysis of the portions at 32°C by the use of a 5 m. column of benzyl cyanide plus silver nitrate on cellite 408[12]. In this procedure all the butene produced was circulated throughout the system, together with reactant ethylene, while a major part of the product hydrocarbons higher than hexene were condensed in the trap.

Specific Surface Area Pore Volume, Pore Size Distribution and Density.— The specific surface area was obtained by the aid of the BET method applied to the nitrogen adsorption isotherm determined at −196°C. The amount of nitrogen adsorbed at the relative pressure of 0.967 gave the the pore volume, including pores smaller than 300 Å in radius. Furthermore, the desorption isotherm was determined on three kinds of catalysts, A-, AI- and AII-4. On the basis of the isotherm, the pore size distribution was calculated by the aid of Barrett's method[13]. The catalyst density was measured by the helium displacement method[14] at 20°C.

Experimental Results

Catalyst Activity for Ethylene Polymerization. —The data on the pressure decrease in the experiments of series A are found to follow the following rate equation proposed for the ethylene polymerization by Koizumi et al.[3], provided that the reaction does not proceed too far:

$$-\mathrm{d}p/\mathrm{d}t=kP/(1+b(P_0-P)) \qquad (1)$$

or upon integration,

$$(P_0-P)/t=(P_0+1/b)\ln P_0/P-k/b \qquad (2)$$

In the equations, P_0 is the initial pressure of ethylene, P is the observed ethylene pressure at time t, k is the rate constant, and b is a

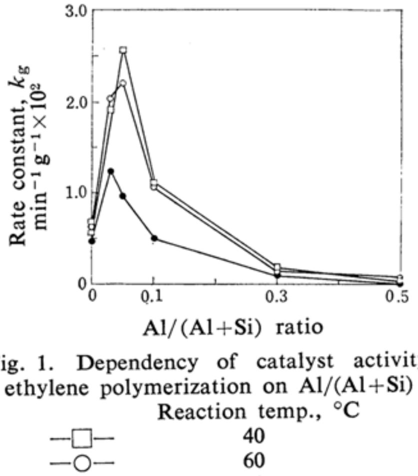

Fig. 1. Dependency of catalyst activity for ethylene polymerization on Al/(Al+Si) ratio.

Reaction temp., °C
—□— 40
—○— 60
—●— 100

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[11] S. S. Kistler, *J. Phys. Chem.*, **36**, 52 (1932).

[12] F. van de Craats, *Anal. Chim. Acta*, **14**, 136 (1956).

[13] E. P. Barrett, L. G. Joyner and P. P. Halenda, *J. Am. Chem. Soc.*, **73**, 373 (1951).

[14] F. O. Wiig and A. J. Juhola, ibid., **71**, 561 (1949).

TABLE II. CATALYST ACTIVITY, SPECIFIC SURFACE AREA, AND OTHER MATTERS ON CATALYSTS A-, AI- AND AII-5

Catalyst	k_g 40°C	k_g 100°C	F_b 40°C	F_b 100°C	Specific surface area m²/g.	Pore volume cc./g.	Average pore radius Å
	$\times 10^2$ min.$^{-1}$ g.$^{-1}$						
A-4	1.24	0·53	0.72	0.84	278	0.344	24.7
AI-4	1.68	0.37	0.59	0.73	403	0.252	12.5
AII-4	1.41	0.43	0.69	0.79	576	1.500	52.0

constant. In this paper, k_g, which gives the rate constant per gram of the catalyst, is used as a comparative measure of the catalyst activity. It decreases with the increasing temperature (refer to Fig. 1), but the Arrhenius plot of the k_g is not linear.

In Fig. 1, the k_g is plotted against the Al/(Al+Si) ratio, and a maximum is produced in the narrow range from 0.03 to 0.05. On the other hand, the values of k_g for catalysts A-, AI- and AII-4 are listed in Table II, which includes also the data on the specific surface area and the other matters. The k_gs have been found to be almost the same among the three catalysts.

