Study on Nickel Oxide-Silica-Alumina Catalyst for Ethylene Polymerization. II. Catalyst Structures Related to Catalyst Activity

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Our preceding paper[1] presented the results concerning the catalyst activity for ethylene polymerization and the selectivity in butene-isomer formation which were obtained for a series of nickel oxide-silica-alumina catalysts. The catalysts contained progressively increasing amounts of alumina with a fixed nickel oxide content. The results showed that both the activity and the selectivity change in a particular manner that is greatly dependent on the alumina content. In the present study, the catalysts were successively treated with hydrogen and carbon monoxide to remove nickel oxide, and the catalyst acidities before and after the treatment have been measured, along with the determinations of the changes in the activity and specific surface area. The valence state of nickel has also been determined. The results may serve for the elucidation of catalyst structure which, in turn, determines the activity.

Experimental

Catalyst Acidity.—The acidity was determined on a separate sample drawn from the same batch as the catalysts used in the activity test in the preceding paper[1]. The procedure of the determination is dependent on the chemisorption measurement of quinoline or ammonia. In this study, the quinoline chemisorption method was adopted, and the data were in some cases supplemented with the ammonia chemisorption method.

The quinoline chemisorption measurement was made by means of the technique developed by Mills et al.[2], using an apparatus of a more simplified design developed by Hara et al.[3] Prior to the chemisorption the catalyst sample was successively heated at 500°C in a stream of dry air for fifteen hours and a stream of purified nitrogen for three hours. The quinoline chemisorption and subsequent flushing of the sample with nitrogen at the flow rate of 300 cc./min. were made at 300°C.

The ammonia chemisorption was pointed out by Tamelle[4], Milliken et al.[5], Webb[6], and Voltz[7] as

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

[2] G. A. Mills, E. R. Boedeker and A. G. Oblad, *J. Am. Chem. Soc.*, **72**, 1554 (1950).

[3] N. Hara, M. Ikeda and K. Mita, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zassi*), **56**, 377 (1953).

[4] M. W. Tamelle, *Discussions Faraday Soc.*, **8**, 270 (1950).

[5] T. H. Milliken, Jr., G. A. Mills and A. G. Oblad, ibid., **8**, 279 (1950).

[6] A. N. Webb, *Ind. Eng. Chem.*, **49**, 261 (1957).

[7] S. E. Voltz and S. W. Weller, *J. Phys. Chem.*, **62**, 574 (1958).

serving as a measure for the catalyst acidity. In this study, the method of Voltz was followed, and the chemisorption measurement was conducted in a static system at a fixed ammonia pressure of 35 mmHg at 60°C (the polymerization temperature). Each molecule of quinoline or ammonia chemisorbed was considered to correspond to one acid site, and the acidity data were given in the form of mmole equivalent base (quinoline or ammonia)/g. catalyst.

Removal of Nickel Oxide from Catalyst.—It would be desirable to divide the observed acidity of the catalyst into the individual contributions of the catalyst components. This would be possible if nickel oxide could be removed without causing irreversible changes in the silica-alumina support. In this respect, Schuit et al.[8] developed a very convenient method for removing nickel at a comparatively low temperature. In their study on nickel-on-silica catalysts, nickel was converted to nickel carbonyl by treatment with carbon monoxide at atmospheric pressures to remove it from the catalysts, and then the changes in the specific surface area and average pore radius caused by the removal were investigated. This method of romoval has been followed in this study with some modifications: after having been thoroughly reduced at 450°C under high pressure ($50\sim100$ kg./cm^2) of hydrogen for a week, the catalyst was treated with flowing carbon monoxide at high pressure (150 kg./cm^2) at 150°C for a week. Schuit et al.[8] stated that the removal of nickel seldom proceeded quantitatively when the coprecipitated catalysts were treated. It has been proved in the present study, however, that by the treatment at the higher pressure and temperature, more than 99% of the nickel can be removed from the coprecipitated catalysts. The catalyst acidity and the activity as well as the specific surface area were determined, in the same manner as described previously[1], on the catalyst samples thus depleted of nickel oxide (hereafter denoted as catalyst $\mathrm{A'}$).

