



The role of H₂ in n-butane isomerization over Al-promoted sulfated zirconia catalyst

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ABSTRACT

C, H, N-elemental analyzer, and NH₃-TPD, FTIR, XPS and reactor system are used to investigate the function of hydrogen in n-butane isomerization over the Al-promoted (3 mol% as Al₂O₃) sulfated zirconia catalyst (Al/SZ). Findings show relatively stable Al/SZ catalyst activity at 250 °C with H₂ introduction; however it decreases very quickly when N₂ replaces H₂. Deactivation is attributed to coke formation. The main components of coke are graphite and polymeric hydrocarbons. Activity can be recovered about 70% when H₂ is admitted again. Conversely, catalytic activity is lower but more stable in the presence of H₂ than in that of N₂ at 150 °C. Findings also show that activity cannot be restored if n-butane conversion is down to zero (i.e., the catalyst is completely deactivated). This study infers that H₂ reacts with coke at 250 °C, but inhibits isobutane formation and cannot react with coke at 150 °C. Catalytic activity restoration is via the reaction between coke and adsorbed hydrogen on the Brønsted acid sites. Although many researchers report that decayed sulfated zirconia regenerates by burning coke off with oxygen, this work finds that the fouled catalyst regenerates, though not completely, by hydrogen, provided it is not fully deactivated.

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1. Introduction

Alkylate products, produced from alkylation of C₃–C₅ alkenes with isobutane, improve octane number and gasoline quality, and replace aromatics and methyl tertiary butyl ether (MTBE). Their quality improvement is currently becoming an important subject in petroleum refineries. Isobutane can be produced by n-butane isomerization. Both liquid and solid acid catalysts can be used, but the commercial process changes to solid acid catalysts due to environmental considerations. Sulfated zirconia (SZ) and other sulfated metal oxides exhibit a strong acidity, allowing them to catalyze butane isomerization at low temperature [1].

Rapid deactivation seriously disadvantages sulfated zirconia, so many researchers attempt to elucidate the cause of deactivation and prevent it. Several factors may cause SZ catalyst deactivation: (1) coke deposit formation on the catalyst surface [2,3], (2) reducing Zr₄⁺ to Zr₃⁺ by hydrocarbon reaction [4], (3) sulfate group attenuation owing to reduction by hydrogen [5], (4) change of sulfur charge [6], (5) change of zirconia phase from tetragonal to monoclinic [7], and (6) poisoning by water [8]. Coke deposition is the main cause of catalyst deactivation, so coke deposition control and/or the reduction of coke deposition rate prolongs catalytic life.

Two kinds of reaction pathways are proposed for isomerization over solid acid, one is monomolecular, and the other is bimolecular [9,10]. The bimolecular mechanism involves C₆⁺ carbenium ion formation, followed by cracking and subsequent hydride transfer/desorption steps [9,11]. Hydrocarbons of larger molecules adsorbed on the catalyst surface do not desorb easily at the reaction temperature and accumulate as coke or coke precursors [11]. In other words, catalyst decay prevails more with a bimolecular reaction mechanism than with a monomolecular mechanism [12].

SZ promoted with small amounts of Al (Al/SZ) significantly enhances catalyst activity and stability for n-butane isomerization at 250 °C in the presence of H₂ [13,14]. The optimum Al₂O₃ content is 3 mol%. Moreover, the catalyst activity of Al/SZ is higher than Pt/SZ for n-butane isomerization in the presence of H₂ [15]. Canton et al. [16] further studies the influence of a small addition of alumina onto zirconia structure and microstructure. Recently, Sun et al. [17] reports that Al-promoted mesoporous sulfated zirconia increases steady state conversion compared with unsupported SZ and catalytic activity is highest with 3 mol% Al₂O₃ contents. Catalytic activity and stability improvement attributing to Al₂O₃ helps stabilize the sulfate complex on oxides and enhances the number of acid sites with intermediate strength [18]. The promoting mechanism of the main group element Al is different from that of transition metals. Mou and co-workers [19,20] reports that Al-promoted SZ retards phase transformation from tetragonal to monoclinic and balances distribution of acid site strength with an

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enhanced amount of weak Brønsted acid sites, so catalytic activity and stability improve. However, the hydrogen role in Al-promoted SZ has not been investigated.

This study prepares aluminum-promoted sulfated zirconia and designs testing methods for investigating the role of hydrogen in the n-butane isomerization reaction. The current work examines catalyst characteristics by several characterization techniques for elucidating the cause of catalyst deactivation.

2. Experimental

2.1. Catalyst preparation

The methods for preparing SZ are already described elsewhere [19,21]. Hexadecyl trimethyl ammonium bromide (2.5 g, Aldrich) is dissolved in a solution of 115 g water and 22.4 g HCl (37 wt%), followed by 5.99 g of 70 wt% Zr(O-nPr)₄ in added 1-propanol. After stirring for 30 min, (NH₄)₂SO₄ in 23.0 g water is introduced to the solution (the molar ratio of SO₄/Zr is about 0.7). The solution is stirred for 1 h at room temperature, then transferred into a polypropylene bottle and heated at 100 °C for 3 days. The precipitate is filtered and washed with de-ionized water, ethanol, and de-ionized water consecutively, finally drying at 100 °C for 12 h. Aqueous alumina sulfate is introduced into the uncalcined sulfated-ZrO₂ via the incipient wetness impregnation technique to obtain the Al-promoted SZ with nominal 3 mol% Al₂O₃, calculated on the weight basis of ZrO₂. The slurry is stirred for 1 h and oven-dried at 100 °C for 12 h. Solid particles are then calcined for 5 h at 650 °C in static air, thus obtaining the Al/SZ catalyst.

