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The Gas-Phase Hydrogenation of Benzene Using Phosphate-Supported Nickel Catalysts

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The gas-phase hydrogenation of benzene was studied on a series of nickel catalysts supported on alumina–aluminum phosphate (AAP), magnesia–alumina–aluminum phosphate (MgAAP), SiO_2, and kieselguhr. Measurements of the reaction rates at 110°C, 3.5 atm, and GHSV = 42,000 showed the phosphate-supported Ni catalysts to be less active than catalysts supported on SiO_2 or kieselguhr. Additionally, the relative reate on Ni/MgAAP was dependent on the reduction temperature employed during pretreatment. Comparison of the hydrogenation rates and the sulfur capacity toward thiophene poisoning versus the irreversible hydrogen uptake of the various catalysts indicated that the reduced activity of phosphate-supported Ni was due to metal–support effects and that only sites which exhibited strong hydrogen chemisorption were active for benzene hydrogenation.

INTRODUCTION

There has been considerable interest in recent years in the use of phosphate-based materials as supports for metallic catalysts (*1*). Due to their unique physical and structural properties, modifications of aluminum phosphate (AP), such as alumina–aluminum phosphate (AAP) (*2, 3*), magnesia–alumina aluminum phosphate (MgAAP) (*4, 5*), and silica–aluminum phosphate (*3, 6*), have been extensively reported as suitable supports for hydrogenation catalysts. Metals such as Ni, Rh, and Pt have been successfully deposited on AP-type materials and reportedly exhibit improved activity toward liquid-phase hydrogenation reactions when compared with similar catalysts prepared using more conventional supports, such as SiO_2, Al_2O_3, or TiO_2. To a large extent, however, this improvement in apparent activity has been traced, not to a true increase in the intrinsic activity of the catalyst, but rather to better transport of reactants and products within the large pores which are characteristic of phosphate-based supports (*2, 5*).

Another feature of interest found in AP-type supports is their apparent ability to interact with metals resulting in obvious changes in the chemisorptive, electronic, and catalytic properties of the deposited metal. Nickel supported on AP has been shown to exhibit a suppression of its normal H_2 chemisorptive capacity when reduced at high temperatures, much as is observed in "SMSI" supports (*7, 8*). In addition, anomalous magnetic behavior has also been observed for Ni/AAP and Ni/MgAAP (*9, 10*). These magnetic studies have indicated that AAP-type supports do not interact with the metal via the same mechanism of other interacting supports, and this is reflected in their respective catalytic properties. For example, Ni supported on AAP and MgAAP and reduced at high temperature shows catalytic behavior to-

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ward both ethane hydrogenolysis and CO hydrogenation, which is markedly different from what has been observed for both a noninteracting Ni/SiO$_2$ and a SMSI Ni/Nb$_2$O$_5$ (*11*).

Due to the uniqueness of AP-supported catalysts, we have been extensively studying the catalytic behavior of these materials. In this paper we report on the behavior of such catalysts on a simple reaction, the gas-phase hydrogenation of benzene, where no significant transport effects are present to confound the resulting apparent activity. Additionally, we also report on the use of sulfur poisoning as a probe for the hydrogenation sites in said reaction. For comparison, more conventional supports such as SiO$_2$ and kieselguhr were also included in this study.

EXPERIMENTAL

Catalyst preparation and characterization. The catalysts used in this study consisted of a commercial Ni/kieselguhr (Harshaw Ni-0104) which was determined to contain 40 wt% Ni^0 after reduction; and a series of 20 wt% Ni supported on SiO$_2$ (Davison grade 59), an alumina–aluminum phosphate with Al/P = 2, and a magnesia–alumina aluminum phosphate with Mg : Al : P = 2 : 18 : 5. The method for the preparation of the various modified AAP supports has been described previously (*2*, *4*). The necessary amounts of aluminum nitrate, magnesium nitrate, and phosphoric acid were dissolved in a common solution and added, simultaneously with a 1 : 1 ammonium hydroxide solution, while adjusting the rate of addition of the two solutions in order to maintain the pH fixed at 9. The resulting slurry was filtered, washed, and, while still wet, used directly for mix-mulling with nickel carbonate. The Ni/SiO$_2$ catalyst was also prepared by mix-mulling, after first sizing the support through a 100-mesh screen and wetting it with deionized water. All catalysts were dried, calcined in air at 350°C, crushed, and sized to 20–40 mesh prior to evaluation.