In the ethylene polymerization, a major part of the broduct is usually butene, while a part of the product consists of the trimer and the higher polymers. The fraction of the amount of ethylene converted to butene in the total polymerization product (the fraction is designated as F_b hereafter) is given approximately by $2(P_b+10)/(P_0-P+10)$, where P_b is the pressure rise caused by the evaporation of that butene which has been condensed in the trap during the polymerization, and 10 (mmHg) stands for the vapor pressure of the butene in the circulatory system. The values of F_b at the different reaction temperatures of 40, 60 and 100°C are plotted in Fig. 2 as a function of the Al/(Al+Si) ratio. Comparison of the figure with Fig. 1 discloses that F_b is lowest for the catalyst of the highest k_g.

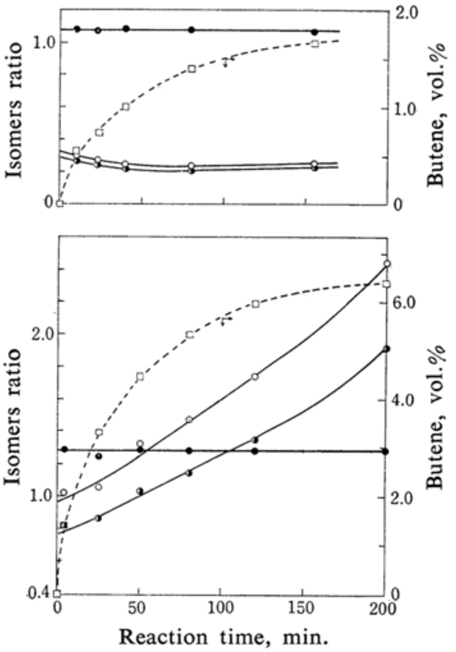

Fig. 3. Change in butene-isomers ratio with progress of polymerization.
Above, results on catalyst A-1. Below, results on catalyst A-3 at 40°C.

Isomers ratio
—◑— *cis-*/1-butene
—○— *trans-*/1-butene
—●— *trans-*/*cis-*
···□··· Amount of butene (vol.%) in circulating gas.

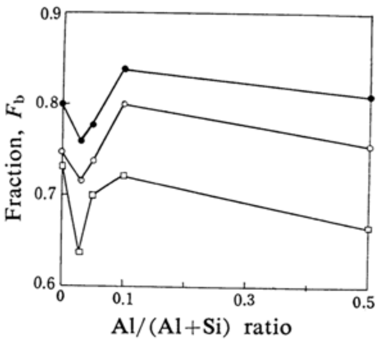

Fig. 2. Dependency of ethylene fraction converted to butene in total ethylene polymerized on Al/(Al+Si) ratio.

Reaction temp., °C
—□— 40
—○— 60
—●— 100

Catalyst Performance in the Selectivity of Isomer Formation.—Additional data from the experiments of series B give information on the distribution of butene isomers but not any on the rates of polymerization. The data are exemplified in Fig. 3, showing the reaction at 40°C on catalyst A-1 with no aluminum and on A-3 with some aluminum[15]. As regards catalyst A-3, both the ratios of *cis-* and *trans-*2-butene to 1-butene tend to increase with the duration of reaction time. This is the case with all the catalysts with aluminum,

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[15] There has been found hardly any evidence of the presence of isobutene.

more or less pronounced according to the aluminum contents, but it is not the case with the catalysts with no aluminum. Emphasis should be laid on the fact that throughout all the catalysts the ratio between two 2-butene isomers is maintained at values approximate to 1 regardless of the amount of butene formed[16]. Anyhow, the isomer composition at the beginning of the reaction is far removed from the thermodynamical equilibrium composition[19].

Specific Surface Area, Volume and Size of Pore and Density.—Figure 4 shows the specific surface area (S) and the pore volume (V) as respective functions of the Al/(Al+Si) ratio. The S shows a maximum at the ratio of 0.05; as the ratio increases further, it gradually decreases to about a half of the S of catalyst A–1 with no aluminum. The V is largest at catalyst A–1 and decreases, at first rapidly and then more slowly, with the increasing ratio. The average pore radius calculated from the values of S and V is plotted against the ratio and shows a minimum at the ratio corresponding to the maximum of S.

