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Strong Metal–Support Interactions in Nickel/Titania Catalysts: The Importance of Interfacial Phenomena

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Nickel catalysts supported on silica and titania have been prepared by wet impregnation. The uncalcined catalysts, after an initial mild reduction at 623 K, have been treated by heating in hydrogen or argon at successively higher temperatures up to 923 K. The activity and selectivity of the catalysts have been determined under flow conditions at 1 bar pressure for the hydrogenolysis of *n*-hexane at 548 K, for the hydrogenolysis of ethane over the temperature range 478–673 K, and for the CO/hydrogen reaction at 548 K. Hydrogen adsorption isotherms have been measured and the specific metal surface areas determined using the Langmuir equation for dissociative adsorption to determine the monolayer coverage. Mean crystallite diameters have been determined by X-ray line broadening. Ni/titania catalysts exhibit normal hydrogen chemisorption properties after reduction at 723 K, although adsorption is suppressed after thermal treatment at 923 K. X-Ray line broadening measurements indicate a mean particle size of 8.0 nm after reduction at 723 K, and 13.3 nm after heating to 923 K. Activity measurements, after reduction at 723 K, show excellent agreement between the specific activities of the Ni/silica and Ni/titania catalysts for the hydrogenolysis of *n*-hexane and ethane. All these results are consistent with literature data for these reactions. However, for the CO/hydrogen reaction the specific activity of the Ni/titania catalyst is a factor of 50 higher than that of the Ni/silica catalyst. After heating at 923 K, there was a large decrease in the activity of the Ni/titania catalysts for *all* the reactions investigated. It is concluded that the enhanced activity of the Ni/titania catalysts for the CO/hydrogen reaction cannot be due to strong metal–support interactions (SMSI) *as defined in the literature*. A model of the Ni/titania system is presented which emphasizes the importance of considering the interface between the metal and the partially reduced support. It is proposed that new active sites created at the interface are responsible for the high specific activity of these catalysts for the CO/hydrogen reaction.

INTRODUCTION

Interest in titania-supported metal catalysts has increased rapidly since the observation by the Exxon group that metals supported on titania could exhibit unusual properties. After reduction at moderately high temperatures, for example, it was observed that the ability of the metals to adsorb hydrogen or carbon monoxide was greatly suppressed (*1–5*). This phenomenon is not restricted to titania-supported catalysts; similar effects have been observed using other "easily reducible" transition metal oxide supports (*2*). Indeed, the possibility that the support may modify the properties of a metal particle has long been recognized (*6*). Acidic supports have the capacity to interact strongly with metal crystallites, withdrawing electrons and leaving an electron-deficient metal particle; basic supports, or supports promoted with alkali metals can cause an increase in the electron density of the metal. Recent work has uncovered many other examples of metal–support effects, and strong metal–support interactions (SMSI) now appear to be quite widespread. The occurrence, or absence, of an SMSI is critically dependent

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on the experimental conditions used in the catalyst preparation (*7–34*).

Since in all cases SMSI reduce the capacity of a metal to adsorb hydrogen or carbon monoxide it might be anticipated that the development of an SMSI would be accompanied by a loss of catalytic activity. This is found to be the case for the hydrogenation of benzene (*7, 33, 34*), the dehydrogenation of cyclohexane (*33*), and for the hydrogenolysis of ethane (*20*) or *n*-hexane (*10, 34*).

It is surprising, therefore, that titania-supported catalysts should exhibit exceptionally high activity in the reaction of CO with hydrogen. High activity in the CO/hydrogen reaction was first reported by Vannice and Garten (*9*) for Ni/titania catalysts, and these results have been confirmed by other groups of workers (*24, 25, 31, 32*). Recently, it has been found that titania-supported Rh, Ir, Pt, and Pd also exhibit high activity for the CO/hydrogen reaction (*23, 35, 36*).

The origin of these SMSI is still unclear. However, since the interaction occurs most readily with reducible oxide supports, and at a temperature which reflects the relative ease of reduction of the support (*2, 19, 30*), the preferred explanation involves an electronic interaction between a small metal particle and a partially reduced (semiconducting) support. Horsley (*37*) has calculated that a metal atom situated at an oxide ion vacancy could interact sufficiently strongly with a Ti^{3+} cation, probably with electron transfer to the metal, to account for the observed effects of SMSI. Although there is disagreement as to the magnitude and/or direction of electron transfer, this model is at least reasonable in the case of the platinum metals where the particle sizes are very small (about 1 nm), and where the metals are easily reduced.

For Ni catalysts, however, where the particle sizes from X-ray line broadening experiments are calculated to be about 10 nm (*9, 21, 32, 34*), it is more difficult to envisage an interaction with the support which would prevent the metal particles from adsorbing hydrogen or carbon monoxide.

In earlier publications (*24, 25*) we have shown that after reduction for 1 h at 723 K Ni/silica and Ni/titania catalysts have very similar properties. For example, they have similar capacities to adsorb hydrogen and carbon monoxide, similar specific activities for the hydrogenation of benzene, and for the hydrogenolysis of *n*-hexane. All the evidence is that these catalysts are not affected by SMSI. However, these same Ni/titania catalysts have exceptionally high activities in the CO/hydrogen reaction (in agreement with literature data). These conflicting results have led us to propose (*24, 25*) that the enhanced activity of titania-supported catalysts in the CO/hydrogen reaction is specific to this reaction. Furthermore, the enhanced activity does not appear to be due to changes in the surface properties of the nickel particles, which has led us to suggest that the titania is *directly* involved in the CO/hydrogen reaction.

The purpose of this paper is to present further experimental evidence that the high activity of titania-supported catalysts in the CO/hydrogen reaction is not associated with the normal type of SMSI described in the current literature.

EXPERIMENTAL

Catalyst preparation. Catalysts containing 10% Ni (nominal composition by weight of the reduced catalyst) were prepared by the wet impregnation method, using a solution of nickel nitrate (Fisons, AnalaR reagent). After wetting the support with the solution, excess water was removed by rotary evaporation at 343 K. The impregnated catalysts were dried in air at 400 K for 16 h, and stored in a vacuum desiccator. Samples to be used for catalytic or chemisorption experiments were further dried at 400 K for 16 h immediately prior to use.

The supports used for the catalysts were Davison silica (type 57, a mesoporous silica having a surface area of 290 $m^2\ g^{-1}$), and

Degussa titanium dioxide (type P25, fumed titania, nonporous, 80% anatase and 20% rutile, having a surface area of 50 m^2 g^{-1}). The titania used was a different batch from that used previously (*24–26*), and was chosen to exclude the possibility that our earlier data were not typical of this type of titania.

