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Alumina–Aluminum Phosphate as a Large-Pore Support and Its Application to Liquid Phase Hydrogenation

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Studies were conducted on the preparation of several compositions of alumina–aluminum phosphate and their resulting physical properties. It was observed that by varying the stoichiometry of the precipitates, surface areas and pore size distributions could be controlled. High alumina content invariably yielded materials with high surface area and small pores while high aluminum phosphate resulted in smaller surface area and larger pores. Some of the large-pore support gels were mixed with nickel salts to produce catalysts which were found to be highly active for the liquid phase hydrogenation of 2-ethylhexenal. The relative activities were successfully correlated with catalyst average pore radii and surface areas.

INTRODUCTION

The use of pure metal for heterogeneous catalysis is uncommon. In some cases, finely divided powders and metal gauzes have been used, but generally industrial metal catalysts are dispersed within a support such as clay, silica, or alumina. In addition to providing an economic incentive due to the reduced level of metal required, the support can aid the stability of the catalyst by providing a barrier to sintering, allowing exposure of higher surface area of the metal and increasing the mechanical strength of the catalyst (*1*). Some evidence also exists of metal–support interactions and their role in affecting reaction parameters (*2*).

The observed activity of a catalyst in a heterogeneous system depends, among other factors, on the surface area which is accessible to the reactants. It is important to recognize that in porous catalysts it is not only the total surface area which governs the reaction but also the average pore size and the pore size distribution. For some reactions the total surface area, as measured by nitrogen physisorption, does not truly represent the available surface for reaction. It is conceivable that large organic molecules will be restricted from entering cavities of small size and, therefore, only the active sites found within large pores contribute significantly to the reaction. One example of a diffusion-limited reaction of particular importance to the chemical industry is the hydrogenation of liquid feedstreams using supported nickel catalysts. When using a liquid feedstream, severe diffusion problems can be encountered. The reactants must diffuse through the liquid phase and into the catalyst pores for reaction to occur, and diffusion coefficients in liquid phases are extremely small. To overcome these limitations, catalytic metals employed in liquid phase hydrogenations are usually supported on large-pore refractory materials, such as selected kieselguhr or alumina (*3*).

The use of alumina–aluminum phosphate (AAP) as a catalyst support has received little attention in the open literature. A recent review by Moffat discusses the physical and catalytic properties of aluminum phosphate and includes AAP, but makes no mention of its utility as a catalytic support (*4*). In a series of papers, Marinas and coworkers studied the surface properties of aluminum phosphate and its use as a cracking and hydrogenation catalyst (*5–9*). A

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number of U.S. patents dating back to 1948 have been granted on this subject (*10*). In 1975, Pine described an AAP which was resistant to surface area loss when contacted with water and could successfully be used as a catalyst support (*11*). Recent reports describe the preparation of large-pore, thermally stable AAP and a magnesia modification which are readily prepared from easily handled materials (*12–14*).

The physical and chemical characteristics of AAP appear to make it suitable as a catalytic support. Aluminum phosphate is structurally similar to silica, since both the phosphorus and the aluminum atoms are tetrahedrally bonded to oxygen, and can exist in six structures analogous to silica. The structural similarity between silica and aluminum phosphate, the widespread utility of silica–alumina, and the high porosity of these materials prompted us to examine the use of AAP as a large-pore catalytic support.

In the present work we have examined various compositions of AAP with respect to surface and pore properties and evaluated their use as a support for nickel in liquid phase hydrogenations. For a probe reaction, the hydrogenation of 2-ethyl-2-hexenal to the saturated alcohol was chosen because of its industrial importance and the relatively mild conditions at which the reaction can proceed. This reaction was recognized as exhibiting diffusion limitations (*15*) and as such would provide a realistic example on the use of AAP as a large-pore catalytic support.

