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Models of Metal–Support Interactions in Phosphate- and Niobia-Supported Catalysts

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Magnetic studies were conducted on supported nickel catalysts in order to elucidate changes in the bulk structure of the ferromagnetic nickel upon high-temperature reduction and inducement of metal–support interactions. The catalysts consisted of 10% Ni/Nb_2O_5, 9% Ni/Nb_2O_5–SiO_2, and both 7 and 20% Ni on modified aluminum phosphate (AP). Catalysts supported on AP exhibited a change from the normal magnetization–temperature behavior of bulk nickel when reduced at high temperatures. Higher temperature and longer reduction times were required to make this change apparent in the higher loading catalysts. Niobia-supported catalysts did not show any deviation from the normal magnetic behavior of bulk Ni, regardless of the reduction conditions. They did, however, exhibit an apparent loss of Ni metal and a decrease in crystallite size upon treatment at 600°C for 16 h. The difference in magnetic behavior of Ni depending on the supports can be explained if one considers the Ni/AP to interact through bulk alloy formation, but the Ni/Nb_2O_5 through an encapsulation-compound formation mechanism. © 1985 Academic Press, Inc.

INTRODUCTION

It has been widely reported that the chemisorptive and catalytic behavior of many supported metal catalysts can be affected by the choice of support, in particular when dealing with supports that can interact with the active metal (*1–3*). In a number of instances, the choice of support can cause a metal to completely lose its hydrogen chemisorptive capacity while retaining its catalytic activity. This suppression of H_2 chemisorption phenomenon was first observed in the late 1970's and dubbed "strong metal–support interaction" or "SMSI" (for a recent review see Ref. (*4*)). The idea that H_2 chemisorption suppression was indicative of SMSI led to a number of reports in which the suppression of chemisorption was immediately equated with SMSI and all supports that caused a suppression of hydrogen chemisorption were considered to be similar.

Recent attempts have been made to classify and differentiate metal–support interactions. Ko *et al.* proposed a hierarchy to rank the strength of metal–support interactions based on the behavior of catalysts toward hydrogen chemisorption and chemical probe reactions, such as ethane hydrogenolysis and CO hydrogenation (*5*). They were successful in ranking Ni catalysts supported on niobia and extended their hierarchy to include titania. This hierarchy, however, fails when one examines supports which are not reducible transition metal oxides, but which can still cause a suppression of H_2 chemisorption. This point is illustrated for aluminum phosphate-containing (AP) supports. A suppression of hydrogen chemisorption is observed for Ni/AP catalysts when reduced at high temperatures (>500°C) (*6*), but chemical probes have shown that the kinetic behavior of these materials in catalytic reactions is different from that observed for the more traditional "SMSI" supports, i.e., TiO_2 or Nb_2O_5 (*7*). In fact, phosphate materials do not obey the hierar-

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chy to rank metal–support interactions. Magnetic work has also shown a difference between AP and TiO_2 in the way these two supports affect the metal (*8, 9*). Thus, there appears to be more than one cause leading to the suppression of hydrogen chemisorption.

In this work we report on a comparison magnetic study of Ni/Nb_2O_5, Ni/Nb_2O_5–SiO_2, and Ni/AP, in order to elucidate the events leading to so-called strong metal–support interactions in metals supported on chemically different supports. As detailed below, different behavior of the metal was observed over the different supports, indicating the existence of different mechanisms leading to metal–support interactions.

EXPERIMENTAL

Catalysts. The niobia catalysts used in this study consisted of 10% nickel supported on Nb_2O_5 and 9% Ni supported on a silica which had been coated with approximately a monolayer of Nb_2O_5 (Ni/Nb_2O_5–SiO_2). The preparation and characterization of both of these catalysts, and the experimental evidence for niobia-monolayer coverage of the latter, has been presented in previous publications (*10, 11*). The phosphate catalysts consisted of a small crystallite 7% Ni on alumina–aluminum phosphate (AAP), and a larger crystallite 20% Ni on magnesia–alumina–aluminum phosphate (MgAAP). These two will be collectively called "phosphate-supported." The preparation and characterization of these catalysts have also been described previously (*6, 9*).

