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Evidence for Metal-Support Interactions in Phosphate-Supported Nickel Catalysts

Recent work on strong metal-support interactions (SMSI) has been fueled, in part, by Exxon's pioneering work on the behavior of supported Group VIII metals on titania (*1*, *2*). When metals such as Pt, Os, Ir, or Ni are supported on TiO_2 and reduced at elevated temperatures, typically greater than 500°C, a suppression of the normal hydrogen chemisorption is observed. This reduced chemisorption has been attributed to the existence of strong interactions between the support and the metallic particles and is catalytically evident in Fischer–Tropsch reactions where the activity is significantly greater and shows a different product distribution from metals supported on the more conventional SiO_2 or Al_2O_3 supports (*3*).

Other investigators have observed some of the characteristics of metal-support interactions using nonmetal oxide supports. Martin and Dalmon (*4*) observed a suppression of the normal H_2-chemisorption of Group VIII metals supported on silica when the materials were reduced at temperatures in excess of 900°C. Chen and White have observed SMSI behavior when silicon carbide is used as a support (*5*), and Marinas and co-workers (*6*) have inferred the existence of metal-support interactions on nickel–aluminum orthophosphate catalysts based on the kinetic behavior of such catalysts during hydrogenation reactions.

We have recently observed evidence supporting the existence of interactions between nickel metal and aluminum phosphate supports. Nickel supported on phosphate-containing materials, such as aluminum phosphate, mixed alumina-aluminum phosphate, and mixed magnesia–alumina–aluminum phosphate, exhibit the suppression of hydrogen chemisorption which is characteristic of SMSI states, when reduced at high temperatures. This note reports some of our more recent observations.

All catalysts used contained nominally 20% nickel after reduction and were prepared by mix-mulling the corresponding support and nickel carbonate with water. Silica (Davison Grade 59), alumina (Harshaw Al4100P), and titania (Harshaw Ti0720) powders were first passed through a 100-mesh screen and dry-blended with nickel carbonate prior to mix-mulling. All other supports were coprecipitated using the necessary nitrate salts, phosphoric acid, and ammonium hydroxide, at a fixed pH, following the method described by Kehl (*7*). A mixture of ammonium hydroxide and ammonium bicarbonate was used as the precipitant for the magnesia–alumina support. Following precipitation, filtration, and washing, the wet filter cakes were used directly for blending with nickel carbonate. Catalysts were dried at 120°C for 20 h and calcined at 350°C in air for 10 h. Afterwards they were sized 20–40 mesh prior to reduction.

Hydrogen uptake was determined using a conventional pulsed chemisorption system (*8*). The samples of catalyst used for chemisorption measurements were reduced *in situ* at the desired temperature for approximately 18 h in a hydrogen stream, followed by a 2-h argon flush at the temperature of reduction. The apparent dispersions were calculated using the method of Bartholomew *et al.* (*9*) which accounts for the fraction of unreduced metal remaining in the catalyst. The extent of reduction of the metal was measured by titrating the re-

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duced catalyst with oxygen at 500°C and assuming that only the metal was oxidized. Blank experiments were performed on the support materials to ensure that partial reduction of the support was not significant relative to the metals. In no case was hydrogen chemisorption observed for the supports, and subsequent measurement of the O_2 uptake was negligible compared to that of the corresponding finished catalyst.

The nickel crystallite size of the reduced materials was determined by magnetization measurements using the low field technique. Measurements were made in a Cahn Model 6602-4 Faraday apparatus. Approximately 5 mg of sample were reduced at 500°C and subjected to magnetization measurements in fields up to 10 kOe at 25 and −196°C. The average particle diameter was calculated using the low field approximation of the Langevin equation (*10*).

The results of the chemisorption experiments and the crystallite size determinations for all the catalysts tested are summarized in Table 1. In agreement with the published results of other investigators, we observe the characteristic suppression of hydrogen chemisorption for titania-supported nickel catalysts when the material is reduced at elevated temperatures, although some lowering of the expected chemisorption is observed even at the lower reduction temperature. Measurements of the extent of reduction and the nickel crystallite size indicate that the diminished chemisorption is due to the inducement of the SMSI state and not to sintering of the metal. For comparison, catalysts using silica and alumina supports were also subjected to these measurements and were found to possess normal H_2 chemisorption characteristics regardless of the reduction temperature.