Valence State of Nickel in Catalyst.—The valence state of nickel was evaluated by precise reduction of the nickel oxide with hydrogen. The reduction was conducted according to the method of Hill et al.[10] in a circulatory flow system similar in construction to that used for the catalyst activity test in the preceding paper[1]. The catalyst sample weighing about 5 g. was placed in a catalyst tube and was pretreated in the same way as for the activity test[1], followed by introduction of hydrogen from an attached gas burette into the system to a pressure of 500 mmHg. Two U-traps were placed in the circulating system and were cooled at -78°C to remove the water vapor formed by reduction. The reduction was made at 540°C in a circulating current of hydrogen maintained at about 500 mmHg by frequent introductions of hydrogen from the gas burette. It was continued until the hydrogen consumption diminished to such a small extent as 0.1 cc. (N. T. P.)/g. catalyst·day. The reduction durations ranged from 7 to 15 days according to the reducibility. After the reduction was completed, the volume of hydrogen necessary for keeping the final pressure of the entire system exactly at 500 mmHg was measured. The system was evacuated again at 540°C for 3 hr., followed by the immediate introduction of hydrogen to the pressure of 500 mmHg. The difference between the volumes of hydrogen introduced before and after the evacuation gave the hydrogen consumption for the reduction of the nickel oxide. The processings of evacuation and the subsequent introduction of hydrogen were done in such a way as to minimize the error of overestimating the hydrogen consumption, which error might result from a considerable amount of hydrogen chemisorption on the reduced catalysts.

Experimental Results

Catalyst Activity after Nickel Oxide Removal.—In the preceding paper[1], the catalyst activity for ethylene polymerization was expressed in terms of the rate constant per gram of catalysts A (k_g). For the sake of a convenient comparison between the k_g and the activity of corresponding catalysts $\mathrm{A'}$ after the nickel oxide removal, the activity of the latter catalysts is given by a rate constant based on the amount of silica-alumina contained in 1 g. of the original catalysts A but not in 1 g. of catalysts $\mathrm{A'}$. The rate constant defined in this manner will be conventionally denoted by k_g of catalysts $\mathrm{A'}$[11]. The results are listed in Table I, which includes the k_g for catalysts A. The table shows that catalysts $\mathrm{A'}$, the silica-alumina residues from catalysts A, give poor activities which are lower than several hundredths of the activities of the corresponding catalysts A, with the exception of catalyst A-6, with a large aluminum content[12]. The ethylene

TABLE I. DECREASE IN ACTIVITY AFTER NICKEL OXIDE REMOVAL

Catalyst	Al/(Al+Si) ratio	k_g at 40°C $\times10^2\mathrm{min}^{-1}\mathrm{g}^{-1}$	k_g at 40°C after NiO removal $\times10^2\mathrm{min}^{-1}\mathrm{g}^{-1}$
A-1	0	0.68	0.0058
A-2	0.03	2.04	0.028
A-3	0.05	2.57	0.077
A-4	0.11	1.18	0.066
A-5	0.30	0.18	—
A-6	0.50	0.075	0.055

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[8] G. C. A. Schuit and L. L. van Reijen, "Advances in Catalysis and Related Subjects", X, Academic Press Inc. Publishers, New York and London (1958), p. 243; G. C. A. Schuit and N. H. de Boer, *J. Chim. Phys.*, **51**, 482 (1954). Recently, this method was followed by Morikawa et al.[9] for their study of supported nickel catalysts.

[9] K. Morikawa and F. Nozaki, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **64**, 1562 (1961).

[10] F. N. Hill and P. W. Selwood, *J. Am. Chem. Soc.*, **71**, 2522 (1949).

[11] The rate constant defined in this way is 0.996 times the value of the rate constant based on 1 g. of catalysts $\mathrm{A'}$.

[12] With respect to propylene polymerization, Clark[13] reported that when the oxides of metals in group V and higher of the periodic table were supported on silica-alumina they gave an increase in the activity over silica-alumina alone.

[13] A. Clark, *Ind. Eng. Chem.*, **45**, 1476 (1953).

polymerization seems to proceed on the active sites on which nickel oxide is acting effectively.