The pore size distribution curves are given in Fig. 5 for catalysts A–, AI– and AII–4.

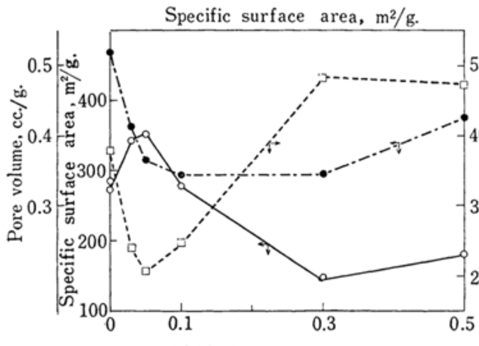

Fig. 4. Specific surface area, pore volume, and average pore radius as a function of Al/(Al+Si) ratio.
—○— Specific surface area
···●··· Pore volume
···□··· Average pore radius

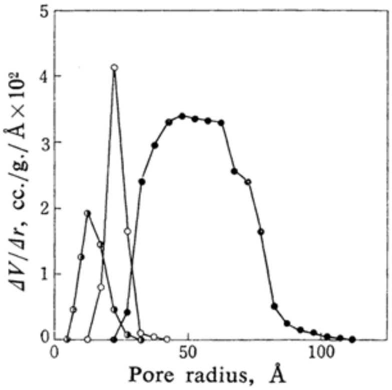

Fig. 5. Pore size distribution curves.
—○— Catalyst A–4
—◑— Catalyst AI–4
—●— Catalyst AII–4

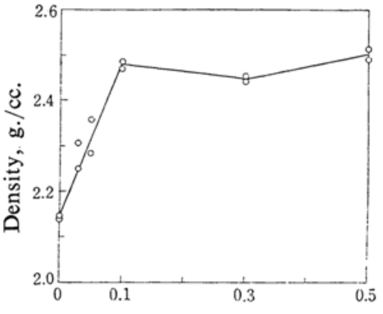

Fig. 6. Density as function of Al/(Al+Si) ratio.

The distribution curves differ markedly from each other, even though the catalysts have the same composition. The pore radii corresponding to the maximum in the curves ($\Delta V/\Delta r_{\max}$) are 22.5, 12.5 and 47.5 Å for catalysts A–, AI– and AII–4 respectively.

Figure 6 shows the plot of the density vs. the Al/(Al+Si) ratio. The density at first rises rapidly with the increasing ratio, and it remains nearly constant in the range above 0.1.

Discussion

Specific Activity per Unit Surface Area.—As regards catalysts A–, AI– and AII–4, comparison of the pore size distribution curves (Fig. 5) or of the pore radii at $\Delta V/\Delta r_{\max}$ with the k_g (Table II) reveals no direct relationship existing between them. Moreover, catalyst A–3 with the smallest pore radius, gives the highest k_g (compare Fig. 1 with Fig. 4). These facts may lead to the reasonable assumption that the polymerization takes place uniformly along the pore well. Under this assumption, the specific catalyst activity per unit surface area (hereafter denoted by k_s) can be obtained

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[16] In this connection, Foster et al.[17] stated that, in the isomerization of 1-butene to 2-butene isomers on a clay catalyst, the ratio of trans- to cis-isomer was kept at values approximate to 1 independent of conversion, whereas Lucchesi et al.[18] pointed out that in the isomerization on a silica-alumina catalyst the ratio increased.

[17] N. F. Foster and R. J. Cvetanovic, *J. Am. Chem. Soc.*, **82**, 4274 (1960).

[18] P. J. Lucchesi, D. L. Baeder and J. P. Longwell, ibid., **81**, 3235 (1959).

[19] The thermodynamical equilibrium composition of butene isomers at 40°C has been calculated on the basis of the physical constants given by Kilpatrick et al.[20], as follows: 1-butene, 4.2%: *cis*-2-butene, 13.3%: *trans*-2-butene, 82.5%.

