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Metal–Support Interactions in Supported Nickel Catalysts: Difference in Chemical Behavior between Phosphate and Niobia Supports

It was recently reported (*1*) that nickel catalysts supported on phosphate-containing materials, when reduced at high temperatures, suppress hydrogen chemisorption. This behavior is typical of SMSI oxide supports such as titania and niobia (*2–4*). However, in later magnetic studies (*5–7*), a shift in the Curie temperature was found to accompany metal–support interactions for nickel catalysts on phosphate-containing supports, but not on titania. Thus, there seems to be a subtle difference between these two classes of materials, and apparently hydrogen chemisorption is unable to differentiate them.

We have shown that for niobia-supported nickel, chemical probes other than hydrogen chemisorption can be used to provide a more complete characterization on the nature of interaction (*8*). In particular, the behavior of SMSI systems with respect to ethane hydrogenolysis and carbon monoxide hydrogenation has been established. We, therefore, proceeded to study the same two test reactions over phosphate-supported nickel. As reported below, a significant difference was found in the chemical properties of phosphate- and niobia-supported nickel. These results reinforce the notion that there are different mechanisms for metal–support interactions, as suggested by earlier magnetic studies (*6, 7*).

The preparation of the two phosphate-containing supports used in this study, $Al_2O_3 \cdot 2AlPO_4$ and $4MgO \cdot 13Al_2O_3 \cdot 10AlPO_4$, was described elsewhere (*1*). Basically they were coprecipitated using the necessary nitrate salts, phosphoric acid, and ammonium hydroxide at a fixed pH as suggested by Kehl (*9*). The 7% Ni/$Al_2O_3 \cdot 2AlPO_4$ catalyst was prepared by ion exchange (*7*), and the 20% Ni/$4MgO \cdot 13Al_2O_3 \cdot 10AlPO_4$ catalyst, by blending the support with nickel carbonate (*1*).

The catalysts were reduced *in situ* in flowing hydrogen (3 liters/h) at either 573 or 773 K for 1 h for the kinetic studies. These reduction conditions were chosen to coincide with those used earlier for Ni/Nb_2O_5 catalysts (*8*), so that a direct comparison of support behavior would be possible. Table 1 summarizes previous results on the characteristics of nickel catalysts on the two phosphate-containing supports, and on niobia which is included for comparison. For brevity we shall refer to these catalysts in the following discussion by the notations defined in the first column of Table 1. The two important parameters are the percentage reduction and the average crystallite size. They were used to calculate the total amount of surface nickel atoms, on which the activity is based. The percentage reduction reported in Table 1 for the first four samples was directly measured by using a commercial thermogravimetric system (Cahn 113) operated under flow conditions identical to those used in the reactor (*4*). In general the extent of reduction compares well with that of the same catalysts reduced for 16 h in a static system (*7*).

Ethane hydrogenolysis and CO hydrogenation were studied with a microreactor operated in a differential mode at atmospheric pressure. The experimental procedure was identical to that used earlier (*8*). Table 2 summarizes the results for ethane hydrogenolysis for all the samples. No conver-

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TABLE 1

Summary of Supported Nickel Catalysts

Sample	Catalyst	Reduction	% Reduction	Average crystallite diameter (nm)
AAP-573	7% $Ni/Al_2O_3 \cdot 2AlPO_4$	573 K, 1 h	0	—
AAP-773	7% $Ni/Al_2O_3 \cdot 2AlPO_4$	773 K, 1 h	90	3[a]
MgAAP-573	20% $Ni/4MgO \cdot 13Al_2O_3 \cdot 10AlPO_4$	573 K, 1 h	20	4[a]
MgAAP-773	20% $Ni/4MgO \cdot 13Al_2O_3 \cdot 10AlPO_4$	773 K, 1 h	100	4[a]
NB-573	2% Ni/Nb_2O_5	573 K, 1 h	100[b]	4[b]
NB-773	2% Ni/Nb_2O_5	773 K, 1 h	100[b]	4[b]

[a] From Ref. (*7*).

[b] From Ref. (*4*).

sion was found for sample AAP-573, as it was not reduced under the condition used. Sample MgAAP-573 was found to behave very similarly to silica-supported nickel (*10*), indicating a minimal support effect. This observation is consistent with the previous work (*1*), which showed a negligible suppression of hydrogen chemisorption for this catalyst reduced at 573 K. After a reduction at 773 K, both samples AAP-773 and MgAAP-773 exhibited a significant decline in ethane hydrogenolysis activity, in parallel with a strong suppression in hydrogen chemisorption (*1*). Thus, results in Table 2 clearly demonstrate a support effect for the two phosphate-containing supports. If a comparison is made between these materials and niobia under identical reduction treatments, then it becomes obvious that samples NB-573 and NB-773 are less active and show a less negative hydrogen partial pressure dependence. This could simply mean that niobia is a more interacting support. On the other hand, the possibility of a different mechanism of interaction should not be overlooked.

