Study of Nickel Oxide - Silica - Alumina Catalysts for Ethylene Polymerization. III. The Performance of the Catalysts in Ethylene Polymerization and Butene Isomer Formation and Its Dependence on the Nickel Oxide Content

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The activity of a particular series of nickel oxide-silica-alumina catalysts for ethylene polymerization and the selectivity in the formation of butene isomers have already been studied.[1,2] The catalysts used differed in aluminum content, though they all had the same nickel content.

To obtain more detailed knowledge about the relation between the catalyst performance and the catalyst composition, the study has recently been extended to another series of catalysts which are the same in aluminum content but different in nickel content. The results of this study will be presented here, and the effects of the addition of aluminum and nickel upon the catalyst performance will be discussed on the basis of these and the previously-obtained results.

Although the performance of nickel-containing catalysts has been studied by some other investigators,[3-7] most of their papers deal with

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[1] H. Uchida and H. Imai, This Bulletin, **35**, 989 (1962).

[2] H. Uchida and H. Imai, ibid., **35**, 995 (1962).

[3] S. Kawaguchi and K. Kihara, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **75**, 15 (1954).

[4] A. Ozaki, ibid., **77**, 888 (1956).

[5] S. Kawaguchi, *J. Phys. Chem.*, **61**, 394 (1954).

[6] V. C. F. Holm, G. C. Bailey and A. Clark, *Ind. Eng. Chem.*, **49**, 250 (1957).

[7] A. Takahashi, N. Mogi, H. Takahama and Y. Mita, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **66**, 473 (1963).

the catalytic activity and not with the selectivity. The only exception is the paper recently published by Takahashi et al.,[7] who state that a high selectivity in the 1-butene formation can be obtained by the use of a nickel oxide-silica-alumina catalyst suspended in a medium of cyclohexane.

Experimental

The catalysts required for this study were prepared in the same way as those designated as "catalysts A" in the previous paper.[1] In other words, they were prepared by mixing a solution of sodium silicate with a solution of aluminum and nickel nitrates and then forming the resulting precipitate into granules 1—2 mm. in size. In this case, the aluminum content of the catalyst, expressed as the Al/(Al+Si) atomic ratio, was fixed at 0.05, and the nickel content, expressed as atom.% nickel (defined by $100\times\mathrm{Ni}/(\mathrm{Ni}+\mathrm{Si}+\mathrm{Al})$), was varied over the range from 0 to 8.

Their catalytic performance was studied by conducting two series of experiments on ethylene polymerization with the catalysts. One series of experiments (Series A) was carried out in order to determine the catalytic activity, while the other series (Series B) was carried out in order to determine the selectivity in the formation of butene isomers. The apparatus used for these experiments, which included a circulatory flow system, was the same as that used in our previous study.[1] In the two series of experiments, the reaction temperature was 40°C and the initial ethylene pressure was 345 mmHg. In the experiments of Series A, 5 ml. of a catalyst was used to form the catalyst bed in the cell (catalyst cell), and the two U-shaped traps, joined, respectively, to the entrance and exit tubes of the cell, were cooled in a dry ice - methanol bath. During each experiment, the pressure drop in the system was recorded at intervals. In the experiments of Series B, 1 ml. of a catalyst was used to form the catalyst bed in the cell, and the traps were cooled in an ice bath so that the butenes formed might be maintained in the circulating gas. A small portion of the circulating gas was withdrawn at intervals from the gas circulation system and analyzed for butene isomers by gas chromatography.

The following physical properties of the catalysts were measured by the methods described in previous papers:[1,2] catalyst acidity, specific surface area, and total pore volume. The total pore volume as measured by the present method represents the sum of the volumes of pores smaller than 300Å in radius. Moreover, in order to see the effects of the addition of nickel on the physical properties of catalysts, samples of the catalysts were depleted of nickel, and then the resultant changes in physical properties were measured. The nickel was removed by the method described in a previous paper,[2] namely, by reducing the original catalyst in a stream of hydrogen and then treating the reduced catalyst at 150°C with carbon monoxide under high pressure until it showed no sign of the presence of nickel.