[20] J. E. Kilpatrick, E. J. Prosen, K. S. Pitzer and F. D. Rossini, *J. Research Nat. Bur. Standards*, **36**, 559 (1946).

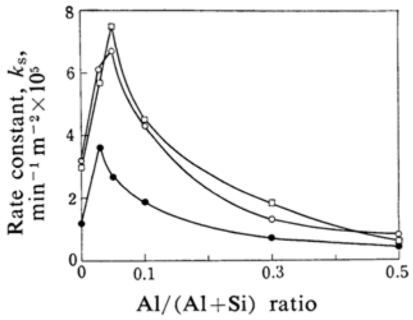

Fig. 7. Rate constant of ethylene polymerization per unit surface surface area given as function of Al/(Al+Si) ratio.

Reaction temp., °C
—□— 40
—○— 60
—●— 100

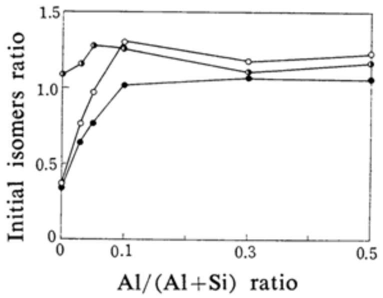

Fig. 8. Dependency of initial ratio of isomers on Al/(Al+Si) ratio.

Initial isomers ratio
—●— *cis*-/1-butene
—○— *trans*-/1-butene
—◑— *trans*-/*cis*-2-butene

by dividing k_g by S, and it is shown in Fig. 7 as a function of the Al/(Al+Si) ratio. The figure shows a maximum of the k_s at the Al/(Al+Si) ratio where the maxima of k_g and S appeared. The high k_g is therefore to be attributed to the high k_s as well as to the large S.

The structures of the catalyst responsible for the high k_s will be described in the next paper[21].

Selectivity in the Formation of Butene-isomers.—The tendency in the ratio of *cis*- or *trans*-2-butene to 1-butene to increase with the reaction time may be due to the increasing amount of 2-butene isomers converted from the 1-butene which has been once present in the gas phase as the desorbed product. Nevertheless, it by no means follows that all the 2-butene isomers are produced by way of the desorbed 1-butene. In this connection, Fig. 3 reveals that the ratio of cis- or trans-isomer to 1-butene is not reduced to zero even at a very short period of the reaction.

Applying the method proposed by Schneider et al.[22] to their study of the catalytic isomerization of *n*-butenes, Foster et al. plotted the ratio of the product isomers (for instance, the ratio of cis- to trans-isomer) against the corresponding per cent conversion of the reactant isomer (for instance, 1-butene), and obtained the ratio between the product isomers at zero conversion by extrapolation of the plot. This procedure is now followed; the extrapolation to $t=0$ of the plots in Fig. 3 results in the initial ratio at zero extent of the polymerization. The initial ratios thus obtained are shown in Fig. 8 as a function of the Al/(Al+Si) ratio. Both the initial ratios of cis- and trans-isomers to 1-butene increase with the increasing aluminum content up to the highest value at the Al/(Al+Si) ratio of 0.1, beyond which they remain almost constant. In contrast, the initial ratio between the two 2-butene isomers remains at about 1 throughout the aluminum content of the present study, except for a slight maximum at the content corresponding to the maximum of the k_g.

The initial isomers ratio thus obtained gives the relative rates for the formation of the two isomers. There are, then, the following relations:

$$r_{01}/r_{02}=[\text{cis-}]/[\text{1-butene}] \quad \text{at } t=0$$

$$r_{03}/r_{01}=[\text{trans-}]/[\text{1-butene}] \quad \text{at } t=0$$

$$\text{and } r_{03}/r_{02}=[\text{trans-}]/[\text{cis-}] \quad \text{at } t=0 \qquad (3)$$

where r_0 is the initial rate of formation, and the subscripts 1, 2 and 3 stand for 1-butene, *cis*- and *trans*-2-butene respectively. On the other hand, the initial rate of ethylene polymerization (r_0) is given by

$$r_0=r_{01}+r_{02}+r_{03} \qquad (4)^{23)}$$

Eq. 3 being combined with Eq. 4, r_{01}, r_{02} and r_{03} can be evaluated, if r_0 is known. In this connection, the initial polymerization rate based on the unit surface area can be calculated with the aid of Eq. 1, in which k_s, in place of k_g, is taken into account[24]. Figure 9 shows the calculated r_{01}, r_{02} and r_{03} based on the unit surface area at a fixed pressure (345 mmHg) and at a fixed temperature (40°C) as a function of the Al/(Al+Si) ratio. The figure reveals that, as the aluminum content is varied, the

