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NOTES

Compositional Effects on the Thermal and Structural Stability of Aluminum Phosphate Catalytic Materials

Metal oxides are ideally suited as supports for metal catalysts because of their characteristic thermal stability, low cost, and physical durability. In many instances, the surface area, porosity, and chemical nature of the oxide support can affect supported metal-catalyzed reactions. These effects can be significant in the case of mixed oxides, where compositional effects can vary the support's characteristics (*1, 2*).

A number of studies have been reported on the binary oxide system of alumina–aluminum phosphate (AAP) (*3–8*). This interest is due, in part, to the electronic and structural similarities between AAP and silica–alumina. However, because of inconsistencies in the methods of preparation (*4*), much of the work in the literature is not directly comparable, and many questions are yet unanswered concerning the nature of these binary oxides. Recently, consistent methods of preparation have been adopted to yield well-defined precipitates of AAP (*5*). This paper presents the results of a study on these well-defined, nonstoichiometric AAPs which indicate the effects of composition on the physical, chemical, and structural properties of these materials.

Materials ranging in P/Al from 0.06 to approximately 1 were prepared according to the method of Kehl, which has been described in detail elsewhere (*9, 10*). Aluminum nitrate and phosphoric acid were dissolved in a common solution. This solution was added together with an aqueous ammonium hydroxide solution into a well-stirred container of distilled water. The rate of addition of the two solutions was regulated to maintain a constant pH of 8. The precipitate formed was filtered, washed, oven-dried at 120°C, and later calcined in air at 500°C overnight.

Surface area and pore characteristics were obtained by nitrogen adsorption at −196°C using a Micromeritics 2600 surface area analyzer. X-ray analysis was performed using a Rigaku X-ray diffractometer. Mo*Kα* and Cu*Kα* radiation were used to measure the particle size, using line broadening techniques, after thermal treatments at temperatures of 500, 850, 1000, and 1400°C. Use of Mo*Kα* radiation allowed for particle size determination down to ca. 30 Å.

The composition of the various AAP materials is denoted throughout this paper by the use of a stoichiometric shorthand notation. For example, a P/Al ratio of 0.10 is chemically equivalent to a stoichiometry of $9Al_2O_3 \cdot 2AlPO_4$. This will be abbreviated as 9A2AP. This nomenclature is used only for convenience and does not imply a physical mixture of two distinct compounds.

The resulting BET surface area, pore volume, and pore size distribution for AAPs of differing stoichiometric ratios agree well with previous reports (*4, 5*). The effect of P/Al on the pore size distribution is shown in Fig. 1 and a listing of the obtained BET surface areas is given in Table 1. Examination of the pore size distributions and specific surface areas, as a function of P/Al ratio, indicates that the higher the Al content of the binary oxide, the more its surface area resembles that of Al_2O_3. Thus, it might be suggested that the material is a physical mixture of two metal oxides rather than a true microcomposite. If this were the case, however, it would be expected that such mixtures would exhibit bimodal pore distri-

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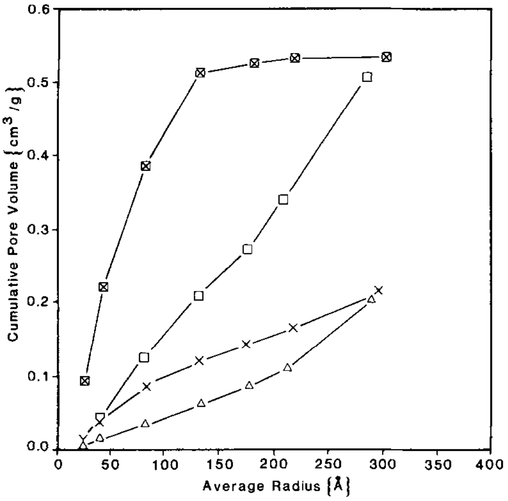

FIG. 1. Cumulative pore volume as a function of pore radius for AAPs of varying compositions. (△) Al*PO; (×) A8AP; (□) A2AP; and (☒) 9A2AP.

butions. As Fig. 1 shows, this is not the case, indicating that each AAP is a true chemical microcomposite.

The characteristics of chemical microcomposites are influenced by a number of factors, such as the preparation method or the chemical stoichiometry (*1, 4, 10*). Since all the materials studied here were prepared using a consistent procedure, this cannot be a significant factor in the explanation of the results. Therefore, chemical stoichiometry (i.e., the local chemical environment of the Al and P) would seem to be of greatest importance.

The thermal stability of AAP samples of varying P/Al ratios was examined by the techniques of both DTA and X-ray diffractometry (XRD) of sequentially heated samples. The temperature at which DTA exhibited a sharp exothermic signal was believed to indicate the onset of transformation from an amorphous to a crystalline phase, and thus an indication of the thermal stability of the material. These results are summarized in Table 1. Results for Al_2O_3 are also included for comparison. The most striking result noted, for the AAPs, is that at lower concentrations of P the microcomposite retained its amorphous nature to higher tem-

TABLE 1

Material Properties of Alumina–Aluminum Phosphates

Sample	P/Al	BET area (m²/g)	T1	T2	Crystalline phases present after calcination at T (°C) 500[a]	500[b]	850	1000	1400
γ-Al_2O_3	0	—	1080	1230	—	γ-Al_2O_3	—	δ-Al_2O_3	α-Al_2O_3[c]
8AAP	0.06	220	1340	—	γ-Al_2O_3	am.	—	trid. γ-Al_2O_3	trid. γ-Al_2O_3
9A2AP	0.10	240	1020	1360	γ-Al_2O_3	am.	am.	trid. γ-Al_2O_3	trid. γ-Al_2O_3
2AAP	0.20	180	1030	—	am.	am.	—	trid. γ-Al_2O_3	trid. γ-Al_2O_3
A2AP	0.50	105	870	—	am.	am.	trid. γ-Al_2O_3	trid. γ-Al_2O_3	trid. α-Al_2O_3
A4AP	0.67	—	1040	—	am.	am.	—	—	—
A8AP	0.80	70	880	—	am.	am.	trid. γ-Al_2O_3	trid. γ-Al_2O_3	trid. α-Al_2O_3
Al*PO	0.94	60	None	—	trid.[d]	am.	trid.	—	trid.

