



Research paper

Comparative study of *n*-butane isomerization over $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3\text{-ZrO}_2$ and HZSM-5 zeolites at low reaction temperatures

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ABSTRACT

The effects of acidity and pore structures of alumina-promoted sulfated zirconia (SZA) and two HZSM-5 zeolites with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios on reaction properties of *n*-butane conversion were comparatively investigated. The results demonstrated that monomolecular isomerization reaction predominated at 433–533 K for SZA catalysts and bimolecular pathway predominated at 573–673 K for HZSM-5 zeolites. For both samples, the amount of coke deposits was considerably low. The differences in catalytic behavior were caused by different acid properties and pore structures. The strength and stability of catalytic Brønsted acid sites determine the conversion rate of *n*-butane and the deactivation rate of catalysts, respectively. While the contributions of monomolecular and bimolecular pathway, as well as the products distributions are depended on the pore structures and influenced by the density of catalytic Brønsted acid sites.

1. Introduction

The skeletal isomerization of *n*-butane to isobutane is of significant with respect to academic study in understanding of reaction mechanism in acid catalysis. Two most intensively studied catalysts are anion-promoted zirconia [1–5] and acidic zeolites [6,7] in recent years. Despite the large amount of studies have attempted to explain the “structure-reactivity” relationship of each catalyst in *n*-alkane isomerization, no a systematically investigation has been made on general consensus between catalyst properties and catalytic behaviors over different catalysts.

Possible reaction routes for *n*-butane on acid catalysts include cracking, dehydrogenation, and isomerization, depending on the catalyst properties and reaction conditions. All of these reactions are initiated by the protonation of C–C or C–H bonds of alkane molecules to form a five-coordinated carbonium ion by Brønsted acid sites [8]. The catalytic properties of solid acid catalysts usually depend on the strength and density of Brønsted acid sites [9–12]. It is believed that the acid strength strongly affects activation barriers for reactions involving cationic transition state, such as alkane cracking, isomerization, and alkylation, while weakly influences the reactions that require activated complexes with low charge [13,14]. Generally, both the sulfated zirconia and zeolite catalysts are considered having superacidic sites, which are responsible for the formation of cationic transition state in alkane conversion. Thus, investigating the relationship between conversion rate of *n*-butane and acid strength of catalysts can help one to

understand the ability of proton transfer from Brønsted acid sites to the reactant.

Another subject being worth studying is the reaction mechanism, i.e. the pathways for products formation from the cationic transition state. The conversion of *n*-butane on acid catalysts usually proceed by two mechanisms: monomolecular (intramolecular) and bimolecular (intermolecular) pathway. There are numerous studies focused on the effects of reaction conditions on the reaction behavior of alkane conversion, but only a few of investigations aimed at the influence of catalysts properties. In general, low partial pressure of reactant and low conversion level favor the monomolecular reaction. The monomolecular reaction of light alkane can be classified into three types: cracking to yield a smaller alkane and an alkene, dehydrogenation to a corresponding alkene and a hydrogen molecule [15,16], and isomerization to a corresponding isomer molecule [7,17,18]. In addition, the higher temperature can also promote monomolecular reaction because of the high activation barrier to form cationic transition state. By contrast, the bimolecular reaction, which is energetically more favored, requires higher concentration of unsaturated intermediates and produces disproportionation products and corresponding isomers. Moreover, the diffusion limitation of three-dimensional microporous zeolites must be accounted into to establish a sound structure-diffusion-activity relationship [19,20].

The goal of this investigation was to comparatively study the “structure-reactivity” relationship for *n*-butane isomerization over alumina-promoted sulfated zirconia (SZA) and HZSM-5 zeolites. The

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contributions of monomolecular and bimolecular pathways are determined. The origin and properties of acidity over SZA and HZSM-5 zeolites are analyzed in detail. The determining factors that control relative rates of mono/bimolecular pathway are identified. This knowledge would allow one to predict the conversion rate and products distribution of *n*-alkane conversion over solid acid catalysts with changing reaction conditions and catalyst properties.

2. Experimental

2.1. Catalyst preparation

Al-promoted sulfated zirconia, designated as SZA was obtained by the same method reported in our previous study [4]. First, the pseudo-boehmite powder (AR, 67 wt.%) was mixed with distilled water in a vessel. Then, HCl solution (36–38 wt.%) was added dropwise under vigorous stirring at 343 K and an aluminum hydroxide gel was formed. The weight ratio of pseudo-boehmite, water, and HCl solution was 2: 9: 1. Subsequently, an appropriate amount of highly hydrated nanosized zirconium hydroxide (30 nm, 48.2 wt.% of ZrO₂), purchased from Xuancheng Jingrui New Material Cl. Ltd., was added and the Al-Zr hydroxide gel was obtained. After 2 h of stirring, the sulfuric acid (AR, 98 wt.%) was added dropwise under vigorous stirring. The weight ratio of ZrO₂, Al₂O₃, and sulfuric acid was 78:4:18. Finally, the sulfated mixture was stirred for another 2 h, dried at 383 K for 12 h, and calcined at 923 K for 2 h in a furnace under a static air atmosphere.

HZSM-5 zeolite with SiO₂/Al₂O₃ = 38 were synthesized by hydrothermal method using sodium silicate and aluminum sulfate as silicon and aluminum source and *n*-butylamine as organic template. After crystallization at 453 K for 24 h and washing by water, Na-ZSM-5 was obtained. Removal of template was carried out at 823 K for 4 h in a muffle furnace. The final HZSM-5, designed as HZSM-5-38 was obtained by ion exchange of NH₄NO₃ solution and another calcination at 823 K for 4 h. HZSM-5 with SiO₂/Al₂O₃ = 200 was purchased from the Catalyst Plant of Nankai university and designed as HZSM-5-200.

