JOURNAL OF CATALYSIS 59, 303–310 (1979)

Structure of NiO–SiO$_2$ Catalyst for Ethylene Dimerization as Observed by Infrared Absorption

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Received January 3, 1979

Nickel oxide–silica catalysts were prepared by precipitation from an acidic solution of a nickel salt–sodium silicate mixture, and the structure of prepared catalyst was examined by infrared absorption spectra. Two types of nickel–hydrosilicate, montmorillonite and antigorite, are formed in the catalysts, the relative abundance of which is indicated by ir bands at 710 and 665 cm^{-1}. It is shown that the higher the final pH in precipitation, or the higher the Ni/SiO$_2$ ratio in the starting mixture, the more the formation of antigorite. The NiO/SiO$_2$ catalysts thus prepared are activated for ethylene dimerization by evacuation at elevated temperatures, giving two optimum temperatures, about 100 and 600°C. The first activation is ascribed to a montmorillonite-type site, while the second activation is ascribed to an antigorite-type site.

INTRODUCTION

It is well-known that nickel oxide–silica exhibits a high activity for the dimerization of lower olefins, even at room temperature (*1–3*). In the previous paper from this laboratory, it has been shown that the deuterium involved in the catalyst appears in the product butene by way of the isomerization, and not of the dimerization, and the active site responsible for the dimerization was suggested to consist of a low valent nickel ion and an acid (*4*). In fact nickel oxide which is active for C_2H_4–C_2D_4 equilibration acquires an activity for ethylene dimerization upon addition of nickel sulfate, which is known to be an acid (*5*).

However, little is known about the real species or structure of the active part of the catalyst, which may be significantly affected by the method of preparation of the catalyst. Therefore, it is worthwhile to study the correlation among the conditions of catalyst preparation, catalyst structure, and catalytic activities. In this paper the effects of pH during precipitation on their structures and activities are examined.

EXPERIMENTAL

Catalysts. Nickel oxide–silica was prepared by adding sodium hydroxide solution (0.1 *N*) slowly into a mixed aqueous solution of sodium silicate, nickel sulfate or nitrate, and sulfuric or nitric acid at 60°C with stirring until the pH of mother liquid reached a certain value, and then by allowing the precipitate to stand for 3 hr at room temperature. The ratio of sodium silicate to nickel was varied, while the initial concentrations of sodium silicate and acid were fixed at 1.5 *N*. The final pH value was varied from 6 to 12.7. The precipitate thus obtained was washed thoroughly with distilled water and was dried at 120°C. The dried precipitate was

0021-9517/79/110303-08$02.00/0

TABLE 1

Catalyst Preparations

Catalyst No.	pH	Starting material	Ratio of NiO to SiO_2 in starting material	Color of catalyst after calcination
A-6	6	Na_2SiO_3, $NiSO_4$, H_2SO_4, NaOH (Group 1)	1:4	Yellowish white
A-6.7	6.7	Group 1	1:4	Slight yellow
A-7.4	7.4	Group 1	1:4	Yellowish green
A-8	8	Group 1	1:4	Brownish green
A-9	9	Group 1	1:4	Greenish brown
A-10	10	Group 1	1:4	Blackish brown
A-10.5	10.5	Group 1	1:4	Blackish brown
A-11	11	Group 1	1:4	Greenish black
A-12	12	Group 1	1:4	Black
A-12.7	12.7	Group 1	1:4	Black
B-4	7.5	Na_2SiO_3, $Ni(NO_3)_2$, HNO_3, NaOH (Group 2)	1:30	Brownish yellow
B-10	7.5	Group 2	1:11	Yellowish green
B-24	7.5	Group 2	1:4	Blackish green
B-34	7.5	Group 2	1:2.5	Blackish green
B-56	7.5	Group 2	1:1	Black
B-66	7.5	Group 2	1.5:1	Black
B-73	7.5	Group 2	2:1	Black
B-80	7.5	Group 2	3.2:1	Black
B-85	7.5	Group 2	4:1	Black
B-90	7.5	Group 2	7:1	Black

found to contain sodium ion up to 0.38 mEq/g. Thus, it was again washed with successive portions of a 5% ammonium nitrate solution and then with hot distilled water. The amount of sodium ion remaining in the catalyst after washing with ammonium nitrate solution was confirmed to be less than 3 ppm by atomic absorption spectrometry of an HCl extract. The thermal decomposition of the dried precipitate was carried out at 550 to 650°C for 1 hr in the air. All the catalysts prepared are tabulated in Table 1.