BET surface area and pore size distributions of the unreduced catalysts were measured using N$_2$ sorption at 77°K. X-Ray diffraction was performed using a Philips 3100 automatic powder diffractometer to ensure that the metal was well dispersed and that the AAP supports were in the amorphous state (*12*).

Hydrogen uptake was determined at room temperature using a conventional pulsed chemisorption system (*13*). The samples of catalyst used for chemisorption measurements were reduced *in situ* at the desired temperature (either 300 or 500°C) for 16 h in a hydrogen stream followed by a 2-h Ar flush at 400 to 500°C. Blank chemisorption experiments were performed on the supports to ensure that any H$_2$ uptake by the partially reduced supports was not significant relative to the metals. The extent of reduction was determined using pulse O$_2$ titration at 450°C, as described in previous work (*7*).

The Ni crystallite diameter of the reduced materials was determined by magnetization measurements using the low-field technique. Measurements were made using a Cahn 6602-4 Faraday apparatus modified to include a flow-through sample hang-down tube. Approximately 5 mg of sample was reduced in H$_2$ overnight and then evacuated for at least 1 h at the temperature of reduction prior to cooling to room temperature. Magnetic measurements were performed in fields up to 10 kOe at 25 and −196°C. From measurements of the magnetization versus field curves, the average particle diameter was calculated using the low-field approximation of the Langevin equation (*14*)

$$v = \frac{v^2}{v} = \frac{3kT}{M_{\mathrm{sp}}H}\frac{M}{M_{\mathrm{s}}}$$

where M_{sp} = the spontaneous magnetization of Ni, M_{s} = the saturation magnetization obtained by extrapolation to infinite field at 77°K, and H = magnetic field. Crystallite diameters were calculated by assuming spherical particle shape.

TABLE 1

Summary of Ni Catalysts Studied

Catalyst	BET surface area (m^2/g)	Median pore radius (Å)	Reduction temp (°C)	H_2 uptake (μmole/g)	Crystallite diam (Å)
20% Ni/SiO_2	260	100	500	170	50
40% Ni/kieselguhr	170	70	500	120	>100
20% Ni/AAP	220	100	500	7	40
20% Ni/MgAAP(LT)	220	130	300	80	40
20% Ni/MgAAP(HT)	220	130	500	20	40

Reaction studies. Benzene hydrogenation was conducted using a 7.5-mm-i.d. fixed-bed reactor with in-line gas chromatographic analysis. One-half gram of the catalyst was loaded into the reactor and reduced overnight at 500°C prior to any reaction studies. The MgAAP-supported catalyst was also reduced after an overnight reduction at only 300°C. The reactant liquid feed consisted of 15 wt% benzene in cyclohexane. This dilution was found necessary to prevent temperature increases due to the exothermicity of the hydrogenation process. Feed rates were 20 ml/h, 8 liters/h, and 8 liters/h for the liquid feed, hydrogen, and nitrogen, respectively. This corresponded to approximately a 10-fold H_2 excess and a GHSV = 42,000. The reaction was studied at 110°C and 3.5 atm. Reaction products were sampled periodically to follow the extent of the reaction.

Sulfur-poisoning studies were conducted using 1 g of catalyst and the same liquid feed, but with 150 ppm of sulfur added as thiophene. Nitrogen diluent was not used in the poisoning studies. All other conditions were kept the same, resulting in a considerable deactivation within an 8-h period. All the poisoning studies were conducted using a separate reactor setup and fresh catalyst samples in order to avoid any cross-contamination of the clean feed.

