

The Effect of Supports on the Chemisorptive Properties of Catalysts

I. Magnetic Studies of Nickel Catalysts

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Studies were conducted on the chemisorptive and magnetic properties of supported nickel catalysts in order to investigate the effect of metal-support interactions on different support materials. The catalysts consisted of both 7 and 20% nickel supported on SiO₂, Al₂O₃, TiO₂, alumina-aluminum phosphate (AAP), and magnesia-alumina-aluminum phosphate (MgAAP). For catalysts supported on phosphate-containing materials, the inducement of metal-support interactions was accompanied by both a lowering of the Curie temperature and a change in chemisorptive behavior. Irreversible hydrogen chemisorption was suppressed, as is typical of strong metal-support interactions (SMSI) materials, but a significant reversible chemisorption was still evident. In contrast, the inducement of SMSI in TiO₂-supported catalysts showed no change in Curie temperature and no reversible hydrogen chemisorption. The different behaviors observed in the various materials have been attributed to different mechanisms responsible for the inducement of the metal-support interactions. © 1985 Academic Press, Inc.

INTRODUCTION

The behavior of some metals supported on reducible transition metal oxides is unusual. These materials show normal hydrogen chemisorption when reduced at low temperatures but exhibit a diminished sorption capacity when the reduction is conducted at elevated temperatures. This behavior has been explained in terms of strong metal-support interactions (SMSI) and has received considerable attention from both industrial and academic researchers in the last few years (for a recent review, see Ref. (1)). The most commonly studied examples of SMSI are noble metals or nickel supported on titania (2, 3). Recently, it has been reported that some non-transition metal oxides, such as silica (4), silicon carbide (5), and aluminum phosphate (6) are also capable of interacting with metals to suppress normal hydrogen chemisorption.

Many tentative explanations have been offered to explain this phenomenon, such as morphological changes in the active

metal (7), electronic interactions (1), alloying (8), and encapsulation (9). The exact nature of the interaction, however, remains obscure. As part of an effort to identify techniques for measuring active site densities in catalysts, we have been studying the magnetic and chemisorptive behavior of nickel metal supported on various materials. By doing so we hope to better define the existence and extent of metal-support interactions in systems of catalytic interest.

EXPERIMENTAL

A series of catalysts was prepared containing two different nominal levels of nickel, 7 and 20%, using the following supports: silica, alumina, titania, alumina-aluminum phosphate (AAP), and magnesia-alumina-aluminum phosphate (MgAAP). The preparation of the supports and the high nickel content catalysts has been described previously (10, 11). The 7% nickel catalysts were prepared on alumina, titania, and AAP using ion-exchange techniques. The finely powdered support was slurried into an aqueous solution of nickel nitrate

equivalent to 10% metal loading. The pH was adjusted to 6.3 and the temperature raised to 55°C with constant stirring. Exchange was allowed to proceed for 4 h while periodically adjusting the pH of the solution, if necessary, to keep it constant. After this time period the slurry was filtered, thoroughly washed, and dried overnight at 120°C. No calcination was performed on these catalysts prior to reduction. The 7% Ni on silica catalyst was prepared by precipitation of nickel onto a colloidal suspension of silica gel (12).

Magnetization measurements were performed using a Cahn Model 6602-4 Faraday apparatus capable of producing fields up to about 10 kOe and incorporating a thermostatted sample section with flow-through capability. Prior to magnetic measurements, approximately 5 mg of catalyst were reduced *in situ* overnight (unless otherwise noted) at the desired temperature, followed by evacuation for 2 h at the reduction temperature. The magnetization at constant field strength, typically 5 kOe, was measured as a function of temperature by decreasing the temperature at a rate of about 2°C/min and charting the results using an X-Y recorder. A thermocouple located ca. 5 mm below the sample bucket was used to monitor the temperature. The average nickel crystallite size was obtained by measuring the magnetization versus field behavior at 25 and -196°C and using the low field approximation of the Langevin equation (13).