Changes in Specific Surface Area and Pore Volume by Nickel Oxide Removal.—The specific surface area and the pore volume of catalysts A′ are expressed in m^2 and cc. respectively of the silica-alumina contained in 1 g. of catalysts A. The area thus defined, in place of the surface area based on 1 g. of catalysts A′, may lead to an easier understanding of the effect of nickel oxide addition on the change in the catalyst surface area. Figure 1 presents the results as a plot against the Al/(Al+Si) ratio, together with the plot for a series of catalysts A. The former plot lies a little above the latter plot over the whole range of aluminum content examined in this study[14]. The result is the opposite of that of Schuit[8], who stated a decrease in the specific surface area of nickel-on-silica catalysts from which nickel had been driven out.

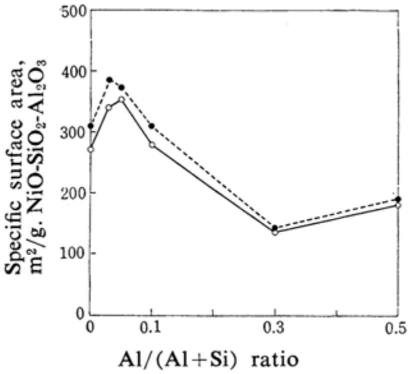

Fig. 1. Change in specific surface area by nickel oxide removal as function of Al/(Al+Si) ratio.
—○— Catalysts A
--●-- Catalysts A′

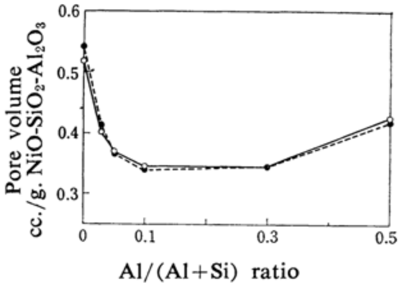

Fig. 2. Change in pore volume by nickel oxide removal as function of Al/(Al+Si) ratio.
—○— Catalysts A
--●-- Catalysts A′

Definite tendencies in the change of the pore volume have scarcely been found between the catalysts A and corresponding catalysts A′ (refer to Fig. 2).

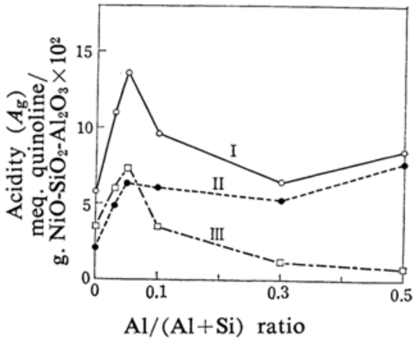

Fig. 3. Catalyst acidities before and after nickel oxide removal as function of Al/(Al+Si) ratio.
—○— Catalysts A
--●-- Catalysts A′
--□-- Difference between acidities of catalysts A and A′

Catalyst Acidity.—Figure 3 shows the acidity (denoted by A_g) determined by the quinoline chemisorption method for the two series of catalysts A and A′, plotted against the Al/(Al+Si) ratio. Again, the acidity for the catalysts A′ for the sake of convenience, is expressed in mmole equivalent (meq.) quinoline chemisorbed on the silica-alumina contained in 1 g. of the original catalysts A. The plot for catalysts A (plot I) tends to rise rapidly, to pass through a maximum at a Al/(Al+Si) ratio of about 0.05, and to fall off gradually with the increasing aluminum content. The plot for catalysts A′ (plot II) lies below plot A, and the difference between the two plots (plot III), which is larger in the range of the higher acidity of catalysts A, is a measure of the acidity resulting from the nickel oxide. A small amount of nickel oxide can in some cases produce a large number of acid sites, besides those of silica-alumina alone[15]. It should be noted, further, that the numbers of acid sites thus produced are greatly dependent on the aluminum content.

Valence State of Nickel in Catalyst.—The result is shown in Fig. 4 as a plot of the atom ratio of hydrogen consumed for reduction to

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[14] Since the specific surface area of catalyst A-2 decreased by 2.5% of the original area after the catalyst underwent the hydrogen treatment at 450°C and subsequent oxidation at 500°C with air, the increase in the specific surface area can not be ascribed to the treatments other than the nickel oxide removal.