Results

Activity for Ethylene Polymerization.—From the data obtained in the experiments of Series A, the rate constant for ethylene polymerization at 40°C over a unit quantity of a catalyst, hereafter denoted by k_g, is calculated by the aid of the equation proposed by Koizumi et al.[8] (Eq. 1):

$$-\mathrm{d}P/\mathrm{d}t=k_g wP/\{1+(P_0-P)\} \qquad (1)$$

where P_0 (mmHg) is the initial pressure of ethylene; P (mmHg), the ethylene pressure at the reaction time, t (min); w, the quantity of catalyst used, and b, a constant. The rate constant, k_g, thus calculated is plotted against the nickel content of the catalyst in Fig. 1.

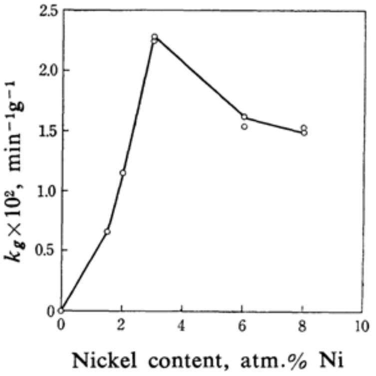

Fig. 1. Dependence of catalyst activity for ethylene polymerization on nickel content.

The plot shows a maximum at about 3 atm.% nickel; this finding is consistent with that of Holm et al.[6]

Selectivity in the Formation of Butene Isomers.—From the data obtained in the experiments of Series B, three butene-isomer ratios (concentration ratios), *trans*-2-/1-butene, *cis*-2-/1-butene, and *trans*-2-/*cis*-2-butene, were calculated and plotted against the reaction time, t. The plots were then extrapolated to $t=0$ to give the initial butene-isomer ratios.[9] The initial butene-isomere ratios thus obtained are given in Fig. 2 as functions of the nickel content of the catalyst. With the increase in the nickel content, the *cis*-2-/1-butene and *trans*-2-/1-butene ratios both decrease very slowly in nearly the same manner, and then rapidly. In contrast, the *trans*-2-/*cis*-2-butene ratio remains nearly the same (about 1) over the whole range of nickel content studied, though it becomes slightly greater at 3 atm.% nickel, where the highest value of k_g was found.

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[8] M. Koizumi and S. Taga, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kwagaku Kwaishi*), **64**, 794 (1943).

[9] For details of this procedure, see Ref. 1.

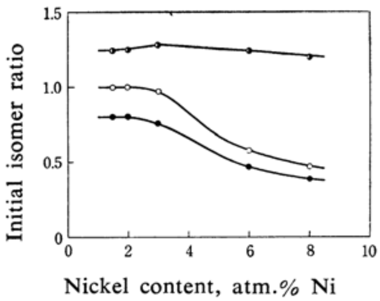

Fig. 2. Dependence of initial butene-isomer ratios on nickel content.
Initial isomer ratio
○ *trans*-2-/1-butene
● *cis*-2-/1-butene
◑ *trans*-2-/*cis*-2-butene

Catalyst Acidity.—The catalyst acidity is expressed in millimole equivalents (meq.) of quinoline chemisorbed on a specified quantity of a catalyst sample. In the case of the original catalyst sample containing all three oxides, nickel(II) oxide, silicon oxide, and aluminum oxide, the acidity, A_g, is the numerical value determined for 1 g. of the catalyst sample. On the other hand, in the case of the nickel-depleted catalyst sample (which contains only two oxides, silica and alumina), the acidity, A_g', is the numerical value determined for that quantity of the nickel-depleted catalyst sample which has been produced from 1 g. of the original catalyst (i. e., the catalyst containing all three component oxides). In Fig. 3, the acidity values, A_g and A_g', determined for the catalysts used in this study are plotted against the nickel content of the original catalyst. The plot of A_g shows a maximum at 3 atm.% nickel. Whereas the plot of A_g' shows a minimum at the same nickel content. Therefore, it may be seen that the removal of nickel results in a decrease in the catalyst acidity, though the extent of the decrease is not directly related to the nickel content of the catalyst.

