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Support Effects in Nickel Catalysts

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Silica- and silica–alumina-supported Ni catalysts have been prepared by wet impregnation, and their activities determined for the isomerisation and hydrogenolysis of n-hexane, for the hydrogenation of benzene, and for the CO/H_2 reaction. The results show that the Ni/SiAl catalysts have normal activities for the hydrogenation of benzene and for the CO/H_2 reaction, but that their activity for the hydrogenolysis of hexane is much lower than that of an equivalent silica-supported catalyst. Possible reasons for the suppression of hydrogenolysis activity over Ni/SiAl catalysts are considered. Contamination of the metal surface by sulphur from the support is excluded for a number of reasons. It is concluded that due to the influence of the support the Ni particles are modified either electronically or structurally. Comparison with Ni/titania catalysts shows that it is possible by varying the support to prepare Ni catalysts having normal activities for the hydrogenation of benzene which, on the one hand, have unusually low activities for hydrogenolysis reactions (Ni/SiAl), or, on the other hand, have unusually high activities for the CO/H_2 reaction (Ni/Ti). It is suggested that for catalysts where a metal-support interaction may operate, the use of benzene activity data rather than hydrogen chemisorption data may offer a more reliable method of determining specific activities, and hence of determining the extent of metal-support effects.

INTRODUCTION

High surface area supports, usually oxides, are used extensively in industry for the preparation of metal catalysts. The traditional view of the support is that of a passive, inert carrier, whose sole function is to improve the efficiency of the metal catalyst by increasing the dispersion and stability of the metal particles. Gradually, it has emerged that the support may play a more active role (*1*). In fact, various authors some 25 years ago had demonstrated that altering the semiconducting properties of a support affected the catalytic activity of metals (see, e.g., Ref. (*2*) and references therein), but this work received little attention until recently when there was a resurgence of interest in metal-support effects, stimulated by reports that metals supported on transition metal oxides could have unusual properties (for a summary, see Ref. (*3*)).

In the specific case of nickel catalysts, Taylor *et al.* (*1*) have found that the activity of silica–alumina-supported nickel is much lower than silica-supported nickel for the hydrogenolysis of ethane. We have previously reported (*4*) that when supported on a very high surface area acidic silica–alumina, nickel loses the capacity to convert hexane into smaller hydrocarbons. However, the same catalyst retains its activity for hydrogenation and dehydrogenation reactions, since it is observed that the isomerisation of hexane continues unabated over catalysts which are inactive for hydrogenolysis. These unusual properties were attributed also to a metal-support interaction. It was tentatively suggested that the nickel was preferentially adsorbed at aluminum sites on the surface of the support, with the result that very small nickel particles (approaching monodispersion) were produced. It was suggested that these nickel particles were too small to have bulk properties, and so the hydrogenolysis reaction, which is very sensitive to changes in the properties of a metal, was inhibited.

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Hydrogenation, which is an insensitive reaction, would be much less affected, and so the observed changes in selectivity could be accounted for.

When a catalyst is found to be less active than anticipated there is always a concern that the effect is caused by contamination of the metal surface by impurities from the support. The silica–alumina used in the previous work contained residual sulphate (0.7% wt), so in order to investigate the possibility that the results were due to contamination, and also because of the developing interest in metal-support interactions, it was decided to perform some further experiments, using different methods of catalyst activation, and covering a wider range of catalysed reactions.

EXPERIMENTAL METHODS

Catalysts. The nickel/silica–alumina catalyst used in this work had been prepared in a previous investigation (*4*) by impregnation of the support (Akzo Chemie N.V., fluid cracking catalyst; 14% alumina; surface area, 612 $m^2 g^{-1}$; pore volume 0.73 $cm^3 g^{-1}$) with a solution of nickel nitrate in distilled water. The impregnation was performed by the incipient wetness technique. The catalyst (containing 7% wt Ni, and referred to as Ni/SiAl) was dried for 16 h at 400 K, and stored in a vacuum desiccator. For comparison, a silica-supported catalyst (Ni/Si) was prepared, also by impregnation, which contained 5% wt Ni on silica (Davison Grade 57; surface area 300 $m^2 g^{-1}$). A 5% Ni/TiO_2 catalyst was prepared by wet impregnation of Degussa P25 titanium dioxide, and dried and stored as before.

