Isomerization of n-butane over Pd–SO$_4$/ZrO$_2$ catalyst: Prospects for commercial application

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HIGHLIGHTS

- Pd promoted sulfated zirconia catalyst Pd–SZ was prepared after proprietary procedure.
- Catalytic properties were studied in n-butane isomerization upon parameters variation.
- At low H$_2$/C$_4$ ratios catalyst shows high conversion and selectivity performance.
- Catalytic stability was unchanged during 90 h resource test exposed to 20 ppm H$_2$O.
- n-Butane isomerization technology may be simplified by making use Pd–SZ catalyst.

ARTICLE INFO

ABSTRACT

Increase in productivity of the refineries and improvement the fuel quality demands to engage isobutane as a key feedstock for producing both alkylates and oxygenated additives. Substantial growth of isobutane output via isomerization of n-butane poses a real technological challenge. The goal of this study is to investigate performance of Pd promoted sulfated zirconia catalysts (Pd–SZ) in n-butane isomerization. The physical–chemical characteristics of various anion-modified zirconia catalysts (XRD and IR spectra, BET surface) are presented. It was observed that Lewis acid sites of medium and strong strength and two types of Brönsted acid sites exist. Approximately 90–97% of zirconia is in tetragonal phase.

The influence of parameters on conversion of n-butane and selectivity towards isobutane was investigated by varying the temperature (90–290 °C), pressure (15–26 bar), WHSV (0.5–5 h^{-1}), and molar ratio H$_2$/C$_4$ (0.08–3). Mainly, temperature and H$_2$/C$_4$ ratio are responsible for increasing the effectiveness of the process. At H$_2$/C$_4$ = 0.08–0.3 the apparent activity of Pd–SZ catalyst was high enough to reach the equilibrium conversion of n-butane to isobutane at 140 °C value, that is, ∼65%. The best results were obtained on Pd–SZ granules in the form of 2 mm trilobe. Water impact and the catalyst lifetime were studied in the pilot setup. Endurance testing of Pd–SZ catalyst in course of 90 h showed its sustained operation at H$_2$O concentration up to 20 ppm without loss of activity.

The estimated process specifications on Pd–SZ catalyst were compared to a conventional process; potential benefits of making use Pd–SZ catalyst are emphasized and discussed.

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1. Introduction

The industrial importance of upgrading light hydrocarbons (HC) in refineries and gas processing plants has increased dramatically since the adoption by many countries of new regulations affecting fuel quality. The upgrading may be accomplished by means of light paraffin C$_5$–C$_6$ isomerization, isobutane alkylation by olefins, isobutene dimerization and hydrogenation, or by MTBE synthesis. In order to increase productivity of oil refineries, the gaseous paraffin fractions including butane and isobutane should be engaged in production of high-octane motor fuel constituents. However, a shortage of isobutane (i-C$_4$) in refineries essentially limits its application as a raw material. Boosting of isobutane production via n-butane (n-C$_4$) isomerization could provide a solution to this problem. Isomerization of n-C$_4$ is in high demand for i-C$_4$ alkylation by butenes. Alkylates contain no aromatics and are considered as key components in production of high-quality blending fuels that satisfy strict environmental regulations [1].

In the past century, a number of isomerization technologies were commercialized [2]: isomerization at high temperatures (360–440 °C) over fluorinated Pt/alumina catalysts; isomerization at medium temperatures (250–300 °C) over Pt/zeolite catalysts; isomerization at low temperatures (120–190 °C) over Pt/Al$_2$O$_3$–Cl catalysts; isomerization at low temperatures (120–200 °C) over Pt anion-modified zirconia catalysts. For now, some of them are

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just of historical interest. Most of these technologies were applied for C_5–C_6 isomerization, one of them – for C_4 isomerization. Every approach has its advantages and disadvantages; this is why the quest for new isomerization catalysts and technologies is still continuing.

Catalysts on the basis of anion-modified zirconia were found to be highly active for light paraffin C_5–C_6 isomerization [3–6]. With these catalysts, the main reaction routes were isomerization and cracking. However, their significant drawback was low catalytic stability. It was shown in [3,4] that introduction of Pt or Pd as hydrogenating–dehydrogenating agent and carrying out the process in hydrogen atmosphere allows for continuously high catalytic activity and selectivity, predominantly for the paraffin isomerization route [7]. In particular, Pt-promoted sulfated ZrO_2 catalysts (Pt–SZ) exhibit high activity for paraffin C_5–C_6 isomerization that is close to that of Pt–Cl/Al_2O_3, although the catalyst can deactivate permanently when exposed to high temperatures [8]. Later it was shown that the use of Pd in ZrO_2 modified by sulfate-ion is preferable at low temperatures, up to 150–180 °C [9], which provides higher activity in comparison with Pt–SZ in the low-temperature process area. Also, promoting of SZ by Pd improves the catalytic stability in n-C_4 isomerization compared to SZ [10], which is probably due to preventing the accumulation of carbonaceous deposits on the catalyst [11].

Catalysts for C_5–C_6 isomerization on the basis of ZrO_2 modified by various anions form the new generation of isomerization catalysts that are free from some disadvantages of Pt–Cl/Al_2O_3. Such catalysts are commonly used now in the industry for production of isomerate of light paraffin fractions C_5–C_6 with research octane number (RON) 87 [3]. Successful application of Pt–SZ in light paraffin isomerization suggests that in the long term, the new catalysts may substitute conventional chlorinated alumina catalysts.