Reduction and magnetic measurements. The magnetic properties of the catalysts were determined using a Cahn Model 6602-4 Faraday System using a 4-in. magnet capable of fields up to ca. 10 kOe. The microbalance was connected to a gas handling manifold and vacuum line capable of operating below 10^{-6} Torr. All catalyst reductions were performed *in situ*, using purified and dried hydrogen. Because of the experimental configuration, the reductions were performed statically, in a hydrogen atmosphere at 400 Torr. The reduction procedure was as follows: approximately 5 mg of catalyst were loaded into the sample bucket and the system was evacuated for about 1 h. The temperature was then raised to the desired value while pumping, then hydrogen was admitted to 400 Torr. After the desired reduction period, the system was pumped for 1 h at the reduction temperature to remove any adsorbed species, and the sample was cooled. Reduction temperatures ranged between 300 and 600°C for periods extending up to 64 h.

Crystallite size distributions were determined by measuring the magnetic field dependence of the magnetization at room temperature and liquid-nitrogen temperature and fitting the room-temperature data to the Langevin function, initially assuming a log normal crystallite size distribution. The standard tests for superparamagnetism were used in order to ascertain the superparamagnetic nature of the sample and the correctness of the equations used in the calculations (*12*). Curie temperatures were determined by observing the change in magnetization, at a constant magnetic field of 5 kOe, as the temperature was programmed at 1 to 2°C/min between room temperature and ca. 400°C. The temperature was measured using a thermocouple placed inside the vacuum envelope and about 5 mm below the sample bucket. In most experiments only the heating curve was measured but in some, both a heating and cooling curve were obtained and found to be reproducible to within 2°C. The resulting curve was normalized at 25°C and compared with theoretical curves for superparamagnetic or ferromagnetic materials of varying crystallite size and Curie temperature. The details of the computational techniques have been described in detail in previous publications (*9, 13*).

The apparent reducibility of the catalysts was obtained by extrapolating the low-temperature magnetization-field curve to infi-

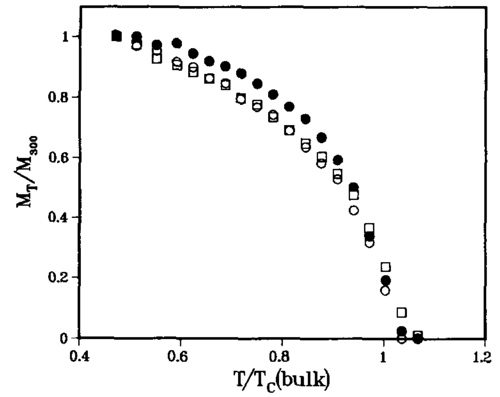

FIG. 1. Magnetization–temperature curves for 10% Ni/Nb_2O_5. Reduction treatments were: (●) 500°C, 1 h; (○) 600°C, 16 h; and (□) 600°C, 64 h.

nite field (plotted as M vs $1/H$) and comparing the obtained relative saturation magnetization to that obtained for a pure bulk-Ni standard. The ratio of the saturation magnetization of the sample of interest to that of a similar fraction of pure bulk nickel metal was taken to be equal to the portion of the Ni present as Ni(0), i.e., Ni(0)/Ni(total). Because of uncertainties in the absolute value of the nickel loading in the catalysts, the values reported for Ni(0)/Ni(total) are probably only accurate to 10%.