2.2. Characterization

The surface area and pore size distribution of catalysts are determined by nitrogen desorption at –196 °C with a Micromeritics TriStar 3000 instrument. For determining catalyst acidity, NH₃-TPD is performed in a flow apparatus. A sample 0.1 g is activated in helium at 400 °C for 1 h. The system is then cooled under helium to 100 °C. At 100 °C, NH₃ is adsorbed till saturation. Then the sample is heated to 820 °C at a heating rate of 7 °C/min to desorb NH₃. Aluminum and sulfur contents are determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) using a PerkinElmer ICP 4300 instrument.

The types of coke deposited on the used catalyst are analyzed using an X-ray photoelectron spectroscope (Thermo VG Scientific, ESCALAB 250) fitted with a monochromatic Al K α radiation (1486.8 eV) X-ray source, under a residual pressure of $\sim 1 \times 10^{-9}$ Torr. Binding energy is calibrated to Zr in ZrO₂, BE = 182.7 eV because of electrostatic charging.

This work adopts the method described by Föttinger et al. [22] for characterizing acidic sites in both fresh and used catalysts. The infrared spectra are recorded with a BIO-RAD Digilab FTS-40V FT-IR spectrometer. Coke content of the used catalyst is determined by the Elementar Vario EL C, H, N-elemental analyzer.

2.3. Catalytic reaction

The isomerization of n-butane to isobutane is carried out in a fixed-bed reactor and operated at atmospheric pressure. 1.0 g of the catalyst is loaded into the reactor and then pretreated in dry air for 3 h at 450 °C. Thereafter, the catalyst is cooled to 250 °C (or 150 °C). Subsequently, the reaction is performed with three different modes (Table 1).

In mode I, the reaction starts with 250 °C using hydrogen as a carrier gas (step I). The carrier gas is shifted to nitrogen (step II) when conversion is nearly unchanged. Then, the carrier gas changes back to hydrogen (step III). Mode II is similar to mode I except that step

Table 1
Operation mode.

Mode	Operating temperature (°C)	Carrier gas			
		Step I	Step II	Step III	Step IV
I	250	H ₂	N ₂	H ₂	–
II	250	H ₂	N ₂ ^a	H ₂	–
III	150	H ₂	N ₂	H ₂	N ₂

^a In this step, reaction proceeded until catalyst was fully decayed.

II proceeds until complete catalyst decay. The operating procedure in mode III is the same as that in mode I except the reaction is carried out at 150 °C and an additional step in which the carrier gas is shifted to nitrogen (step IV).

The weight hourly space velocity (WHSV) of n-butane is set at 0.62 h⁻¹ and n-butane/H₂ ratio is 1/10 (v/v). Effluent gas analysis uses a gas chromatograph (Varian 3800) equipped with a 50-m plot AL/M column and FID.

3. Results and discussion

3.1. Catalyst characterization

The surface area, composition, and acidity characteristics of the fresh catalyst are listed in Table 2. Note that the higher measuring temperature is the larger ratio of Lewis acid to Brønsted acid (L/B) because the number of Brønsted acid sites reduces with raising measuring temperature [23]. In order to obtain the actual ratio of L/B in isomerization reaction, the measuring temperature for the used catalysts is the same as the reaction temperature.

The XRD results show that the Al/SZ catalysts are mainly tetragonal phase. No change is detected by XRD in the crystalline phase for used catalysts.

3.2. n-Butane isomerization at 250 °C

In elucidating the fact that the Al/SZ catalyst for n-butane isomerization is more active and stable in the presence of hydrogen than other gases, this reaction uses operating mode I and mode II at 250 °C and analyzes the coke content of used catalysts at the end of each step.

3.2.1. Catalytic activity and selectivity

Fig. 1 shows the mode I result. Conversion at step I is about 50% at the very beginning of the run, declining gradually and slightly to a relatively stable level of about 44% after 5 h. However, when the carrier gas changes from hydrogen to nitrogen (step II), conversion decreases very quickly because of catalyst decay. These conversion variations are similar to those reported previously [24]. When hydrogen is admitted again (step III), conversion suddenly drops from 4.7% to 1.7% due to competitive adsorption of hydrogen with n-C₄ onto active sites, increasing gradually to 29%, and stabilizing thereafter. The conversion does not completely recover to the step I level, but is much higher than that at the end of step II.

Table 2
Characteristics of the fresh catalyst.

Item	Value
BET S.A. (m ² /g)	101
Sulfur (wt%)	1.3
Al (wt%)	1.3
L/B ^a at 150 °C	1.75
L/B ^a at 200 °C	2.01
L/B ^a at 250 °C	2.14

^a Ratio of Lewis acid sites to Brønsted acid sites.

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