Catalyst activation. Samples of the dried catalyst were calcined in air at 770 K for 2.5 h. These samples, together with decomposed samples (i.e., samples heated in air at 570 K), were reduced *in situ* in a U-tube microreactor in flowing hydrogen. Some samples were reduced by heating rapidly to 770 K and holding at this temperature for 16 h, other samples were reduced by temperature-programming (7 K/min) to 723 or 773 K, and holding at the upper temperature for 1.5 h.

Activity measurements. The activity and selectivity of these catalysts has been determined for the hydrogenolysis of hexane, the hydrogenation of benzene, and the hydrogenation of carbon monoxide.

Benzene experiments. Samples (usually, sufficient sample was used to give 2 mg Ni in the reduced catalyst) were placed in a silica glass reactor attached to a stainless-steel gas manifold, and reduced as described above. After reduction, the samples were cooled to 333 K. Benzene (Koch Light, thiophene-free, sulphur content <5 ppm vol.) was injected into the hydrogen stream using a motor-driven syringe. The flow of hydrogen was controlled by a Negretti and Zambra controller. The benzene/hydrogen mixture was homogenised by passage through a heated mixing volume consisting of a cylinder (length 11.5 cm, diameter 5.5 cm) packed with Raschig rings, and then flowed down through the catalyst. The activity of the catalyst was determined over a 30-min period by removing samples of the effluent with a gas syringe at 10-min intervals, and analysing by injection into a Perkin–Elmer F33 gas chromatograph (FID detector) fitted with a 3-m column packed with 10% triscyanoethoxypropane on Chromosorb P). The peak areas were measured automatically using an Infotronics CRS 308 electronic integrator.

At the completion of each test, the benzene/hydrogen flow was interrupted, and the sample heated to the next higher temperature, when a further activity test was performed. Each sample was tested at 333, 353, 373, 383, 393, 403, 413, and 423 K. The experimental conditions used were 4.436 mol benzene/h/gNi, and a hydrogen/benzene ratio of 20:1.

Hexane flow experiments. On completion of the benzene experiments, or immediately after reduction if fresh samples were being used, the activities of the catalysts were determined for the hydrogenolysis and isomerisation of hexane. The catalyst was heated to 548 K, and hexane (Phillips Petroleum Co., 99.99%) was injected into the hydrogen stream, again by using a motor-driven syringe. The activity of the catalysts was determined under flow conditions over a 2-h period, samples of effluent being removed at 30-min intervals and analysed using the F33 gas chromatograph, which in this case was fitted with a 6-m column packed with silicone fluid (20%) on Chromosorb P.

The experimental conditions were 3.008 mol hexane/h/g Ni and a hydrogen/hexane ratio of 5.58 : 1.

Hexane pulse experiments. The activities of the Ni/SiAl catalyst samples were determined under pulse conditions for the conversion of hexane at temperatures in the range 573 to 693 K. Pulses of hexane (1 μl) were injected into a hydrogen stream passing over the sample (0.200 g), and the products were analysed as before. Several pulses were injected at each reaction temperature.

CO/hydrogen experiments. After reduction, the sample (containing 2 mg Ni) was cooled to 423 K, and the CO/H_2 mixture (British Oxygen Co. special gas, CO/H_2 ratio 1 : 3) set at a flow rate of 1.2×10^6 cm^3 gas mixture/g Ni/h. The temperature was raised quickly to 553 K, and the activity and selectivity of the catalyst was determined over a 1.5-h period by analysing the effluent using a Perkin–Elmer F11 gas chromatograph fitted with a thermal conductivity detector and a Poropak N column (to determine the concentrations of CO, CO_2, CH_4, and C_2H_6). Simultaneously, the hydrocarbon products, up to C_6, were analysed using the F33 gas chromatograph.

The standard conditions were CO/H_2 ratio = 1 : 3; T = 553 K; atmospheric pressure; CO flow rate = 13.38 mol CO/g Ni/h.