[15] The increase in the acidity caused by an addition of metal oxides, such as chromium oxide, copper oxide, and other oxides of the transition metals, to silica-alumina over that of silica-alumina alone has already been pointed out by Clark[13] and Fisher et al.[16]

[16] K. A. Fisher and G. Brandes, *Erdoel u. Kohle*, **9**, 81 (1956).

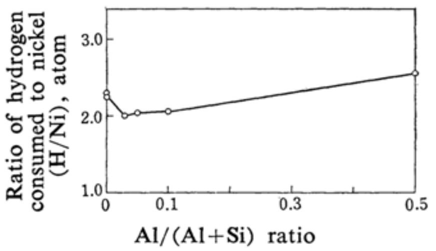

Fig. 4. Hydrogen consumption plotted against Al/(Al+Si) ratio.

nickel vs. the Al/(Al+Si) ratio. Nickel exhibits a normal valence of 2 in the Al/(Al+Si) range from 0.03 to 0.1, while on the sides both of decreasing and increasing aluminum contents valences a little higher than 2 are found. Concerning the valence of nickel in catalysts, Holm et al.[17] reported the normal valence of 2 for series of impregnated and coprecipitated nickel oxide-silica-alumina catalysts containing silica and alumina in the ratio of 9 : 1 with a wide range of nickel oxide contents. The present result is consistent with the result of Holm et al. in the sense that the valence is 2 for the catalysts with relatively small aluminum contents. On the other hand, Selwood[18] obtained a valence higher than 2 for nickel in nickel oxide-on-alumina catalysts. The slight valence increase in the range of higher aluminum content may be explainable in view of Selwood's result, since the larger the aluminum content, the larger the amount of nickel oxide which can be combined with alumina. However, no interpretation of the higher nickel valence for catalyst A-1 with no aluminum is possible.

Discussion

Relationship between Catalyst Activity and Acidity.—Previous papers dealing with the nickel oxide-silica-alumina catalysts indicated no direct relationship between the catalyst activity for olefin polymerization and the catalyst acidity[19,20]. As shown in Fig. 5[21], a simple plot of the activity (k_g) against the acidity (A_g) does not show such a relationship, either. Regarding dual-oxide catalysts, however, it was not infrequently possible to obtain a definite relationship between them[4,22,23], and hence the present data will be treated in further detail.

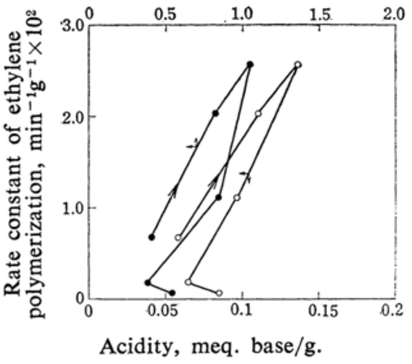

Fig. 5. Plots of catalyst activity vs. acidity.
—○— Acidity by quinoline chemisorption method (300°C)
—●— Acidity by ammonia chemisorption method (60°C)
The arrow on the line indicates the order of increasing aluminum content.

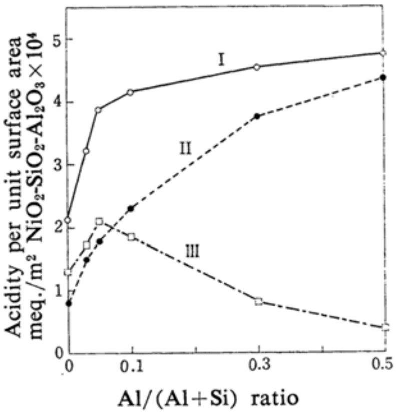

Fig. 6. Plots of acidity per unit surface area vs. Al/(Al+Si) ratio.
—○— Catalysts A
--●-- Catalysts A′
-·-□-·- Difference between acidities of catalysts A and A′

The preceding paper[1] of this series established that the specific activity per unit surface area of the catalyst and the specific surface area are the major factors determining the catalyst activity for ethylene polymerization on the nickel oxide-silica-alumina catalysts. In the present work, it has been determined that the nickel oxide has no appreciable effect on the surface area of silica-alumina and, therefore, that the increased activity is not due to an increase in the specific surface area. In order

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

18) P. W. Selwood, "Advances in Catalysis and Related Subjects", III, Academic Press Inc. Publishers, New York and London(1951), p. 28.