The nickel content of calcined catalyst samples was determined by wet analysis. Samples were dissolved in a 25% solution of HF in 2 *M* HNO_3; the resulting solutions were boiled to codistil off unreacted HF, and then analysed by atomic absorption spectrophotometry. The compositions, in weight percent Ni, were found to be 8.5% Ni/TiO_2 and 9.9% Ni/SiO_2. For convenience we label these catalysts Ni8.5Ti and Ni9.9Si.

Activation procedure. A silica glass reactor was used for activity measurements. This consisted of two concentric tubes with the sample being supported on a sintered disc fitted in the inner tube. Gas mixtures passed down through the catalyst bed, and up through the outer tube. The reactor was fitted with ball and socket joints to allow connection to a stainless-steel manifold.

Samples (60 mg) of the dried, uncalcined, catalysts were mixed with 30–60 mesh silica gel (140 mg) and placed in the reactor. The reactor was flushed with hydrogen (flow rate 1.67×10^5 cm^3 g Ni^{-1} h^{-1}) and heated at 5 K min^{-1} to 623 K, where reduction was continued for 1 h. The activity of the catalyst was determined (see below), and then a series of further treatments were performed by heating in hydrogen for 0.5 h at 723, 823, and 923 K. After each treatment the catalyst was cooled to the appropriate reaction temperature and the activity determined.

To investigate the role of hydrogen in the high-temperature activation process, a parallel set of experiments was performed in which all subsequent treatments after the initial activation procedure were carried out under argon. The procedure was to flush the system with argon at the reaction temperature, heat in argon at the new activation temperature for 0.5 h, and then cool to the reaction temperature, still under argon. These catalysts are designated Ni8.5Ti/Ar.

At the completion of the series of activity measurements, the samples were cooled to room temperature, flushed with argon, and passivated by injection of several small pulses of air into the argon stream. Passivated samples were examined by X-ray diffraction.

In separate experiments, samples of the titania-supported catalyst were reduced at 773 K for 16 h, in order to compare directly our results with published data (*20*).

Chemisorption experiments. The adsorption of hydrogen (B.O.C. 99.995% purity, used without further purification) by the reduced samples was determined using a conventional glass volumetric apparatus. This consisted of a dosing volume, a U-tube silica sample holder which allowed *in situ* pretreatment of the catalysts, an oil diffusion-pumped vacuum system, and a gas handling line. Pressures were measured using Bell and Howell high-precision pressure transducers which, together with the dosing volume, were thermostatted at 300 K.

The catalyst samples (300 mg) were activated *in situ* using the same conditions as for catalyst testing, after which the apparatus was evacuated for 0.5 h while maintaining the sample at the final activation temperature. The sample was then cooled to room temperature and the evacuation was continued for a further 16 h, the final pressure being $<10^{-4}$ N m^{-2}. A hydrogen adsorption isotherm was measured at 273 K, with 1 h being allowed at each point for the attainment of equilibrium. The monolayer coverage was calculated using the Langmuir equation for dissociative adsorption. Specific metal surface areas were determined by assuming that each Ni atom adsorbs 1 H atom, and that each H atom occupies 0.065 nm^2.

Measurement of n-hexane hydrogenolysis activity. The activity of the catalyst for the hydrogenolysis of *n*-hexane (Phillips Petroleum Co., 99.99% purity) was determined at 548 K under continuous flow conditions. Temperatures were maintained to ±1 K by a Eurotherm controller operating an electric microfurnace; sample temperatures were measured using a thermocouple situated in a thermowell adjacent to the sample. Hexane was injected by a motor driven syringe, through a stainless-steel T-piece, into the hydrogen carrier gas. The steel tubing was heated to 340 K to ensure rapid evaporation and mixing of the hexane with the hydrogen. The liquid hourly space velocity of *n*-hexane was 1.35 mol hexane g Ni^{-1} h^{-1}. The hydrogen flow was 1.25 dm^3 h^{-1}, and the molar ratio of hydrogen to hexane was 5.58 : 1.

The activity and selectivity of the catalysts was determined by extracting samples of the effluent with a gas syringe and analyzing using a Perkin Elmer F33 gas chromatograph having a flame ionisation detector, and fitted with a 3.5 m 20% w/w silicone fluid on Chromosorb P column. The areas of the product peaks were determined using an Infotronics 308 integrator. To minimize catalyst deactivation, only a single analysis was performed after exposing the sample to the hydrogen/hexane flow for 20 min. The hexane was then turned off, and the samples reactivated in hydrogen (or argon) at the next higher temperature (see activation procedure).

Measurement of ethane hydrogenolysis activity. There are few data in the literature on the hydrogenolysis of *n*-hexane over Ni catalysts. Most work has been concerned with the hydrogenolysis of ethane, even though useful information can be obtained from the product distributions produced in the hydrogenolysis of larger molecules. To allow direct comparison between our results and published data, the activity of the titania-supported catalyst was determined for the hydrogenolysis of ethane in the temperature range 478–673 K. An ethane/hydrogen mixture (10% ethane, B.O.C. special gas, impurities were methane (0.002%), ethene (0.013%), propane (0.025%)) was passed over the prereduced catalyst heated to 478 K, at a flow rate of 6 × 10^5 cm^3 ethane g Ni^{-1} h^{-1}. Samples of the products were removed with a gas syringe after 2, 5, 10, 15, and 20 min, and analyzed using the F33 gas chromatograph. The ethane/hydrogen mixture was turned off and the sample heated in hydrogen to the next test temperature. The ethane/hydrogen mixture was passed over the catalyst again and the activity determined as before. When sufficient data had been collected to allow a reliable activation energy to be determined, the sample was reactivated for 0.5 h in hydrogen at the next higher temperature; the activity was then determined as before.

Measurement of activity in the CO/hydrogen reaction. Fresh samples of catalyst (60 mg) were activated as described above. The sample was cooled to 420 K, where the activity is very low, so that the flow of the CO/hydrogen mixture (B.O.C. special gas, 25% CO/75% H_2) could be set accurately. The flow, controlled by a Negretti and Zambra M2545 flow controller, was set at 1.342 × 10^5 cm^3 CO g Ni^{-1} h^{-1}. The CO/H_2 mixture was turned off and the sample heated to 548 K under flowing hydrogen. When the temperature had stabilized, the CO/H_2 mixture was turned on and, after 15 min, a 1 cm^3 sample of the effluent gas was removed using a gas syringe. Half this sample was injected into the F33 gas chromatograph to determine the distribution of hydrocarbons; the remainder was injected into a Perkin Elmer F11 gas chromatograph (with a thermal conductivity detector) fitted with a Porapak N column, to determine the concentrations of CO, CO_2, and CH_4. After correcting for the different sensitivities of these compounds, the activity was determined by combining the data from the F11 and F33 analyses.

