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The Selective Isomerization of *n*-Hexane over Nickel on Silica–Alumina Catalysts

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The isomerization of *n*-hexane to branched chain isomers has been investigated over a range of nickel on silica–alumina catalysts containing between 5 and 16% nickel by weight. It is found that a 7% Ni catalyst has a high activity and selectivity for isomerization, but that catalysts containing more than about 10% Ni produce methane as the main product at temperatures above 633 K. The 7% Ni catalyst has an activity and selectivity which is comparable to a commercial platinum catalyst operating under the same experimental conditions. Hydrogen reduction experiments show that the nickel is present as zerovalent nickel, but X-ray and magnetic measurements do not correspond to bulk nickel metal. It is suggested that the active site in the 7% Ni catalyst is a zerovalent nickel atom probably attached to an aluminium ion. A mechanism is proposed for the isomerization reaction in which a nickel atom first abstracts a hydride ion from a hydrocarbon molecule forming a secondary carbonium ion, which then isomerizes to a tertiary carbonium ion on an adjacent oxide ion, before, finally, addition of the hydride ion gives the saturated isomer.

INTRODUCTION

The conversion of straight-chain hydrocarbons into branched-chain isomers is an important industrial process used to increase the octane number of petroleum. The reaction is catalyzed by bifunctional catalysts, e.g., platinum or palladium metal combined with an acidic oxide (*1*, *2*). Weisz (*1*) has shown that the mechanism involves dehydrogenation of the hydrocarbon to an olefin on a metal site, transfer of the olefin via the gas phase to an acidic oxide site where the olefin is isomerized by a carbonium-ion mechanism, and return of the isomerized olefin to a metal site where finally it is hydrogenated to a saturated isomer. With Pt catalysts, providing the Pt content of the catalyst is greater than about 0.3% by weight, the rate-determining step is isomerization at the acidic site. The overall activity of the catalyst can be enhanced by using more acidic oxides (*2*).

The choice of the metallic component of a bifunctional catalyst has in the past been restricted to Pt or Pd. This choice has been governed by the recognition that each individual metal has characteristic properties in hydrocarbon reactions. Both Pt and Pd are very efficient at hydrogenation and dehydrogenation reactions, and both metals have little tendency to produce undesirable cracked products. Consequently, most development work on isomerization and reforming catalysts has concentrated on modifying and improving existing platinum catalysts. This work has resulted in the development of a family of bimetallic reforming catalysts, of which Pt/Re catalysts are the most important.

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Much less attention has been given to the possibility of using metals other than Pt or Pd in isomerization catalysts. Nickel, for example, has not been investigated because it is known that metallic nickel has a very high tendency to cause complete hydrocracking of hydrocarbons to methane. However, it is now known that interactions between a metal and an "inert" support can result in a catalyst whose properties are substantially different from those of the pure metal. For example, even platinum, which normally interacts only weakly with any type of support, has been found (*3*) to interact with titania supports in such a way as to alter significantly the capacity of the Pt to chemisorb hydrogen. Nickel interacts strongly with oxygen supports (*4*). Therefore, it is to be expected that under the correct conditions unusual chemical properties may be obtained with supported nickel catalysts.

This paper presents some results of an investigation into the selective isomerization of *n*-hexane at atmospheric pressure over a range of nickel catalysts supported on an acidic silica–alumina support.

EXPERIMENTAL METHODS

Catalysts. Catalysts containing 5, 7, 10, 13, and 16% by weight nickel were prepared by impregnating a silica–alumina support (Akzo Chemie N.V., fluid cracking catalyst, 14% Al_2O_3; surface area, 612 m^2 g^{-1}; pore volume, 0.73 cm^3 g^{-1}) with solutions containing the appropriate concentration of nickel nitrate. The prepared catalysts were dried and decomposed to the oxide form by heating in air from room temperature to 570 K over a period of 1.5 hr. The catalysts were cooled to room temperature and stored in sealed glass bottles until required.

A 7% Ni/Al_2O_3 catalyst was prepared by the same method using an alumina support (Akzo Chemie N.V.; surface area, 358 m^2 g^{-1}).