Temperature-programmed reduction. The reducibility of the catalysts, and of the silica-alumina support (which contained 0.7 wt% sulphate), was investigated using temperature-programmed reduction (TPR). Samples (0.200 g) were placed in the reactor and reduced by heating (7 K/min) in a hydrogen/argon mixture (5% hydrogen). The quantity of hydrogen consumed was determined by passing the gas mixture first through the reference side of a thermal conductivity detector, then through the sample, through a cold trap (cooled in a propanol slush bath), and back through the sample side of the detector. The signal from the detector was displayed on a chart recorder. The TPR apparatus was calibrated by measuring the area of the peak produced during the reduction of analytical-grade copper oxide.

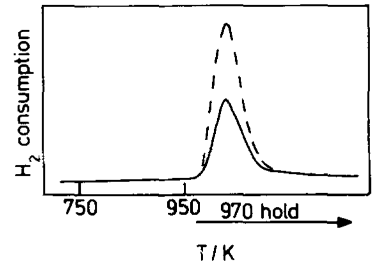

FIG. 1. Temperature-programmed reduction of the silica–alumina support for a fresh sample (broken line), and a sample prereduced for 16 h at 770 K (solid line).

RESULTS

Temperature-Programmed Reduction

The silica–alumina support contains 0.7% wt of sulphate, so it is necessary to consider the possibility that the unusual properties previously reported for nickel deposited on this support (*4*) arise because of sulphur poisoning. Figure 1 shows that the support consumes a considerable amount of hydrogen in a TPR experiment when the temperature reaches about 970 K. The reduction corresponds to the conversion of about 20% of the sulphate into hydrogen sulphide and water. This represents 14.6 μmol of hydrogen sulphide per g support. Figure 1 also shows the quantity of hydrogen consumed by the support after this had been prereduced for 16 h at 770 K (these were the conditions used previously to reduce the nickel catalysts). The reduc-

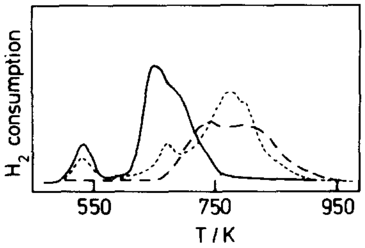

FIG. 2. Temperature-programmed reduction of Ni catalysts, Ni/Si (solid line), Ni/SiAl decomposed (dotted line), Ni/SiAl calcined at 823 K (broken line).

tion in this case corresponds to the formation of 6.8 μmol of hydrogen sulphide. The difference in the two TPR experiments, representing the amount of sulphate reduced in 16 h at 770 K, is 7.8 μmol. For the 7% Ni catalyst, this corresponds to 4.37×10^{18} S atoms per g catalyst, and the catalyst contains 7.18×10^{20} Ni atoms per g. Since previous X-ray and magnetic measurements have indicated that the nickel is well dispersed (*4*), it seems unlikely that sulphur contamination is a problem.

Nickel Catalysts

Figure 2 shows TPR profiles for the reduction of the two catalysts after decomposition at 570 K, and for the silica–alumina catalyst after calcination for 2.5 h at 823 K. The degree of reduction is 100, 91, and 87%, respectively, for the silica-supported catalyst, for Ni/SiAl after decomposition at 570 K, and for Ni/SiAl after calcination at 823 K. These results confirm the earlier data (*4*), and show that almost complete reduction of the nickel will occur in a very short time in isothermal experiments at 770 K. The difference in the TPR profiles for the two catalysts after decomposition at 570 K indicates that the silica–alumina has more effect on the reducibility of the nickel oxide. However, this may only be because of an increased dispersion of the oxide, since the position of the main reduction peak is not consistent with the presence of mixed oxide phases, such as Ni silicate or aluminate.

Hydrogenolysis of Hexane in Pulse Experiments

In the previous work it was found that catalyst Ni/SiAl had a very high selectivity for isomerisation of hexane and a very low activity for hydrogenolysis. Table 1 compares the previous data with measurements made in the present work. The catalyst has changed somewhat during storage, and now

TABLE 1

Activity and Selectivity of Ni/SiAl Catalyst under Pulse Conditions[a]