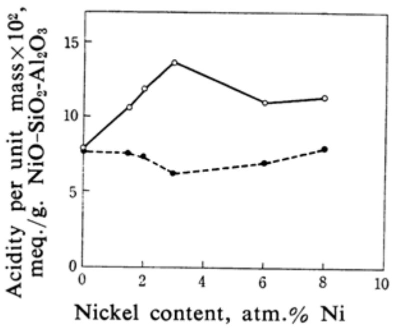

Fig. 3. Acidities per unit mass plotted against nickel content.
—○— Acidity before removal of nickel (A_g)
···●··· Acidity after removal of nickel (A_g')

Specific Surface Area and Total Pore Volume.—When the original catalyst contains all three component oxides, the specific surface area, *S*, and the total pore volume, *V*, are the surface area (in m^2) and the total pore volume (in ml.) of 1 g. of the catalyst. On the other hand, in the case of a nickel-depleted catalyst sample, the specific surface area, *S'*, and the total pore volume, *V'*, are the surface area (in m^2) and the total pore volume (in ml.) of that quantity of the nickel-depleted catalyst sample which has been produced from 1 g. of the original catalyst. In Fig. 4, the four quantities, *S*, *S'*, *V*, and *V'*, are plotted against the nickel content of the original catalyst. As the nickel content increases, both *S* and *S'* first increase, then vary less markedly over the range from 2 to 6 atm.% nickel, and finally decrease. On the other hand, both *V* and *V'* remain nearly the same over the whole range of nikel content studied. Except for a pair of catalyst samples—an original catalyst and the nickel-depleted sample produced from this, the specific surface area of a nickel-depleted catalyst (*S'*) is generally smaller than the specific surface area of the original (*S*) ; on the other hand, the total pore volume of a nickel-depleted catalyst (*V'*) is a little greater than the total pore volume of the original (*V*).

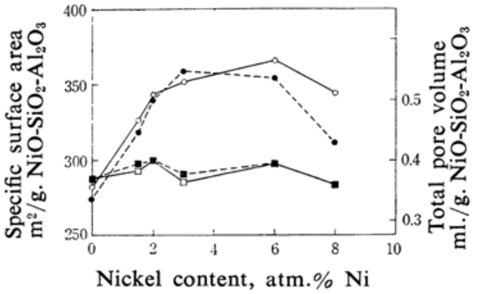

Fig. 4. Specific surface area (*S*) and total pore volume (*V*) of the catalyst samples before and after nickel oxide removal plotted against nickel content.
Circle, *S* Square, *V*
Empty mark, before the removal
Full mark, after the removal

Discussion

The Relationship between Activity and Acidity.—Before considering the relationship between the catalytic activity for ethylene polymerization and the catalyst acidity, let us study, for a moment, the relation between the specific activity, k_s, and the specific acidity, A_s. The specific activity, i. e., the activity based on the unit surface area of the catalyst, is obtained by dividing k_g by S. Similarly, the specific acidity, i.e. the acidity based on the unit surface area of the catalyst, is obtained by dividing A_g by S.

Figure 5 shows a plot of k_s as a function of the nickel content. Since, in the case of acid catalysts,[10-12] k_s is linearly correlated with A_s, one may suspect that a similar relationship will be found between the k_s and A_s, or more roughly between k_g and A_g, for the present catalysts. However, no such correlation can be found in the present case.

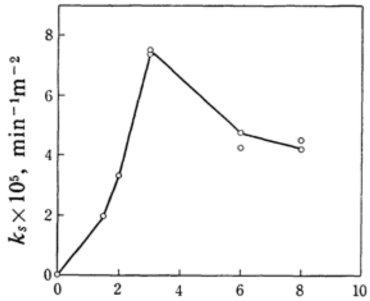

Fig. 5. Specific activity (k_s) as a function of nickel content.

