



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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H₂O, meanwhile, some cations and anions can be converted into surface hydroxyl groups [16–18]. Due to subsequent diffusion of the hydroxyl groups, boehmite can be finally formed. Apparently, the changes in physicochemical properties of the new obtained boehmite would take place. After calcination, a new γ -Al₂O₃ with different properties can be obtained. Compared to hydrothermal treatment of boehmite, rehydration of γ -Al₂O₃ could proceed at relatively low temperature and complete in a short time. Despite several papers have reported about this method [19–21], only the difference in pore structure was concerned whereas differences in other characters were neglected. However, those characters, particularly in crystalline structure and surface acidity, are closely related to catalytic activity. It is because that surface acidity has close relationship with the interactions of active metal (Ni, Co, Mo, etc.) with alumina surface, which directly influence the dispersion and composition of active phase, and subsequent catalytic performance. Therefore, how to adjust the structure and surface property of alumina is a key for preparing catalysts. To understand the effects of rehydration process in detail, herein, the properties of aluminas obtained via a rehydration–dehydration process under different conditions were investigated. The textural, structural and surface properties of aluminas were characterized with N₂-sorption, XRD, SEM, TEM, FTIR ²⁷Al MAS NMR and TPR, respectively.

2. Experimental

2.1. Preparation and hydrothermal treatments

Pseudo-boehmite was precipitated between pH 7.5 and 8.5 at 60 °C from solution of Al₂(SO₄)₃·18H₂O, using a 20 wt% solution of NaAlO₂. The white precipitate was collected, washed with deionized water for several times, and then dried in air at 80 °C overnight. The dried powder then was heated to 500 °C with a heating rate of 2 °C min⁻¹ and remained for 4 h.

Afterwards, 1.0 g of the as-obtained alumina was ultrasonically suspended in 20 ml of deionized water. Then the suspension was transferred into a 40 ml Teflon-lined stainless autoclave that was sealed and heated at 80 °C for 24 h. Thereafter the autoclave was cooled to room temperature naturally, and the resulting suspension was filtered off, dried in air at 80 °C overnight. For the investigation of the effect of rehydration temperature on the properties of samples, similar experiments were conducted at the temperature of 110, 140, 170, 200 and 230 °C. The rehydration samples were labeled as S-80, S-110, S-140, S-170, S-200, and S-230 respectively, according to the temperatures of rehydration. Sample labeled S-0 corresponded to the initial pseudo-boehmite without calcination. The dried samples were calcined in air from room temperature up to 500 °C for 4 h at 2 °C min⁻¹ heating ramp. Calcined samples identified by adding the letter “C” to the nomenclature used for fresh samples.

The NiMo/ γ -Al₂O₃ catalysts were prepared by impregnating alumina extrudate with mixed solution of ammonium heptamolybdate ((NH₄)₆Mo₇O₂₄·4H₂O) and nickel nitrate (Ni(NO₃)₂·6H₂O). Then the impregnated materials were dried overnight in air at 80 °C, and further calcined at 500 °C for 3 h at 2 °C min⁻¹ heating ramp. The as-prepared catalysts were labeled as C-0, C-140, C-170, C-200, and C-230, respectively.

2.2. Activity test

Catalytic activity measurements were carried out in a high-pressure continuous-flow micro-reactor. 10 ml of the catalyst extrude was loaded in the reactor. Prior to reaction, the catalysts were sulfided at 300 °C and 2.0 MPa H₂ pressure for 8 h with a liquid stream containing 3 wt% CS₂ in toluene, liquid hour space velocity

(LHSV) 2.0 h⁻¹, and H₂/feed = 300:1. The model compound (1.0 wt% quinoline and 0.2 wt% CS₂ dissolved in toluene) was then pumped into reactor. The reaction was carried out at a temperature 340 °C, H₂ pressure 2.0 MPa, H₂/feed = 300:1, and LHSV 2.0 h⁻¹. The liquid product was analyzed at Varian 3800 gas chromatograph equipped with CP-5 capillary column and flame ionization detector.

Kinetic experiments were carried out in a 500 ml of autoclave. The reactant (1.0 wt% quinoline and 1.0 wt% CS₂ dissolved in toluene) was transferred into it. Then the catalyst was put into the solution and its amount was fixed at 3.5 wt% of the solution. The initial H₂ pressure was fixed at 2.0 MPa. Before the reaction, the catalysts were sulfided first at 180 °C for 2.5 h and then at 300 °C for 1.5 h, after that the autoclave was cooled to room temperature. The H₂S generated during presulfurization was discharged and then complemented H₂ again. The reaction was performed at 320 °C under mechanical agitation at a rate of 750 rpm. At several time intervals, a series of liquid samples were obtained and analyzed at Varian 3800 gas chromatograph.

2.3. Characterization

2.3.1. X-ray powder diffraction

The X-ray powder diffraction (XRD) patterns of the samples were recorded at room temperature by a Panalytical X'Pert Pro MPD diffractometer (Netherlands) using Cu K α radiation at a scan rate (2 θ) of 5° min⁻¹. The accelerating voltage and applied current were 40 kV and 40 mA, respectively. The crystallite size of samples was calculated through the Scherrer formula ($D = (0.9\lambda)/(\beta \cos \theta)$), where D , λ , β , and θ are crystallite size, wavelength (1.54060 Å), full width at half-maximum intensity (FWHM) of diffraction peaks in radians, and Bragg's diffraction angle, respectively. The crystalline structures were refined with the Rietveld method.

2.3.2. Election microscopy

The morphologies images of as-prepared samples were obtained by an S-4800 field emission scanning electron microscopy (SEM) (FE-SEM, Hitachi, Japan) with an acceleration voltage of 1.5 kV. Partial samples ultrasonically dispersed in ethanol and dropped onto a carbon-coated copper grid for the analysis of transmission electron microscopy (TEM) carried out on a JEM-2100UHR electron microscopy (JEOL, Japan) at an accelerating voltage of 200 kV.

2.3.3. Textural analysis

The specific surface areas and pore size distributions were obtained from nitrogen adsorption–desorption isotherms measured on a Micromeritics TRISTAR 3020 adsorption analyzer (USA) at -196 °C. All as-prepared samples were degassed at 140 °C in vacuum for 6 h prior to adsorption measurements. The surface areas were calculated by the Brunauer–Emmett–Teller method, and the pore size distributions were determined by the Barrett–Joyner–Halenda (BJH) method from desorption branch of the isotherms.

2.3.4. Acidity distribution

The types of surface acid sites on calcined samples were determined through FT-IR pyridine adsorption technique. Measurements performed on a Newus Fourier transform infrared spectrometer (Nicolet, USA). IR spectra recorded at a resolution of 4 cm⁻¹ in the range of 1700–1400 cm⁻¹. Prior to measurement, the samples were degassed in air at 350 °C for 3 h, cooled down and then adsorbed in the saturated pyridine atmosphere at room temperature for 2 h. After adsorption, the infrared spectrum was recorded with the sample temperature fixed at 100 °C while outgassing.

In order to calculate quantitatively the total acidity of calcined samples, thermogravimetric (TG) analysis was employed to record

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