At the completion of this experiment, the sample was heated in hydrogen for 0.5 h at the next higher activation temperature; the activity was then determined as before.

X-ray diffraction. X-Ray powder patterns were obtained with a Philips horizontal diffractometer, using nickel-filtered copper radiation. Samples were used either as smear slides or as cavity mounts.

RESULTS AND DISCUSSION

Chemisorption of Hydrogen

A suppression of the adsorption of hydrogen in titania-supported catalysts is taken to be evidence of the existence of an SMSI. Almost total suppression is observed for the platinum metals supported on titania (*1*, *2*). In the case of nickel a smaller, but nevertheless significant, suppression has been claimed (*9*).

Figure 1 shows the hydrogen adsorption isotherms for the Ni/titania catalyst after reduction at 723 and 923 K, and for the 9.9% Ni/silica and a 40.0% Ni/silica catalyst reduced at 723 K. The specific nickel surface areas calculated from the Langmuir equation are given in Table 1. The use of the Langmuir equation is open to criticism because the heat of adsorption decreases with coverage and, indeed, the Langmuir plots were not very linear. However, both the Temkin and the Freundlich equations were tried also, and both gave equally poor lines. Since we are concerned with a *comparison* of silica-supported and titania-supported catalysts any errors in the estimated surface areas will not alter the conclusions.

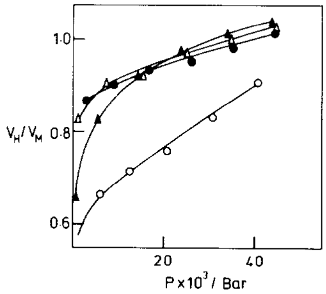

FIG. 1. Hydrogen adsorption isotherms for Ni catalysts. V_H, volume of hydrogen adsorbed at pressure P; V_M, volume of hydrogen adsorbed at monolayer coverage. ○, Ni8.5Ti reduced at 923 K; ●, Ni8.5Ti reduced at 723 K; ▲, Ni9.9Si reduced at 723 K; △, Ni40.0Si reduced at 723 K.

TABLE 1

Specific Nickel Surface Areas Calculated Using the Langmuir Equation

Catalyst	$S_{Ni}(m^2\ g\ Ni^{-1})$
Ni9.9Si	103.7
Ni40.0Si	79.7
Ni8.5Ti/723[a]	51.4
Ni8.5Ti/923[b]	13.0[c]

[a] Sample heated at 723 K.

[b] Sample heated at 923 K.

[c] Represents a minimum value because of nonlinearity of Langmuir plot.

Figure 1 shows for the silica-supported catalysts that as the Ni content is increased, the isotherm exhibits a more distinct break at low pressures. This indicates that the adsorption is becoming more characteristic of bulk nickel.

It is important to note, therefore, that the isotherm for the Ni/titania catalyst reduced at 723 K is very similar to that for the 40.0% Ni/silica catalyst, which suggests that this sample also contains bulk nickel. After activation at 923 K, the isotherm for the Ni/titania catalyst is very different, showing no tendency to reach a limit in the adsorption. This is evidence that the surface of the nickel in this catalyst has been modified by the high-temperature treatment. The obvious explanation, following the literature, would be that the Ni is now subject to a SMSI. However, at these temperatures, the possibility of surface contamination of the nickel by the titania cannot be ruled out. Furthermore, data on the activity of this catalyst (see later) indicate that only part of the nickel has been affected. We think that the isotherm reflects an interaction of *part* of the nickel with the support, the remainder of the nickel remaining unchanged. The important conclusion to be drawn from the isotherms is that after reduction at 723 K, the nickel in our Ni/titania catalyst has normal adsorption characteristics, but after reduction at 923 K, some of the nickel is modified, and adsorbs hydrogen less readily.

The specific nickel areas given in Table 1 emphasize the fact that there is no obvious suppression of hydrogen adsorption for the Ni/titania catalyst reduced at 723 K. The Ni area is only a factor of 2 lower than for the 9.9% Ni/silica catalyst, even though the surface areas of the supports differ by a factor of 6. Activation at 923 K causes the calculated Ni surface area to decrease by a factor of 4. Part of this decline may be due to SMSI. However, quite a large fraction may be due to sintering, as indicated by the X-ray data in the next section.

X-Ray Diffraction

Figure 2 shows the X-ray powder patterns for the Ni/titania catalyst after various activation pretreatments. After reduction at 623 or 723 K sharp lines for anatase and rutile are observed, and the intensities are in the correct ratio (80 : 20). The Ni lines are broad, but clearly visible; the particle size calculated from line broadening is 8.0 nm. After activation at 923 K the powder pattern shows that the titania has undergone the anatase to rutile transformation, and the Ni particle size has increased to 13.3 nm. The anatase to rutile transformation usually requires higher temperatures, but can be catalyzed by metals (*38–40*). It is important when considering possible models for titania-supported catalysts (see later) to recognize that the predominant form of the titania in samples activated at 623 or 723 K is anatase.

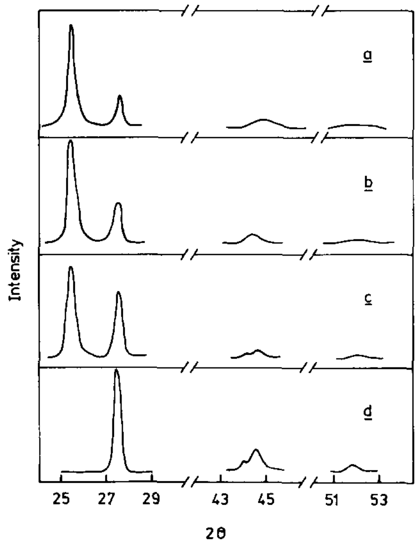

FIG. 2. Portions of the X-ray powder patterns for Ni/titania catalysts activated at (a) 623 K; (b) 723 K; (c) 923 K; (d) 1023 K. Lines correspond to anatase (25.4°), rutile (27.4, 44.0°), and nickel (44.5, 51.8°).

Activation at 1023 K causes all the remaining anatase to convert to rutile, and the nickel lines become sharper. This is further evidence that much of the nickel is unaffected by the high-temperature activation, remaining in the form of large particles, and that at least half of the surface area loss (see Table 1) is due to sintering of the Ni particles (see Fig. 2).

Hydrogenolysis of n-Hexane

The hydrogenolysis reaction is very sensitive to changes in catalyst structure and electronic properties; a reduction in activity by several orders of magnitude has been reported for the hydrogenolysis of ethane (*41*). With larger molecules, such as *n*-hexane, each metal produces a characteristic cracking pattern (*42*). In these cases, changes in both the activity and the selectivity can be used to probe the surface properties of a metal catalyst, and to investigate the influence of the support.