To determine the characteristic activity and selectivity of nickel metal under our experimental conditions, a sample of nickel nitrate was decomposed and reduced *in situ* in the catalytic reactor used for the continuous flow experiments. A 2.9% Ni on silica catalyst, supplied by the Climax Molybdenum Co. Ltd., was also investigated for a similar reason. To establish a comparison with conventional isomerization catalysts, data were also obtained on a 0.5% Pd/zeolite, a 0.5% Pt on fluoride-treated alumina, and a high surface area Mo/MoO_2 catalyst, all supplied by the Climax Molybdenum Co. Ltd.

Supported catalysts were activated prior to the catalytic experiments by reduction for 16 hr at 770 K in flowing hydrogen (GHSV = 500 cm^3 hydrogen/cm^3 catalyst/hr).

Catalytic experiments. Continuous flow experiments were performed using a conventional glass apparatus operating at atmospheric pressure. The hydrogen/hexane mixture used (H_2/hexane = 4) was obtained by passing hydrogen through two bubblers the second of which was thermostatted at the temperature necessary to give the required hexane vapor pressure. The catalyst (3-cm^3 samples) was supported on a glass sinter sealed into a 1-cm-bore Pyrex glass U-tube. Glass beads placed above the sample served as a preheater for the reaction mixture. The U-tube reactor was immersed in a salt bath which gave very steady temperatures over the whole catalyst bed. The hydrogen/hexane mixture was passed downstream through the catalyst bed, and the product gases were analyzed on a Perkin–Elmer F33 gas chromatograph coupled to an Infotronics CRS 308 electronic integrator.

Pulse experiments were performed on a separate microreactor in which 0.2-g samples of catalyst were placed in a 6-mm-bore glass U-tube. Heating was by means of a small wire wound electric furnace, and temperatures were determined to 1 K with a chromel–alumel thermocouple placed

TABLE 1

Activity and Selectivity of Various Catalysts for the Isomerization of *n*-Hexane[a]

Catalyst	Activity[b] (%)	Selectivity[c] (%)	Methane[d] (%)	Temperature (K)
Ni powder	3	0	97	603
2.9% Ni-SiO$_2$[e]	55	0	97	603
7% Ni-Al$_2$O$_3$	0.1	—	—	603
5% Ni-SiO$_2$/Al$_2$O$_3$	2	86	0.2	603
7% Ni-SiO$_2$/Al$_2$O$_3$	40	95	0.7	623
16% Ni-SiO$_2$/Al$_2$O$_3$	33	19	17	548
Mo/MoO$_2$[e]	43	98	0.1	603
Pd/zeolite[e]	48	91	0.2	603
Pt/F$^-$-Al$_2$O$_3$[e]	31	93	0.4	603

[a] Conditions: pressure 1 atm; LHSV = 1.0 (cm^3 hexane)(cm^3 catalyst)$^{-1}$ hr^{-1}; Hydrogen/hexane = 4; sample volume, 3 cm^3.

[b] Activity (%) = [(hexane reacted)/(hexane initial)] × 100.

[c] Selectivity (%) = [(C$_6$ isomers)/(hexane initial)] × 100.

[d] Methane as a percentage of the total products.

[e] Catalysts supplied by the Climax Molybdenum Co. Ltd.

in a thermocouple well close to the sample. Pulses of 1 μl of *n*-hexane were injected into a continuous flow of hydrogen passing down through the sample, and the products were analyzed as before. Measurements were obtained with the catalyst heated to 603, 633, 663, and 693 K.

X-Ray and magnetic measurements. X-Ray powder patterns were obtained on reduced nickel on silica–alumina catalysts using a Debye–Scherrer powder camera with copper $K\alpha$ radiation. Magnetic susceptibility data were obtained by the Faraday method. Physical mixtures of Ni powder and silica–alumina were used for calibration purposes.

RESULTS

Flow Experiments

The results of the continuous flow experiments are given in Table 1. The activity and selectivity data correspond to a time "on stream" of 2 hr. A constant time "on stream" is chosen because the activity of all the samples decays with time, particularly during the first few minutes. The nickel powder and the 2.9% Ni on silica (N2.9-Si) catalysts exhibit the behavior which is characteristic of nickel catalysts (*5–9*). Neither catalyst produces any significant amount of isomerization products. Both catalysts produce methane almost exclusively as the hydrogenolysis products. The only difference between the two catalysts is the activity which, of course, is much higher for the supported (more highly dispersed) nickel.

