



Effects of rehydration of alumina on its structural properties, surface acidity, and HDN activity of quinoline

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ABSTRACT

A series of aluminas were obtained through rehydration–dehydration of the initial alumina under different hydrothermal conditions. To investigate the influences of rehydration temperature on the physicochemical properties of the as-obtained aluminas, several techniques were applied, such as X-ray powder diffraction, nitrogen adsorption, scanning/transmission electron microscopy, Fourier transform infrared, thermogravimetric analysis, and ^{27}Al MAS NMR. The results show that crystal size and morphology of alumina particles changed as the treatment temperature was increased, and alumina crystallites grew mainly along two surface orientations. Consequently, the changes in textural properties of the aluminas took place. In addition, the rehydration process increased not only the weak acid sites but also the strong acid sites, which is closely related to the growth of the (1 1 1) and (1 1 0) surfaces of $\gamma\text{-Al}_2\text{O}_3$. The two type acid sites were originated from coordinately unsaturated four-fold aluminum atoms. TPR for a series of Ni(Mo) catalysts were carried out and the results show that rehydration process increased the surface acidity and basicity of alumina simultaneously, which enhanced the interacting force of Ni and Mo species with aluminas respectively. This interaction is closely related to the hydrodenitrogenation (HDN) activity of quinoline over the corresponding NiMo/ $\gamma\text{-Al}_2\text{O}_3$ catalysts.

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1. Introduction

As one of the most important metal oxides, catalytic alumina, especially $\gamma\text{-Al}_2\text{O}_3$, has been widely used as supports or catalysts in several petroleum refining processes and petrochemical industries, mainly owing to its low cost, high specific surface area, good thermal stability, volatile acidity, and the interaction that it exhibits with deposited transition metals [1–3]. Its catalytic property depends largely on the crystallographic and textural structure. Hence, the control of textural properties (surface area, pore volume, pore size), morphology, and particle size is of the greatest interest to improve the potential of alumina in catalysis and other spectrum. Generally, $\gamma\text{-Al}_2\text{O}_3$ is produced by thermal dehydration reaction of boehmite ($\gamma\text{-AlOOH}$) with different crystalline in the range of 450–750 °C [4], and the morphology of $\gamma\text{-Al}_2\text{O}_3$ stays the same as its precursor (boehmite) during thermal transformation process. Therefore, the preparation procedure and thorough knowledge of boehmite precursor are fundamental to obtain a $\gamma\text{-Al}_2\text{O}_3$ material with excellent performance.

In order to acquire featured $\gamma\text{-Al}_2\text{O}_3$, many strategies in both preparation and modification of boehmite have been developed.

By controlling precipitation conditions, such as basic or acidic reactants [5,6], temperature [7], final pH value [8], various boehmites can be prepared. Nanostructured boehmite with different properties can be obtained by sol–gel method through adjusting hydrolysis and condensation rates of aluminum alkoxide and by variation of temperature, concentration, type of alkoxide, and water-to-alkoxide ratio [9,10]. Furthermore, hypercritical drying conditions [11], surfactant assemblies [12], and other conditions that could influence the texture of boehmite were investigated as well. In recent years, hydrothermal technology has been considered as an alternative method for the modification of boehmite due to its convenient route [13–15]. By controlling the temperature and duration of hydrothermal process not only textural properties, but also surface acidity of boehmite can be adjusted. These properties of the corresponding alumina could be modified as well. However, it is not efficient when the temperature of hydrothermal treatment is relatively low. Besides, longer treating period inhibits the utilization and development of the method.

As far as we are concerned, $\gamma\text{-Al}_2\text{O}_3$ has a similar structure with spinel, but there are many defect sites on the surface of its crystallites. These defect sites, including coordinately unsaturated surface (cus) cations and oxide anions, are the origin of Lewis acid sites and basic sites, respectively. Because of the existence of the coordinately unsaturated aluminum and oxygen atoms on the surface of $\gamma\text{-Al}_2\text{O}_3$ crystallites, rehydration can occur by interaction with

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