EXPERIMENTAL

Catalyst Preparation

The method described by Kehl (*10*) was employed to produce precipitates. Aluminum nitrate, Baker Analyzed assay 97.0% $Al(NO_3)_3 \cdot 9\ H_2O$ minimum, and phosphoric acid, Fisher Certified assay 85.7% H_3PO_4, were dissolved together to obtain a solution. A second, pH controlling solution was prepared using a 1 : 1 volume mixture of NH_4OH, Baker Analyzed assay 29.8% NH_3, with water. Both solutions were slowly added to a well-mixed vessel containing distilled water as a stirring medium while maintaining a constant pH of 8.0. The addition was continued until the aluminum nitrate–phosphoric acid solution was consumed. The resulting slurry was filtered, washed with water, and the percent solids of the resultant cake was obtained using an Ohaus moisture balance. The filter cake was either dried for 20 h at 120°C and calcined for 10 h at 500°C in air to obtain the support itself, or alternatively made directly into a finished catalyst by mix-mulling the AAP gel with nickel carbonate, MCB Reagent assay 45.0% Ni minimum. This was done by using a ratio of 60% solids AAP to 40% nickel carbonate in a Blakeslee Model A717 mixer. The material was dried at 120°C in air for 20 h, then calcined in air at 350°C for 10 h. The resulting catalyst was sieved to 20–40 mesh prior to evaluation. The stoichiometry of the AAP composite was easily controlled by varying the Al/P ratio in the initial solution.

A similar procedure was employed to prepare nickel catalysts on more conventional commercial supports. Silica (Davison Grade 59) and kieselguhr (Fisher Scientific infusorial earth, I-22) were sieved to −100 mesh and dry blended with nickel carbonate. Water was added to form a paste and the components were mix-mulled prior to drying, calcining, and sizing.

The BET surface area and the pore size distribution of the unreduced catalyst were measured using nitrogen adsorption at 77°K (*16*). Average crystallite sizes were measured by the X-ray line-broadening technique. In most instances the crystallite size measurement was obtained on the unreduced sample, and several measurements carried out on reduced catalysts indicated that no agglomeration took place during reduction (*17*). The nickel was reduced in the reactor for 7 h at 400°C with 15 liter (STP) h^{-1} (g cat)$^{-1}$ flowing through the catalyst bed. XRD measurements showed the catalyst to be at least 90% reduced following this treatment.

Catalytic Activity

The liquid phase hydrogenation of *cis*-2-ethyl-2-hexenal was performed in a fixed-bed, continuous-flow reactor. The reactor consisted of a 13-mm i.d. stainless steel tube into which approximately 5 ml of catalyst was loaded. Catalyst activity was tested following reduction at 400°C using a feed consisting of 15 wt% *cis*-2-ethyl-2-hexenal and 85 wt% 2-ethyl-1-hexanol. This dilution was found necessary to prevent temperature increases due to the exothermicity of the reaction. The liquid feed was delivered using a small reciprocating pump at a feed rate of approximately 33 g/h and heated to reaction temperature prior to contacting the catalyst. Hydrogen was flowed at a rate of 3 liter/h and a pressure of 100 psig. The reaction was studied at 50°C. Temperatures in the catalyst bed were controlled and monitored continuously using an embedded iron-constantan thermocouple and were not observed to vary by more than 1° from the desired value during the course of a reaction. The reaction was monitored for a period of 5 h with hourly samples collected and analyzed by GLC.

The catalysts were compared on the basis of their relative activity which was defined as percent conversion of 2-ethyl-2-hexenal to hydrogenated products per gram of nickel. Except as noted later, only the hydrogenation products, 2-ethylhexenol and 2-ethylhexanol, were observed in any of the catalysts evaluated and there was no evidence of side reactions such as isomerization or cracking.