Temperature (K)	Activity[b] (%)	Selectivity[c] (%)	Product distribution (%)						
			C1	C2	C3	iC4	C4	iC5	C5
573	8.3	95.6	1.54	0.30	0.63	0.00	0.62	0.21	1.19
603	20.5	93.0	1.91	0.43	1.10	0.18	0.81	0.87	1.69
603[d]	5.0	98.2	0.2	0.6	1.0	0.0	0.0	0.0	2.0
633	33.8	86.5	2.46	0.49	2.38	0.61	1.56	2.68	3.28
633[d]	7.5	95.3	0.1	0.1	2.8	0.3	0.3	0.5	0.5
663	50.2	66.8	6.97	1.06	7.12	2.08	4.27	5.86	5.92
663[d]	11.1	83.1	0.8	0.3	10.7	1.0	1.0	1.4	1.4
693	58.1	39.9	16.4	3.3	14.2	3.75	8.19	6.96	7.16
693[d]	4.5	33.5	4.7	3.1	41.0	4.2	7.3	4.0	4.0

[a] Sample (200 mg) decomposed by heating in air for 1.5 h at 573 K, then reduced for 0.75 h at 773 K.

[b] Activity defined as percentage hexane converted into all products.

[c] Selectivity defined as percentage of hexane converted into C_6 isomers.

[d] After Ref. (*4*).

TABLE 2

Activity and Selectivity of Calcined Ni/SiAl Catalyst under Pulse Conditions[a]

Temperature (K)	Activity[b] (%)	Selectivity[c] (%)	Product distribution (%)						
			C1	C2	C3	iC4	C4	iC5	C5
573	6.9	98.8	0.18	0.00	0.15	0.00	0.03	0.14	0.66
603	18.5	96.0	0.39	0.10	0.45	0.05	0.42	0.79	1.55
633	29.8	87.6	1.68	0.26	1.64	0.55	1.57	3.12	3.64
663	52.5	67.0	6.38	0.91	5.44	2.06	4.65	6.79	6.76
693	65.0	36.8	20.0	3.6	12.4	3.84	8.50	7.54	7.54

[a] Sample (200 mg) decomposed by heating in air for 1.5 h at 573 K, then calcined in air for 2.5 h at 773 K, and finally reduced for 0.75 h at 773 K.

[b] Activity defined as percentage hexane converted into all products.

[c] Selectivity defined as percentage of hexane converted into C_6 isomers.

has a slightly higher activity for hydrogenolysis. However, except at the higher temperatures, the high selectivity for isomerisation is maintained. Since a very small amount of "normal" nickel can drastically alter the activity of these catalysts for hydrogenolysis it would appear that during storage there has been some change in the catalyst which results in the formation of a small fraction of bulk nickel after reduction. Nevertheless, even after storage, this catalyst is still more than 30 times less active than a 10% Ni/SiAl catalyst (*4*).

Table 2 shows the activity and selectivity data for the present catalyst after calcination at 823 K and reduction at 770 K. Comparison with Table 1 shows that calcination has had little effect either on the activity or the selectivity of the catalyst. Figure 3 shows an Arrhenius plot of the activity against the reciprocal temperature for the present catalyst. The activation energies are calculated to be 130 and 150 kJ mol^{-1} for the decomposed and for the calcined catalyst, respectively. These values are lower than the value of 187 kJ mol^{-1} reported by Ponec and Sachtler (*5*). This may be significant, especially since it has been reported by Ko and Garten (*6*) for the hydrogenolysis of ethane over titania-supported nickel that the activation energy is much lower than for normal nickel (130 compared with 180 kJ mol^{-1}), an effect which these workers have attributed to metal-support interactions. It should be recognised, however, that for the hydrogenolysis reaction the *apparent* activation energy is temperature dependent. Therefore, it is possible that the lower values obtained in this work reflect the different range of temperatures over which the activation energy was measured, rather than being a consequence of metal-support effects.