RESULTS AND DISCUSSION

A summary of the catalysts used in this work, along with the reduction conditions and some pertinent characterization results, is shown in Table 1. The data reveal that all the catalysts exhibited very similar physical properties and, except for the Ni/kieselguhr, metal crystallite size. Because of the physical similarity among the catalysts, any gross difference in chemisorptive or gas-phase catalytic behavior may be directly ascribed to support effects and not to physical limitations or structure sensitivity of the reaction of interest.

As expected, catalysts in which the Ni is supported on phosphorus-containing materials are seen to exhibit a loss of the normal chemisorption capacity when reduced at high temperature (7). This is clearly evident in the Ni/MgAAP catalyst which chemisorbs an expectedly normal amount of hydrogen when reduced at 300°C, but exhibits suppressed hydrogen chemisorption if reduced at 500°C (the low-temperature and high-temperature reductions will be denoted throughout the paper by the notation LT and HT, respectively). XRD showed that this loss of chemisorptive capacity was not the result of Ni crystallite growth or compound formation between Ni and the support and, as shown in previous work, can be readily reversed by oxidation followed by low-temperature reduction of the catalyst (7).

In spite of this loss of the hydrogen chemisorptive capacity, Ni catalysts supported on AAP or modified AAP have been shown to be highly active for liquid-phase hydrogenation reactions. Their high activity, however, is due to the open-pore structure (i.e., high surface area and large pores)

TABLE 2

Reaction Rate for Benzene Hydrogenation
(T = 110°C, P = 3.5 atm, H_2/C_6H_6 = 10, GHSV = 42,000)

Catalyst	Reaction rate (molec/g · s)	Turnover frequency (events/site/s)	
		Based on crystallite diam	Based on H_2 chemisorption
20% Ni/SiO$_2$	1.5×10^{19}	0.05	0.08
40% Ni/kieselguhr	5.8×10^{18}	0.022	0.04
20% Ni/AAP	5.0×10^{17}	0.0012	0.02–0.09
20% Ni/MgAAP(LT)	1.1×10^{19}	0.028	0.06–0.16
20% Ni/MgAAP(HT)	1.8×10^{18}	0.0045	0.04–0.12

which is characteristic of AAP substrates prepared by the method utilized in this work (*2*, *5*). When this diffusion limitation, inherent in liquid-phase reactions, is removed by carrying out the reaction in the gas phase, the relative activities change drastically.

Table 2 shows the results obtained for the rate of benzene hydrogenation over the various catalysts studied. On a catalyst-weight basis, there is a large difference in apparent reaction rates between the different catalysts. Whereas Ni supported on SiO$_2$, kieselguhr, and MgAAP(LT) all show very similar reaction rates, the Ni/AAP and Ni/MgAAP(HT) catalysts exhibit reaction rates which are lower by a factor of 10 to 30. That this lower reaction rate is observed only in the catalysts which showed a suppression of normal hydrogen chemisorption, i.e., Ni/AAP and Ni/MgAAP(HT), is indicative of some relation between the hydrogen chemisorptive sites and the hydrogenation activity.

Table 2 also shows the reaction rates expressed in terms of turnover frequency (TF), that is, the number of transformations occurring per second per site on the catalyst surface. Calculation of the TF based on the measured crystallite diameter yielded relative numbers which again show the activity to be support related and in the order SiO$_2$, MgAAP(LT), kieselguhr, MgAAP(HT), and AAP. If, however, the TF is calculated assuming that only the hydrogen chemisorbing sites take part in the hydrogenation, then the support effect essentially disappears. The large uncertainties shown for the TF of phosphorus-containing materials reflect the fact that hydrogen uptakes were not measured for the same sample used in the reaction and that the uptake is highly dependent on the exact reduction treatment.