Figure 3 shows the variation in the activ-

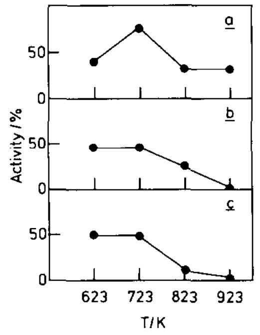

FIG. 3. Activity of Ni catalysts for the hydrogenolysis of *n*-hexane at 548 K, as a function of temperature of activation. (a) Ni9.9Si; (b) Ni8.5Ti; (c) Ni8.5Ti/Ar.

TABLE 2

Activity and Selectivity of Nickel Catalysts for the Hydrogenolysis of *n*-Hexane at 548 K, as a Function of the Activation Temperature

Catalyst	T^a (K)	Activity^b (%)	Product selectivity^b (%)				
			C1	C2	C3	C4	C5
Ni9.9Si	623	40.1	51.0	5.1	9.0	13.8	21.1
	723	75.4	64.3	6.1	9.4	10.0	10.2
	823	31.8	54.6	5.2	8.8	12.2	19.2
	923	30.5	58.2	5.0	8.8	11.1	16.9
Ni8.5Ti	623	46.1	51.8	6.4	9.1	12.5	20.2
	723	46.8	53.2	5.9	9.0	12.7	19.2
	823	23.1	57.5	5.2	8.3	11.3	17.7
	923	0.66	43.7	3.0	7.4	11.2	34.7
Ni8.5Ti/Ar	623	47.8	53.7	6.2	8.3	10.1	21.7
	723	47.8	56.5	5.5	8.2	9.3	20.5
	823	11.1	52.3	4.6	8.9	13.1	21.1
	923	2.8	44.4	4.9	9.5	14.8	26.4

[a] Temperature of activation treatment.

[b] See text for definition.

ity of our catalysts for the hydrogenolysis of *n*-hexane as a function of the temperature of activation. The activity is expressed as conversion defined by the relationship

$$\text{Conversion }(\%) = \frac{(\text{initial } C_6 - \text{final } C_6) \times 100}{\text{initial } C_6}$$

where C_6 is the concentration of *n*-hexane.

Table 2 shows the variation in the product distribution (i.e., selectivity) obtained in the *n*-hexane reaction over these catalysts. The selectivity of product *P* is defined by the relationship

$$S(P)(\%) = \frac{C_n \times 100}{n \sum_{1}^{n} C_n}$$

where C_n is the concentration of hydrocarbon *P* and *n* is the number of carbon atoms in hydrocarbon *P*.

For the silica catalyst, Fig. 3a shows that there is a sharp increase in activity after activation at 723 K. This produces a shift in product distribution (Table 2) from C_4, C_5 to C_1, C_2 hydrocarbons, presumably because of an increasing contribution of secondary cracking reactions at the higher conversion. This increase in activity is probably due to further reduction of nickel oxide on the support, since separate experiments have shown (*34*) that reduction of the nickel is not complete after 1 h at 623 K. Activation at 823 K results in a loss of activity by a factor of 2.5 and the product distribution changes in the expected manner. Further activation at 923 K has little effect on this catalyst, the small increase in selectivity to methane being within experimental error. The loss of activity on heating in hydrogen is not unexpected. It could reflect some degree of sintering of the nickel, or a structural transformation (to expose a greater proportion of (111) planes, for example (*41*)). Whatever the explanation, the effect is small under our experimental conditions and we conclude that in the absence of special effects the specific activity of Ni decreases at most by a factor of 2.5 when heated in hydrogen at 923 K for 0.5 h.

Figure 3b shows the corresponding data for the titania-supported catalyst heated in hydrogen, and Fig. 3c shows the results for the titania catalyst heated in argon (after the preliminary reduction for 1 h at 623 K). In contrast to the Ni/silica catalyst, the activities of the titania catalysts are unchanged after activation at 723 K, either under hydrogen or under argon. This is consistent with the results of other experiments (*34*) which show that titania-supported nickel oxide is completely reduced after heating in hydrogen for 1 h at 623 K.

The selectivity of the Ni/titania catalysts, either after activation at 623 or at 723 K, is very similar to that of the Ni/silica catalyst reduced at 623 K, so it is apparent that their performance in this reaction is characteristic of pure, unmodified nickel. (This is to be expected since there is general agreement that temperatures in excess of 723 K are necessary to induce SMSI.) This point is further established by comparing the specific activities of the Ni/silica and Ni/titania catalysts after activation at 723 K. The specific activities at 548 K, calculated by dividing the activities in Table 2 by the specific metal surface areas in Table 1, are 108 × 10^{-3} molecule s^{-1} Ni^{-1} for Ni/silica and 134 × 10^{-3} molecule s^{-1} Ni^{-1} for Ni/titania. Ponec and Sachtler (*43*), using unsupported Ni powder, obtained a specific activity at 603 K of 650 × 10^{-3} molecule s^{-1} Ni^{-1}. Using their value of 184 kJ mol^{-1} for the activation energy, we calculate a specific activity at 548 K of 16 × 10^{-3} molecule s^{-1} Ni^{-1}. This shows our catalysts to be about 10 times more active, which is reasonable agreement considering the very different particle sizes used in the two cases. More importantly, the results demonstrate the absence of any inhibition of the activity of the Ni/titania catalysts.

It may be noted that the specific activities, which show a slightly higher activity for the Ni/titania catalysts (ratio of activities is 1.28 : 1), agree very well with our data (*25*) obtained previously with samples prepared using a different batch of P25 titania, and tested at much smaller conversions (ratio then found to be 1.21 : 1).

As the temperature of activation is increased, Fig. 3 and Table 2 show that both titania-supported catalysts lose activity. For example, after pretreatment at 923 K the activity has declined by a factor of 71 for the catalyst heated in hydrogen, and by a factor of 17 for the catalyst pretreated in argon. The extent of deactivation is much greater than observed for the Ni/silica catalyst, and we conclude that the deactivation occurs because of a strong interaction with the support. However, it is important to appreciate that the activity determined after heating at 923 K does not necessarily correspond to the activity of the metal in the SMSI state. The specific metal area only declines by a factor of 4 after heating at 923 K (see Table 1), yet the activity declines by a factor of 71. This means that even though the samples continue to adsorb hydrogen (and so all the Ni is not in the SMSI state), most of the activity has been lost. Consequently, the two processes cannot be directly related. We believe that the effect of heating at high temperature is to deactivate almost totally a *fraction* of the nickel, perhaps the smaller nickel particles, leaving the remaining nickel (larger particles?) unaltered. It would have been anticipated that any major change in the surface properties of the Ni particles due to SMSI would have produced a parallel change in product distribution. In fact, although Table 2 shows the anticipated decrease in selectivity to methane as the activity of the Ni/titania catalysts declines, it is significant that even for the least active catalysts (i.e., where a SMSI presumably exists) the product distribution is characteristic of bulk nickel (i.e., giving terminal C–C bond cleavage).