Despite the numerous patents and scientific contributions, the only proven technology of n-butane isomerization known to date is *Butamer* process [2] commercialized in 1941 by UOP and used for isomerization of n-C_4 to i-C_4 over Pt-modified chlorinated alumina catalyst (Pt–Cl/Al_2O_3). The fixed-bed catalytic process is performed in vapor phase at 120–200 °C. To maintain the constant activity of the catalyst, toxic organic chlorides are continuously supplied to the raw stream. The process is notable for high values of n-butane conversion and selectivity. However, serious problems may arise with the catalyst, which is highly sensitive to even smallest admixtures of contaminants in the raw material: allowable content of water $\leqslant$1 ppm, sulfur $\leqslant$1 ppm, and fluorine ~0 ppm. Substantial costs are required to protect the catalyst and to ensure continuous injection of organic chloride and its downstream decontamination. The extremely stringent restriction on the impurities in the feedstock and the ecological concerns, such as the need for recycling of the chlorine products, significantly complicate the wide-spread use of *Butamer*.

The use of sulfated metal oxide catalysts in commercial n-butane isomerization units has obvious benefits of a substantially simpler technology and lower operating costs of i-C_4 production. The process requires no chlorine supply and has lower standards on the trace contaminants in the raw material.

However, unlike in the isomerization of pentane and hexane, the reaction rate of n-butane isomerization over Pt–SZ was 3–7 times lower than that of n-pentane [10,12]. This may be due to the low activity of Pt–SZ and to suboptimal process conditions. The loss of Pt–SZ catalytic activity may be caused by extremely high activation temperature. It was observed by TPR method in [9] that hydrogen reduction of Pt supported on SZ proceeds within 230–270 °C. Partial reduction of surface sulfate to sulfite and sulfide and subsequent removal of sulfur from the surface proceed in the same temperature region. This may significantly decrease the acid function of Pt–SZ. In Pd–SZ catalysts, reduction of palladium on SZ surface occurs at low temperatures 70–90 °C, which prevents destruction of surface sulfates and decrease of the acidity of the catalyst. For this reason, Pd–SZ catalyst has a promising perspective in low-temperature n-butane isomerization.

In most works on n-butane isomerization on Pt–SZ catalysts, the initial H_2/n-C_4 ratio was greater than 1. However, in [10] it was reported that decreasing the molar ratio H_2/n-C_4 below 1 leads to a significant increase in the reaction rate. Thus, it can be assumed that n-butane isomerization mechanism differs from that of C_5–C_6 isomerization [4].

Paraffin isomerization catalysts based on Pd–SZ were studied much less than SZ or Pt–SZ. We argue that Pd as hydro-dehydrogenating metal is preferable to Pt for the following reasons: (i) higher activity at low temperatures 130–170 °C [9], (ii) higher resistance to mercaptans, sulfides and other sulfur impurities in isomerization feed [11], and (iii) substantially lower cost.

The purpose of this article is to analyze the specific properties of sulfated zirconia promoted by Pd (referred to as Pd–SZ catalyst), to demonstrate its capabilities in n-C_4 skeletal isomerization in comparison with conventional catalysts, and to assess the prospects of its commercial application.

2. Experimental

2.1. Catalyst preparation and testing procedures

Samples of anion-modified zirconium oxide were prepared in accordance with the procedure set forth in [13]. Solution of ammonia–oxocarbonate Zr complex prepared as recommended in [14] was dropped into distilled water with vigorous stirring at 97–98 °C. The ZrO_2 concentration in the solution was 0.082 g/g. The concentration ratio between complex solution and aqueous medium [ZrO_2]/[H_2O] was maintained at 0.1. After completing the supply of ammonia–oxocarbonate zirconium complex, the suspension was stirred at the temperature of thermal decomposition until constant pH = 7–8 was reached. After that, the suspension was cooled to 25–30 °C, and the solution of sulfuric acid or other anion-modified agent (ions of tungstate, molybdate, aluminate) was added. Suspension of anion-modified zirconium oxide was kept 1 h under stirring then filtered. The obtained gel was molded by extrusion and the extruded granules were dried at 150 °C. Then palladium was supported on granules from solution of H_2PdCl_4 by incipient wetness impregnation method. Finally, the catalyst samples were dry-air calcined at 600–900 °C. By analogy with SZ, the other anion-modified zirconia samples shall be referred to as MoZ, WZ, and AlZ.

Content of sulfate-ion in the SZ samples was determined with elemental analyzer Elementar Vario EL III by thermal decomposition of samples at 1100 °C. General chemical analysis of the samples was made by ARL-Advant'x X-ray fluorescence analyzer using Rh anode.

The specific surface area of the catalysts was determined by measuring the nitrogen adsorption–desorption isotherms on sorptometer Sorbi N4.1. The total surface area was calculated according to the BET equation.

The structural properties of SZ and Pd–SZ were investigated by X-ray diffraction (XRD) (HZG-4C, Freiberger Präzisionmechanik) using Cu Kα (35 kV, 30 mA) radiation with 2θ ranging from 23° to 75° at a scanning speed of 0.1°/5 s. Crystal size and morphology were investigated by scanning (SEM) and transmission (TEM) electron microscopy using JEM-2010 (JEOL) electron microscope.

In order to determine the nature of the acid sites on SZ and Pd–SZ surface, the studies of infrared spectra of adsorbed CO molecules [15] were performed on IR-spectrometer BOMEM MB 102 at a resolution of 4 cm^{-1} and with accumulation of 256 scans.