Applied Catalysis A, General 554 (2018) 64–70

Contents lists available at ScienceDirect

Applied Catalysis A, General

journal homepage: www.elsevier.com/locate/apcata

Hydrothermal modification of the alumina catalyst for the skeletal isomerization of n-butenes

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ARTICLE INFO

Keywords:
Alumina catalyst
Skeletal isomerization of n-butenes
Hydrothermal treatment

ABSTRACT

Hydrothermal modification of the alumina catalyst of n-butenes skeletal isomerization was investigated. It is shown that during the hydrothermal treatment of γ-Al_2O_3 and subsequent calcination its activity in skeletal isomerization of n-butenes first increases, and then it decreases with a rise of the hydrothermal treatment duration. This behavior is due to a similar change in the content of the strong Lewis acid sites of alumina, which are the active centers of reaction and they can be identified by IR-spectroscopy of the adsorbed pyridine and EPR-spectroscopy of the adsorbed anthraquinone. We report the mechanism of new Lewis acid sites formation at the γ-Al_2O_3 hydrothermal treatment containing X-ray amorphous component.

1. Introduction

Active aluminum oxide (γ-Al_2O_3) is most often used in a series of oxide catalysts and catalyst carriers due to a unique combination of thermal stability, mechanical strength, developed surface and acid-base properties. Its acid properties affect the dispersity of the active component in the catalyst; the acid sites are the active centers in dehydration and isomerization reactions; they are also involved in oligomerization of hydrocarbons [1–10].

The skeletal isomerization of n-butenes (1-butene, trans-2-butene, cis-2-butene) to 2-methylpropene proceeds on the Lewis acid sites of γ-Al_2O_3 by the carbon-ion mechanism, including the stages of n-butene adsorption with formation of carbonium ion of linear structure, its isomerization to the tertiary ion, and desorption of 2-methylpropene [11]. Therefore, γ-Al_2O_3 with a high content of strong Lewis acid sites is used as an industrial catalyst for the skeletal isomerization of n-butenes to 2-methylpropene [12], and it is important to increase its activity [11,12]. For this purpose, chemical modification of γ-Al_2O_3 with oxides by tungsten and boron was carried out [13–16]. However, with an increase in the acidity and conversion of n-butenes, the selectivity to 2-methylpropene is reduced and catalyst surface coking occurs [14]. This is associated with a change in the structure and strength of acid sites during chemical modification. The problem can be solved by increasing the concentration of acid centers γ-Al_2O_3 without using promoters.

Several researches [2] developed a number of methods for controlling the acid properties of the γ-Al_2O_3 surface through the chemical modification and heat treatment, and showed the mechanism of their action. Another new method of acid properties modifying of surface alumina is hydrothermal treatment (HTT) with the calcination to follow: the γ-Al_2O_3 hydration into boehmite proceeds in the hydrothermal conditions, and it is then converted back to oxide with improved catalytic characteristics in results of heating [4–6]. For example, we showed the positive effect of HTT support on the catalytic properties of synthesized alumoplatinum catalysts in the dehydrogenation of propane [4] and of NiMo/γ-Al_2O_3 in the hydrogenation of quinoline [9].

Unfortunately, at the present time in the literature there is no unambiguous opinion on the process of changing the acidity of the alumina support as a product of the γ-Al_2O_3 HTT. In [4–6,9], an increase in the content of Lewis acid sites after HTT is shown. However, the causes and mechanism of acidity growth were not revealed - the authors attribute the results to the formation of a large boehmite, the particles of which have the form of plates [6]. This assumption contradicts the data of [10,11], according to which the boehmite is better crystallized, and the lower is the acidity of γ-Al_2O_3 obtained from it. On the other hand, HTT removes microimpurities of Na, Fe oxides from the alumina. This can also be the reason for the increase in the content of acid sites and their strength [2]. It is probable that hydrothermal modification can increase the acidity of γ-Al_2O_3 by changing its microstructure and/or as a result of the effect of purification from metal oxides.

The purpose of this research work is investigation of the effect of hydrothermal treatment γ-Al_2O_3 on its acid properties and catalytic

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https://doi.org/10.1016/j.apcata.2018.01.024
Received 8 August 2017; Received in revised form 16 January 2018; Accepted 24 January 2018

activity in the skeletal isomerization reaction of n-butenes.

2. Materials and methods

2.1. Preparation of initial alumina and its hydrothermal treatment

Sample aluminum oxide (AO) was obtained by calcinations of high-purity pseudoboehmite Pural SB (molded with distilled water to cylindrical extrudates, d = 4 mm) manufactured by SASOL company. It contained the following microimpurities (g/ton): SiO_2 < 120; Fe_2O_3 < 100; CaO < 50; MgO < 50; Na_2O < 20; K_2O < 20; Ni,Co, Cr, Pb, Mn, Zn < 100. The hydrothermal treatment of aluminum oxide extrudates was performed in stainless steel autoclave (V = 100 ml, without stirring) at 150 °C and heating/cooling rate of 7 °C/min. An AO to water mass ratio was 1:5. On being kept for a certain time, the autoclave was cooled to room temperature and the sample was extracted, and dried at 120 °C for 2 h.

2.2. Methods of research

Thermogravimetric analysis was performed with a STA-449C (Netzsch, Selb, Germany) combined thermogravimetric and differential scanning calorimetric (DSC) analyzer coupled with an Aeolos QMS 403 quadruple mass spectrometer (Netzsch, Selb, Germany) in a temperature range of 30–1000 °C at a heating rate of 10 °C/min in a flow of argon. The concentrations of aluminum hydroxide phases were calculated from the amount of water released in their dehydration.