On the other hand, we have already found that, for a series of nickel oxide-silica-alumina catalysts with different aluminum contents, k_s is more closely related to the difference between the specific acidity values before and after the removal of nickel, $A_s—A_s'$ (where $A_s'=A_g'/S$) than to A_g or A_g itself, and that the relationship between k_s and $A_s—A_s'$ is approximately linear.[2] To see whether such a correlation would hold for the present series of catalysts, we have evaluated the specific acidity difference, $A_s—A_s'$, and plotted the values against the nickel content of the catalyst in Fig. 6.

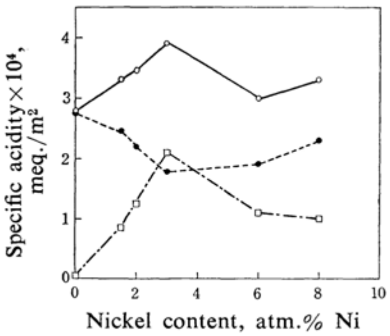

Fig. 6. Specific acidities plotted against nickel content.
—○— Acidity before removal of nickel (A_s)
--●-- Acidity after removal of nickel (A_s')
—·□·— Difference between the above two values (A_s-A_s')

A comparison of this plot with the plot of k_s in Fig. 5 shows a parallel relationship between them. Moreover, a plot of k_s vs. $A_s—A_s'$ for the present series of catalysts agrees with the straight line obtained for the series of nickel oxide-silica-alumina catalysts with different aluminum contents (see Fig. 7).

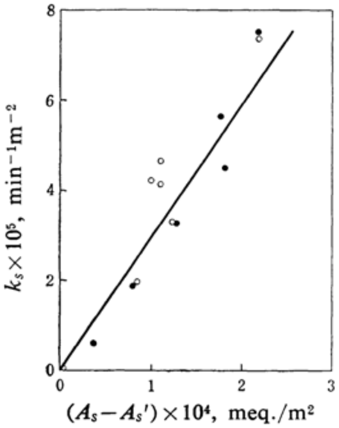

Fig. 7. Specific activity (k_s) plotted against the specific acidity difference (A_s-A_s').
● Previously obtained results[2]

These facts indicate that only the acidity produced by the addition of nickel is closely related to the activity of ethylene polymerization, in other words, only the acid sites due to nickel contribute to the ethylene polymerization. However, it must here be noted that the nickel content is not always proportinal to A_s-A_s', and, hence, to k_s.

The Rates of the Formation of Butene Isomers at the Initial Stage of Polymerization and Their Dependence upon the Nickel Content.—From the data of Figs. 2 and 5, the rates of the formation of three n-butene isomers per unit surface area of catalyst at the initial stage of ethylene polymerization can be calculated by the aid of the following equations:

$$r_{02}/r_{01}=[\textit{cis}\text{-2-}]/[\text{1-butene}]\ \text{at}\ t=0$$

$$r_{03}/r_{01}=[\textit{trans}\text{-2-}]/[\text{1-butene}]\ \text{at}\ t=0$$

$$r_{03}/r_{02}=[\textit{trans}\text{-2-}]/[\textit{cis}\text{-2-butene}]\ \text{at}\ t=0 \quad (2)$$

$$r_0=k_sP_0 \quad (3)$$

$$r_0=r_{01}+r_{02}+r_{03} \quad (4)^{13)}$$

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10) M. W. Tamelle, *Discussions Faraday Soc.*, **87**, 270 (1950).

11) O. Johnson, *J. Phys. Chem.*, **59**, 827 (1955).

12) E. Echigoya, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **76**, 1049 (1955).

13) In the earlier stage of polymerization, where the fraction of ethylene polymerized remained below 0.1, more than 95% of the reaction product was butene.