On the basis of these results it appears that during benzene hydrogenation, only those sites which strongly chemisorb hydrogen are catalytically active. This is not unusual. Indeed, similar trends have been reported for other gas-phase reactions over phosphorus-supported Ni catalysts. In studies of ethane hydrogenolysis, a Ni/MgAAP catalyst reduced at low temperature showed activity and rate-law parameters virtually identical to those of Ni/SiO$_2$; whereas upon high temperature treatment, lower activity and different rate-law parameters were observed (*11*).

Campelo *et al.* have surmised the existence of metal–support interactions in Ni/AlPO$_4$ catalysts by comparing the results of a sulfur-poisoning titration method with metal surface areas determined by BET techniques and X-ray diffraction (*15*). They determined that the number of active sites responsible for the liquid-phase hydrogenation of 1-hexene was much lower than would be expected if all Ni sites were

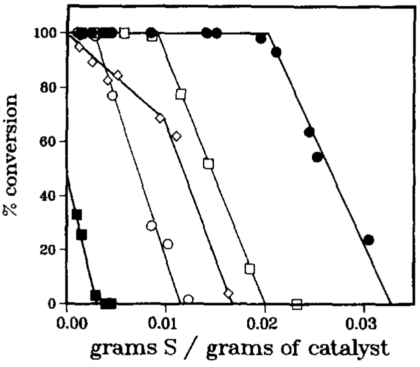

FIG. 1. Benzene hydrogenation activity of supported Ni catalysts as a function of sulfur poisoning during reaction at 110°C, 3.5 atm, $H_2/C_6H_6 = 10$, and GHSV = 25,000. Feed contained 150 ppm sulfur as thiophene. ●, Ni/SiO_2; ◇, Ni/kieselguhr; □, Ni/MgAAP(LT); ○, Ni/MgAAP(HT); ■, Ni/AAP.

equally active. Using this technique, they were able to obtain an estimate of the fraction of active atoms on the metal surface. They concluded that the catalytic activity of Ni was independent of particle size but highly dependent upon the support, with $AlPO_4$ being more interactive than SiO_2.

The integral sulfur capacity of the catalysts in our study was measured by observing the decrease in catalytic activity with time in the conversion of benzene to cyclohexane and extrapolating the linear portion of the decay line to zero conversion. These results are shown in Fig. 1 as percentage conversion versus total sulfur passed over the catalyst. The trend in sulfur capacity is the same as observed for the apparent reaction rate, that is, a decrease in the order SiO_2, MgAAP(LT), kieselguhr, MgAAP(HT), AAP.

The trend in the capacity of the various supported catalysts toward sulfur can be easily understood if one considers it to be directly related to the number of hydrogenation sites and the hydrogenation sites to be only those which strongly chemisorb hydrogen, i.e., those which are not interacting with the support. Therefore, supports such as SiO_2 or kieselguhr, which show little or no interaction (as evidenced by their hydrogen chemisorption), yield catalysts with higher total sulfur tolerance than supports in which interactions occur. Figure 2 shows that a nearly linear relationship exists between the number of Ni atoms capable of chemisorbing hydrogen and the sulfur capacity of the catalyst.

Finally, as can be seen from the slope of the line in Fig. 2, an approximately threefold excess of thiophene was required to completely poison the hydrogenation activity of these catalysts. This is much higher than would be expected in view of reported equilibrium data for sulfur-containing compounds, such as H_2S, in hydrogen (*16*). According to equilibrium studies, one S atom has been shown to sorb on an ensemble of approximately four or five Ni atoms thereby poisoning the activity of the ensemble (*17*). Although it is possible for the poisoning to be nonselective, resulting in a high sulfur-to-nickel ratio, the high ratio observed in these catalysts is most likely due to the high space velocities used during reaction and not to any inherent tolerance toward sulfur. Bartholomew *et al.* (*18*) have observed a similar phenomenon in sulfur-poisoning studies of Al_2O_3-supported Ni and Ni–Mo catalysts and suggested that the presence of adsorbed intermediates may be responsible for the apparent high sulfur tolerance by reversibly occupying active sites which would otherwise be irreversibly poisoned by the sulfur. The observed enhance-