Electron-microscopy studies were performed at the Electron Microscopy Center of Kazan Federal University. Micrographs of the samples were obtained with a Zeiss EVO-50XVP scanning electron microscope (SEM) and with Hitachi HT7700 Excellence transmission electron microscope (TEM) operating at 80 keV.

Powder X-ray diffraction measurements were carried out using a Shimadzu XRD-7000 diffractometer with long-wavelength CuKα radiation and graphite monochromator. The range of 2θ angles was 5°–90° with a step of 0.05°. 2 to 100° with a step of 0.02° and exposure time at each point of 0.24 s without sample rotation. The coherent scattering region (CSR) sizes $D_{(hkl)}$ were calculated using the Scherrer Eq. (1).

$$D_{(hkl)} = K\cdot\lambda/(\beta\cdot\cos\theta) \quad (1)$$

which is limited by the uncertainties in K, the crystallite shape factor, and β, which is the pure diffraction broadening. Diffraction intensities were measured by scanning from 20 to 80° (2θ) with a step size of 0.02° (2θ). The error in determining the CSR size was about 10%.

The porous structure of the samples was studied by the method of low-temperature adsorption of nitrogen with a Quantachrome Autosorb IQ instrument. The adsorption isotherms of nitrogen were obtained at a temperature of −196 °C, the degassing was performed at 150 °C to a residual pressure of 10^{-4} mmHg. Specific surface area (S) was calculated according to the Brunauer-Emmett-Teller method. The pore diameter distribution was calculated by the desorption branch of isotherm using the standard Barrett–Joyner–Halenda method.

The infrared spectrum has been determined for pyridine adsorbed on acidic solids. Experiments were performed using a Bruker Vertex 70 FTIR spectrometer fitted with a mercury–cadmium–telluride (MCT) detector. The measurements were done in transmission mode using a Harrick high-temperature cell. For the FTIR analysis a sample of γ-alumina was prepared in a tablet-shape of 20 mg; its optical density was 20 mg/cm^2. Background spectrum was recorded post-activation at T = 723 K and residual pressure of less than 10^{-3} mbar. Pyridine was dosed onto the catalyst at T = 320 K. Excess of pyridine was evacuated at the same temperature.

EPR measurements were done using commercial BrukerElexsys E 580 X-band (9.6 GHz) machine. For the quantitative measurements, toluene solution of Cu-DETC complex with 4.8(2)*1016 spins per sample was used as a reference. The modeling of EPR spectra and decomposition procedure were done by EasySpin toolbox for MATLAB [12,13].

2.3. Catalytic testing

The catalytic activity of the samples in the course of n-butenes skeletal isomerization was tested in an isothermal flow-through laboratory reactor in the continuous mode at a temperature of 540 °C, gas hourly space velocity (GHSV = Reactant Gas Flow Rate/Reactor Volume) of 200 h^{-1}, raw material to steam ratio of 1:4, and charged volume of the catalyst of 20 cm^3 (13 g, see also Fig. 1S, Supplementary Information). The composition of the starting reaction mixture (n-butenes) and reaction products was analyzed with a Khromos GKh-1000 automated chromatographic complex with heat-conductivity (chromatographic column 8 m with diameter 2.5 mm, phases are brick calcined at 800 °C and 30% of pentaerythritol tetrabutyrate) and flame-ionization detectors (capillary column CP-Al_2O_3/KCl, 25 m, 0.32 mm). The attainment of the steady state by the process was judged from three repeated results of analyses of the contact gas, the error in determining concentrations of components was about 0,5% (relative). The conversion X (%) and selectivity S (%) obtained in the steady state were calculated by the formulas (2) and (3).

$$X = [(\sum N_{n-butenes\ in\ feed} - \sum N_{n-butenes\ in\ contact\ gas})/\sum N_{n-butenes\ in\ feed}]\cdot 100\,\% \quad (2)$$

$$S = [N_{isobutene}/(\sum N_{n-butenes\ in\ feed} - \sum N_{n-butenes\ in\ contact\ gas})]\cdot 100\,\% \quad (3)$$

The error in determining conversion and selectivity was about 1% (relative).

3. Results and discussion

3.1. Properties of the initial γ-Al_2O_3

The initial alumina sample was produced by calcination (550 °C,

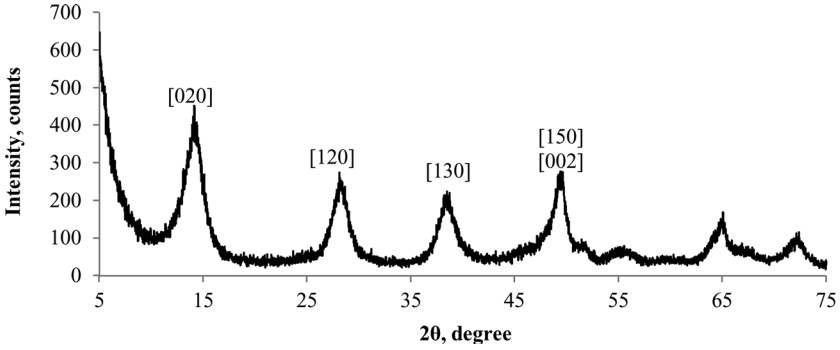

Fig. 1. Diffractogram of a Pural SB sample.