HYDROTHERMAL STABILITY OF ALUMINOPHOSPHATE CATALYST SUPPORTS

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Alumina and aluminophosphate (AP) with Al/P ratio of 6 were subjected to hydrothermal treatment at 750 ° C for up to 48 h. The results indicate that AP had a higher hydrothermal stability than the γ-alumina. The pore size distribution and surface area of AP did not change much under hydrothermal conditions. The pore size distribution of alumina, on the other hand, shifted toward larger pore diameter accompaning with decreasing surface area upon deactivation.

1. Introduction

The material most commonly used as a support for hydrodesulfurization and automotive exhaust catalysts is alumina. It is known [1] that at high temperature (900 ° C) the γ-alumina begins to transform into other structures with loss of surface area. It is therefore of great interest to develop materials with high thermal and hydrothermal stability. In addition, γ-alumina has a fairly broad pore size distribution with a considerable portion of the total surface area in small pores, say pores smaller than 50 Å. Metal in such pores may not be readily accessible to reactant molecules and may also be buried when the catalyst is exposed, perhaps by accident, to high temperature.

Aluminophosphate (AP) has long been known as a catalyst support [2-5]. This interest is due, in part, to the large pore size [6-8]. An almost tailor-designed pore size distribution can be obtained by varying the AP compositions [2,3]. Although the thermal stability of AP has been studied by many researchers [2-6], the hydrothermal stability is seldom reported. The objective of this study is to investigate the hydrothermal stability of AP.

2. Experimental

AP with Al to P ratio of 6 was prepared according to the method of Kehl, which has been described in detail elsewhere [2,7]. Aluminum phosphate and phosphoric acid, both from Merck, were dissolved together to obtain a solution. A second, pH controlling solution was prepared using a 1 : 1 volume mixture of NH_4OH with distilled 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 precipitate formed was filtered, washed, oven-dried at 120 ° C, and later calcined in air at 500 ° C overnight. γ-alumina was obtained by hydrolysis of aluminum isoproproxide (Merck).

Deactivation of dried samples was done by treating the samples at 750 ° C for 4, 24, and 48 h in a furnace while adding water to the furnace (2.5 ml/min). These deactivation conditions are those generally used in testing the hydrothermal stability of cracking catalysts [9].

Specific surface area was obtained by the volumetric method of nitrogen adsorption (Micromeritics 2500). Pore size distribution was determined by the mercury penetration method. Mercury intrusion porosimetry to 60×10^3 psi was effected using a Micromeritics 9300 Pore Size Analyzer (30 Å minimum pore diameter attained). Atomic ratio of Al to P was measured by Inductively Coupled Plasma (Jarrell-Ash 1100).

3. Results and discussion

As shown in fig. 1, the initial surface area of γ-alumina was 213 m^2/g, but decreased by 40% to 128 m^2/g after 48 h deactivation at 750 ° C. However, a remarkable stabilization occurred on the AP sample. The AP sample only lost 5% of its surface area. Therefore, from the point of view of providing support surface

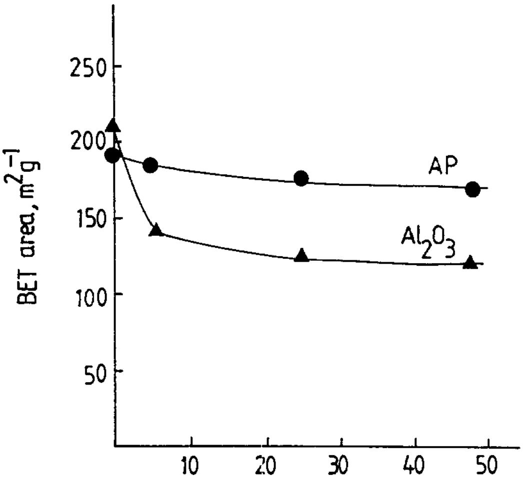

Fig. 1. Influence of hydrothermal treatment on BET surface area. ● AP; ▲ Al_2O_3.

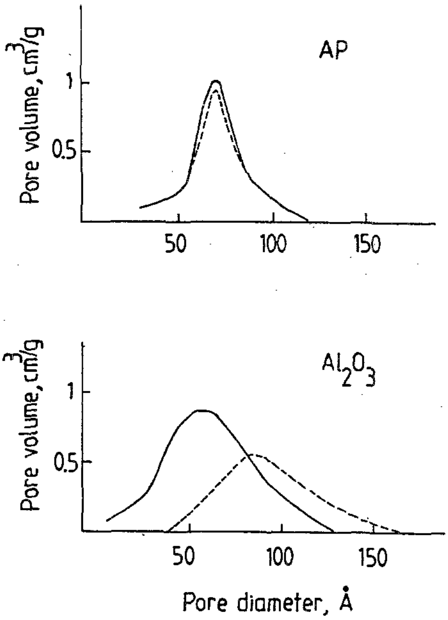

Fig. 2. Pore size distribution for AP and Al_2O_3. ——— before deactivation; ------ after deactivation at 750 ° C for 24 h.

area for metal under severe hydrothermal conditions, AP is much better than the conventional γ-alumina.

Figure 2 shows that the pore size distribution for the AP and alumina are quite different and they also responded differently to hydrothermal treatment. The AP sample has a rather narrow pore size distribution centered around a pore diameter of about 70 Å. It only changed little on hydrothermal treatment. It has been concluded that AP is a true chemical microcomposite, rather than a physical admixture of Al_2O_3 and $AlPO_4$ [2,7]. The unimodal pore distribution shown in fig. 2 are accord with this conclusion.

The alumina sample, on the other hand, has a much broader pore size distribution, which flattened, broader, and shifted towards large pore diameters upon deactivation. The small pores in the alumina thus disappear and the large pores grow larger.

The observed hydrothermal stability of AP is not uncommon in alumina system, where the presence of divalent ions or tetrahedral inclusions are known to result in an increase in hydrothermal stability [1]. The results may be readily explained by considering the $AlPO_4$ and the Al_2O_3 to randomly mix. Pure alumina show its characteristic crystalline structure. The inclusion of the $AlPO_4$ would tend to disrupt alumina structure, affecting the long-range order of the lattice. This would result in the enhancement in hydrothermal stability.

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