Dynamic hydrogen uptake measurements were performed using a conventional pulsed chemisorption system and previously described techniques (6). The extent of reduction of the metal was determined using oxygen titration at 450°C and assuming that only the metal was being oxidized (6). Blank experiments on the support materials alone supported this assumption. Static hydrogen chemisorption measurements were also performed on the samples subjected to the magnetization studies by measuring the decrease in magnetization of

TABLE I
Hydrogen Chemisorption of Ni Catalysts

Catalyst	Temperature of reduction (°C)	Percent reduction	Apparent dispersion
20% Ni/silica	300	100	10
	500	100	10
20% Ni/titania	300	45	3.9
	500	100	0.6
20% Ni/alumina	300	80	8.2
	500	100	7.5
20% Ni/AAP	300	10	3.2
	400	90	4.2
	500	100	0.4
20% Ni/MgAAP	300	40	12.5
	400	90	2.9
	500	100	1.1
7% Ni/silica	400	100	25
7% Ni/titania	300	100	0
	500	100	0
7% Ni/alumina	400	100	12
7% Ni/AAP	300	0	—
	400	70	0
	500	100	0

the catalysts upon admission of hydrogen to a pressure of 20 Torr. After stabilization of the baseline, the system was pumped out in order to measure the amount of reversibly chemisorbed hydrogen (14).

RESULTS AND DISCUSSION

Pulse Chemisorption

Table I summarizes the results of the pulse chemisorption measurements. Some of these results have been previously reported (6), but are included for the sake of completeness. As expected, when nickel is supported on noninteracting supports, such as the conventional silica or alumina, the hydrogen chemisorption characteristics are independent of reduction temperature and are in rough agreement with values of crystallite size. Titania, AAP, and MgAAP, however, exhibit higher hydrogen chemisorption when reduced at low temperature than when reduced at high temperature. This suppression of the normal sorptive capacity has been interpreted as caused by the inducement of metal-support interactions and has typically been used as the test for the existence of SMSI states in sup-

ported-metal catalysts (1-6). For the purpose of this article, a catalyst will be defined to be in a SMSI state if it is shown to exhibit a lower H₂-sorption capacity when reduced at high temperature ($\geq 500^\circ\text{C}$), and if this suppression is reversible upon oxidation, followed by low-temperature reduction. Nickel supported on TiO₂, AAP, or MgAAP conforms to this definition.

Two other features are apparent from examination of the data. Whereas the catalysts prepared on noninteractive supports show almost complete nickel reducibilities at 300°C, this is not necessarily the case for the interactive supports and in particular for the phosphate-based supports. This apparent difficulty in reducing the metal when supported on the interactive supports is probably due to a combination of factors related to the dispersion and the interaction existing within the catalyst. Bartholomew and co-workers have shown that small metal oxide particles are more difficult to reduce than their larger counterparts, particularly when supported on interactive supports (15). They showed that highly dispersed nickel oxide on alumina cannot be readily reduced, even at temperatures as high as 450°C. Further, they interpreted this as resulting from catalyst-support interactions which are existent in highly dispersed nickel on alumina. The ease of reducibility which was exhibited by the 7% Ni on titania is inconsistent, since the previous explanation would argue for the reverse. An alternate explanation is that the different methods employed to prepare the high- and low-loading catalysts influenced the reducibility of the nickel in the finished material.

The second feature that is apparent from examination of Table 1 is that the inducement of metal-support interactions occurs at different temperatures for catalysts with different metal loadings. In fact, for the 7% nickel on AAP and titania catalysts, we were not able to reduce the metal without suppressing the normal H₂ chemisorption. This ease in inducing metal-support inter-

actions is most likely due to the small nickel crystallite size found in these catalysts. Ko *et al.* have shown that for Ni supported on TiO₂ or Nb₂O₅, metal-support interactions may be induced at milder conditions on catalysts exhibiting smaller metal crystallites (16, 17). They showed that reduction in flowing hydrogen at 300°C for 1 h was sufficient to nearly completely suppress the hydrogen chemisorption of a 7% Ni/TiO₂ catalyst with average crystallite diameter of 35 Å. As seen in Table 2, the 7% Ni/TiO₂ and 7% Ni/AAP used in this study both showed average nickel crystallite diameters <30 Å, and as such it is not entirely surprising that the low-temperature reduction was sufficient to fully induce the SMSI state.