RESULTS AND DISCUSSION

Catalyst Characteristics

By varying the amount of reagents used in the preparation of the supports, a number of AAP materials ranging in aluminum : phosphorus ratio between about 1 and 20 were obtained. Figures 1 and 2 show the relation between composition and surface area and median pore radius, respectively, obtained for the various AAP samples prepared after calcination at 500°C.

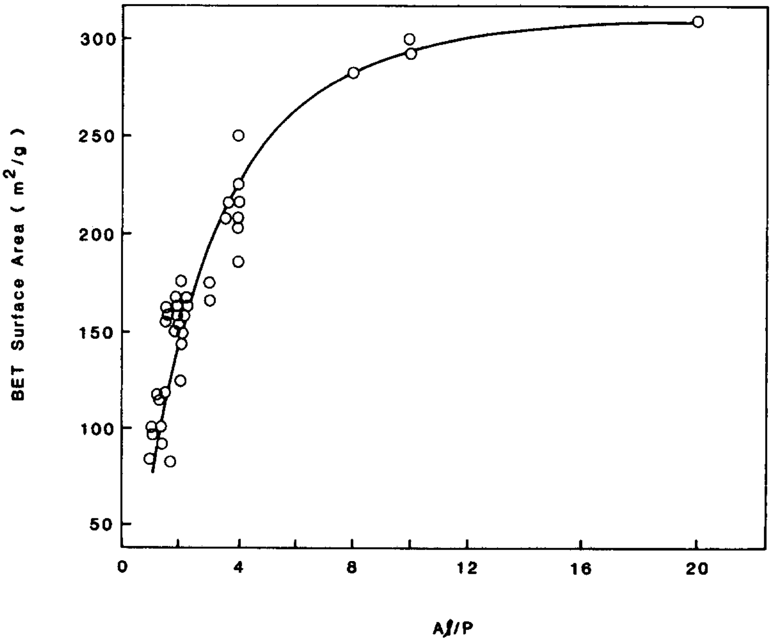

FIG. 1. Surface area vs aluminum to phosphorus atomic ratio for AAP.

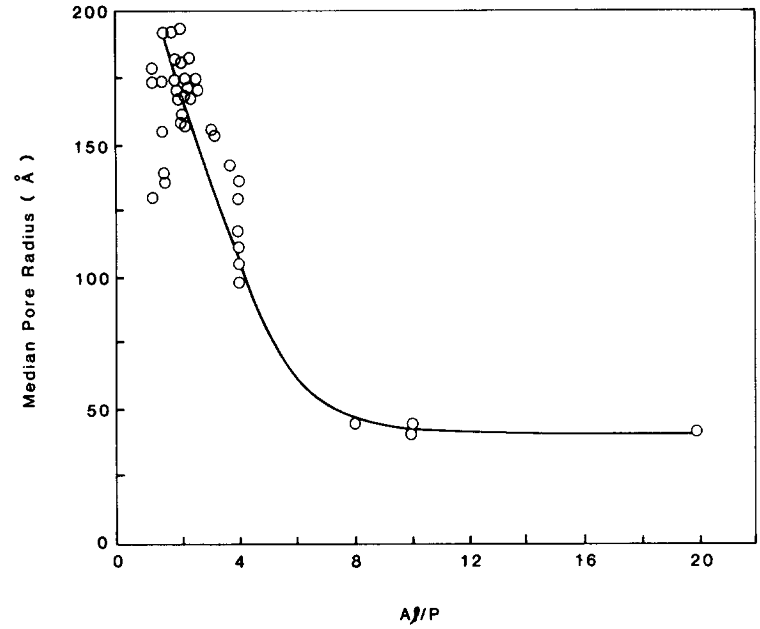

FIG. 2. Median pore radius vs aluminum to phosphorus atomic ratio for AAP.

These figures clearly show the variation in porosity which can be obtained by varying the Al/P stoichiometry. Low concentrations of alumina generally yielded supports of large porosity with pore size distributions consisting largely of >100 Å radii pores. As expected, the large-pore materials had somewhat lower surface areas than the smaller-pore counterparts.