Reoxidation Experiments

When the activity of a catalyst is lower than anticipated it is difficult to ignore the

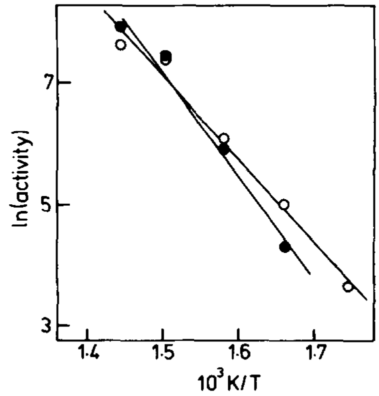

FIG. 3. Arrhenius plots for the hydrogenolysis of hexane over catalyst Ni/SiAl decomposed at 570 K (○), or calcined at 823 K (●).

possibility that the effect is due to surface contamination (*7, 8*). Indeed, in our own work with Ni/titania catalysts (*9*) it has been found that because of sulphur poisoning, catalysts prepared using titania derived from titanium sulphate are completely inactive for the hydrogenation of benzene. Earlier, from TPR experiments, it was established that there is some reduction of residual sulphate in the support. Although the quantity of sulphide produced does not appear to be sufficient to poison most of the nickel surface, some further experiments were performed to exclude poisoning as a possible explanation.

A fresh sample of catalyst Ni/SiAl was calcined in air for 2.5 h at 823 K, and reduced for 16 h at 770 K. The activity and selectivity was then determined for the hexane reaction under pulse conditions. The sample was next reoxidized by heating in flowing air for 16 h at 770 K, a procedure designed to remove any sulphide deposits. The sample was then reduced in hydrogen for 0.75 h at 770 K, the short time being chosen to minimise further sulphate reduction. Figure 4 summarises the data from these two experiments. The agreement is excellent. It seems quite certain that the unusually low activity which we have observed for the hydrogenolysis reaction is not due to surface contamination, at least from sulphide. (The only other impurity reported by the manufacturer is iron (0.02%) which is unlikely to create a problem under our mild activation conditions.)

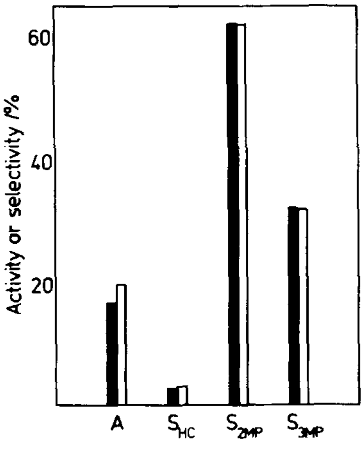

FIG. 4. Activity and selectivity of Ni/SiAl catalysts for the hexane reaction. (■), Fresh catalyst, (□), reoxidized catalyst. A, Activity; S_{HC}, selectivity to cracked products; S_{2MP}, selectivity to 2-methylpentane; S_{3MP}, selectivity to 3-methylpentane.

Flow Experiments

The largest differences which we have observed between nickel catalysts on different supports occur with uncalcined, reduced materials (*9*). Therefore, flow experiments have been performed only on catalysts prepared by heating the uncalcined precursors in hydrogen at 7 K/min to 723 K, and holding at this temperature for 1 h. These mild reduction conditions are sufficient to ensure that most of the nickel is reduced, but minimises the reduction of residual sulphate (see Figs. 1 and 2).

Table 3 summarises the activity data for the hydrogenolysis of hexane, the hydrogenation of benzene, and the hydrogenation of CO, over the Ni/SiAl and Ni/Si catalysts. For the hydrogenation of benzene the activity of catalyst Ni/Si is about twice as high as that of catalyst Ni/SiAl. It is generally accepted that the benzene hydrogenation reaction is insensitive to the structure of a metal surface and so the activity is proportional to the surface area (*10, 11*). The difference in activity by a factor of 2 between the two catalysts is small enough to be attributed to differences in the available nickel surface area. It seems clear that the Ni/SiAl catalyst behaves normally in this hydrogenation reaction. This is borne out by the fact that the activation energies (53.8 kJ mol^{-1} for Ni/SiAl and 54.2 kJ mol^{-1} for Ni/Si) are very similar to each other, and are in close agreement with published values (52.3–54.8 kJ mol^{-1} for catalysts having similar Ni loadings (*11*)). For the hydrogenolysis of hexane, Table 3 shows that the Ni/Si catalyst is more than 2 orders of magnitude more active initially than the Ni/SiAl catalyst, and even under steady state conditions it is still more than 60 times more ac-

TABLE 3

Comparison of the Activities of Nickel Catalysts

Reactant	Catalyst[a]			
	Ni/SiAl	Ni/Si	SiAl/Si[b]	Ti/Si[c]
Benzene	1.5^{d}	3.5^{d}	0.43	0.82
Hexane	0.3^{e}	34.5^{e}	0.0087	0.55
Hexane	0.4^{d}	25.2^{d}	0.016	
CO/H_2	0.5^{d}	1.2^{d}	0.42	33.8
	Selectivity[f]			
C1	88	88		
C2	7	5		
C3	4	3		
C4+	1	4		

[a] All experiments performed using 2 mg Ni in the sample which was reduced by temperature-programming in hydrogen to 723 K at 7 K min^{-1} and holding at 723 K for 1 h.