Procedure. The infrared spectra were recorded at room temperature with a JASCO IRA-2 double-beam spectrometer. Usually 2 mg of catalyst was mixed with 150 mg of KBr and pressed into a disk (600 kg/cm^2). The disk was usually subjected to heat treatment at 400°C under vacuum in the cell prior to the measurement.

The catalytic activity for ethylene dimerization was determined at 20°C by a conventional static system following pressure change from an initial pressure of 230 Torr. Fresh catalyst sample was used for every run after evacuation at different temperatures for 1 hr. Reaction products were analyzed by gas chromatography with a VZ-7 column at room temperature. The specific surface area was determined by adsorption of N_2 at -196°C.

RESULTS AND DISCUSSION

Effect of pH in Precipitation on Composition and Structure of Catalyst

The precipitation from a mixed $NiSO_4$–Na_2SiO_3 (1:4) solution with sodium hydroxide was terminated at different pH values from 6 to 12.7. This series of catalysts is denoted by symbol A followed by the final pH value as shown in Table 1.

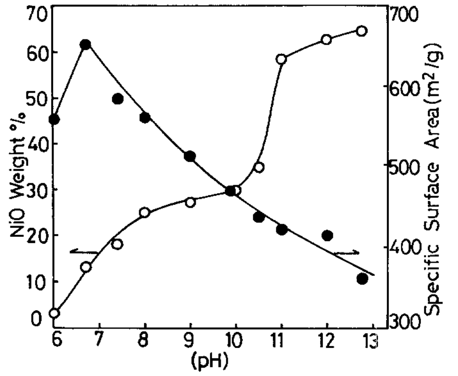

FIG. 1. Nickel oxide content and surface area of A series catalysts as functions of pH in preparation.

Although the composition of starting material was the same, the NiO content increased with increase in pH, particularly at pH values above 6 and 10 as shown in Fig. 1. The change at pH 6 is natural because the precipitation of $Ni(OH)_2$ takes place at this region (*6*), while the change above pH 10 is most likely caused by loss of silica into solution because of a high pH value. Figure 1 also shows that the specific surface area decreases with increase in pH after a maximum at pH 6.7.

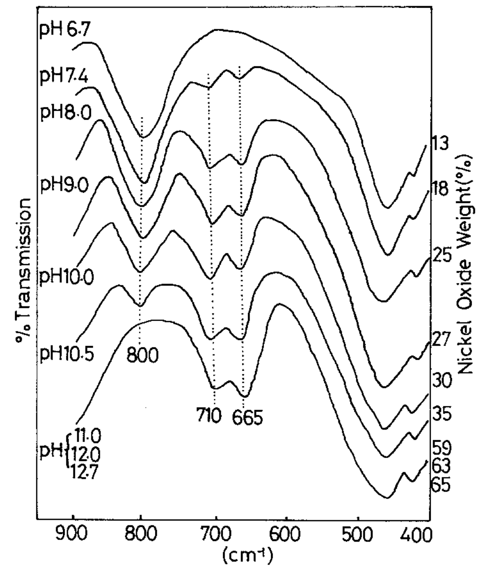

FIG. 2. Infrared spectra of A series catalysts calcined at 550°C.