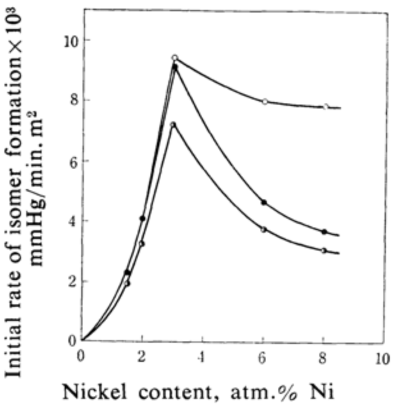

Fig. 8. Dependence of r_{01}, r_{02} and r_{03} on nickel content.
○ : r_{01}, ◑ : r_{02}, ● : r_{03}

where r_{01}, r_{02}, and r_{03} are the rates of the formation of the butene isomers per unit surface area of the catalyst, respectively referring to 1-butene, *cis*-2-butene, and *trans*-2-butene; r_0 is the rate of ethylene polymerization per unit surface area of the catalyst, and the brackets indicate the concentration. In Fig. 8, the rates thus calculated, i. e., r_{01}, r_{02}, and r_{03}, are plotted against the nickel content of the catalyst. As the nickel content is increased, all these rates increase up to their respective maxima at 3 atm.% nickel and then decrease. An interesting fact to note here is that, in the range of nickel content above 3 atm.%, the rate r_{01} decreases more slowly than the rates r_{02} and r_{03}. This fact seems to indicate the possibility of producing 1-butene selectively by the use of a catalyst containing nickel greatly in excess of a certain amount of aluminum.

Active Sites for Dimerization and Isomerization.—For the purpose of explaining the catalytic performance observed in the formation of butene isomers (from ethylene) over nickel oxide-silica-alumina catalysts differing only in aluminum content, it has been postulated in a previous paper[2)] that two kinds of active sites, H^+X^- and H^+Y^-, as pictured by (>Si-O-Ni<) and (>Si-O-Al<) respectively, might be present on the catalyst surface, and that the first-named site would participate in the formation of chemisorbed species of 1-butene from ethylene, while the second site would participate in the rearrangement of the chemisorbed species to form the other *n*-butene isomers as the primary products. The concept of the active site H^+X^- serves to explain the straight line relationship observed between the specific activity, k_s, and the specific acidity difference, A_s—A_s'. However, since three *n*-butene isomers were formed as primary products in ethylene dimerization over the catalyst containing no aluminum,[14)] it might be necessary to correct this concept as follows: the site H^+X^- contributes not only to the formation of 1-butene but also, in some degree, to the rearrangement of the chemisorbed species of 1-butene which forms the other *n*-butene isomers as the primary products. Nevertheless, we can safely say that only the site H^+X^- contributes to the dimerization of ethylene and that all the sites of this type contribute in equal degree, whatever the aluminum and nickel contents of the catalyst may be.

On the other hand, as the following discussion will show, it has now been found that the data hitherto obtained on the selectivity in the formation of butene isomers are too complicated to allow us to assign the site H^+Y^- simply to the silica-alumina combination, >Si-O-Al< . In the butene-isomer formation over the catalysts described in the previous paper, both *cis*-2-/1-butene and *trans*-2-/1-butene ratios at the initial reaction stage (reaction time: $t=0$) rise rapidly as the aluminum content of the catalyst (expressed as Al/(Al+Si) atomic ratio) increases up to 0.1, while above this value of aluminum content, they remain nearly constant. On the other hand, in the butene-isomer formation over the catalysts described in this paper, these isomer ratios decrease, at first very slowly and then rapidly, as the nickel content of the catalyst increases up to a certain limit. These facts suggest that the selectivity might be related to the Al/Ni ratio rather than to either of the other two factors, aluminum content and nickel content.

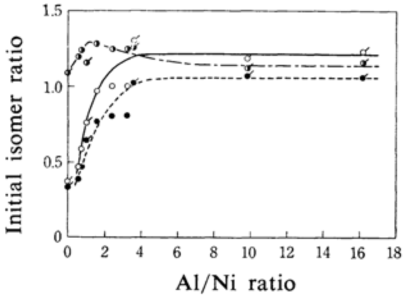

Fig. 9. Dependence of initial isomer ratio on Al/Ni ratio.
○ ○′ *trans*-2-/1-butene
● ●′ *cis*-2-/1-butene
◑ ◑′ *trans*-2-/*cis*-2-butene
The marks with dash indicate the previous date with a series of catalysts containing varying amount of aluminum and a fixed amount of nickel.[2)]

[14)] There is a possibility that the catalyst described as containing no aluminum may happen to be contaminated with a minute quantity of aluminum or some other substance, an impurity which might come from the sodium silicate used as a raw material.