[b] Ratio of the activity of the Ni/SiAl catalyst to that of the Ni/Si catalyst.

[c] Ratio of the activity of a 5% Ni/TiO_2 catalyst to that of the Ni/Si catalyst.

[d] Steady state activity, defined as the percentage of reactant converted into all products.

[e] Initial activity, defined as above.

[f] Selectivity in the CO/H_2 reaction, defined as the percentage of CO converted into each hydrocarbon product.

tive. This is in marked contrast to the results for the hydrogenation of benzene.

We have not reported specific activities for the Ni/SiAl catalyst because there is growing uncertainty regarding the validity of hydrogen chemisorption measurements for catalysts in which metal-support effects may operate (*12–15*). The amount of hydrogen adsorbed on this catalyst has been determined using temperature-programmed desorption both for the freshly reduced catalyst and after reoxidation and reduction. The H/Ni ratios lie in the range 0.01 to 0.02. These low values are inconsistent with X-ray data which indicate a small average particle size. Also, if correct they would give specific activities for the hydrogenaton of benzene about an order of magnitude higher for the Ni/SiAl than for the Ni/Si catalyst. This seems unlikely. We prefer to assume that for some reason the adsorption of hydrogen is unreliable. A similar inconsistency in the adsorption of hydrogen by some alumina-supported nickel catalysts has been reported recently (*16*). Rather than calculate specific activities from adsorption data, we have used the activity of a catalyst for the hydrogenation of benzene as a measure of the amount of metal surface available under reaction conditions. On this basis we have calculated the relative activities of the two catalysts for the hydrogenolysis of hexane and for the hydrogenation of carbon monoxide. Table 3 shows that the Ni/SiAl catalyst has a specific activity (relative to benzene hydrogenation) for the hydrogenolysis of hexane about 50 times less than that of the Ni/Si catalyst.

The hydrogenation of CO has been shown recently to be sensitive to metal-support effects for titania-supported catalysts, with activities varying by up to 2 orders of magnitude (*13, 17, 18*). Consequently, the CO/H_2 reaction may be used also as a probe reaction to investigate metal-support effects. However, as Table 3 shows, our Ni/SiAl and Ni/Si catalysts have similar absolute activities (per g Ni), and almost identical product selectivities. Furthermore, the activities relative to the activity for the hydrogenation of benzene are exactly the same within experimental error. The final column in Table 3 compares the activity of a titania-supported catalyst (5% Ni) with the Ni/Si catalyst. These catalysts have very similar activities for the hydrogenation of benzene and the hydrogenolysis of hexane, but the titania-supported catalyst is much more active in the hydrogenation of CO.

DISCUSSION

The experiments have confirmed the results reported previously (*4*) which showed that a Ni/SiAl catalyst had a very low activity for the hydrogenolysis of hexane, and yet could sustain a high hydrogenation activity in the bifunctional isomerisation of hexane. Furthermore, it has been demonstrated that the suppression of the hydrogenolysis activity is unlikely to be due to surface contamination. We have excluded surface contamination, at least by sulphur poisoning, for a number of reasons. First, quite different prereduction procedures (reduction for 16 h at 770 K, or for 1 h at 723 K, or for 0.75 h at 770 K after a previous 16-h reduction and 16-h reoxidation at 770 K) gave essentially identical catalytic properties. It would appear unlikely that such diverse pretreatments would lead to identical degrees of contamination. Second, the partial pressure of H_2S will be less than 1 ppm, and this, together with the calculation that the total amount of sulphate which is reduced only represents 1 S atom/200 Ni atoms, further argues against sulphur contamination. Finally, the activity of the Ni/silica–alumina and Ni/silica catalysts in the CO/H_2 reaction, are very similar. Since the CO/H_2 reaction over Ni is very sensitive to poisoning by sulphur, it seems unlikely that these two catalysts could have similar activities if one was seriously contaminated.