The structure of catalyst calcined at 550°C was examined by infrared absorption. The ir spectra of catalysts A-6.7 to A-11 are given in Fig. 2. When they are compared with ir spectra of nickel oxide and silica as shown in Fig. 3, it is clear

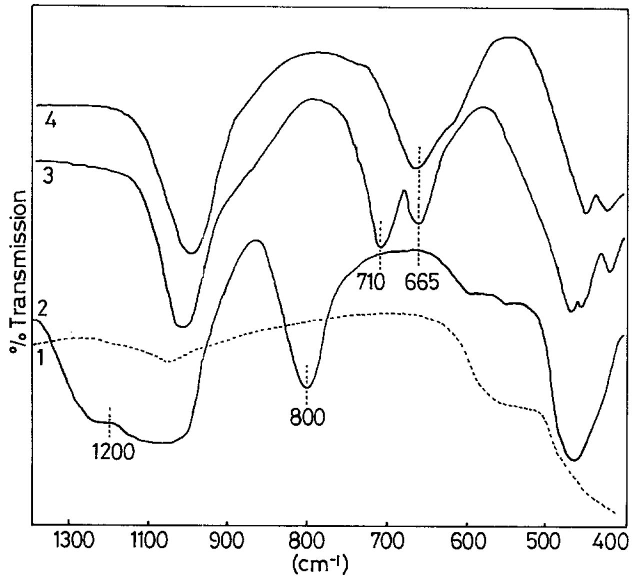

FIG. 3. Infrared spectra of nickel oxide (1), silica gel (2), nickel montmorillonite (3), and nickel antigorite (4).

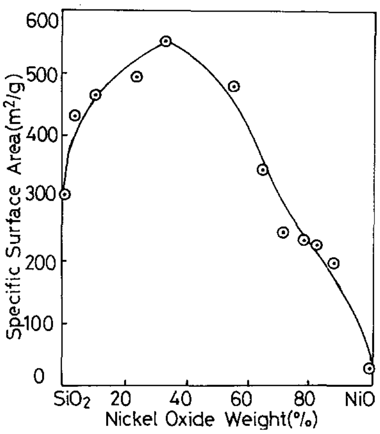

FIG. 4. Variation of specific surface area with composition of B series catalysts.

that new bands are formed at 420, 665, and 710 cm^{-1} except for the catalyst A-6.7, and that the band at 800 cm^{-1} characteristic of silica decreases with increase in pH and is completely lost from A-11. The ir spectra of A-12 and A-12.7 were identical to that of A-11. Thus the enrichment of NiO is evidently caused by dissolution of silica.

Since two types of nickel silicate of layer structure, nickel montmorillonite [$Ni_3(Si_2O_5)_2(OH)_2$] and nickel antigorite [$Ni_3Si_2O_5(OH)_4$], are known (*7*), two samples of nickel hydroxide precipitated on silica gel, which were different in NiO content (I, 24%, and II, 80%), were subjected to hydrothermal treatment at 265 to 270°C (50 to 54 atm) for 30 hr. The sample I was further treated with NaOH solution to remove excessive silica. The X-ray analyses showed that the nickel silicates formed in the samples I and II are, respectively, montmorillonite and antigorite, as evidenced by *d* values of 9.4 and 3.1 Å (mont.), and 7.4 and 3.6 Å (ant.) (*8*).[1] The ir spectra of the two samples are shown in Fig. 3. It is clear that the new bands found with catalysts A-7.4 to A-11 are ascribed to the silicates. Both 710- and 665-cm^{-1} bands have been assigned to Si-O stretching affected by Ni^{2+} for nickel talc and crysotile (*9*).

It is notable in Fig. 3 that the band intensity at 710 cm^{-1} is much stronger than that at 665 cm^{-1} with montmorillonite, while only the 665-cm^{-1} band is observed with antigorite. Thus the two silicates can be distinguished by relative intensities of the two absorption bands. In view of this fact the spectra shown in Fig. 2 seem to show that the nickel silicate formed in the catalyst sample changes from montmorillonite to antigorite as the NiO content of catalyst or the final pH in precipitation increases. In fact, A-8 gave an X-ray diffraction pattern characteristic of montmorillonite, while A-11 gave a broad peak which can be ascribed to antigorite.