In fact, as Fig. 9 shows, both *cis*-2-/1-butene and *trans*-2-/1-butene ratios (at $t=0$) increase as the Al/Ni ratio increases up to 4, but above this Al/Ni ratio they remain nearly constant. On the other hand, the *cis*-2-/*trans*-2-butene ratio is nearly the same throughout the range of the Al/Ni ratio studied, except at an Al/Ni ratio of about 1, where a slight maximum appears in the plot. The trend of the first two plots suggests that all the aluminum in a catalyst can not always be the constituent of the active site capable of accelerating the double-bond shift to form 2-butenes, but that only the aluminum associated in some manner with the nickel, presumably the aluminum joined by an oxygen bond to the nickel as in $(\rightarrow\mathrm{Si{-}O{-}Al{-}O{-}Ni}\leftarrow)$, can be the constituent.

Moreover, the fact that both *cis*-2-/1-butene and *trans*-2-/1-butene ratios (even their highest values) are much smaller than the corresponding ratios calculated from the thermodynamical data for the chemical equilibrium between butene isomers at 40°C[15] leads us to conclude that the aluminum present in excess of an Al/Ni atomic ratio of 4 cannot accelerate the initial double-bond shift. This conclusion is consistent with the geometry of the aluminum-nickel combination, because, on the basis of the reasonable assumption[16] that one nickel atom is located in the center of a tetrahedron with four oxygen atoms at the corners, it may be considered that four aluminum atoms are joined to one nickel atom by oxygen bridges.

In his study of the selectivity in olefin isomerization over acid catalysts, Brouwer[17] explained the variation in the selectivity with the kind of catalyst by applying the concerted or switch mechanism proposed by Turkevich and Smith[18] and by Horiuchi[19]. Our explanation based on the concept of two active sites is similar to Brouwer's in that two kinds of acid sites, H^+X^- and H^+Y^-, are considered. However, the former differs from the latter in that the two acid sites considered in our explanation have different properties, whereas the sites considered by Brouwer are the same. The concerted mechanism alone does not suffice to explain our observation that the activity for ethylene polymerization and the selectivity in the formation of butene isomers change in different ways as the catalyst composition is changed.

The reaction scheme presented in a previous paper[1] can be applied to explain the constancy of the *cis*-2-/*trans*-2-butene ratio observed nearly all over the range of the Al/Ni ratio studied. However, it is not possible to account for the slight maximum appearing in the plot of the isomer ratio at an Al/Ni ratio of about 1.

Summary

The activity of nickel oxide - silica - alumina catalysts in ethylene polymerization and the selectivity in the formation of three *n*-butene isomers as the primary products have been studied by employing a series of catalysts with identical aluminum contents but different nickel contents. Also studied have been the changes brought about by nickel removal in the catalyst acidity and in the specific surface area.

In the series of catalysts studied, the specific activity, i. e., the activity per unit surface area of the catalyst, increases with the increasing nickel content of the catalyst, attaining a maximum at 3 atm.% nickel. When the specific activity is plotted against the difference between the specific acidity values observed before and after the removal of nickel, the plot falls approximately on the straight line obtained with a series of catalysts which are the same in nickel content but different in aluminum content. On the other hand, for all the catalysts used in the present and previous studies, the selectivity is more closely related to the Al/Ni ratio than to either aluminum content or nickel content.

Two kinds of active sites have been presented in order to explain the present observations. One kind of active site is the nickel acid site, which contributes to the polymerization of ethylene while facilitating the isomerization to some extent. The other site is the aluminum acid site in contact with the former; it contributes to the initial-bond shift.

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[15] About the equilibrium composition, see Ref. 1.

[16] C. L. Thomas, *Ind. Eng. Chem.*, **41**, 7564 (1949).

[17] D. M. Brouwer, *J. Catalysis*, **1**, 22 (1962).

[18] J. Turkevich and R. K. Smith, *J. Chem. Phys.*, **16**, 446 (1948).

[19] J. Horiuchi, *Catalyst* (*Shokubai*), **1**, 67 (1948).