RESULTS

The measured magnetization–temperature curves, $M(T)$, for the catalysts after various reduction treatments are shown in Figs. 1–4. For both the niobia and the niobia–silica supported catalysts (Figs. 1 and 2, respectively), it can be seen that, regardless of reduction treatment, the Curie temperature remains virtually unchanged and very close in value to that of bulk Ni. In fact, the slightly higher T_C observed in some measurements is typical of what has been experimentally reported, and is obtained due to paramagnetic contributions of the nickel metal (*14*). One noticeable feature of the Ni/Nb_2O_5 curves is a slight decrease in the curvature of the $M(T)$ curve when a very rigorous reduction treatment is used—16 to 64 h at 600°C. This change in curvature is interpreted as resulting from a decrease in the average Ni crystallite size of the catalyst. The Ni/Nb_2O_5 magnetization–temperature behavior is very characteristic of small crystallite Ni and can be fitted very well by theoretical curves of 370°C Curie temperature and 40- to 80-Å-diameter particle. Similar changes in curvature with higher reduction temperatures were not observed for the Ni/Nb_2O_5–SiO_2 catalysts.

When Ni is supported on a P-containing support, the metal cannot be completely reduced after treatment in hydrogen at 300°C for 1 h. This is in agreement with our previous observations (*6*). Even after reduction at 500°C for 1 h, only a fraction of the Ni can be reduced in the Ni/AAP catalyst. Figure 3 shows the magnetization–temperature behavior of Ni/AAP. In agreement with what has been previously reported for Ni supported on AP, the $M(T)$ curve observed after a 1-h reduction at 500°C shows the expected behavior of small crystallite nickel metal. However, an anomalous concave downward curve shape is observed after a rigorous reduction at 500°C for 16 h (*9*). This anomalous behavior is not observed to change with increasing reduction temperature or time, and indeed the $M(T)$ curve remained unchanged even after treatment for 64 h at 600°C. Figure 4 shows the

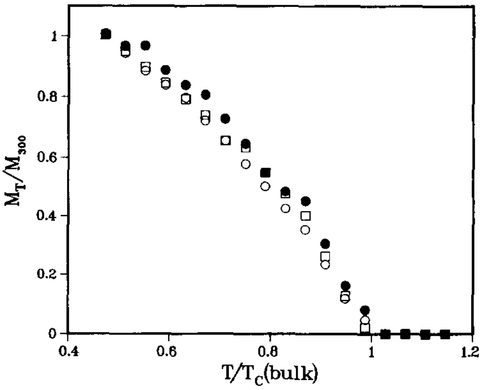

FIG. 2. Magnetization–temperature curves for 9% Ni/Nb_2O_5–SiO_2. Reduction treatments were: (●) 500°C, 2 h; (○) 600°C, 5 h; and (□) 600°C, 16 h.

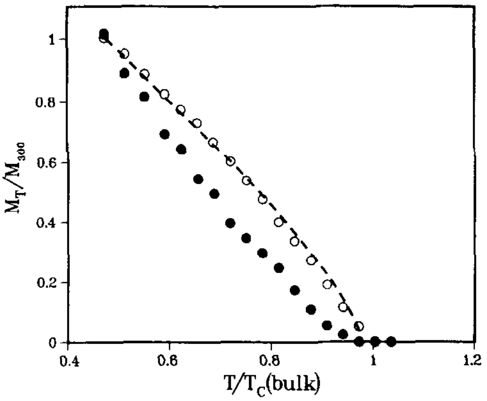

FIG. 3. Magnetization–temperature curves for 7% Ni/AAP. Reduction treatments were: (○) 500°C, 1 h (from Ref. (9)); and (●) 600°C, 16 h. Dashed line is calculated for a 40-Å-diameter particle with a Curie temperature of 330°C.

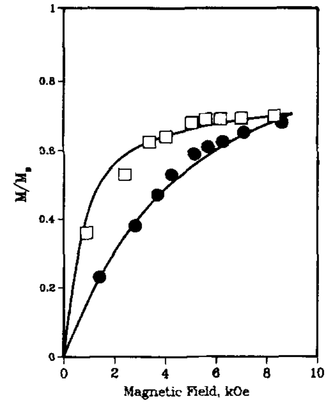

FIG. 5. Magnetization-field curves for 10% Ni/Nb_2O_5 reduced at 500°C, 1 h (☐) and 600°C, 16 h (●). Solid lines are the theoretical curves for the calculated crystallite size distributions shown in Fig. 6.