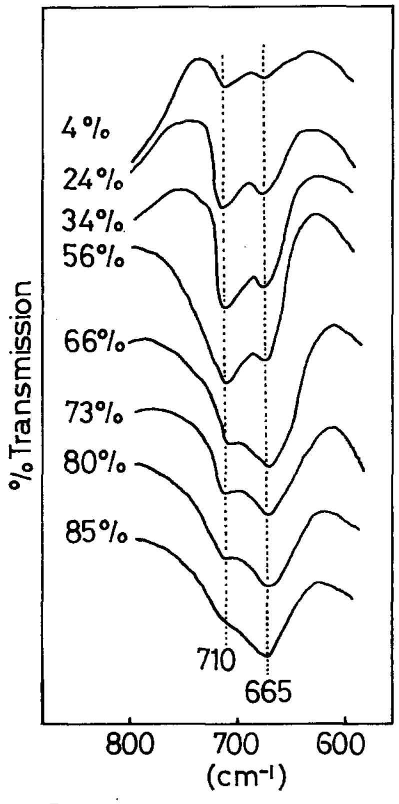

FIG. 5. Infrared spectra of B series catalysts calcined at 550°C.

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[1] Sample I was distinguished from a nickel talc by intense X-ray diffraction lines at 4.5, 2.6, 2.5, and 1.5 Å. The ion exchange capacity of the catalyst preparations as indicated by the presence of unwashable Na^+ is in conformity with a montmorillonite.

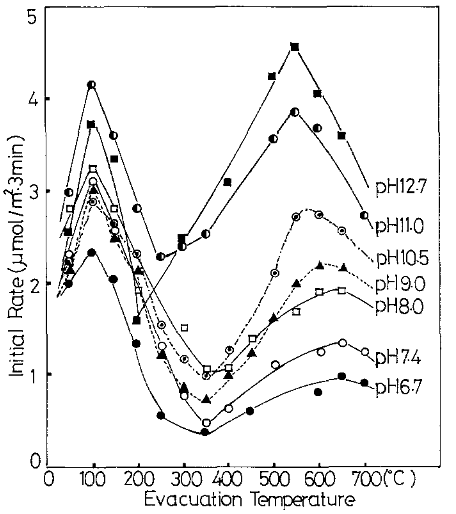


FIG. 6. Variations of initial rate of ethylene dimerization on A series catalysts with evacuation temperature.

In view of the foregoing results, another series of catalysts were prepared starting from different composition of $Ni(NO_3)_2$–Na_2SiO_3–HNO_3 solution in which the concentration of HNO_3 was fixed at 1.5 *N*. The precipitation by sodium hydroxide was terminated at a fixed pH of 7.5. This series of catalysts are denoted by symbol B followed by NiO content (wt%) after calcination. The compositions of starting mixture are given in Table 1.

As shown in Fig. 4, the specific surface area of B series of catalysts attains a maximum at 34% NiO, while the maximum for A series of catalysts lies at 13% NiO. Infrared spectra of B series of catalysts calcined at 550°C are shown in Fig. 5. It is seen that the relative intensity of the 710-cm^{-1} band to the 665-cm^{-1} band changes markedly between B-56 and B-66, indicating a change in the silicate species from montmorillonite to antigorite. Since NiO content in the antigorite is 65%, the changes at around this composition is quite reasonable. In fact the change in predominant species was confirmed by X-ray analyses.

Thus it may be concluded that the nickel silicate species formed in the precipitate changes from montmorillonite to antigorite as the nickel oxide content increases, and that the change can be monitored by ir spectra of calcined sample. When the spectra shown in Fig. 5 are compared with those in Fig. 2, it appears that although both A and B catalysts contain more or less both of the silicates, B catalysts are purer with respect to the silicate species contained. This would be caused by the low pH value adopted in the preparation of B catalysts, since the precipitate formed at a high final pH should be contaminated with that formed at a lower pH.