Magnetic Measurements

Measurements of the magnetization-temperature behavior were performed on the catalysts in order to see if the inducement of the SMSI state was reflected in the bulk electronic properties of the ferromagnetic nickel metal. One of the mechanisms that has been proposed to explain SMSI consists of reduction of the support during the high-temperature reduction, followed by a partial electron transfer between the metal and the support (18). If this electron transfer occurs for a significant number of nickel atoms, it should be reflected in their magnetic behavior and particularly in a shift of the Curie temperature (T_c).

Magnetic parameters of the catalysts were extracted from the experimental magnetization temperature [$M(T, v)$] behavior using the theory derived by Bean and co-workers (19) in which

$$M(T, v) = I_{sp}(T) \cdot \left(\sum v \right) \cdot \left[\coth \frac{I_{sp} v H}{kT} - \frac{kT}{I_{sp} v H} \right], \quad (1)$$

where H is the magnetic field, v is the particle volume, k is Boltzman's constant, and $I_{sp}(T)$ is the saturation magnetization of the bulk material at temperature T . This ex-

TABLE 2
Effect of Support and Metal-Support Interactions
on the Magnetic Properties of Nickel Catalysts

Catalyst	Reduction temperature ^a (°C)	Crystallite diameter (Å)		SMSI?	Curie temp. (°K)
		Field	Temp. Fit		
20% Ni/silica	500	—	≥120	N	640
20% Ni/silica	500	80	65	N	630
20% Ni/titania	500	85	≥120	Y	640
20% Ni/AAP	500	40	70	Y	640
	500	40	55	Y	630
7% Ni/silica	400	≤30	≤30	N	600
7% Ni/alumina	500	50	40	N	600
7% Ni/titania	500	≤30	40	Y	600
7% Ni/AAP	500 (1 h)	≤30	40	Y	600
	500	≤30	^b	Y	^b

^a All reductions were conducted for 16 h unless indicated.

^b Not determinable using Eq. (1).

pression predicts the $M(T, v)$ relationship for particles which are small enough to consist of a single magnetic domain and yields particle sizes in good agreement with those obtained from chemisorption and X-ray diffraction (XRD) measurements where comparisons are valid. For systems in which the Curie temperature is different from that of nickel (631°K), we have presumed that the bulk magnetization of the system follows the Weiss expression for M versus T/T_c for $J = \frac{1}{2}$ (20) and that the saturation magnetization for the unknown is equal to that of Ni at the same reduced temperature ($T_R = T/T_c$). The latter was obtained from the experimental Ni saturation magnetization data of Weiss and Forrer (21).

Figure 1 shows the normalized $M(T)$ data at 5 kOe for two relatively low dispersion Ni/SiO₂ catalysts. The curves in the figure are the calculated curves for 120-Å particles at $T_c = 640^\circ\text{K}$ and 65-Å particles at $T_c = 630^\circ\text{K}$. For comparison, the experimental data for bulk nickel at 4 kOe are also plotted. As one can see, there is little observable difference between $M(T, v)$ for $v = 120$ Å and the bulk curve. From an examination of the family of curves developed for

$M(T, v)$, it was observed that very little change occurs for particle sizes above 120 Å. It is also the case that very little change

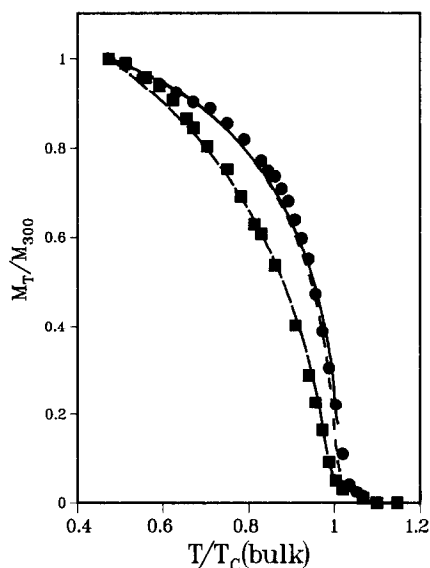


FIG. 1. Magnetization-temperature curves for 20% Ni/SiO₂ catalysts with different dispersions. Average nickel crystallite diameters were 120 (●) and 65 Å (■). Lines represent calculated curves for Ni with 640°K (—) and 630°K (---) Curie temperature and appropriate crystallite diameters. Also shown are experimental results for bulk Ni at 4000 Oe (-.-).