[a] Using Mo$K\alpha$ radiation.
[b] Using Cu$K\alpha$ radiation.
[c] From Ref. (*2*).
[d] Tridymite structure of $AlPO_4$.

peratures, indicating a higher thermal stability. The observed thermal stability enhancement was also carried over to the resulting alumina phase after the crystallization process. This is shown by both 8AAP and 9A2AP, in which the resulting crystalline alumina phase consisted primarily of γ-Al_2O_3, *even after thermal treatment at 1400°C*. This phase predominates to temperatures well above the expected point of transition of γ-Al_2O_3 to α-Al_2O_3 (*11*). It is also interesting to note the preference for the formation of the crystallographic phases of tridymite (for $AlPO_4$) and γ-Al_2O_3 upon initial crystallization, for all AAP samples.

This increase in thermal stability is not uncommon in alumina systems, where the presence of divalent ions or tetrahedral inclusions are known to result in an increase in thermal stability. Since $AlPO_4$ is tetrahedral in structure, the relationship between thermal stability and composition of the AAP materials can be considered to be similar to that of other spinel structures. In fact, the observed results for the AAPs in Table 1 agree very well with the variation of thermal stability for other mixed oxide systems such as silica–alumina (*11*). This enhancement in thermal stability is greatest for low P/Al ratios, suggesting the ability of $AlPO_4$ to disrupt the structural reordering of Al_2O_3 expected at higher temperatures. The lack of this enhancement at higher P/Al ratios is probably due to the crystallization of $AlPO_4$ and a depletion on the Al_2O_3 structure of impurity $AlPO_4$.

The ability of $AlPO_4$ to terminate regular ordering in Al_2O_3 is demonstrated by the X-ray results for the initially calcined AAP samples in Table 1. This data examines each AAP for microcrystallinity down to 30 Å with a Mo*Kα* source, as well as "macrocrystallinity" (>50 Å), using a Cu*Kα* source. The results indicate that although macrocrystallinity does not exist for any of the samples examined, microcrystallinity is apparent at both low and high P/Al ratios, but not for any intermediate values. At the extremes, it is the dominant phase which starts to crystallize.

The observed microcrystallinity at extreme P/Al values, and the amorphous nature of materials with intermediate P/Al may be readily explained by considering the $AlPO_4$ and the Al_2O_3 to randomly "mix" within the microcomposite. Pure materials show their characteristic crystalline structure. The inclusion of the second component would tend to disrupt this structure, affecting the long-range order of the lattice. If only small amounts of the second component are present, the disruption of the crystal lattice is not complete, and some microcrystallinity can still exist. It is interesting to note that while microcrystallinity is exhibited at both high and low P/Al values, only at the low ratio is thermal stability clearly enhanced.

While the overall structure of the resulting amorphous species is not clear, it is suggested that octahedral AlO_6 most likely is responsible for the termination of the $AlPO_4$ structure. Of the two coordination sites for Al expected to be found in AAP, the octahedrally coordinated aluminum would have the most disrupting effect in the long-range order of $AlPO_4$, since tetrahedral AlO_4 would be expected to easily replace tetrahedral $AlPO_4$ with only minor structural disruption. Recent NMR studies by workers at Phillips Petroleum on the structure of AAP lend further validity to this view (*12*). Their results indicate that, regardless of the P/Al ratios, the materials are not simply coprecipitated mixtures of Al_2O_3 and $AlPO_4$.

The persistence of the γ-phase of Al_2O_3 during the crystallization process is indicative of the relationship between octahedral and tetrahedral Al in AAP. The structure of γ-Al_2O_3 contains considerably more octahedral AlO_6 sites than either the α- or the η-phases. Therefore, if the majority of tetrahedrally coordinated Al in AAP are bound in the form of $AlPO_4$, upon crystallization, the remaining alumina should be predominately octahedral in nature and hence in a "γ-Al_2O_3-like" form as long-range crystallinity develops. As for the presence of tridymite found in $AlPO_4$ upon crystallization of the AAP, its formation can be explained by steric considerations. It has been suggested by Peri (*3*) that tridymite is the favored form of $AlPO_4$ due to the requirement that hydroxyls bond to both Al and P. Thus, it is not surprising that upon crystallization of AAP the γ-Al_2O_3 and tridymite phases predominate.

In summary, it has been shown that phosphorus, when coprecipitated in a 1 : 1 mixture or less with aluminum, can form an amorphous binary oxide with physical and textural properties which indicate that it is a true microcomposite and not just an admixture of the individual materials. The ratio of P/Al greatly affects the textural properties, as well as the thermal stability and microcrystallinity of the samples. In the limit, as P/Al approaches zero, increased thermal stability exists, and microordering occurs at high and low concentrations of P, but not at intermediate values.

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