The greater loss of activity of the titania-supported catalyst heated in hydrogen rather than in argon (see Table 2) may indicate that the creation of an SMSI is accelerated under reducing conditions. However, it should be noted that even heating in argon results in a much greater loss of activity for the Ni/titania catalyst than for the Ni/silica catalyst. We conclude that after reduction an SMSI can be produced in Ni/titania catalysts by heating under an inert atmosphere at higher temperatures. Valigi *et al.* (*44*) have observed a similar effect for Re/titania catalysts.

There are no published data on the hydrogenolysis of *n*-hexane over Ni/titania catalysts with which to compare our results. Therefore, we have determined also the activity of our catalysts for the hydrogenolysis of ethane, using experimental conditions similar to those used in the literature.

Hydrogenolysis of Ethane

Table 3 gives the results for the experiments on the hydrogenolysis of ethane over the Ni/titania catalyst. For experiments a, b, and c, the results show that the activity declines by a factor of 2.1 between 723 and 823 K, and overall by a factor of 16.8 between 723 and 923 K. The initial decrease is almost identical to that found for the hydrogenolysis of hexane (see Table 2); the overall decline is rather less, but this may partly

TABLE 3

Activity of Ni/Titania Catalysts for the Hydrogenolysis of Ethane

Experiment[a]	Activation treatment		Test temperature (K)							Relative activity[b]
	T (K)	Time (h)	478	548	573	598	623	648	673	
a	723	1.0	0.13	3.02	—	—	—	—	—	1.00
b	823	0.5	0.06	1.44	—	—	—	—	—	0.48
c	923	0.5	—	0.18	—	—	—	—	—	0.058
d	773	16.0	—	0.80	5.14	26.28	—	—	—	0.266
e	923	0.5	—	0.09	0.67	3.43	12.90	—	—	0.043
f	923	0.5	—	—	0.33	2.93	10.63	—	—	0.036
g	1023	0.5	—	—	—	0.25	1.12	3.74	11.1	0.004

[a] Experiments a, b, and c performed on a single sample subjected to successive heat treatments. Experiments d, e, f, and g performed on a single sample subjected to successive heat treatments.

[b] Activity calculated at 548 K.

reflect the uncertainties associated with measuring very low activities. The pattern of changes in activity for both the hexane and ethane experiments is broadly similar, so either reaction can be used to monitor changes in catalytic properties associated with SMSI.

The specific activity of our Ni/titania catalyst at 478 K, after reduction at 723 K, is 7.3×10^{-4} molecule s^{-1} Ni^{-1}. This is in very good agreement with the value quoted by Sinfelt (*45*) for Ni/silica (6.7×10^{-4}) the value obtained by Ryndin *et al.* (*46*) for Ni/silica at 473 K (7.6×10^{-4}), and the values reported by Sárkány and Tétényi (*47*) for samples of Ni black ($2.4–5.0 \times 10^{-4}$).

Our value for Ni/titania, therefore, shows no evidence of suppression of activity after reduction at 723 K. Moreover, the specific activity after activation at 923 K is reduced by less than a factor of 3. We conclude that after reduction at 723 K the Ni/titania catalyst has properties which are typical of pure nickel, and even after activation at 923 K the specific activity is consistent with the retention of pure nickel properties.

To obtain more detailed information on the nature of the nickel in our catalysts after activation at high temperatures, or after longer reduction times (compare Ref. *20*), a further set of experiments was performed (experiments d, e, f, g in Table 3). Activation energies were calculated from the Arrhenius plots which are shown in Fig. 4. The results are given in Table 4. After heating for 16 h at 773 K the activity has declined by less than a factor of 4 (compare experiments a and d in Table 3).

This contrasts sharply with the data of Ko and Garten (*20*) who found that after reduction at 773 K for 16 h a Ni/titania catalyst had a specific activity lower by a factor of 1000 than that of a Ni/silica catalyst. It should be noted, however, that the specific activities which they quote have been calculated assuming 100% dispersion of the

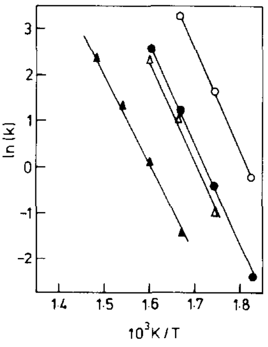

FIG. 4. Arrhenius plots for the hydrogenolysis of ethane over Ni/titania catalysts. The curves correspond to experiments d (○), e (●), f (△), and g (▲) in Table 3.

TABLE 4

Activation Energy for the Hydrogenolysis of Ethane over Ni/Titania Catalysts, Subjected to Different Heat Treatments

Experiment[a]	$E_A{}^b$(kJ mol^{-1})
d	190
e	177
f	160
g	160
Ref. (*20*)	130

[a] See Table 3 for details of heat treatment.

[b] Activation energy.

nickel on the titania. This is not meant to be a correct assumption, but was necessitated by the fact that they could not determine specific metal areas by hydrogen chemisorption. If we use the value for the dispersion of our catalyst after reduction at 723 K (8.9%) the specific activity calculated from Ko and Garten's results would still be about two orders of magnitude lower than we find after a similar pretreatment.

In our experiments, when the pretreatment temperature is increased, eventually to 1023 K, the relative activity (see Table 3) is found to decline by a factor of 250. Thus, our catalyst after reduction for 0.5 h at 1023 K has a similar activity to the catalyst used by Ko and Garten after reduction for 16 h at 773 K. However, as Table 4 shows, the catalysts are not equivalent. With our catalyst, as the temperature of activation is increased, there is a decrease in the activation energy from 190 down to 160 kJ mol^{-1}. However, Ko and Garten (*20*) quote an activation energy of 130 kJ mol^{-1} for their Ni/titania catalyst.

Typical values for the activation energy for the hydrogenolysis of ethane are difficult to establish. For unsupported nickel powders, Sárkány and Tétényi (*47*) quote values from 171 to 189 kJ mol^{-1}; and for Ni/silica, values of 184 (*46*), 160–170 (*48*), and 163 kJ mol^{-1} (*49*) have been reported. For highly dispersed Ni/silica catalysts Sárkány and Tétényi quote values from 138 to 220 kJ mol^{-1}.