The 7% Ni on alumina (N7-Al) catalyst, on the other hand, is almost completely inactive under the same conditions. We interpret this to mean that this catalyst does not contain bulk metallic nickel.

The silica–alumina-supported catalysts have a completely different activity and selectivity to either the silica-supported or the alumina-supported catalysts. The 5% Ni catalyst (N5-SiAl) has a very low activity but quite a high selectivity for isomerization, and very little tendency to form methane. The 7% Ni catalyst (N7-SiAl) has a much higher activity (note, however, the higher temperature used) and a very high selectivity. Catalyst (N16-SiAl), even at 548 K, has a high activity but a low selectivity, and a moderate tendency to form methane.

These results may be compared with similar data obtained on the same apparatus for a high surface area Mo/MoO_2 catalyst (*12*) and two commercial catalysts, a palladium on rare earth-exchanged zeolite, and platinum on a fluoride-treated alumina. All three of these catalysts have activities and selectivities which are characteristic of the metals. We note that the catalyst (N7-SiAl) has a selectivity and activity comparable to a platinum reforming catalyst.

Pulse Experiments

The results of the pulse experiments are summarized in Figs. 1–4. The detailed product distributions obtained with the four catalysts are given in Table 2. In all cases the experimental points correspond to the average of three or four pulse experiments. Figure 1 shows the variation in activity and selectivity with nickel content of the catalyst at one representative temperature (603 K). The activity rises very sharply with nickel content above 7% Ni and reaches a maximum of 92% conversion at 13% Ni before decreasing to 78% at 16% Ni. This decrease occurs because both the nickel and the oxide support form cracked products. The oxide forms propane by cracking a C_6 molecule at a central carbon atom; the high activity of the 13% Ni catalyst is partly due to the high concentration of propane in the products (27.5% as compared with 16% for the 16% Ni catalyst).

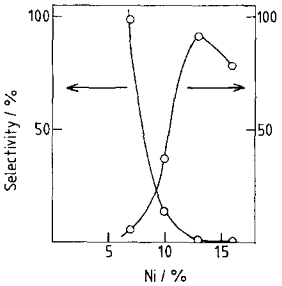


FIG. 1. Activity and selectivity as a function of nickel content for n-hexane isomerization over nickel/silica–alumina catalysts at 603 K.

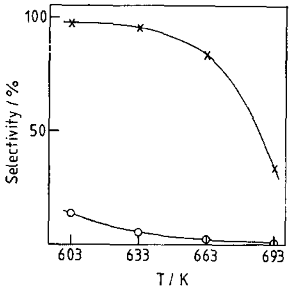


FIG. 2. Selectivity as a function of temperature for n-hexane isomerization for catalysts N7-SiAl (×) and N10-SiAl (○).

The selectivity for isomerization reactions falls very sharply between 7 and 10% Ni, mainly as a consequence of the higher activity of the 10% Ni catalyst for the methanation reaction (13.7% as compared with 0.2%). The results for the pulse experiments in Fig. 1 are consistent with the data from the flow experiments in Table 1 for the N5-SiAl, N7-SiAl, and N16-SiAl catalysts. In both cases the high nickel content catalyst has a low selectivity for isomerization. On the other hand, all the information points to the 7% Ni catalyst having unusual and interesting properties.

Further results comparing the 7 and 10% Ni catalysts are shown in Fig. 2, which illustrates the effect of temperature on the selectivity of the two catalysts. The 10% Ni catalyst has a low selectivity which further decreases slowly with increasing temperature. The 7% Ni catalyst has a high selectivity which remains fairly constant up to 633 K, but then decreases rapidly at higher temperatures.

