



International Conference on Oil and Gas Engineering, OGE-2016

## Supported sulfated zirconia catalysts for isomerization of n-hexane

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### Abstract

Sulfated zirconia catalysts supported on SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> were prepared and studied. Phase composition of the catalysts, acidic properties in CO adsorption, and textural characteristics were assessed. Activity of the catalysts in isomerization of n-hexane was measured. Alumina was shown to be a promising support for the synthesis of such catalysts. A new step of additional sulfation after platinum deposition was proposed for the synthesis of alumina-supported catalysts. It was found that strong Lewis acid sites with CO absorption bands at 2210 and 2224 cm<sup>-1</sup> are formed in the catalysts. The yield of the sum of hexane isomers for the alumina-supported catalysts reached 80 wt.%.

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Peer-review under responsibility of the Omsk State Technical University

**Keywords:** Isomerization; sulfated zirconia; supported catalysts; platinum

### 1. Introduction

Isomerization of light gasoline fractions is an efficient process for the production of gasolines that completely meet the requirements of Customs Union Technical Regulation for class 5 [1]. The system based on sulfated zirconia is a highly efficient catalyst for the isomerization process [2]. Such catalysts are highly active and selective and operate in a favorable temperature range of 140-180°C; however, they are quite expensive and require a complicated production technology, which includes the step of zirconium hydroxide reprecipitation. The introduction of active

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component into the porous matrix of support can be used to synthesize sulfated zirconia systems without reprecipitation step. On the other hand, the use of support with the developed specific surface area can increase the catalyst surface [3] virtually without a loss in its strength. The second essential aspect is that the deposition facilitates the formation of small crystal zirconia particles by the high-temperature calcination, which owing to spatial separation cannot agglomerate to form larger particles [4-12]. This results in stabilization of the tetragonal phase of zirconia, which is active in the isomerization reaction.

The work aimed to investigate the sulfated zirconia catalysts supported on  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ , which were synthesized by thermal decomposition of zirconium salts in the pores of supports. The effect of different conditions of the synthesis on the chemical and phase composition, textural characteristics, acidic properties and catalytic performance in isomerization of n-hexane was studied.

## 2. Experimental

### 2.1. Catalyst preparation

Porous matrices of silica and alumina calcined at  $600^\circ\text{C}$  served as supports for the catalysts. The study was performed with the KSK-1 silica manufactured at the Salavat catalyst plant. Alumina was synthesized under laboratory conditions from aluminum hydroxide (Sasol). Textural characteristics of the supports are listed in Table 1. The supports were evacuated and then impregnated with a solution of sulfated zirconia with subsequent high-temperature calcination at  $650\text{--}800^\circ\text{C}$ . The samples are denoted as SZ/ $\text{SiO}_2$  and SZ/ $\text{Al}_2\text{O}_3$ , respectively. To increase the content of active component, one to three impregnations were carried out; the number of impregnations is indicated as index X that stands after the support name (SZ/support-X). Between impregnations, the samples were dried and calcined at  $500^\circ\text{C}$ . After calcination, the catalysts were sulfated with a 5 N solution of sulfuric acid and then calcined in a muffle furnace at  $500^\circ\text{C}$ . Platinum was deposited on the synthesized systems from a solution of hexachloroplatinic acid. This was followed by activation of the catalysts in flowing air at a temperature of  $500^\circ\text{C}$ . The effect of sulfuric acid concentration was investigated at the step of additional sulfation after platinum deposition. In this series, catalysts with deposited platinum were impregnated with a  $\text{H}_2\text{SO}_4$  solution having the concentration of 1-4 N, and then calcined in flowing air at  $500^\circ\text{C}$ .

### 2.2. Catalyst characterization

The content of Pt,  $\text{ZrO}_2$  and  $\text{SO}_4^{2-}$  ions in the tested samples was measured on a Varian-710ES inductively coupled plasma atomic emission spectrometer under the following conditions: plasma power, 1.1 kW; plasma-generating flow of argon, 13.5 L/min; auxiliary flow of argon, 1.5 L/min; analytical wavelengths, 343.823 nm (Zr), 214.424 nm (Pt), and 181.972 nm (S).

The pore structure parameters of the samples were examined on a Sorptomatic-1900 instrument. The phase composition were studied on a D8 Advance (Bruker) diffractometer using parallel  $\text{Cu-K}\alpha$  radiation in the  $2\theta$  angular range from  $5$  to  $80^\circ$ . A scanning step was  $0.05^\circ$ ; and a time of signal integration, 5 s/step.

IR spectra of the samples were recorded on a Shimadzu 8300 Fourier spectrometer with a resolution of  $4\text{ cm}^{-1}$  and spectra accumulation from 100 scans. To take the spectra, the samples were pressed into pellets without a binder, their density was  $24 \times 10^{-3}\text{ g/cm}^2$ . A pellet was placed in a cuvette intended for the high-temperature pretreatment of a sample, adsorption of CO, and recording the spectra at the liquid nitrogen temperature ( $-190^\circ\text{C}$ ). Prior to the adsorption, the sample was heated in a vacuum at  $500^\circ\text{C}$  for 1 g. Adsorption of CO was performed at a pressure of 0.1-10 Torr.

### 2.3. Catalytic tests

The catalytic studies were carried out in a flow setup with a reactor having a stationary layer of the catalyst. The catalyst fraction with the particle size of 0.25-0.75 mm was loaded into reactor. The supported catalysts were activated directly in the catalytic setup in a flow of purified hydrogen for 2 h at a temperature of  $270^\circ\text{C}$ . The catalytic reaction was conducted in a temperature range of  $140\text{--}220^\circ\text{C}$  at a pressure of 1.5 MPa, liquid hourly space

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