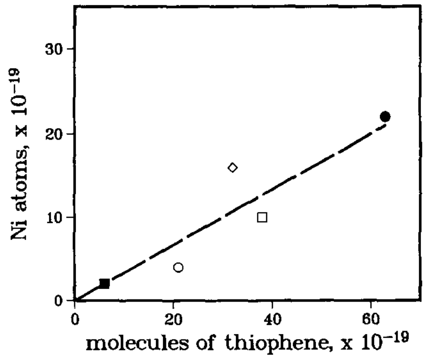

FIG. 2. Correlation between Ni capable of strong H_2 chemisorption and amount of thiophene required for complete deactivation. ●, Ni/SiO_2; ◇, Ni/kieselguhr; □, Ni/MgAAP(LT); ○, Ni/MgAAP(HT); ■, Ni/AAP.

ment in the sulfur capacity over expected equilibrium results is most likely a function of reaction variables such as temperature, pressure, hydrogen/benzene, and space velocity. As such, although sulfur capacity provides a direct comparison of the relative number of hydrogenation sites, it is not possible to use values obtained in this manner to count the absolute number of active hydrogenation sites in the supported Ni catalysts.

CONCLUSIONS

The present study shows that there is a strong support effect in phosphate-supported Ni catalysts toward the gas-phase hydrogenation of benzene and the extent of the metal–support interaction is dependent on the exact reduction temperature employed. Comparison of the hydrogenation rates and sulfur capacity of the various catalysts indicated the existence of a strong correlation between the strongly hydrogen chemisorbing sites and the active hydrogenation sites.

REFERENCES

1. For a recent review of phosphate catalysis, see Moffat, J. B., *Catal. Rev. Sci. Eng.* **18,** 199 (1978).
2. Marcelin, G., Vogel, R. F., and Swift, H. E., *J. Catal.* **83,** 42 (1983).
3. Aramendias, M. A., Borau, V., Jimenez, C., and Marinas, J. M., *React. Kinet. Catal. Lett.* **18,** 335 (1981).
4. Marcelin, G., Vogel, R. F., and Kehl, W. L., "Scientific Bases for the Preparation of Heterogeneous Catalysts, III," p. 169. Elsevier, Amsterdam, 1983.
5. Marcelin, G., Vogel, R. F., and Swift, H. E., *Ind. Eng. Chem. Prod. Res. Dev.* **23,** 41 (1984).
6. Campelo, J. M., Garcia, A., Luna, D., and Marinas, J. M., *Bull. Soc. Chim. Belg.* **91,** 131 (1982).
7. Marcelin, G., and Vogel, R. F., *J. Catal.* **82,** 482 (1983).
8. Tauster, S. J., Fung, S. C., and Garten, R. L., *J. Amer. Chem. Soc.* **100,** 170 (1978).
9. Marcelin, G., and Lester, J. E., *Prepr. Div. Petrol. Chem. Amer. Chem. Soc.* **28,** 553 (1983).
10. Marcelin, G., and Lester, J. E., *J. Catal.* **93,** 270 (1985).
11. Ko, E. I., and Marcelin, G., *J. Catal.* **93,** 201 (1985).
12. Vogel, R. F., and Marcelin, G., *J. Catal.* **80,** 492 (1983).
13. Freel, J., *J. Catal.* **25,** 139 (1972).
14. Selwood, P. W., "Chemisorption and Magnetization." Academic Press, New York, 1975.
15. Campelo, J. M., Garcia, A., Luna, D., and Marinas, J. M., *J. Chem. Soc. Faraday Trans. 1* **80,** 659 (1984).
16. Oliphant, J. L., Fowler, R. W., Pannell, R. B., and Bartholomew, C. H., *J. Catal.* **51,** 229, (1978).
17. Ng, C. F., and Martin, G. A., *J. Catal.* **54,** 384 (1978).
18. Bartholomew, C. H., Weatherbee, G. D., and Jarvi, G. A., *J. Catal.* **60,** 257 (1979).