2.2. Catalytic activity tests

n-Butane isomerization reactions were conducted in a tubular packed-bed reactor (12 mm inner diameter) under atmospheric pressure. The catalyst powder (80–180 μm) was placed in the middle of reactor and activated at 623 K for SZA catalysts and 823 K for HZSM-5 zeolites in a flow of air (30 mL/min) for 30 min. Subsequently, the catalysts were swept with N₂ for 10 min and cooled down to desired reaction temperature. Afterwards, *n*-butane was fed into the reactor without carrier gas at a WHSV of 1.98 h⁻¹. The compositions of feed and products were analyzed by a Bruker 450 gas chromatograph as described in our previous study [17]. The *n*-butane used in this study was purchased from Keyuan Gas Co., LTD and had a purity higher than 99.995%. Before the reactor, a trap containing 30 g H-Y zeolite was used as adsorbent to remove any olefin impurities present in the *n*-butane feed. The concentration of butene remaining in the butane feed after the trap was below the detection limit of our GC (0.001%) [17]. The internal diffusion limitation of HZSM-5 zeolites on the *n*-butane conversion was ruled out by Weisz-Prater criterion (see section S3 in the Supporting Information).

2.3. Catalyst characterization

The X-ray diffraction (XRD) measurements were performed at an X'pert PRO MPD diffractometer (PANalytical Company, Netherlands), with Cu K_α radiation at 40 kV and 40 mA, running from 5 to 75° for SZA catalysts and to 65° for HZSM-5 zeolites at a speed of 10°/min. The nitrogen adsorption-desorption measurements were carried out on two Quadrasorb SI instruments: a mesopore analyzer for SZA sample and a micropore analyzer for HZSM-5 zeolites at 77 K. Prior to measurements,

the SZA sample was evacuated at 623 K for 4 h and HZSM-5 zeolites at 573 K for 6 h for the complete removal of adsorbed moisture. The total surface was calculated by Brunauer-Emmet-Teller isothermal equation and the total pore volume was determined from the nitrogen adsorbed volume at P/P₀ = 0.990. The micropore surface area and volume of HZSM-5 zeolites were calculated with the *t*-plot method. The external surface area and mesopore volume were obtained by the calculated total values minus the corresponding micropore values. The pore size distributions of SZA and HZSM-5 samples were calculated by BJH method and quenched solid density function theory model, respectively, using the adsorption branch of N₂ adsorption-desorption isotherms. The carbon contents on the surface of used catalysts were determined by a high-frequency infrared carbon sulfur analyzer (HX-HW8B).

The pyridine adsorption FTIR experiments were conducted the same protocols reported in the literature [18]. A Bruker FTIR spectrometer (SENSOR 27) at a spectroscopic resolution of 2 cm⁻¹ and a MCT liquid nitrogen cooled detector were employed. The pretreatments and measurements of samples were achieved in a research-grade diffuse reflectance accessory (the PIKE Technologies DiffusIR) equipped with a unique monolithic ellipsoidal reflector permanently fixed in place – eliminating the need for repositioning the focus optics for sample placement. The sample cup was also purchased from PIKE Technologies with a 10 mm diameter and 2.3 mm deep. All spectra were recorded with the absorbance function and the amounts of pyridine adsorbed on the Brønsted and Lewis acid sites were determined by the integrated areas of absorbance bands in the infrared spectra according to the method proposed by Emeis [21].

The acidity of samples was measured by NH₃-TPD equipped with a thermal conductivity detector (TCD). About 0.1 g of sample (20–40 mesh) was pretreated at 823 K for 30 min under flowing He atmosphere. Then, the sample was cooled down to 323 K and saturated with ammonia. After flushing the physical adsorbed ammonia at 323 K for 1 h, the sample was heated to 1173 K at a rate of 10 K/min in He flow. For HZSM-5 zeolites, the preheat temperature (823 K) is higher than the maximum temperature of ammonia desorption. While for SZA catalyst, there were two desorption peaks higher than the preheat temperature (823 K). This preheat temperature was chosen to avoid sulfur loss at a temperature higher than 823 K, at which temperature, about 95% of water adsorbed on the surface was desorbed [22].

3. Results

3.1. Reaction properties for *n*-butane isomerization

Fig. 1 shows the catalytic behaviors of three different catalysts versus reaction temperature for *n*-butane conversion. The following differences can be found for different catalysts: (1) SZA catalyst favors much lower temperature (433–533 K) than HZSM-5 zeolites (> 573 K); (2) different variations in the rate of *n*-butane conversion with increasing the reaction temperatures. The initial rate of *n*-butane conversion over SZA increased with elevating reaction temperature from 433 to 473 K, while decreased when the temperature further rose. While for HZSM-5, the catalytic activity increased monotonically with the elevation of temperature. The activity over HZSM-5-38 was always strikingly higher than that over HZSM-5-200 sample at 573–773 K; (3) incommensurate rates for deactivation and coke deposition. As shown in Fig. 1 and Fig. S1 in the Supporting Information, the activity of SZA catalysts significantly declined in the initial 5 min of reaction, then decreased much more slowly. After 1 h of reaction, at least 80% of initial activity was lost for SZA under our reaction conditions (Fig. 1a), while only a very small amount of coke deposits was detected (Table 1). By contrast, HZSM-5 zeolites exhibited much slower deactivation rates than SZA catalyst in spite of higher amounts of coke deposits over HZSM-5-38 (Table 1). The decreases in activity for HZSM-5 were less than 10% after 3 h of reaction at all conditions used in this study. Thus,

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