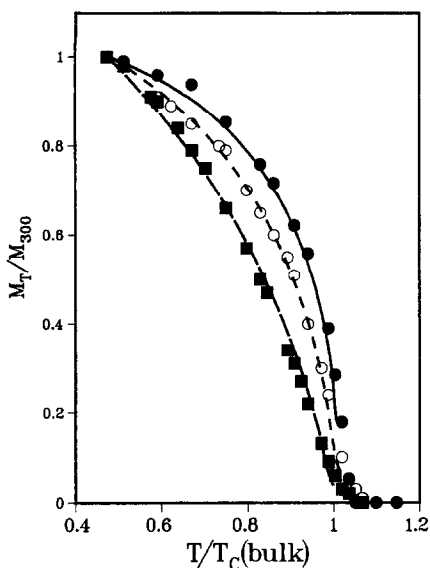


FIG. 2. Magnetization-temperature curves for 20% Ni catalysts. Supports used were TiO_2 (●), AAP (○), and MgAAP (■). Lines are calculated for Ni with Curie temperatures and diameters of 640°K, 120 Å; 640°K, 70 Å; and 630°K, 55 Å, respectively.

is apparent in the normalized $M(T, v)$ curves for particles less than 30 Å in size.

Figure 2 presents the data for the other

20% Ni catalysts after high-temperature reduction, along with the theoretical curves which best fit the data (to $\pm 10^\circ\text{K}$ in T_c and ± 10 Å in diameter). For the fully reduced 20% Ni catalysts, the Curie temperatures are within experimental error of bulk nickel, in agreement with reports by other investigators (22). The particle sizes range from 55 to 120 Å depending on support (and/or preparation methods).

The magnetic behaviors of the 7% Ni catalysts are more diverse. Figure 3a presents the data for 7% Ni/ Al_2O_3 and 7% Ni/ SiO_2 , Fig. 3b that for 7% Ni on TiO_2 . These catalysts behave as predicted for small crystallites of a ferromagnetic material of less than 40 Å in size and Curie temperature about 600°K. For the 7% Ni/ TiO_2 , there does appear to be a systematic deviation between the experimental points and the predicted curves, in that the low-temperature points are consistently high and the high-temperature points are low. This was also the case for the 20% Ni on AAP, MgAAP, and one of the 20% Ni on SiO_2 catalysts, but not so noticeable in those cases. The $M(T)$ data for the 7% Ni/AAP catalyst reduced at