M(*T*) behavior of the higher loading, and larger Ni crystallite, Ni/MgAAP. The resulting *M*(*T*) curves show the Ni to exhibit normal Curie temperatures even after reduction at temperatures up to 600°C for 16 h; however, a slight, but definite, Curie temperature lowering was observed after 64 h at 600°C.

Measurements of the magnetization-field dependence, *M*(*H*), were used to derive the nickel crystallite size distributions and average crystallite diameters for all the catalysts. Figure 5 shows typical *M*(*H*) results obtained at 25°C for the Ni/Nb_2O_5 catalyst, following 500°C/1 h and 600°C/16 h reductions. Also shown are the calculated *M*(*H*) curves corresponding to the derived crystallite size distributions, which are shown in Fig. 6. Clear differences in the apparent Ni crystallite diameters are observed for this system, depending on reduction conditions.

Table 1 summarizes the Curie temperature results, as well as the measured average crystallite diameter and Ni(0) fraction for the catalysts under study at an assort-

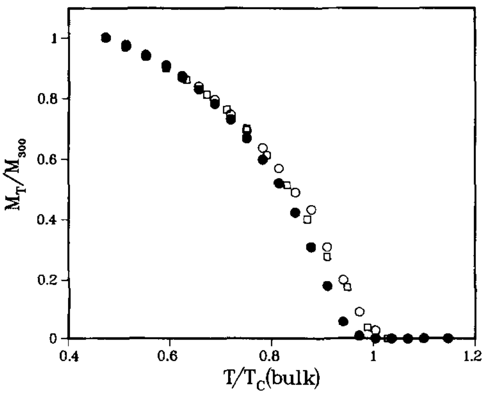

FIG. 4. Magnetization–temperature curve for 20% Ni/MgAAP. Reduction treatments were: (○) 500°C, 1 h; (☐) 600°C, 16 h; and (●) 600°C, 64 h.

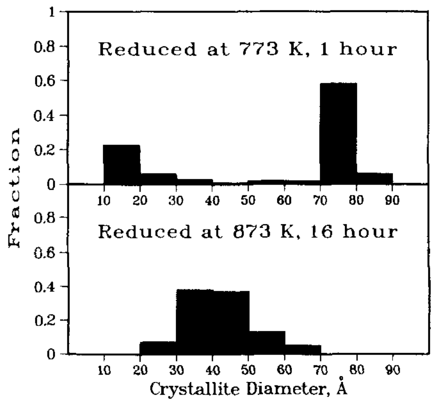

FIG. 6. Calculated crystallite size distributions for Ni/Nb_2O_5.

TABLE 1

Summary of Magnetic Results for Supported Ni Catalysts

Catalyst	Reduction conditions	Average crystallite diameter[a] (nm)	$\frac{\text{Ni(0)}}{\text{Ni(total)}}$	Curie temperature[b] (°C)
10% Ni/Nb_2O_5	300°C, 1 h	7.5	1	370
	500°C, 1 h	7.5	1	370
	600°C, 16 h	4.5	0.55	370
	600°C, 64 h	4	0.55	370
9% Ni/Nb_2O_5–SiO_2	500°C, 2 h	4.5	0.6	360
	600°C, 5 h	4.5	1	360
	600°C, 16 h	3.5–4.5	0.8	370
7% Ni/AAP	300°C, 1 h	—	0	—
	500°C, 1 h[d]	3	0.2	330
	500°C, 16 h[d]	3	1	[c]
	600°C, 16 h	3	1	[c]
	600°C, 16 h	3	1	[c]
20% Ni/MgAAP	300°C, 1 h	4	0.2	360
	500°C, 1 h	4	0.45	370
	500°C, 16 h[d]	4	1	360
	600°C, 16 h	4	1	360
	600°C, 64 h	4	1	320

[a] By field dependence method. Results are accurate to 1 nm.