The product distributions obtained for the 7 and 10% catalysts at various temperatures are shown in Figs. 3 and 4, respectively. The concentration of C_6 isomers falls in parallel with the fall in selectivity, (see Fig. 2). However, the

TABLE 2

Product Distributions (%) from Pulse Experiments

	7% Ni				10% Ni				13% Ni				16% Ni			
	603[a]	633	663	693	603	633	663	693	603	633	663	693	603	633	663	693
CH_4	0.2	0.1	0.8	4.7	13.7	42.1	75.5	94.5	36.2	86.0	96.6	98.9	49.9	85.5	96.7	99.0
C_2H_6	0.6	0.1	0.3	1.3	1.3	4.1	2.9	0.0	18.7	6.6	0.0	0.0	21.0	4.5	0.0	0.0
C_3H_8	1.0	2.8	10.7	41.0	7.2	14.9	7.4	2.5	27.5	9.4	2.3	0.6	16.0	6.1	2.2	0.7
$(CH_3)_2CHCH_3$	0.0	0.3	1.0	4.2	4.4	4.2	1.2	0.2	3.5	0.9	0.1	0.0	1.9	0.6	0.1	0.0
C_4H_{10}	0.0	0.3	1.0	7.3	18.8	13.3	5.3	1.7	10.8	3.0	0.7	0.3	7.2	2.2	0.7	0.2
$(CH_3)_2CHC_2H_5$	0.0	0.5	1.4	4.0	15.1	3.7	1.6	0.5	0.8	0.2	0.0	0.0	0.8	0.2	0.1	0.0
C_5H_{12}	0.0	0.5	1.4	4.0	26.6	12.1	3.7	1.1	2.2	0.6	0.2	0.1	2.8	0.8	0.2	0.1
$(CH_3)_3CC_2H_5$	2.0	2.3	2.3	1.1	0.8	0.2	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$(CH_3)_2CHC_3H_7$	63.7	60.9	51.9	22.8	8.2	3.6	1.5	0.5	0.1	0.1	0.0	0.0	0.3	0.8	0.0	0.0
$C_2H_5(CH_3)CHC_2H_5$	32.4	32.1	28.8	9.5	4.2	1.8	0.8	0.3	0.1	0.0	0.0	0.0	0.1	0.0	0.0	0.0
Activity (%)	5.0	7.5	11.1	4.5	36.9	37.0	42.0	48.4	91.5	90.5	86.3	87.9	78.0	83.7	92.4	93.3
Selectivity (%)	98.2	95.3	83.1	33.5	13.2	5.7	2.4	0.7	0.2	0.1	0.0	0.0	0.4	0.8	0.0	0.0

[a] Temperatures (°K).

interesting point here is that the decrease in selectivity is matched by an increase in the concentration of propane. Since it is probable that both the isomerization and the propane-forming reactions occur on acidic sites on the oxide, it would appear that as the temperature is raised there is a greater tendency for cracking to occur rather than isomerization. It is also interesting that methane (which probably originates on the nickel) constitutes only about 5% of the products even at 693 K.

The product distribution for the 10% Ni catalyst is quite different (Table 2). At 603 K the largest single product is isopentane followed by isobutane. Clearly a considerable amount of isomerization still occurs, but the increased methanation activity of the catalyst results in the removal of one or two CH_4 molecules from the original C_6, or isomerized C_6 molecules. The methane concentration increases sharply with temperature. This presumably accounts for the fact that the propane concentration first increases, due to the increasing activity of the oxide, but then decreases at higher temperatures.

The product distributions for the 13 and 16% Ni catalysts (Table 2) show the high preponderance of cracked products, even at 603 K, and the overwhelming tendency toward the formation of methane at the higher temperatures.

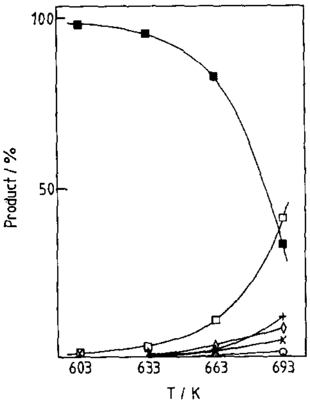


FIG. 3. Product distribution as a function of temperature for catalyst N7-SiAl. ×, C_1; ○, C_2; □, C_3; +, C_4; ◇, C_5; ■, C_6.