The variations of specific surface area as shown in Figs. 1 and 4 suggest that the silicate formation results in increase in the specific surface area while the formation of montmorillonite gives rise to higher surface area than that of antigorite.

Effect of Catalyst Composition on Ethylene Dimerization Activity

In Fig. 6, the ethylene dimerization activities per surface area of A series of catalysts are plotted against the evacuation

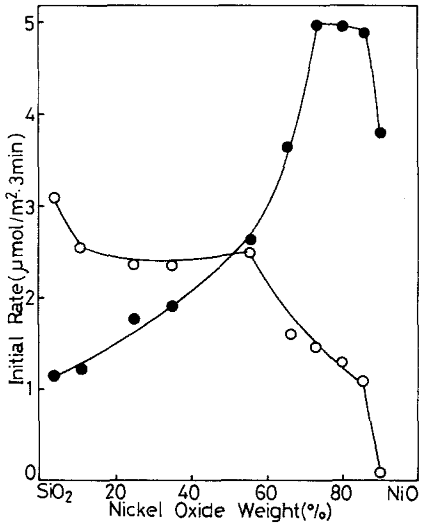


FIG. 7. Variations of initial rate of ethylene dimerization with composition of B series catalysts. ○, evacuated at 100°C; ●, evacuated at 600°C.

temperature at which the catalyst was pretreated for 1 hr. All of these catalysts exhibit two maxima of dimerization activity at 100°C and at 550 to 650°C, and a minimun at 200 to 350°C as reported previously (*1*, *4*). It is notable that the value at the second maximum is more extensively affected by the final pH in the catalyst preparation. Although the increase in final pH gives rise to the formation of antigorite, it is accompanied by an increase in nickel oxide content. Thus the effect of nickel oxide content on the activity variation should be examined. The B series of catalysts would be more relevant to this question since these catalysts are prepared at a fixed final pH of 7.5.

The specific dimerization activities per surface area of B catalysts activated at two optimum temperatures, 100 and 600°C, are given as functions of nickel oxide content (wt%) in Fig. 7. It is disclosed that there are two regions of catalyst composition below 60% and above 70%, in which one of the specific activities remains almost constant irrespective of nickel oxide content. In other words, the catalytic activity is proportional to surface area in that region, suggesting two different active substances on the catalyst surface depending on the region. Indeed the two regions mentioned above coincide with the regions in which montmorillonite or antigorite is predominantly formed as demonstrated by the results shown in Fig. 5.

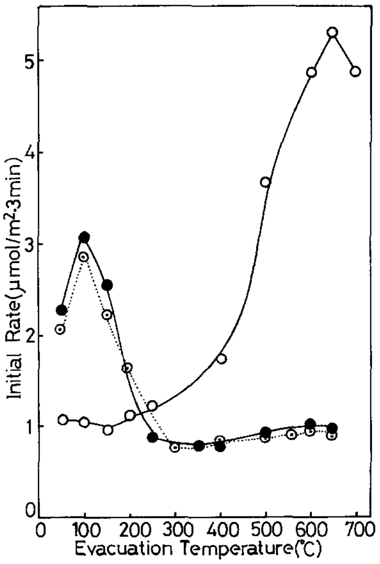


FIG. 8. Variations of initial rate with evacuation temperature. ●, B-4 catalyst; ⊙, hydrothermally synthesized catalyst (sample I); ○, B-85 catalyst.

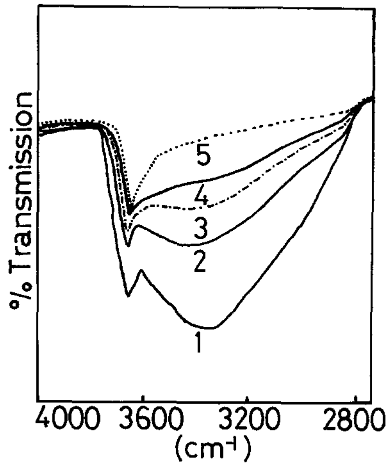
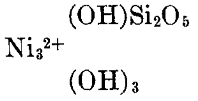


FIG. 9. Hydroxyl absorption by A-11 catalyst evacuated at room temperature (1), 100°C (2), 200°C (3), 300°C (4), and 400°C (5) for 1 hr, respectively.