19) M. Koizumi, *Chemical Researches* (*Kagaku no Kenkyu*) 9, 1 (1951).

20) J. P. Hogan, R. L. Banks, W. C. Lanning and A. Clark, *Ind. Eng. Chem.*, **47**, 752 (1955).

21) The figure is included with the acidity data determined by means of the ammonia chemisorption method, which data are always higher than the corresponding data obtained by the quinoline chemisorption method.

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

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

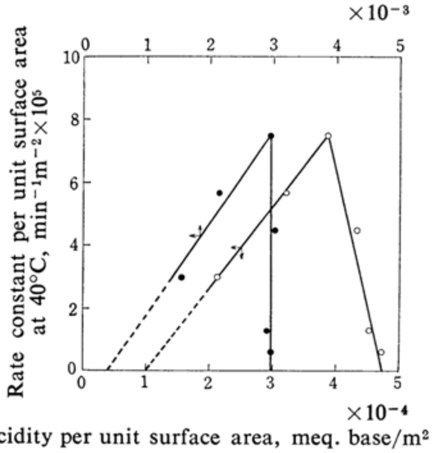

Fig. 7. Relationship of rate constant per unit surface area to acidity per unit surface area.
—○— Quinoline chemisorption method (300°C)
—●— Ammonia chemisorption method (60°C)

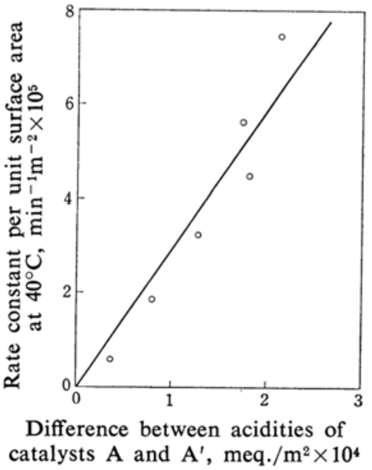

Fig. 8. Rate constant per unit surface area plotted against difference between acidities of catalysts A and A′.

to examine the possible relationship of the specific activity to the acidity, the acidity is likewise considered on the basis of unit surface area (denoted by A_s); namely, the A_g in Fig. 3 is divided by the surface area in Fig. 1 to result in the acidity based on the unit surface area of the catalysts. The A_ss are shown in Fig. 6 with separate plots of I and II for respective series of catalysts A and A′ as a function of the Al/(Al+Si) ratio. Plot I rises rapidly in the range of the Al/(Al+Si) ratio from 0 to 0.05 and more slowly in the range of higher ratios with the increasing aluminum content. In contrast to this, plot II rises monotonously with the increasing content, as is usually the case with silica-alumina catalysts[24,25]. Further, the difference between the two plots, which indicates the acidity produced on the unit surface area of the catalysts with nickel oxide (denoted by A_{sNi} hereafter), is shown by plot III as a function of Al/(Al+Si) ratio. Plot III is quite different in tendency from plot I, showing a maximum at the Al/(Al+Si) ratio of 0.05.

The direct relationship of the catalyst activity to the acidity is to be given rather by the plot of k_s against A_s than by that of k_g against A_g. Of the two acidities, namely, A_s with catalysts A, and A_s with nickel oxide (A_{sNi}), only the latter acidity gives an approximate straight line when plotted against the k_s (refer to Figs. 7 and 8). In view of this fact, combined with the extremely low activity of catalysts A′ as compared with that of catalysts A, it can be concluded that only the acid sites produced with nickel oxide act effectively for the ethylene polymerization and that the individual acid sites thus produced promote the polymerization to an equal extent, regardless of the aluminum contents.