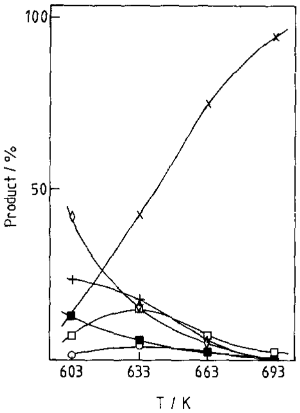


FIG. 4. Product distribution as a function of temperature for catalyst N10-SiAl. For key to symbols, see Fig. 3.

Effect of Calcination on Catalytic Activity

In order to investigate the effect of mild calcination on the activity of the 7% Ni catalyst, a sample was calcined in air in the reactor for 2.5 hr. It was then cooled to room temperature, flushed with hydrogen, and heated to 603 K, and its activity was measured. It was found that the calcination treatment had caused the activity to increase by almost 50%, while the selectivity remained almost constant at 97%.

X-Ray and Magnetic Measurements

X-Ray powder photographs were obtained on reduced samples containing 7, 10, and 16% Ni. By comparison with a reference sample containing 3% Ni powder and 97% silica–alumina it was established that the powders examined contained very little detectable metallic nickel. No indication of nickel oxide was observed, so it is assumed that although no particular precautions were taken to prevent re-oxidation of the reduced catalysts by exposure to air, little bulk oxidation can have occurred. The 7% Ni sample gave no clear lines at all. The 10 and 16% Ni samples gave diffuse lines, the positions of which corresponded to metallic nickel. The line intensities, measured with a microdensitometer, corresponded to about 1% metallic nickel in the 10% nickel sample, and about 1.5% metallic nickel in the 16% sample.

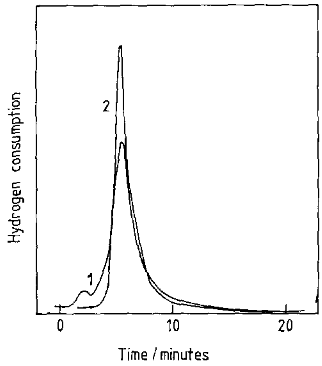


FIG. 5. Reduction curve for uncalcined (curve 1) and calcined (curve 2) catalyst N7-SiAl.

The magnetic susceptibility of the reduced samples was determined using the Faraday method. Once again comparison with a nickel powder showed that very little bulk nickel was present in the reduced (and then air-exposed) samples. The results corresponded to about 0.5% metallic nickel in the 10% Ni sample and 1.2% metallic nickel in the 16% sample.

Reduction Characteristics of the 7% Ni on Silica-Alumina Catalyst

Samples of uncalcined and calcined (2.5 hr at 823 K in air) catalyst (N7-SiAl) were reduced at 770 K in an argon/25% hydrogen stream, and the hydrogen consumed in the reduction was monitored using a thermal conductivity detector. The reduction curves are shown in Fig. 5. The uncalcined sample contains a small peak before the main peak corresponding to about 4 to 5% of the total area of the reduction curve. It is also different from the calcined sample in having a lower peak maximum and a broader, more pronounced tail. The area under the curve for the calcined sample corresponds to 104% reduction (a value above 100% probably arises from calibration errors), and for the uncalcined sample corresponds to 98% reduction. In both cases reduction is almost complete within about 10 min. Clearly the long reduction times used in the earlier experiments were unnecessary. We see that in both these catalysts the divalent nickel is very easily reduced to zerovalent nickel. However, the X-ray data, the magnetic data, and the catalytic properties do not correspond to the presence of metallic nickel in bulk form. We shall discuss these results in more detail later.

DISCUSSION

The tendency for bulk metallic nickel to convert hydrocarbons selectively into methane is well known (*5–9*), and is confirmed under our experimental conditions by the results for a nickel powder catalyst and a nickel on silica catalyst (Table 1). The nickel on silica catalyst shows the extent of hydrogenolysis to methane which is possible even with a very low loading of nickel on a support which is essentially inert. We presume that this catalyst must also contain bulk nickel; that is, nickel particles which are large enough to have the properties characteristic of the bulk metal.