TABLE 2

Kinetic Results for Ethane Hydrogenolysis over Supported Nickel Catalysts

Sample	E_A[a] (kJ/mol)	n[b]	m[b]	Activity at 478 K (molecule/s/surface Ni atom)
AAP-773	194	0.9	−1.5	8.0×10^{-7}
MgAAP-573	160	0.9	−1.8	1.4×10^{-4}
MgAAP-773	175	0.9	−1.5	2.0×10^{-6}
NB-573[c]	176	1.1	−1.1	1.1×10^{-6}
NB-773[c]	180	1.0	−1.2	1.2×10^{-7}

[a] Determined from the temperature dependence of the reaction rate, at ethane and hydrogen partial pressure at 0.03 and 0.2 atm, respectively.

[b] Exponents in the experimental power rate law, $kp_E^n p_H^m$, where p_E and p_H correspond to ethane and hydrogen partial pressure, respectively.

[c] From Ref. (*8*).

In fact, studies of CO hydrogenation over these catalysts revealed very different behavior between phosphate- and niobia-supported nickel (Table 3). First, the catalysts on phosphate-containing supports are about a factor of 5 to 10 less active than those of niobia. Second, samples AAP-773, MgAAP-573, and MgAAP-773 all produced predominantly methane with no olefins. This difference in product distribution is shown in Table 3 in terms of the C_2^+/CH_4 ratio. Thus, the phosphate-supported nickel catalysts did not display any of the characteristics previously established for SMSI supports in CO hydrogenation (*8*). Their behavior was actually similar to that of silica-supported nickel (*11*). Obviously the nature of interaction is different between the two classes of interacting supports.

On the basis of magnetic results, it was suggested that the mode of interaction in phosphate-containing supports is a bulk phenomenon due possibly to alloy formation, whereas in SMSI supports it is a sur-

TABLE 3

Kinetic Results for CO Hydrogenation over Supported Nickel Catalysts

Sample	Activation energy, kJ/mol		Activity at 548 K ($\times 10^{-2}$ molecule/s/surface Ni atom)		CO Conversion (%)	C_2^+/CH_4[b]
	E_{CH_4}	E_{CO}	N_{CH_4}	N_{CO}		
AAP-773	89	89	0.24	0.27	1.2	0.04
MgAAP-573	113	112	0.48	0.68	1.4	0.14
MgAAP-773	127	119	0.30	0.39	1.5	0.11
Nb-573[a]	112	112	1.9	4.2	2.6	0.53
NB-773[a]	128	99	2.6	3.5	1.3	0.63

[a] From Ref. (*8*).

[b] C_2^+ denotes the sum of hydrocarbon products from C_2 to C_5.

face phenomenon (*7*). The kinetic results obtained in this study are consistent with this interpretation. For Ni/Nb_2O_5 catalysts, the presence of migrating oxide on the crystallite surface has been speculated to be the cause for a low ethane hydrogenolysis activity (through site blocking) and a high CO hydrogenation activity (through the creation of active sites at the interface) (*8*). In the case of phosphate-supported nickel, if the interaction is indeed due to a change in bulk property alone, then there would not be a surface oxide species. Consequently, one would not expect as severe a suppression in ethane hydrogenolysis activity, nor an enhancement in CO hydrogenation activity. Such a trend agrees with the observed results. Within the group of phosphate-supported catalysts, sample MgAAP-573 is expected to have the least perturbation in its bulk property because of the large crystallite size and mild reduction treatment. It is thus not surprising that this sample showed the highest ethane hydrogenolysis activity. Another interesting point is that although both phosphate- and niobia-supported nickel catalysts suppress irreversible hydrogen chemisorption, the former has been found to exhibit some reversible hydrogen chemisorption (*7*). This could result in a higher hydrogenation activity, accounting for the observed lack of olefinic products.

In summary, this study demonstrated that different mechanisms for metal–support interactions exist. Since for a given support, the interaction may manifest itself differently with respect to different test reactions, it is important to characterize an interacting system with several chemical probes. Our use of the same set of chemical probes enabled us to differentiate chemical behavior between phosphate- and niobia-supported nickel. Such an approach should be applicable to similar systems.

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