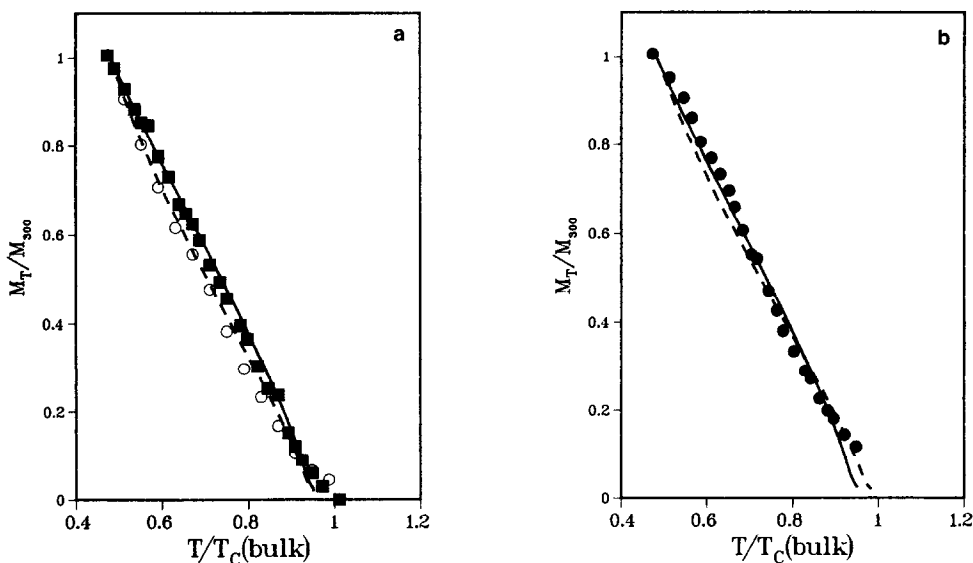


FIG. 3. Magnetization-temperature behavior for 7% Ni catalysts. Supports used were: (a) alumina (■) and silica (○), and (b) titania (●). Lines are calculated for: (a) 600°K, 40 Å (—) and 600°K, 30 Å (---) and (b) 600°K, 40 Å (---) and 590°K, 35 Å (—).

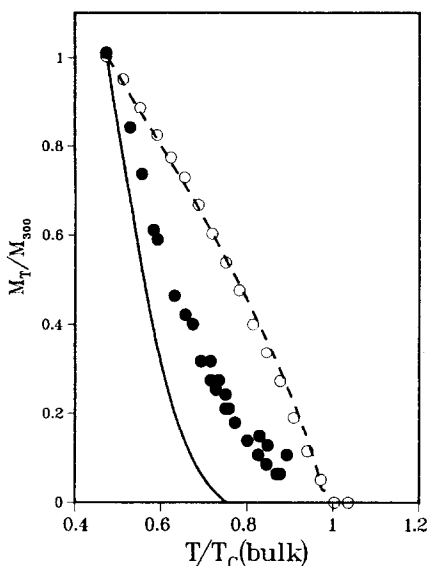


FIG. 4. Magnetization-temperature behavior for 7% Ni/AAP catalyst after reduction at 773°K for 1 (○) and 16 h (●). Dashed line is calculated for $T_c = 600^\circ\text{K}$ and 40-Å diameter. Solid line is reported results for NiP alloy (Ref. (23)).

500°C for 1 and for 16 h are given in Fig. 4 along with the theoretical curve for 40-Å particles having a Curie temperature of 600°K, which fits well the data on the sample receiving 1 h of reduction. An interesting feature is observed on the 16-h results; whereas ferromagnetic Ni normally exhibits an upwardly concave $M(T)$ curve shape, the 16-h data show the reverse curvature. This anomalous behavior is so pronounced that the experimental points could not be satisfactorily fitted using Eq. (1), regardless of the crystallite size or curve temperature used in the fit. This behavior is unusual but not unknown. Iida (23) has demonstrated that this behavior is found in amorphous NiP alloy films, and his data are also presented in Fig. 4. This film contained 16% P and showed no X-ray evidence for crystalline Ni or Ni_3P . Iida noted that other nickel-metalloid alloys exhibit this anomalous $M(T)$ behavior.

Table 2 summarizes the results of the Curie point and crystallite size determinations. Examination of the table shows that a

reduction in crystallite size results in a slight decrease in Curie temperature to ca. 600°K, regardless of support. Also, different magnetic behavior can be seen in Ni catalysts prepared on different supports which exhibit suppression of hydrogen chemisorption and hence are labeled "SMSI."

Several reasons can be proposed for the observed lower T_c in the high-dispersion catalysts. First, that interactions between small crystallites and the support lead to electron transfer and T_c changes. Second, that Ni^{2+} present in the incompletely reduced particle alters the magnetic behavior. Third, that impurities in the support itself react with the nickel to form interstitial compounds or alloys. Any of these explanations is consistent with the observation that changes in T_c are observed in higher dispersion, lower loading catalysts.

Several reports can be found in the literature which support the claim that many magnetic properties, including T_c , are dependent on the degree of dispersion of the ferromagnet. Abeledo and Selwood (24) and Carter and Sinfelt (25) studied the magnetic behavior of highly dispersed silica-supported nickel catalysts and concluded that Curie temperature decreased with increasing degree of dispersion. On the other hand, reports can also be found which state that Curie temperature is independent of particle size for such diverse systems as nickel films in the thickness range 25 to 100 Å (26), cobalt particles down to 20 Å (27), and iron particles between 15 and 100 Å in diameter (28). A recent study by Derouane and co-workers (29), using supported nickel catalysts, concluded that Curie temperature is indeed independent of dispersion but highly dependent on the presence of Ni(II) ions. They explained that previous work reporting dispersion effects on magnetic properties was probably in error due to incomplete reduction of the nickel precursor. Certainly, the presence of Ni^{2+} (with appropriate charge compensation anion—probably O^{2-}) would be expected to alter the electronics of a Ni cluster.