Possible structure of active sites

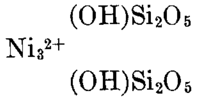
It is suggested by the above results that there are two types of active sites which are closely related to the two nickel silicates. The montmorillonite-type (Type M) sites are activated by evacuation at above room temperature up to 100°C, while the antigorite-type (Type A) sites are activated above 250°C up to about 600°C. If this is the case, the twin peak activation curve as shown in Fig. 6 should be simplified by purifying the active sites. Indeed, the hydrothermally synthesized catalyst (sample I montmorillonite) exhibits a single peak as shown in Fig. 8. Catalysts B-4 and B-85 also exhibit single but different maxima at 100 and 650°C, respectively. Although B-4 and sample I are different in NiO content, the specific activities are strikingly in agreement, suggesting a similar concentration of same active sites on the surface. It is reasonable that the low nickel oxide content in B-4 gives rise to little chance to form antigorite, resulting in exclusive formation of montmorillonite, while in B-85 antigorite is exclusively formed because of the high nickel oxide content.

It is thus very likely that there are two types of active sites, and that the difference in their optimum activation temperatures is traced back to the difference in silicate structures. In the structure of antigorite, one silica layer of the type $(Si_2O_5)^{2-}$ is combined with an octahedral layer of the type $Ni_3^{2+}(OH)_6$, while in montmorillonite, one octahedral layer is sandwiched between two silica layers, in conformity with the formulas:



$$\begin{array}{ll} & (OH)Si_2O_5 \\ Ni_3^{2+} & \\ & (OH)_3 \end{array}$$

antigorite



$$\begin{array}{ll} & (OH)Si_2O_5 \\ Ni_3^{2+} & \\ & (OH)Si_2O_5 \end{array}$$

montmorillonite

Thus the OH groups bound to Ni^{2+} are located inside the silica layers of montmorillonite, while in antigorite, they are mostly exposed to the basal plane. Although it is uncertain whether active sites are formed on basal planes or on edge planes, the above difference in the coordination states of the nickel ion should give rise to the observed difference in activation temperature.

The activation of NiO or NiO–SiO$_2$ catalysts by evacuation at elevated temperatures is known to be caused by surface dehydration (*1*, *4*, *10*). In this connection it is to be noted that the activation of type A sites requires temperatures above 230°C, the decomposition temperature of $Ni(OH)_2$, in contrast to the lower temperatures required for the type M sites. It is suggested that removal of the OH group from the nickel ion is required to activate the type A sites. The lower activation temperature for the type M sites suggests that the type M sites are covered with water molecules when they are exposed to ambient atmosphere. It is reasonable that the adsorbed water is removed by evacuation at around 100°C.

Figure 9 illustrates the variation of ir absorption by A-11 catalyst with evacuation at increasing temperatures. The broad band at around 3300 cm^{-1}, ascribable to adsorbed water and hydroxyls, is mostly removed by evacuation at 400°C, while the sharp band at 3645 cm^{-1}, usually observed with $Ni(OH)_2$, remains even after evacuation at 400°C. (Evacuation at 500°C or above could not be made in the ir cell.) Since the 3645-cm^{-1} band was also observed with montmorillonite, the 3645-cm^{-1} band for the evacuated catalyst should be the lattice OH located inside the silica layers. The results given in Fig. 9 are not very revealing but qualitatively in agreement with the above speculation.

Since the active species for the dimerization is likely made up of an acidic component and nickel ion as mentioned, the possible relevance of nickel silicate in giving acidic properties should also be discussed. This subject will be treated in a forthcoming paper, explaining why the activity of the type M site decreases by activation above 100°C.

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