The nickel on alumina catalyst, in complete contrast, has virtually no activity for hydrogenolysis or for isomerization under the same experimental conditions. We conclude that this catalyst does not contain bulk nickel, otherwise a large amount of methane should have been produced. Isomerization over any of these oxide-supported catalysts almost certainly occurs by a bifunctional mechanism. With the nickel on alumina catalyst isomerization does not occur either because the catalyst does not contain sufficiently acidic sites, or because the nickel is inactive for dehydrogenation and hydrogenation reactions. The problems associated with the reduction of alumina-supported nickel are well known (*4, 10, 11*). However, some reduction to metallic nickel would have been expected for a catalyst which had not been precalcined in air at high temperatures. Our main concern is with the nickel on silica-alumina supports, so suffice it to say at this stage that very contrasting behavior is observed between Ni/SiO_2 and Ni/Al_2O_3 catalysts.

Consider now the Ni on silica–alumina and Ni on silica catalysts. The rate of methane formation (Tables 1 and 2), taken as the activity multiplied by the methane concentration, increases in the order N5-SiAl < N7-SiAl < N16-SiAl < N2.9-Si, with the activity increasing by a factor of 10^4 between N5-SiAl and N2.9-Si. We consider it most unlikely that this very large difference in activity for the formation of methane could occur if the N5-SiAl catalyst contained bulk metallic nickel. Similarly, the N7-SiAl catalyst must contain only a very small amount of metallic nickel. The N16-SiAl catalyst, on the other hand, has quite a high activity for the formation of methane even at fairly low temperatures (548 K), so we suspect that this catalyst contains a small amount of metallic nickel.

It is clear that catalysts containing around 5 to 10% Ni on silica–alumina have unusual catalytic properties. They have very low methanation activities, comparable, in fact, to a commercial Pd or Pt catalyst (Table 1).

Figure 1 shows that above 10% Ni the selectivity for the isomerization reaction decrease rapidly. Table 2 shows that this occurs because of the rapidly increasing methanation activity rather than because of a loss of isomerization activity. Thus, with the 10, 13, or 16% nickel there is a significant concentration of branched C_4 or C_5 isomers. We interpret this to mean that with all four catalysts isomerization is occurring quite rapidly, but with catalysts containing more than 10% Ni the rate of formation of methane from any other hydrocarbon is very high, so that methane becomes the major product for the 13 and 16% catalysts. The stepwise nature of methane formation from higher hydrocarbons is evident from the data at 603 K for the 16% Ni catalyst. The product concentrations decrease in the order $C_1 > C_2 > C_3 > C_4 > C_5 > C_6$.

Further information concerning the nature of the reactivity of the 7 and 10% Ni catalysts can be obtained from Figs. 3 and 4. The selectivity of the 7% catalyst decreases with increasing temperature. However, this is mainly because of an increase in the concentration of propane formed. We expect that the propane originates from a hydrocracking reaction on acidic oxide sites. Such central scission of hydrocarbon molecules is characteristic of an oxide-catalyzed hydrocracking reaction, but is not expected to occur on a metallic nickel catalyst. Under conditions of higher pressure where such hydrocracking reactions are suppressed we would expect that the 7% catalyst would continue to have a high selectivity for isomerization reactions even at high temperatures.

In contrast, the decreased selectivity observed with the 10% catalyst (and also with the 13 and 16% catalysts) is due almost entirely to the rapid increase in the rate of formation of methane. Clearly the 7% catalyst is fairly unique. The question which remains is why should a nickel catalyst have a very low activity for methanation? The relevant data concerning this catalyst are as follows: The support is 86% SiO_2 and 14% Al_2O_3, and has a surface area of 612 $m^2\ g^{-1}$. The nickel loading is 7% by weight. Reduction of the nickel is complete in a few minutes at 770 K. Neither X-ray nor magnetic measurements conform to metallic nickel.