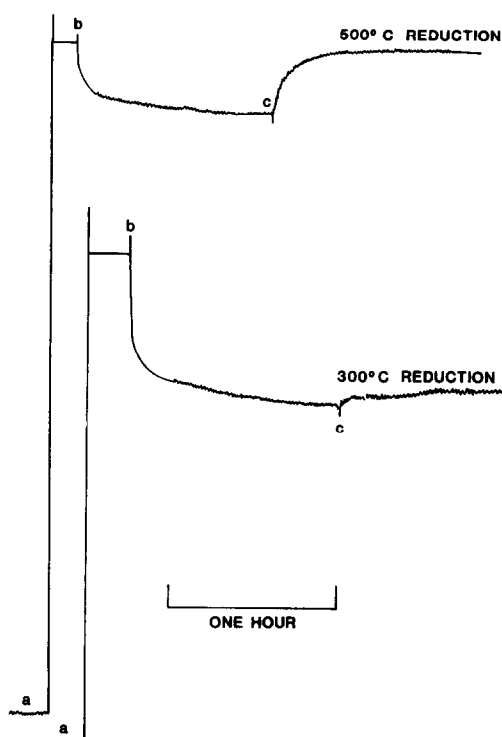


FIG. 5. Effect of reduction temperature on the chemisorptive properties of 20% Ni/MgAAP. Events of note are (a) field on, (b) hydrogen added, and (c) system evacuated. Procedure is detailed in the text.

Regardless of the cause leading to the low T_c in the small crystallite nickel catalysts, the resulting T_c appears to be affected only slightly when the metal is supported on SiO_2 , Al_2O_3 , or TiO_2 . Ni supported on AAP, however, behaves like small crystallite nickel following an initial 1-h reduction but exhibits anomalous magnetic behavior after overnight reduction. This unique change in magnetic behavior of Ni/AAP, upon long-term reduction, leads us to believe that the mechanisms responsible for the observed H_2 -chemisorption suppression in Ni/AAP and Ni/ TiO_2 are different, and hence there is more than one type of "SMSI."

As further evidence for the existence of more than one type of "SMSI," the chemisorptive properties of the catalysts under static conditions were studied. Static che-

misorption has the advantage of differentiating between reversible and irreversible, or weak and strong, adsorption modes. The measurements were performed by observing the decrease in magnetization as hydrogen came in contact with the catalyst. The fractional decrease in magnetization, due to both reversible and irreversible chemisorption, was taken to be roughly equal to the total metal dispersion (14). After stabilization, the system was pumped and the remaining fractional magnetization loss taken to be due to the irreversible chemisorption. Figure 5 shows the effect of inducing SMSI on the 20% Ni/MgAAP catalyst in a typical experiment. Table 3 summarizes the results of these experiments. As in the Curie point determinations, a clear distinction appears in the behavior of the catalysts. Catalysts which use noninteracting supports, i.e., silica, show only irreversible chemisorption, the value of which agrees well with the pulse chemisorption results and with the crystallite size measurements. When nickel is supported on titania, no hydrogen chemisorption is observed after the inducement of the SMSI state. When the nickel is supported on a phosphate-containing support, however, a significant reversible chemisorption is observed, particularly after the inducement of the SMSI state. The observed reversible chemisorption does not appear to be related to the pre-SMSI chemi-

TABLE 3
Effect of Support and Metal-Support Interactions on Hydrogen Chemisorption

Catalyst	SMSI?	Loss of magnetization	
		Reversible	Irreversible
20% Ni/silica	N	0	0.11
20% Ni/titania	Y	0	0
20% Ni/AAP	Y	0.09	0
20% Ni/MgAAP	N	0.02	0.27
	Y	0.09	0
7% Ni/titania	Y	0	0
7% Ni/AAP	Y	0.08	0

sorption and, in fact, was of similar magnitude for all the catalysts evaluated.