Acid Site Produced with Nickel Oxide.—If an extension of Thomas' proposal[25] for silica and other binary oxide mixtures, in which he postulates the formation of protons from residual water to satisfy the valence deficiencies associated with the unit cell, is applied conventionally to the present three-component catalysts, two kinds of acid sites, as pictured respectively by models I and II in Fig. 9, may be formed. On the other hand, the preceding paper[1] suggested the existence of two kinds of acid sites, H^+X^- and H^+Y^-, on the catalysts, one of which acts effectively for the ethylene polymerization and the other one of which acts effectively for the isomerization between

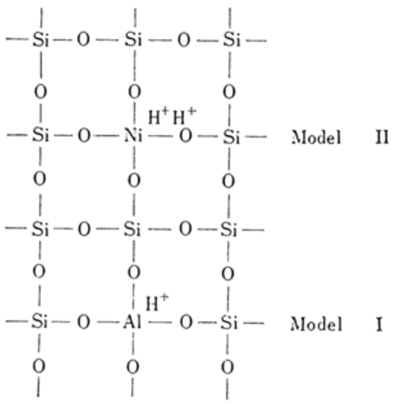

Fig. 9. Structures of acid sites.

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[24] V. C. F. Holm, G. C. Bailey and A. Clark, *J. Phys. Chem.*, **63**, 129 (1959).

[25] C. L. Thomas, *Ind. Eng. Chem.*, **41**, 2564 (1949).

the product butene-isomers. Taking into account the linear relationship observed between the k_s for the polymerization and A_{sNi}, H^+X^- would correspond to the acid site given by the model II.

The model II proposed for the acid site H^+X^- can explain the observed relationship between the A_{sNi} and the aluminum content of the catalysts. The acid site represented by model II is brought about by the condensation of hydroxyls existing at the interface between silica and nickel oxide particles. This suggests that the acid sites could be increased in number according as the particles of nickel oxide and silica are more finely dispersed, consequently according to the increasing specific surface area of the catalyst granules. As for the present series of catalysts containing a fixed amount of nickel oxide with varying amounts of alumina, the specific surface area is greatly dependent on the alumina contents[26], and the plot of the specific surface area against the aluminum content is recognized as running approximately parallel with the same plot of A_{sNi} (compare Fig. 6 with Fig. 1). The fact that nickel in the catalysts of high A_{sNi} is divalent is another support for the model.

Moreover, the decreasing tendencies in the activity and the acidity with the increasing aluminum content in the $Al/(Al+Si)$ range above 0.05 may be partially due to the more frequent formation of the nickel oxide-alumina compound, which gives neither the high activity[19] nor the acidity.

The fact that the initial rates of formation of three *n*-butene isomers and the A_s due to silica-alumina both depend on the aluminum content might lead to the assumption that the acid site H^+Y^- as pictured by model I acts as the site for the isomerization. However, nothing decisive can be established until further experimental data are available with respect to the catalysts with a wide range of the ratio between nickel and aluminum. The matter will be dealt with in one of the succeeding papers of this series.

Summary

After nickel oxide is removed from the catalysts consisting of nickel oxide, silica, and alumina, the catalysts usually show a much lower activity than the original catalysts, with a slight increase in the specific surface area.

The acidity of the original catalysts indicates a maximum at the $Al/(Al+Si)$ ratio of 0.05 and diminishes to some extent after the removal of the nickel oxide. The difference between the acidities before and after the removal of nickel oxide, which is a measure of the acidity originating from nickel oxide, is larger in the range of the higher acidity of the original catalysts. The valence state of nickel is found to be 2 in the $Al/(Al+Si)$ range from 0.03 to 0.1, while it is a little higher than 2 with both decreasing and increasing aluminum contents.

Very few definite relationship have been found between the catalyst activity and acidity. However, when both the activity and the acidity originating from nickel oxide are considered on the basis of the unit surface area, an approximately linear relationship is found between them. The structure of the acid site produced by an addition of nickel oxide is discussed from the view point of an extension of Thomas' proposal for silica and other binary oxide mixtures.

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[26] Milligan et al.[27] stated that in the dual-oxide system (e. g. nickel oxide-alumina), one oxide (e. g. alumina) might exhibit a protective action against crystallization, resulting in finer particles of the other oxide.

[27] W. O. Milligan and L. Merten, *J. Phys. Chem.*, **50**, 465 (1946); H. B. Weiser, W. O. Milligan and G. A. Mills, ibid., **52**, 942 (1948).