It appears that our values for the activation energy, even after activation at 1023 K, correspond to the value for pure nickel. The much lower value found by Ko and Garten may correspond to nickel in the SMSI state. We believe the results indicate that in our catalyst, even after activation at 1023 K, a small amount of nickel (0.4% as judged by the activity data) remains uncombined with the titania, and the measured activity is due to this residual nickel metal. If this is correct, then it is possible that even the low activity measured by Ko and Garten for Ni/titania overestimates the activity of the nickel in the SMSI state, because there may be a contribution from a small residual amount of comparatively very active metallic nickel.

We have observed a similar effect before (*10*), where it was found for nickel on silica-alumina catalysts that the activity for hydrogenolysis was very small providing the metal loading was kept low enough to prevent metallic nickel particles being formed. As soon as this limit was exceeded the hydrogenolysis activity increased by about three orders of magnitude.

Our conclusion from the results for the hydrogenolysis of hexane and ethane is that activation at temperatures below 823 K has little effect on the characteristics of the nickel present in the Ni/titania catalysts.

It is relevant to enquire why our titania-supported catalyst differs so much from that used by Ko and Garten. The most obvious difference between the catalysts is the metal loading, 8.5% in our case, 2% in their case. It is possible that at the higher loading used in our experiments the nickel particle size is larger and so a much longer time is required for the metal to transform into the SMSI state. Indeed, since the titania has a surface area of only 50 m^2 g^{-1} it is possible that 8.5% Ni exceeds the amount of nickel which the support can accommodate in the SMSI state.

The important conclusion we draw from

our hydrogenolysis experiments is that our catalysts do not exhibit SMSI unless very high temperatures are used for the activation. Even then, the properties of the catalysts are more correctly interpreted as being due to a contribution from a small fraction of residual metallic nickel, than as a result of SMSI affecting the whole of the nickel. We now consider our CO/hydrogen experiments in the light of these observations.

CO/Hydrogen Experiments

Figure 5a shows the activity of the silica-supported catalyst for the methanation reaction after heating at different temperatures. There is an increase in activity between 623 and 723 K of about the same order of magnitude as observed for the hydrogenolysis of hexane, and most probably this is again due to further reduction of the nickel at 723 K. Heating at higher temperatures results in a small decrease in activity, which parallels closely the behavior observed in the hexane experiments. The specific activity of this catalyst at 548 K, after reduction at 723 K, is calculated to be 11×10^{-3} molecule s^{-1} Ni^{-1}. This value may be compared with published data for Ni/silica catalysts, namely, 7×10^{-3} (*50*), 5.0–14.4 $\times 10^{-3}$ (*51*), 14.8×10^{-3} (*9*), and, for a Ni(100) surface 40×10^{-3} (*52*). The excellent agreement confirms the reliability of our experimental procedures.

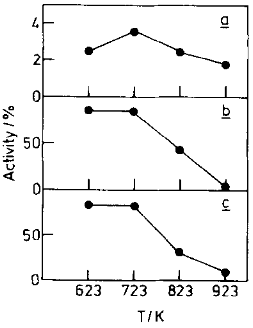

FIG. 5. Activity of Ni catalysts in the CO/H_2 reaction at 548 K as a function of temperature of activation. (a) Ni9.9Si; (b) Ni8.5Ti; (c) Ni8.5Ti/Ar.

TABLE 5

Activity and Selectivity of Nickel Catalysts in the CO/H_2 Reaction after Different Heat Treatments

Catalyst	T^a (K)	Activity[b] (%)	Product selectivity[b] (%)				
			C1	C2	C3	C4	C5
Ni9.9Si	623	1.2	87.2	7.2	5.6	—	—
	723	1.7	86.7	6.9	5.7	0.7	—
	823	1.1	86.4	7.5	6.1	—	—
	923	0.9	79.3	9.9	9.3	1.5	—
Ni8.5Ti	623	40.6	100.0	—	—	—	—
	723	40.1	99.9	0.1	—	—	—
	823	20.3	71.8	12.7	11.7	3.8	—
	923	2.1	36.2	23.8	23.4	12.5	4.1
Ni8.5Ti/Ar	623	39.5	100.0	—	—	—	—
	723	39.1	100.0	—	—	—	—
	823	14.5	60.9	13.9	15.9	5.8	3.5
	923	4.5	44.5	14.0	20.0	11.0	10.5

[a] Temperature of heat treatment.
[b] See text for definition.

Table 5 shows that all the Ni/silica catalysts produce predominantly methane, although significant amounts of higher hydrocarbons are produced also. The selectivity in this reaction is very dependent on temperature, H_2/CO ratio, pressure, and conversion, but *under comparable conditions* the selectivity to methane can be used to probe the nature of the active site. At temperatures around 550–575 K, bulk nickel produces methane almost exclusively (*52, 53*). At low dispersions Ni/silica catalysts also produce more than 95% methane. However, as the dispersion increases so does the concentration of higher hydrocarbons (*50, 51*). The selectivity of our Ni/silica catalyst after reduction at 723 K agrees very well with data for catalysts having similar dispersions (*50, 51*).

Table 5 indicates that after activation of the Ni/silica catalyst at higher temperatures, the selectivity to methane decreases. Higher temperatures will reduce the dispersion, so this shift in selectivity is opposite to the expected trend. This may be due to migration of Ni into the silica to give Ni^{2+} ions which interact with the nickel particles to create sites having a lower hydrogenation activity. It is interesting that for Ni/alumina catalysts, where reduction of nickel is much more difficult, the concentration of higher hydrocarbons can be very high (*51*, *54*).

Figures 5b and c show that the activity of the titania-supported catalysts is much higher than that of the Ni/silica catalyst. The activity remains high after heating at 723 K, but then decreases sharply to a low value after heating at 923 K. The decrease in activity is slightly greater for the sample heated in hydrogen but, just as in the hydrogenolysis of hexane, a substantial loss of activity occurs under argon also.

Table 5 shows that the selectivities of the Ni/titania catalysts are very different from that of the Ni/silica catalyst when comparisons are made at equivalent conversions. The high selectivity of the Ni/TiO_2 catalyst to methane at high conversions may be due to a localized overheating of the active metal because, as Fig. 6 shows, there is a linear correlation between selectivity to methane and activity. The CO/hydrogen reaction is very exothermic, so overheating is possible. Separate experiments on these catalysts (*34*) have confirmed that the selectivity at low conversions for fresh catalysts reduced at 723 K is similar to the selectivity given in Table 5 for catalysts heated at 923 K. Vannice and Garten (*9*), using a 1.5% Ni/titania catalyst obtained a selectivity to methane at 524 K of 30%. Bartholomew *et al.* (*51*), using a 2.8% Ni/P25-titania catalyst, obtained a selectivity to methane of 70% for an impregnated catalyst, and 30% for a precipitated catalyst. These values are in reasonable agreement with our results.