The observed chemisorptive and magnetic changes in Ni/AAP, and the similarity between the $M(T)$ curves of this system and the NiP alloys indicate that partial reduction of the phosphate support and reaction with the Ni to form an NiP alloy may be occurring during high-temperature reduction. Reaction with the support or support impurities would be a relatively slow diffusional process at the reduction temperatures employed, making the process apparent only when small crystallites are involved. Presuming that one has essentially a surface reaction with a mean diffusion distance of 5 Å, this would produce an impurity level of ca. 35% of the saturation limit in a 100-Å-diameter particle but ca. 90% of saturation in a 20-Å particle. Of course, the surface properties of any size crystallite would be equally influenced by this quasisurface phenomenon. The magnitude of the impurity element concentration necessary to yield the observed reductions in T_c can be estimated from data on bulk Ni alloys (30). For alloys of nickel with non-magnetic elements, the values of T_c at 5 at.% of the impurity are ~570 (Cu), ~520 (Zn), ~500 (Al), and ~450°K (Si). Thus, the reduction is dependent on the valence of the impurity. In the iron-phosphide system, Fe₃P and Fe₂P are both ferromagnetic and have T_c values about 70% (690°K) that of pure iron. Comparable reductions in the nickel T_c upon introduction of phosphorous as either an alloying element or in compound formation would result in the reduction of T_c to ca. 420–500°K which appears to be in the region of the observed values.

Support for the hypothesis that Curie temperature reductions in the phosphate-containing catalysts are due to impurity diffusion into the nickel is given by the reduction time dependence of the $M(T)$ curves of the 7% Ni/AAP catalysts. It is most likely that the time dependence for this change is due to a solid-state diffusion process. Attempts to clearly induce these changes in

the high-loading catalysts by reduction at higher temperatures for a longer period of time were not successful due to sintering of the metal particles.

Titanium is also capable of forming alloys with nickel. However, examination of the alloy phase diagrams and the changes in bulk Curie temperature for the alloys show that as little as 5% titanium in the bulk would reduce the Curie point of nickel metal by about 200°C (31). Clearly, this cannot be the process by which SMSI is induced in these materials.

It would seem reasonable to postulate, therefore, that the lack of magnetic changes observed in the Ni/TiO₂ catalysts are due to a lack of bulk changes in the nickel. This postulate is in agreement with results recently reported by a number of investigators which propose a model for "SMSI," in titania, in which the active metal is encapsulated by a titanium suboxide, TiO_x (9, 22, 32–34). According to the encapsulation model, during high-temperature hydrogen reduction, the titania is partly reduced and migrates to the metal surface, covering the active sites and affecting the chemisorptive and chemical behavior of the catalyst. This model can also explain the lack of any significant magnetic changes in Ni/TiO₂ catalysts. Indeed, the results of the magnetic experiments indicate that SMSI on titania must be due to a strictly surface phenomenon and as such is different from the SMSI observed for phosphate-containing supports.

The nature of the reversible chemisorption with phosphate-type supports is still a mystery, but it would seem reasonable to say that is probably due to the formation of new types of active sites on the catalyst when it undergoes the transition into the alloy state. These active sites still chemisorb hydrogen, but with a different binding energy. Some nickel phosphides have been reported to behave as hydrogenation catalysts which would indicate that they are capable of chemisorbing some hydrogen (35). The fact that the same kind of phenomenon

is not observed on titania-based catalysts is further indication of the different mechanisms leading to the metal-support interaction in each case.

CONCLUSIONS

This work has shown there are at least two mechanisms by which strong metal-support interactions can be induced in supported nickel catalysts and the resulting type of interaction is dependent on the support. The mode of interaction can be readily distinguished by the catalyst's chemisorptive and magnetic behavior. When nickel is supported on a phosphate-containing support, the inducement of SMSI is detectable by changes in the chemisorptive properties and by changes in the magnetic behavior. This is most likely due to the formation of a bulk alloy with P. For TiO_2 , and presumably other reducible metal oxides, the SMSI state is a surface phenomena which affects the chemisorptive properties without affecting the bulk properties of the materials.

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