When nickel carbonate was mix-mulled with AAP gels to make finished catalysts, it was observed that, upon calcination, the surface areas increased somewhat, while the porosities decreased slightly. Table 1 gives the physical properties of the various nickel catalysts studied. These catalysts were prepared so that a range of Al/P ratios could be investigated and included the end member of the series, Ni on "$AlPO_4$." Due to the preparation procedure used, the so-called "$AlPO_4$" is not a true stoichiometric phosphate, but rather an AAP with Al/P ~ 1 (*18*). Also, for reference, catalysts prepared using silica and kieselguhr as supports were included. Catalyst A was found to have high surface acidity, as deemed by its high activity for alcohol dehydration (*19*). Consequently, an additional preparation (Catalyst B) was made in which the acid sites were neutralized by the addition of a small amount of an alkali metal, 1% K_2O by impregnation, prior to calcination (*20, 21*).

It is apparent from Figs. 1 and 2 that, for mixed AAP catalysts, an increase in surface area is observed as the ratio Al/P increases. The pore size distribution, however, shifts toward smaller pore sizes with this increase. Figure 3 demonstrates that the addition of nickel generally shifts the pore size distribution toward smaller pores, presumably by occupying some of the pore volume, but does not appreciably distort the distribution profile. The surface area and porosity trends were not observed to continue to the end member, i.e., $AlPO_4$.

The X-ray powder diffraction patterns of the nickel catalysts were recorded between 5 and 75° 2θ. The spectra showed the support to be amorphous to X-rays even after calcination to 500°C. This is in accordance with results reported by Kehl (*12*) who claimed that the alumina and aluminum phosphate are not merely a physical admix-

TABLE 1

Physical Characteristics of 20% Nickel Catalysts

	A	B	C	D	E	F	G	H
Support	$4Al_2O_3 \cdot AlPO_4$	$4Al_2O_3 \cdot AlPO_4 + 1\% K_2O$	$Al_2O_3 \cdot 2AlPO_4$	$Al_2O_3 \cdot 8AlPO_4$	$Al_2O_3 \cdot 20AlPO_4$	$AlPO_4$	SiO_2	kieselguhr
Surface area (m^2/g)	290	280	225	161	92	114	265	111
Pore volume (cm^3/g)	0.46	0.47	0.64	0.44	0.29	0.32	0.85	0.10
Average pore radius (Å)	31.6	33.8	57.2	54.6	62.6	55.9	64.1	18.8
Median pore radius (Å)	39.9	40.4	102	130	138	90.3	104	25.1
Volume percentage of pore radii (Å)								
200–300	0.5	2.8	16.4	31.0	31.8	16.0	2.6	1.7
100–200	1.6	11.7	34.5	26.2	27.5	29.7	53.3	5.4
50–100	30.0	25.4	23.2	15.1	15.4	25.6	34.6	12.0
40–50	17.8	10.4	6.2	4.7	5.2	7.7	2.2	6.4
30–40	18.1	13.5	7.0	6.7	7.8	8.5	1.5	14.4
20–30	18.2	21.0	8.5	10.3	9.7	8.9	2.4	15.7
<20	13.8	15.0	4.4	6.0	2.5	3.6	3.4	44.5

ture but in fact form a new composition in which crystallization of individual phases is mutually inhibited. By contrast, some crystallinity was observed for nickel oxide in the calcined material, although it was highly dispersed. Typical NiO crystallite sizes were less than 40 Å and were not observed to grow with reduction to Ni metal. The catalysts prepared using SiO_2 or kieselguhr exhibited much larger crystallites of average diameter in the range of 80–100 Å.