[b] To nearest 10°C.

[c] Anomalous $M(T)$ curve shape. $T_c < 300°C$.

[d] From Ref. (*9*).

ment of reduction conditions. In this case, we also see a difference in behavior between the different catalysts. The Ni/Nb_2O_5 was easily reduced under very mild conditions and showed an apparent loss of Ni(0), and a decrease in crystallite diameter, when subjected to temperatures of 600°C. The apparent decrease in crystallite diameter was evidenced by both a change in the $M(H)$ dependence (*12*) and in the curvature of the $M(T)$ curve (Fig. 1). The Ni/Nb_2O_5–SiO_2 and the Ni/AP catalysts were significantly more difficult to reduce, as evidenced by the low Ni(0)/Ni(total) values obtained after low-temperature reduction. Once reduced, however, they did not undergo any significant changes in either Ni(0) content or crystallite size regardless of the treatment temperature. The slight drop in Ni(0)/Ni(total) observed for Ni/Nb_2O_5–SiO_2, falls within the experimental error of the measurement.

DISCUSSION

The Curie temperature results observed for the Ni/Nb_2O_5 and Ni/Nb_2O_5–SiO_2 catalysts are very much in line with those previously reported for TiO_2-supported Ni, in which no significant change in the magnetic behavior was observed upon high-temperature reduction and inducement of "SMSI" (*8, 9, 15*). Phosphate-supported catalysts, however, do show changes in magnetic behavior with more rigorous reduction treatments. This change in the magnetic behavior has been previously observed in low loading, small crystallite Ni/AAP (*9*), but up to now had not been observed in the larger crystallite catalysts (such as the 20% Ni/MgAAP). The lowering in the Curie temperature in these catalysts clearly cannot be due simply to changes in crystallite size or to the formation of nonferromagnetic compounds. The apparent time–temperature dependence in inducing an observable T_c shift, indicates that these changes are brought about by a slow process. If we accept that the Curie point lowering is due to some sort of "alloy" formation between a reducible species in the support (most likely the phosphorus) and the nickel metal (*9*), then the time–temperature dependence may be ascribed to the solid–solid diffusion between the Ni and the other moiety. Clearly, the time required to make this effect observable in a small crystallite is less than that required for a comparable effect in a larger crystallite.

The effect of reduction on the crystallite size and the apparent Ni(0) content of the Ni/Nb_2O_5 catalyst is unusual, since there is an apparent loss of ferromagnetic Ni(0) when the catalyst is given a rigorous reduction treatment. Simoens *et al.* recently reported on TEM and FMR studies into the morphological changes that occur to Ni/TiO_2 when reduced at different temperatures (*15*). They too observed an apparent Ni(0) loss when the SMSI state was first induced by reduction at 550°C for 1 h. This apparent loss, however, was most likely due to redispersion of the ferromagnetic Ni into smaller, superparamagnetic crystallites (as evidenced by TEM), which would have gone undetected by FMR.

In the case of Ni/Nb_2O_5, redispersion cannot be the reason for the observed apparent decrease in Ni(0) content since the low-temperature magnetic measurements will account for nearly all the Ni(0), including the superparamagnetic crystallites. At the onset of SMSI (reduction at 500°C for 1 h) all of the Ni is accounted for as Ni(0) and it is only after prolonged, high-temperature reduction (600°C, 16 h) that an apparent loss of Ni(0) is evident. Furthermore, the apparent decrease in crystallite size indicates that it is not just the smaller crystallites reacting with the support, since this would lead to a larger average Ni diameter for the remaining nickel.

