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Effect of γ-Al_2O_3 hydrothermal treatment on the formation and properties of platinum sites in Pt/γ-Al_2O_3 catalysts

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ABSTRACT

The effect of hydrothermal treatment (HTT) of γ-alumina on the state of its surface functional cover, anchoring of hexachloroplatinate, and properties of platinum sites was investigated. Hydrothermal treatment of γ-Al_2O_3 was found to increase the fraction of surface bridging OH groups and concentration of Lewis acid sites (LAS) and alter the metal complex–support interaction. Adsorption of hexachloroplatinate on the support surface is accompanied mainly by the formation of outer-sphere complexes, which are characterized by a lower reduction temperature. As a result, dispersion and electronic state of supported platinum are changed. Influence of γ-Al2O3 hydrothermal treatment on the catalytic properties of Pt/Al2O3 in n-hexane transformations and propane dehydrogenation was demonstrated. The revealed effect of γ-Al_2O_3 hydrothermal treatment on the formation of platinum sites in Pt/Al_2O_3 catalysts can be of fundamental importance for the steps of supported system synthesis where solid phase is contacting with water and aqueous solutions (impregnation and drying).

1. Introduction

A unique combination of the surface acid-base properties and pore structure makes γ-alumina a convenient support for metal catalysts, in particular Pt/γ-Al_2O_3 [1,2]. Platinum-on-alumina composites are widely used in gasoline reforming and isomerization of normal alkanes C_5–C_6 [1,3]. The preparation procedure of Pt/γ-Al_2O_3 catalytic systems includes several steps: deposition of active metal usually from an aqueous solution of $H_2[PtCl_6]$, drying, and thermoactivation. Many works [1,4–15] consider the regularities of active site formation at each synthesis step. The accumulated data provided substantial advances not only in understanding the main transformations of a precursor compound during the synthesis of supported catalysts, but also in the deliberate synthesis of this catalytic system with specified properties by introducing changes into a certain step.

The metal complex–support interaction at the deposition step can affect properties of the final catalyst; the interaction strongly depends not only on the chemical composition of precursor, but also on the nature of surface adsorption sites [4–9,13–15]. The adsorption sites of γ-Al_2O_3 are represented both by the hydroxyl groups and the Lewis acid sites (LAS). The relative content of certain functional groups on the oxide surface is determined to a great extent by phase homogeneity of the support. Changes in the phase composition of support may occur due to uncontrolled effect of water during the catalyst synthesis and storage. It was found that even at room temperature the action of water on γ-Al_2O_3 leads to the formation of aluminum trihydroxide phase [16–20]:

$$\gamma\text{-}Al_2O_3 + 3H_2O \rightleftarrows 2Al(OH)_3 \quad (1)$$

The formation rate and type of $Al(OH)_3$ modifications (gibbsite, bayerite) depend on the temperature, exposure time, and pH of the medium [18–20].

The most pronounced changes in the phase composition of alumina support are observed under hydrothermal conditions, which can take place both during pretreatment of the support and drying of the catalysts after contacting with aqueous solutions. The hydrothermal treatment (HTT) of γ-Al_2O_3 at temperatures up to 350 °C leads to boehmite [18,21–26]:

$$\gamma\text{-}Al_2O_3 + H_2O \rightleftarrows \gamma AlO(OH) \quad (2)$$

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HTT produces changes in the pore structure of γ-Al_2O_3 [18,21,22,24–26]. Efficient control of the temperature and exposure time made HTT applicable to the synthesis of aluminum oxides with variable texture characteristics [21,22]. Thus, variation of the HTT temperature in the range of 100–350 °C led to alumina with specific surface area of 200 to 70 m^2/g and effective pore diameter of 90 to 340 Å [22].

However, data concerning the effect of HTT on the acid-base properties of γ-Al_2O_3 surface are quite scarce. Recently, IR spectroscopy of adsorbed pyridine was used to demonstrate that HTT of γ-alumina at 200 °C for 6 h decreases the total concentration of LAS from 342 to 42 μmol/g [25]. Qualitative data indicating the effect of HTT on the state of hydroxyl cover of the γ-Al_2O_3 surface are reported [23,24]. An IR spectroscopy study [24] revealed that HTT of γ-Al_2O_3 at 140 °C followed by calcination at 550 °C increases the intensity of absorption bands at 3676 and 3731 cm^{-1} during the first 2 h of the treatment (these bands were assigned by the authors to the OH stretching vibrations of the bridging group bound to tetrahedrally and octahedrally coordinated aluminum atoms and the terminal group bound to octahedrally coordinated aluminum atom). A more prolonged treatment (6–24 h) decreases the intensity of these absorption bands. Meanwhile, a 24 h HTT produces nearly a twofold increase in the concentration of weak LAS, as shown by IR spectroscopy of adsorbed pyridine.

The goal of the present work was to acquire quantitative data about the effect of γ-Al_2O_3 interaction with water under hydrothermal conditions on the relative content of various functional groups on the alumina surface. Besides, it was great important to determine the extent to which changes in the composition of functional cover of the support surface could alter its adsorption properties toward $H_2[PtCl_6]$ and the nature of nascent platinum sites in Pt/γ-Al_2O_3 catalysts.