We conclude that the low activity of catalyst Ni/SiAl in the hydrogenolysis reaction is caused by a change in catalytic properties due to the influence of the support. A similar result, and conclusion, has been reported by Taylor *et al.* (*1*) who studied the hydrogenolysis of ethane under flow conditions. They observed that the specific activity for the ethane reaction of a 10% Ni/silica–alumina catalyst was 50 times lower than that of a 10% Ni/silica catalyst. This is similar to the difference observed in the present work between the activity of nickel catalysts for benzene hydrogenation and hexane hydrogenolysis.

In our pulse experiments, the difference in activity between the Ni/SiAl catalyst and a normal Ni catalyst was found (*4*) to be greater than 3 orders of magnitude. Under flow conditions, the difference was only a factor of 50. This suggests that in the normal catalyst (but not in the Ni/SiAl catalyst) there are initially some sites of exceptionally high activity which rapidly become deactivated. This raises the possibility that for demanding reactions, such as hydrogenolysis, only a fraction of the metal surface in a catalyst is active for a particular reaction. It is well known that the activity of different crystal planes can vary by up to a factor of 10 (*19*), but it is usually assumed that all the atoms within each surface are equally active, although the possible importance of coordinatively unsaturated metal atoms (in edges or at corners) has also been considered (*20, 21*).

The Role of the Support

Previously (*4*) it was postulated that the high selectivity of the 7% Ni/silica–alumina catalyst for isomerization reactions might be due to a very high dispersion, essentially a monodispersion, of the Ni. In view of the fact that this same catalyst has now been shown to have normal activity for the CO/H_2 reaction it may be more correct to assume the presence of (small) Ni particles rather than a monodispersion.

In general terms it can be envisaged that the effects which we have observed could arise either because the nickel particles are altered electronically or structurally. Electronic effects could arise because silica–aluminas are highly acidic and have electron-withdrawing sites on the surface (*22*). A nickel particle deposited on such a support may become electron deficient, and this could affect the adsorption of reactant molecules and hence the catalytic activity. The effect of electron withdrawal will be dependent on particle size. Our X-ray and magnetic measurements (*4*) indicated that the nickel is well dispersed, but it is impossible to know whether all the particles will be small enough to lose their bulk properties. Since there will be a range of particle sizes there could be some larger particles whose electronic properties will be essentially unaffected by interaction with the support. This should give the catalyst a residual activity proportional to the fraction of nickel present in larger particles. The fact that the activity of the Ni/SiAl catalyst in pulse experiments is so low suggests either that there are no larger particles present at all (which does not seem likely) or that the influence of the support is not electronic. Furthermore, if electronic effects are operating it is strange that the CO/H_2 reaction should be unaffected. Whereas the hydrogenation of benzene might not be sensitive to small changes in the electron density of the nickel surface, it is surprising that no effect whatsoever is observed for the CO/H_2 reaction, particularly since this reaction is found to be very sensitive to metal-support effects in titania-supported catalysts (*13, 17, 18*).

The second type of metal-support interaction which could arise in the Ni/SiAl catalyst is a change in the structure of the nickel particles. There is evidence that even with silica as a support, variations in the activity of nickel catalysts in hydrogenolysis reactions can occur (*19*). It is possible that structural changes could affect the hydrogenolysis reaction but not affect the hydrogenation of benzene or the CO/H_2 reaction, providing that each of these reactions required a special type of active site. It has been suggested recently for the CO/H_2 reaction over Pd catalysts that only a fraction of the total surface atoms constitute active sites (*23*). It is possible that a similar situation exists for the hydrogenolysis reaction, but not for the hydrogenation of benzene.

It is not possible at this stage to differentiate between electronic and structural interactions. Indeed, to some extent these two parameters will be mutually interdependent. However, the present work offers some evidence that hydrogenolysis reactions over nickel catalysts require a special type of site, which is different from the site required for the hydrogenation of benzene or for the CO/H_2 reaction, and which is sensitive to metal-support interactions.

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