Reports in the literature concerning the mechanism of SMSI in TiO_2-supported catalysts have lately been concentrated on the migration of suboxide species (*16–20*). The presence of such a species on the surface, by diffusion either through or over the metal crystallite, explains many of the features of TiO_2-supported systems. Ni/Nb_2O_5 behaves kinetically very similarly to Ni/TiO_2 toward several chemical probes, and as such it is reasonable to expect the two systems to follow the same mechanism of interaction. Thus, we propose the following model which is consistent with both kinetic and magnetic data. At low-reduction temperature (ca. 500°C) a suppression of chemisorption is already observed (*10*) for the Ni/Nb_2O_5 catalysts, but no changes are evident in their magnetic behavior. This supports the idea that SMSI in Ni/Nb_2O_5 is strictly a surface phenomenon at these temperatures and could indeed be caused by the partial encapsulation of the Ni crystallites by a niobium suboxide species. With a more severe reduction treatment at 600°C for 16 h, the suboxide species on the metal surface increases in concentration and reacts with the nickel metal to form an outer layer of a Nb–Ni compound. The nickel in this compound, which is probably in the form of nickel niobate, loses its ferromagnetic character and accounts for the observed decrease in overall nickel content. At the same time, this compound formation creates a "cherry-pit" type crystallite with a Ni(0) core. This core still exhibits all the magnetic characteristics of the metal, most notably the Curie temperature, but is of reduced diameter. This picture is consistent with the apparent decrease in crystallite size.

An attempt was made to ascertain the presence of nickel niobate by X-ray diffraction. Unfortunately, niobia itself was reduced to NbO_2 under the severe reduction treatment used (600°C, 16 h). The diffraction pattern of the spent catalyst is thus complex and makes an unambiguous identification of other phases difficult. However, indirect evidence of a surface compound comes from kinetic results, which show a significant suppression in the CO hydrogenation activity of the Ni/Nb_2O_5 catalyst reduced at 600°C for 16 h (*11*). By comparison, the Ni/Nb_2O_5–SiO_2 catalyst, which does not contain sufficient niobium to completely react with all the nickel, is more active after the same reduction treatment, indicating the lesser extent of surface compound formation. Magnetic results for this sample also show a much smaller decrease in either the average crystallite diameter or the total nickel content. Apparently, the lower availability of niobia in Nb_2O_5–SiO_2 makes it a less interacting support than bulk Nb_2O_5, even though the mechanism of interaction appears to be the same (*11*).

Ni/AP shows the complete opposite behavior from Ni/Nb_2O_5 and Ni/Nb_2O_5–SiO_2 upon heat treatment. It exhibits a clear shift in Curie temperature, indicating a bulk phenomenon which is affecting the electronic nature of the Ni. Upon high-temperature reduction for extended periods of time, however, it exhibits constant crystallite size and metal content.

We have previously addressed the issue of different mechanisms leading to suppression of H_2 chemisorption in Ni/TiO_2 and Ni/AP catalysts (*9*). This indeed appears to also be the case with Nb_2O_5-supported materials. Both the magnetic results and previous kinetic measurements of the behavior of both of these types of catalysts toward ethane hydrogenolysis and CO hydrogenation, indicate that although the materials behave similarly when reduced at sufficiently low temperatures to prevent the onset of "SMSI," their behavior is quite different as metal–support interactions are induced by reducing at higher temperatures.

On the basis of the magnetic results it can be proposed that the mechanism for interaction between the niobia and the nickel does not involve any bulk changes in the metal, but most likely is a surface phenomenon, somewhat akin to that proposed for titania (*9*). The surface phenomenon is most likely encapsulation of the metal, which ultimately leads to compound formation as the migrating oxide species react with metal crystallites. This is somewhat different to what is observed for Ni/TiO_2, where encapsulation is also suggested (*16–18*), but no XRD evidence of compound formation was found even after hydrogen treatment at temperatures as high as 800°C. Phosphate, on the other hand, can interact with Ni by inducing bulk changes in the metal. This was clearly demonstrated in the case of small crystallites (*9*) and has now also been shown for larger crystallite catalysts, as evidenced by the lower T_c observed for Ni/MgAAP. It has been established that for either mechanism (surface versus bulk), the extent of metal–support interactions is stronger for the smaller crystallites under comparable pretreatments.

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