Catalytic Activity

The availability of the active nickel metal within the pores of the catalyst becomes

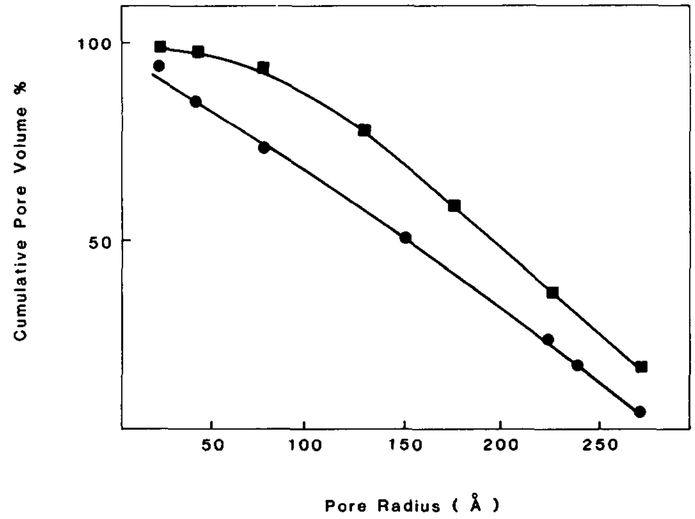

FIG. 3. Pore size distribution for an $Al_2O_3 \cdot 2AlPO_4$ composite, ■; same material after Ni addition, ●.

TABLE 2

Hydrogenation of 2-ethyl-2-hexenal Using 20% Nickel/AAP Catalysts

Support	Al/P (Atom)	Relative activity
$4Al_2O_3 \cdot AlPO_4$ + 1% K_2O	9	60
$Al_2O_3 \cdot 2AlPO_4$	2	100
$Al_2O_3 \cdot 8AlPO_4$	1.25	120
$Al_2O_3 \cdot 20AlPO_4$	1.1	80
$AlPO_4$	1	85
SiO_2	—	70
kieselguhr	—	11

critical for diffusion-limited reactions. In separate experiments we have observed a catalyst particle size influence on the apparent catalytic activity, indicating diffusion limitations (*15*). Examination of Table 1 would intuitively indicate that catalysts with low Al/P ratios should be better liquid phase catalysts by virtue of their larger pores.

When the conversion of 2-ethyl-2-hexenal to its hydrogenated products is employed as a measurement of catalytic activity and diffusion limitations, we find, as shown in Table 2, that activity progressively increases as the Al/P ratio decreases, until it reaches a maximum at Al/P ~ 1.25. This decrease in the relative activity for high phosphate materials, i.e., Al/P < 1.25, is not entirely surprising if one considers the corresponding decrease in surface area. In fact, a good correlation between hydrogenation activity and surface properties can be observed if one imagines the reaction to take place only in the largest pores. Figure 4 shows that the term which we call the "effective surface area," (ESA) defined by calculating the product of the BET surface area and the volume fraction of the pores with radii between 200 and 300 Å, closely mimics the resulting hydrogenation activity trend for the range of AAP compositions studied. Although we chose to define the ESA of a catalyst in terms of the volume fraction of the pores, an almost identical correlation is obtained by using the surface area fraction within the same pore size range.

The choice of range of pore size for the definition of ESA was purely arbitrary and was chosen only because it yielded a good correlation with activity. However, studies of solute diffusivities into catalyst pores have shown that significant diffusional hindrance can occur into liquid-filled pores even when the pore radius exceeds the solute molecular radius by a factor of 30 (*22*). Since the molecular radius of 2-ethyl-2-hexenal, as calculated on the basis of its liquid density, is in the range of 2–4 Å, the choice of 200–300 Å pores as the main contributor to the catalytic activity does not seem unreasonable since only within this pore range can diffusion occur virtually unrestricted.