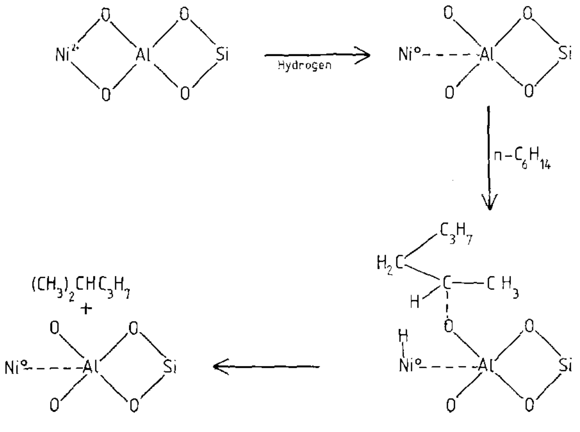
The surface area (which corresponds to 569 $m^2\ g^{-1}$ assuming that the nickel does not significantly increase the surface of the support) and the Ni loading correspond to 79 $Å^2$ per Ni atom, assuming a random distribution of Ni atoms over the whole surface. It is possible that the stronger interaction between Ni^{2+} and Al_2O_3 results in the selective adsorption of Ni at aluminium sites in the lattice which make up 14% of the surface area. In this case each Ni ion would be allocated about 11 $Å^2$, more than sufficient, since the alumina itself is dispersed throughout the SiO_2

matrix, for all the nickel ions to be initially, at least, adsorbed on isolated surface sites. Each Ni ion would be separated from other Ni ions by several atomic distances. On reduction with hydrogen, Ni^0 atoms are formed, judging by the quantity of hydrogen consumed. These atoms would not be expected to be stable as isolated atoms, and migration leading to clustering and crystallite formation should occur at the temperatures used for reduction (770 K). However, the evidence (X-ray, magnetic, catalytic selectivity) is that bulk nickel is not present. Therefore, we must assume that if Ni crystallites are formed, they are so small that they do not have the properties of bulk metal.

There has been much interest in recent years (*13–20*) in the properties of very small metal particles, particularly in the size range 10 to 50 Å. Boudart (*17*) has reviewed the evidence that the specific activity of a metal for a given reaction may depend on the particle size of the metal. He has introduced the terms *structure-sensitive* or *demanding* to describe reactions where a crystallite size effect is observed, and *structure-insensitive* or *facile* for reactions where no such effect is found. Oliver *et al.* (*21*) have argued that the hydrogenation of butadienes on Ni catalysts is structure-sensitive, and Coenen *et al.* (*22*) have found a similar effect for benzene hydrogenation over nickel. However, it has also been pointed out (*23*) that the maximum variation in activity with crystallite size is less than a factor of 10. In our catalysts the activity for methane formation varies by a factor of 10^4. Consequently, we do not consider it likely that the observed variations are caused by a particle size effect.

The unusual properties of the nickel in our 7% catalyst may arise because of interaction with the support. Other workers have suggested that the catalytic properties of metals can be modified by the support. In the particular case of Ni/Al_2O_3 methanation catalysts, Ross (*8*) has suggested that there are two forms of nickel: metallic (bulk) nickel which gives methane from CO/H_2 mixtures, and nickel associated with the support which gives higher hydrocarbons. There is an obvious parallel between our catalyst, which has a very low activity for methane formation, and Ross's type 2 nickel, which forms higher hydrocarbons rather than methane.

It is interesting, as Clarke has pointed out (*24*), that olefin hydrogenation seems to occur on single metal sites, whereas alkane hydrogenolysis requires two contiguous sites. On this basis it is possible that isolated zerovalent nickel, attached to aluminium sites on the support, is responsible for the dehydrogenation/hydrogenation part of the isomerization reaction, but cannot effectively catalyze hydrogenolysis. A possible way in which this could occur is shown in Scheme 1.



In the first step divalent nickel is reduced by hydrogen to zerovalent nickel. This is bound either to an oxygen ion, as suggested by Ross (*8*), or possibly directly to an aluminium ion. The nickel abstracts a hydride ion from an *n*-hexane molecule, which then undergoes isomerization via a carbonium-ion mechanism on an adjacent oxygen ion. The transfer of the hydride ion back to the tertiary carbonium ion produces the saturated branched isomer which desorbs into the gas phase. This mechanism, although plausible, awaits confirmation. Further work is in progress to elucidate the nature of the active nickel in this catalyst.

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