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21) At present it can at the most be pointed out that the density of the catalyst granule is not directly correlated to the specific activity, as can be seen by a comparison of Fig. 6 with Fig. 7.

22) V. Schneider and P. K. Frolich, *Ind. End. Chem.*, **23**, 1405 (1931).

23) At the beginning of polymerization, all the ethylene polymerized may be assumed to produce butene[6].

24) Since k_g was evaluated from the data at the subsequent stage of the reaction, the calculation is rather uncertain, but the initial rates obtained may be adequate for the comparative discussion in this study.

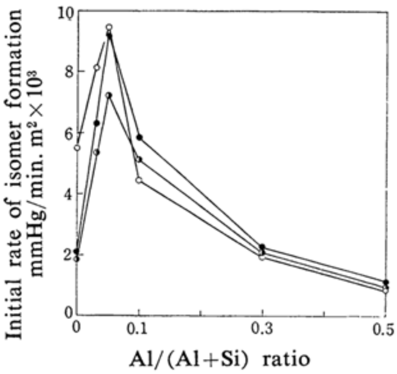
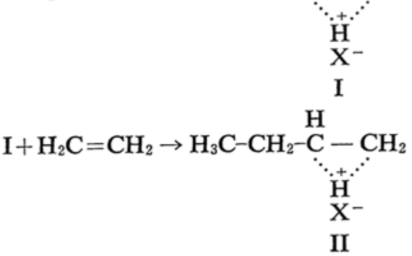


Fig. 9. Dependency of initial rates of isomer formation on Al/(Al+Si) ratio.
—○— Initial rate of 1-butene formation
—◑— Initial rate of *cis*-2-butene formation
—●— Initial rate of *trans*-2-butene formation

initial rates r_{01}, r_{02} and r_{03} change in approximately the same manner as r_0, rising with the increasing aluminum content until a maximum is attained at the Al/(Al+Si) ratio of 0.05 and decreasing with the further-increasing content. However, a closer examination of Figs. 8 and 9 reveals that not all the rates change in exactly the same manner; on the catalyst with the highest r_0, the cis- and trans-isomers are formed about four times as fast as on the catalyst with no aluminum, whereas 1-butene is formed only 1.7 times as fast as the rate on the catalyst with no aluminum.

Effects of Aluminum Addition on Catalytic Activity for Polymerization and Selectivity in Isomer-formation.—All the mechanisms which have been proposed for the hydrocarbon reactions on the acid catalysts, such as the carbonium ion mechanism, the hydrogen transfer mechanism, and the others[25], as well as the mechanism proposed by Horiuchi[26], predict the formation of a chemisorbed species of 1-butene on the catalysts when the mechanisms are applied to the dimerization of ethylene. For instance, the carbonium ion mechanism modified by Lucchesi et al.[18] indicates the following scheme[27];



$$\mathrm{H_2C{=}CH_2 + H^+X^- \rightarrow \underset{\substack{\cdot\cdot\overset{+}{H}\cdot\cdot \\ X^-}}{H_2C - CH_2}}$$

I

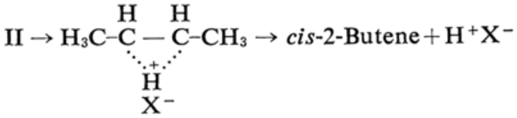
$$\mathrm{I + H_2C{=}CH_2 \rightarrow H_3C\text{-}CH_2\text{-}\underset{\substack{\cdot\cdot\overset{+}{H}\cdot\cdot \\ X^-}}{\overset{H}{C} - CH_2}} \qquad (5)$$