The close correlation reveals the extent of the diffusion limitation of the reaction and extends beyond the AAP family of supports. Figure 5 shows the correlation between hydrogenation activity and effective

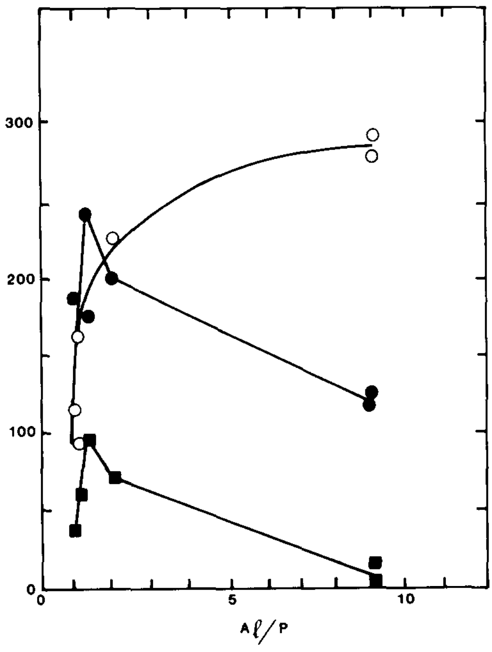

FIG. 4. Relations between support composition expressed as Al/P (atom) for a series of nickel catalysts. ○, BET surface area (m^2/g); ●, relative hydrogenating activity (a.u.); ■ "effective" surface area as detailed in text.

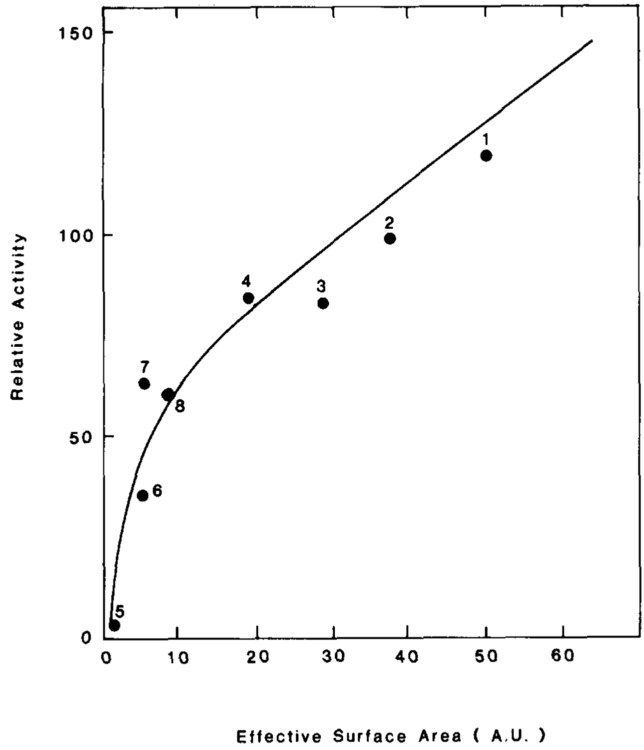

FIG. 5. Effect of "effective" surface area on the relative hydrogenating activity for a series of 20% Ni catalysts: (1) Catalyst D, (2) Catalyst C, (3) Catalyst E, (4) Catalyst F, (5) Catalyst H, (6) Catalyst A, (7) Catalyst G, (8) Catalyst B.

surface area for a series of Ni catalysts ranging in pore size from a nearly inaccessible Ni on kieselguhr (median pore radii = 25 Å) to the large pore Ni–AAP. A nearly linear relation is observed for effective surface areas larger than 20 m^2/g, as expected if reactivity is proportional to accessibility. For low ESA values, the correlation deviates from a simple straight line relationship indicating that, although not quite as accessible, reaction still occurs within smaller pores, or perhaps on the outer surface.

CONCLUSIONS

A new family of hydrogenation catalysts in which nickel is dispersed within a composite support of alumina–aluminum phosphate appears to be well suited for liquid phase hydrogenation. This catalytic material can be prepared with high nickel dispersion and, by varying the AAP composition, an almost tailor-designed pore size distribution can be obtained.

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