2. Experimental

2.1. Sample preparation

The study was carried out using γ-Al_2O_3 purchased from Condea Chemie GmbH; its grain size was 0.1–0.25 mm. This aluminum oxide was a high-purity: according to the manufacturer specification sodium and iron content was equal to 0.003 and 0.021 wt%, respectively. HTT was performed in titanium autoclaves. The alumina samples were placed in the autoclaves and flooded with distilled water. The ratio of solid and liquid phases was maintained constant at 1:25 (wt) in all the experiments. The HTT temperature and time were varied from 50 to 200 °C and from 0.5 to 12 h, respectively. After the treatment, the support samples were separated from the liquid phase by filtration and dried in air and then in a drying oven at 120 °C. For further investigations, the alumina samples after HTT and drying were used with or without thermal treatment in a muffle furnace at 550 °C. Prehistory of the alumina samples is always clarified in the text.

In the synthesis of supported platinum-on-alumina catalysts, aqueous solutions of hexachloroplatinic acid with a specified concentration, which were prepared from crystalline hydrate $H_2[PtCl_6]\cdot 6H_2O$ (pure grade, Aurat), were used as precursors. The adsorption isotherms of $H_2[PtCl_6]$ on alumina supports were obtained by the separate sample method with the weight ratio of support to $H_2[PtCl_6]$ solution equal to 1:25 (20 ± 1 °C). The pH values of the solutions were controlled using an InLab Easy BNC combined electrode (Mettler Toledo) on a SevenMulti device (Mettler Toledo). Platinum concentration in the solutions was determined photometrically. The method is based on the formation of a stained complex with tin chloride in a hydrochloric solution [27].

Samples of supported platinum catalysts were prepared by impregnation of support in an excess of $H_2[PtCl_6]$ solution. The amount of platinum in the solution was less than or equal to the adsorption capacity of the support. Platinum adsorption was carried out for 20 min. In this case, virtually a complete adsorption of platinum from the solution was attained; dissolution of the support and passage of Al^{3+} into solution could be neglected due to a very low rate of the process [28]. After the impregnation, the samples were carefully washed with water to remove non-chemisorbed solution components from the pore space of the support and then dried in air at room temperature. These samples were denoted as $H_2[PtCl_6]/Al_2O_3$.

For platinum content determination samples were dried at 120 °C and then calcined at 550 °C. Platinum content was measured photometrically. Preliminarily, the weighted samples were dissolved with H_2SO_4 in the presence of HCl and H_2O_2.

2.2. Methods of sample investigation

2.2.1. X-ray diffraction (XRD)

Phase composition of the γ-Al_2O_3 samples subjected to HTT was determined by XRD on a Bruker D8 Advance diffractometer (recording with the Bragg-Brentano focusing) using monochromatic Cu *K*α radiation (λ = 1.5418 Å) in an angle range $2\theta = 5–80°$ and a step size of 0.1°. Identification was made using the ICDD PDF-2 database (2006) (no. 10-425 and no. 21-1307). The fraction of boehmite forming from γ-Al_2O_3 under hydrothermal conditions was estimated from the area of reflection (0 0 2), which is typical of this phase, using a calibration curve.

2.2.2. Scanning electron microscopy (SEM)

The effect of γ-Al_2O_3 HTT on the morphology of oxide surface was investigated by the SEM method with a JSM-6460 LV (JEOL) instrument, using Au-coated samples and acceleration voltage of 20 kV.

2.2.3. ^{27}Al and ^{195}Pt magic angle spinning nuclear magnetic resonance (MAS NMR)

^{27}Al MAS NMR spectra were recorded at a Larmor frequency of 104 MHz on an Avance-400 (9.4 T) NMR spectrometer (Bruker) equipped with a SB4 multinuclear sensor (MAS). The tested samples were placed in 4 mm zirconia rotors and spun at the magic angle (54°44′) with a frequency of 10^4 Hz. Single-pulse experiments were carried out with the following parameters: pulse width 2.5 μs, pulse-delay time before quantization 6.5 μs, pulse repetition time 0.5 s, window width 20.8 kHz, number of data points 4000, total number of pulses 1024. Chemical shifts are referenced with respect to 1 M $AlCl_3$ aqueous solution. The relative content of structural aluminum–oxygen polyhedra (aluminum in tetrahedral, pentahedral and octahedral environments) in the samples of support was found from the ^{27}Al MAS NMR spectra. For quantitative analysis, the obtained NMR spectra were deconvoluted using the Pearson VII function [29], and each band was integrated.

The ^{195}Pt MAS NMR spectra of $H_2[PtCl_6]/Al_2O_3$ samples were taken at a Larmor frequency of 86 MHz using an aqueous solution of $H_2[PtCl_6]$ with the concentration 0.03 M as external standard. The pulse time was 13 μs, pulse-delay time before quantization 16 μs, pulse repetition time 0.7 s, window width 70 kHz, number of data points 16,000, and total number of pulses 4096.

2.2.4. Low-temperature nitrogen adsorption

The nitrogen adsorption–desorption isotherms on the alumina samples were obtained at 77 K in a volumetric vacuum static unit ASAP-2020 (Micromeritics). Before measurements, the samples subjected to HTT at different temperatures were calcined at 550 °C for 3 h. The Brunauer-Emmett-Teller specific surface area S_{BET} was