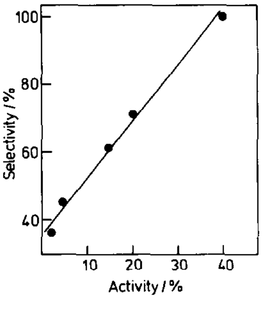

FIG. 6. Correlation between activity and selectivity to methane for Ni/titania catalysts in the CO/H_2 reaction.

The specific activity of our Ni/titania catalyst for the CO/hydrogen reaction at 548 K, after reduction at 723 K, is 508×10^{-3} CO molecule s^{-1} Ni^{-1}, which is nearly 50 times greater than the specific activity of our Ni/SiO_2 catalyst. (Under similar experimental conditions, Vannice and Garten (*12*) quote a turnover number for their Ni/P25-titania catalyst which is one-fourth the activity of their Ni/Cabot-titania catalyst studied earlier (*9*). Very approximately this corresponds to a specific activity for their Ni/P25-titania catalyst at 548 K of 400×10^{-3} CO molecules s^{-1} Ni^{-1}.) Bartholomew *et al.* (*51*) obtain a specific activity at 525 K of 4.7×10^{-3}, also for a Ni/P25-titania catalyst, but they were using much smaller partial pressures of CO and hydrogen. Overall, there is reasonable agreement between our specific activities and selectivities and data in the literature for samples reduced at 723 K.

We obtain the same very high specific activities, and the same high selectivity toward higher hydrocarbons. Furthermore, our results for the chemisorption of hydrogen, for the hydrogenolysis of *n*-hexane, and for the hydrogenolysis of ethane *on these same catalysts* are all consistent with literature data for *normal metallic nickel* catalysts.

Figure 7 summarizes the data presented in this paper. There is a smooth decrease in catalytic activity and hydrogen adsorption capacity for the Ni/titania catalysts as the temperature of activation is increased. However, the decline in the amount of hydrogen adsorbed is less than the decline in catalytic activity, so that although the two processes may be related it appears that hydrogen chemisorption does not give a reliable measure of the number of active sites for these reactions. The fact that the catalytic activity is not directly proportional to the metal surface area as measured by hydrogen chemisorption suggests that only a

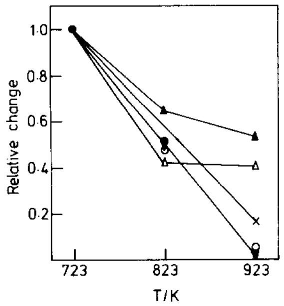

FIG. 7. Relative changes in properties of Ni catalysts as a function of the temperature of activation. ▲, activity of Ni9.9Si in the CO/H_2 reaction; △, activity of Ni9.9Si in the *n*-hexane reaction; ×, hydrogen adsorption on Ni8.5Ti; ●, activity of Ni8.5Ti in the CO/H_2 reaction; ▼, activity of Ni8.5Ti in the *n*-hexane reaction.

fraction of the available metal surface is active, and that these special sites can be eliminated without a corresponding loss of total metal surface.

The loss of hydrogen adsorption capacity and hydrogenolysis activity is anticipated if the metal is in the SMSI state. However, the parallel loss of activity in the CO/hydrogen reaction is not expected since the *enhanced* activity in this reaction is supposed to be due to the existence of an SMSI. Our results show that under conditions where an SMSI is *absent* (as judged by normal hydrogen adsorption, hexane hydrogenolysis activity, ethane hydrogenolysis activity, and typical activation energy in ethane hydrogenolysis) we still observe high activity in the CO/hydrogen reaction and high selectivity to higher hydrocarbons. We conclude that the enhanced activity of titania-supported Ni catalysts for the CO/hydrogen reaction is not due to SMSI *as defined in the literature*. It is necessary to consider more carefully the nature of the SMSI in these catalysts.

SMSI in Ni/Titania Catalysts

In the literature SMSI are taken to indicate a state in which through interaction with the support the *surface* of a metal particle is modified, probably because of an exchange of electrons with the support. For easily reducible transition metal oxides this interaction is thought to be between a metal atom and a surface cation, via a surface anion vacancy. This effect need not be restricted to reducible oxides since surface vacancies can be created in alumina or silica by high-temperature dehydration reactions. An interaction between a *small* metal particle and the support may result in a modification of the surface of the metal. However, for larger metal particles it is unreasonable to expect such a surface modification except after very long activations at high temperatures, and certainly not after 1 h at 623 K.

There is evidence that metal particles wet the titania surface, and develop a "pillbox" morphology (*3–5*). However, this thinning process will not lead to a modification of the properties of the surface metal atoms until the metal particle is less than three to four layers thick (<1 nm). Our X-ray data show evidence of particle *growth* after high-temperature activation (Fig. 2). Although this cannot be taken as proof that the particles are thick, the sharpness of the lines does suggest a minimum thickness >1 nm.

The significant observation which we have made is that a high specific activity in the CO/hydrogen reaction can be obtained even when the type of SMSI referred to in the literature is absent, i.e., after very mild reduction for 1 h at 623 K.

A model for the Ni/Titania System

It is not possible to describe the Ni/titania system with great confidence. However, the following model is consistent with the data currently available. We propose for systems such as the Ni/titania system, which contain large particles, that any special support effects will be restricted to the interfacial region, at the point of contact between the metal and the support. We are concerned with *interfacial* metal–support interactions (IMSI).

Figure 8 shows the stages in the development of the Ni/titania system as the temper-

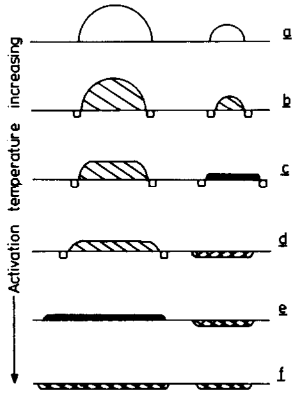

FIG. 8. Interactions in the Ni/titania system as the activation temperature is increased. ⌓, NiO; ◒, bulk Ni metal; ▬, surface Ni (≤1 nm) in the SMSI state; ▩, Ni in a partially ionized subsurface state; □, oxygen anion vacancy.

ature of activation is increased. After the initial reduction of the nickel oxide (Fig. 8a), the surface consists of bulk nickel metal particles of varying size, and anion vacancies on the support adjacent to the metal–support interface (Fig. 8b). As the temperature of activation is increased, the SMSI develops and the particles wet the surface, become flattened, and spread out. This process will not occur at a precise moment: instead there will be a gradual change in the nickel particles. At some intermediate point (Fig. 8c), the smallest particles will have spread out and have a thickness less than about 1 nm. These particles will no longer have nickel-type properties, they may not adsorb hydrogen, and they will exhibit different catalytic properties. Further heating (Fig. 8d) will result in migration of the nickel atoms into the subsurface layers of the support, where they will exist as ions. (There is evidence of such a process for Fe/titania (*27, 28*) and Re/titania catalysts (*44*). This "ionic" form of nickel will have an extremely low catalytic activity (compare Ni ions in alumina). Eventually, as Fig. 8e shows, all the bulk nickel will have disappeared to be replaced by a surface Ni phase. At this stage the catalytic properties will correspond to nickel in the total SMSI state (TSMSI). After a sufficient time the final stage will be reached (Fig. 8f), where no zero-valent nickel remains.