II

where H^+X^- represents the acid site. If with no rearrangement, the chemisorbed species II leads to 1-butene as the desorbed product,

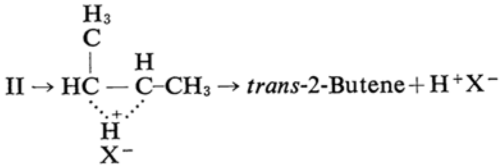
$$\mathrm{II \rightarrow 1\text{-}Butene + H^+X^-} \qquad (6)$$

while, with rearrangement, it leads to either one of the 2-butene isomers by way of III or IV respectively.



$$\mathrm{II \rightarrow H_3C\text{-}\underset{\substack{\cdot\cdot\overset{+}{H}\cdot\cdot \\ X^-}}{\overset{H}{C} - \overset{H}{C}}\text{-}CH_3 \rightarrow \mathit{cis}\text{-}2\text{-}Butene + H^+X^-}$$

III (7)



$$\mathrm{II \rightarrow \underset{\substack{\cdot\cdot\overset{+}{H}\cdot\cdot \\ X^-}}{H\overset{\overset{H_3}{C}}{\underset{|}{C}} - \overset{H}{C}}\text{-}CH_3 \rightarrow \mathit{trans}\text{-}2\text{-}Butene + H^+X^-}$$

IV (8)

The scheme represented by 5—6 can explain the simultaneous formation of the three isomers as the initial dimerization products and can explain also the constant ratio of about 1 between the two 2-butene isomers regardless of the duration of the reaction time, provided that rearrangement 7 can proceed at a rate equal to that of rearrangement 8 and provided also that the direct rearrangement between III and IV can be excluded at the low temperature.

However, the above scheme can not explain the present experimental facts on the catalyst selectivity related to the aluminum content, as is shown below. According to the above scheme, both the polymerization and the isomerization are to take place on the same site, H^+X^-. The increase in polymerization activity, which comes from the increase in the surface concentration of polymerization sites, can not, therefore, be expected to change the selectivity in initial butene isomer formation, whereas the experimental facts demonstrate that both the polymerization activity and the selectivity are changed by the addition of aluminum, and, moreover, that the changes take place in different manners (cf. Figs. 1 and 8).

The fact thus seems to be too complicated to be explained in terms of the above scheme, in which only one kind of acid site was considered. In this respect, we should like to suggest that, in addition to H^+X^-, another kind of acid site, H^+Y^-, which could serve as the site for the rearrangements II → III and II → IV, might be present on the catalyst and

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25) Cf. L. Schmering and V. N. Ipatieff, "Advances in Catalysis and Related Subjects", II, Academic Press Inc., New York (1949), p. 21.

26) J. Horiuchi, *Catalyst* (*Shokubai*), **1**, 67 (1948).

27) For convenience, the mechanism is discussed from this point of view.

that H^+X^- and H^+Y^- could be separately increased in number by the addition of aluminum. The experimental facts capable of demonstrating the presence of the two kinds of acid sites will be described in the next paper.

Summary

The activity for the ethylene polymerization per unit mass of the catalyst has been found highest for the catalyst with the Al/(Al+Si) ratio of 0.05. The high activity is ascribed to the high specific activity per unit surface area as well as to the large specific surface area of the catalyst. The pore sizes scarcely produce any effect on the catalyst activity.

Even at a very short reaction time, the three isomers of *n*-butene are produced simultaneously. The ratios both of *cis*- and of *trans*-2-butene to 1-butene increase with the reaction time more or less according to the aluminum content, whereas for all the catalysts the ratio between the two 2-butene isomers is kept at values approximate to 1. At the zero extent of reaction, the former ratios, given as a function of the aluminum content, show an increase with the progressively increasing content up to the highest value at the Al/(Al+Si) ratio of 0.1, while the latter remains nearly constant throughout all the catalysts.

For the sake of a convenient explanation of the change in the selectivity as well as in the activity related to the aluminum content of the present catalysts, two kinds of acid sites are suggested as possibly present.

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