When a catalyst support contains $AlPO_4$, a behavior typical of SMSI-type materials is observed, i.e., suppression of hydrogen chemisorption upon high-temperature reduction. This behavior is observed regardless of other components found in the support, such as MgO or Al_2O_3, but it is absent whenever phosphate is deleted in the preparation as evidenced by the normal H_2 chemisorption results obtained from Ni sup-

TABLE 1

Hydrogen Chemisorption and Crystallite Diameters of 20% Supported Nickel Catalysts

Support	Temperature of reduction (°C)	Hydrogen chemisorption (μmol/g)	Percentage reduction	Apparent dispersion (%)	Average crystallite diameter (Ångstroms)
SiO_2	300	160	100	10.0	
	500	170	100	10.5	45
TiO_2	300	30	45	3.9	
	500	10	100	0.6	85
Al_2O_3	300	110	80	8.2	
	500	130	100	7.5	90
$Al_2O_3 \cdot 2AlPO_4$	300	[a]	10	[a]	
	400	65	90	4.2	
	500	7	100	0.4	40
$4MgO \cdot 13Al_2O_3 \cdot 10AlPO_4$	300	78	40	12.5	
	400	45	90	2.9	
	500	19	100	1.1	40
$2MgO \cdot 3Al_2O_3$	300	—	0	—	
	400	241	85	17.0	
	500	384	100	21.0	30

[a] Too small for accurate measurement.

ported on mixed magnesia–alumina. As with other SMSI materials, the effect of the high-temperature reduction can be partially reversed by oxygen treatment (*1*). Oxidation at 400°C of the 500°C-reduced materials, followed by reduction at 300°C, restored high H_2 chemisorption characteristics.

An interesting trend was observed concerning the metal reducibility which is observed in these catalysts. Whereas, catalysts supported on silica or alumina showed almost complete reducibility at 300°C, this was not the case on the other oxides. Bartholomew and co-workers have shown that highly dispersed nickel, supported on interacting oxides, is not easily reduced to the metallic state (*9, 11*). Comparison of the titania and alumina catalysts, having similar crystallite size, indeed shows the difficulty of reducing nickel which is supported on an interacting support. A similar comparison can be made between silica and the aluminum phosphate-containing materials. The magnesia–alumina-supported catalyst showed no appreciable reducibility at 300°C, in spite of its lack of metal-support interactions when fully reduced. This is not entirely surprising, however, if one considers the high dispersion of the nickel crystallites present on this support. In fact, similarly dispersed catalysts, supported on alumina, have been reported to only partially reduce at temperatures as high as 450°C (*9*).

We have no explanation for this unusual effect of phosphate on the chemisorptive properties of nickel. Any of the many reported explanations for the inducement of the SMSI state may apply to these catalysts. It is, however, an interesting phenomenon which may have catalytic implications. Obviously, much work remains to be done to fully understand the phosphate system.

REFERENCES

1. Tauster, S. J., Fung, S. C., and Garten, R. L., *J. Amer. Chem. Soc.* **100,** 170 (1978).

2. Tauster, S. J., Fung, S. C., Baker, R. T. K., and Horsley, J. A., *Science* **211,** 1121 (1981).

3. Vannice, M. A., and Garten, R. L., *J. Catal.* **56,** 236 (1979).

4. Martin, G. A., and Dalmon, J. A., *React. Kinet. Catal. Lett.* **16,** 325 (1981).

5. Chen, B.-H., and White, J. M., *J. Phys. Chem.* **86,** 3534 (1982).

6. Campelo, J. M., Garcia, A., Luna, D., and Marinas, J. M., *Appl. Catal.* **3,** 315 (1982).

7. Kehl, W. L., U.S. Patent 4,210,560 (1980).

8. Freel, J., *J. Catal.* **25,** 139 (1972).

9. Bartholomew, C. H., Pannell, R. B., and Butler, J. L., *J. Catal.* **65,** 335 (1980).

10. Selwood, P. W., *in* "Chemisorption and Magnetization." Academic Press, New York, 1975.

11. Mustard, D. G., and Bartholomew, C. H., *J. Catal.* **67,** 186 (1981).

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