The changes in the activities of the various reactions which we have investigated may be interpreted using this model. It is fairly certain that in our catalysts we do not pass beyond stage (d), i.e., there is always residual bulk nickel present. Consequently, our activities decline in parallel with our hydrogen adsorption data because a fraction of the nickel transforms into the TSMSI state and becomes inactive, but the larger nickel particles retain normal properties. The fact that Ko and Garten (*20*) observe a different activation energy for the ethane hydrogenolysis reaction for their 2% Ni/titania catalyst may indicate that it is easier to arrive at stage (e) because of a smaller average particle size.

The Active Site in the CO/H_2 Reaction over Ni/TiO_2 Catalysts

Figure 9a is a representation of the interface between a Ni particle and the titania surface, corresponding to stage (b) in Fig. 8. It is proposed that at the interface between the metal and the support, anion vacancies are created, possibly as a result of hydrogen spillover from the metal. The Ti^{3+} ions at the vacancy could influence the

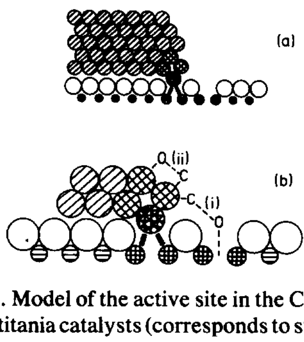

FIG. 9. Model of the active site in the CO/H_2 reaction over Ni/titania catalysts (corresponds to stage (b) in Fig. 8). ⊘, normal Ni atom; ⊗, $Ni^{\delta\delta-}$ atom; ●, $Ni^{\delta-}$ atom; ○, oxide ion; ⊕, Ti^{3+} ion; ⊖, Ti^{4+} ion; ▮, SMSI.

course of the CO/hydrogen reaction in a number of ways, e.g. (1) direct involvement of the support (a) by forming a bond to the oxygen atom in a CO molecule, or (b) by adsorbing a CO molecule via the C atom; (2) indirect involvement of the support (a) by exchanging electrons with the metal, or (b) by changing the architecture of the metal particle.

The first possibility, that is the direct intervention of the support by forming a bond to a CO molecule, is the process which we have suggested previously (*25*). This is illustrated in Fig. 9b (i) for the case where Ti^{3+} interacts with the oxygen atom of a CO molecule; the other possibility, i.e., adsorption of CO at a Ti^{3+} site alone, is not illustrated. In this model, the enhanced activity of the titania-supported Ni catalyst would arise because of the creation of a new type of active site at the Ni/TiO_2 interface. This model would account for the special role of reduced titania, and also for the fact that Ni/titania catalysts deactivate very rapidly (*34*). (This could occur, for example, by blocking of Ti^{3+} sites with oxygen from CO molecules.) However, it is less easy to account for the fact that the activation energy for this reaction is similar over Ni/titania catalysts as over other Ni catalysts (*12, 55*).

The second alternative, i.e., indirect involvement of the support, requires either a modification of the electronic properties of the metal atoms near the interface, or a change in the shape of the metal particles. In Fig. 9b (ii), we have indicated an electron transfer from the support to the metal, which is consistent with other published data (*37, 56*), although Vannice and Garten (*9*) originally proposed an electron transfer in the opposite direction.

It is important to emphasize that our model differs from previous models because support effects are restricted to the atoms at the interface. The high electron density at the Fermi level in the metal will ensure that electronic perturbations are smoothed out within a very few atomic distances.

There is disagreement in the literature concerning the mechanism and the rate-determining step in the CO/H_2 reaction. Dissociation of CO is generally considered to be the first step, but it is uncertain whether the rate-determining step is the dissociation of the CO, or the subsequent hydrogenation, or the desorption of the products (*57–59*). It is possible that a change in the electron density on the Ni atoms as shown in Fig. 9b will affect the catalytic properties by increasing the rate of dissociation of CO molecules, or by increasing the rate of desorption of hydrogenated products.

Serious weaknesses in the electronic model at present are the absence of clear evidence of a significant degree of electron transfer for polycrystalline samples, and the fact that even for single crystal samples, where a large degree of electron transfer is detected (*60*), the activity for the CO/H_2 reaction is only a factor of three higher than for unsupported Ni.

The final, possible role of the support is in modifying the architecture of the metal particle. There are reports that metal particles supported on titania tend to wet the oxide surface (*3–5*), although the TEM evidence for this has been questioned (*61*). If correct, this change in the architecture of the metal particles could account for the enhanced activity. However, since no equivalent changes are observed in the activity for hydrogenolysis, a mere change in particle shape seems unlikely to be the reason for the enhanced activity.

The CO/H_2 Reaction over Other Titania-Supported Metal Catalysts

In this paper our main concern has been with the Ni/titania system, and with the importance of the interface between the metal and the support. However, it is possible that similar IMSI also operate with other metals. The observation (*36*) that the activity of most metals supported on titania is high for the CO/H_2 reaction suggests a common explanation. We suggest that this may be a consequence of IMSI rather than

SMSI as has been proposed previously. Similarly, the dramatic changes in selectivity which can be obtained when different supports are used could be due also to IMSI.

Another feature of our IMSI model is that it implies that only a small fraction of a metal surface is active in the CO/H_2 reaction. As yet this cannot be reconciled with the observed decrease in activity with increasing dispersion (*62, 63*). However, a similar proposal has been made for Pd/titania catalysts (*64*).

CONCLUSIONS

The main conclusion of this work is that very high activity and selectivity in the CO/H_2 reaction can be obtained under conditions where SMSI are absent. It is proposed that the role of the titania is to create new active sites at the interface between the metal particles and the support, either through a direct or an indirect intervention of the support. Although either is feasible there is some preference for a model in which there is direct involvement of Ti^{3+} cations exposed at anion vacancies in a partially reduced titania surface.

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