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Investigation of factors influencing catalytic activity for *n*-butane isomerization in the presence of hydrogen on Al-promoted sulfated zirconia

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Abstract

Two series of Al-promoted sulfated zirconia with 3 mol% Al_2O_3 content were prepared. In one case, zirconium–aluminum hydroxide has been aged at room temperature; in the other case, zirconium–aluminum hydroxide has been synthesized at 373 K under hydrothermal condition. For the two series of samples, the influence of the synthesis parameters such as ageing time, the amount of ammonia added, and zirconium concentration on catalytic activity for *n*-butane isomerization in the presence of hydrogen were investigated. Moreover, Al-promoted sulfated zirconia with a high surface area (174 m^2/g) can be obtained by properly adjusting synthesis parameters under hydrothermal condition at 373 K. The catalytic data showed that this material had similar catalytic activity to a conventional Al-promoted sulfated zirconia with a low surface area (98 m^2/g). The characterization of the samples revealed that the catalytic activity was directly correlated with sulfur content rather than surface area, sulfate density and the total number of Brønsted acid sites. The synthesis of the precursors of hydroxides before sulfation is a crucial step for catalytic activity of the samples in *n*-butane isomerization.

Keywords: H/D exchange; Sulfated zirconia; *n*-Butane; Isobutane; Hydrogen; Isomerization; Hydrothermal synthesis

1. Introduction

Transformation of hydrocarbons is of prime economic importance in the petrochemical industry [1]. Generally, the transformation occurs under strong acidic conditions. For example, liquid superacids such as SbF_5/HF or SbF_5/HSO_3F can activate alkanes at temperatures below 273 K [2]. However, the drawback of liquid acids is that they are corrosive and difficult to recover and reuse. As a replacement of liquid acids, solid acids exhibit a promising alternative because of their environmental friendly characteristics (non-corrosiveness, ease of handling, and easy to recover and reuse).

Among solid acids, sulfated zirconia has attracted much more attention because it can transform *n*-butane into isobutane at relatively low temperature such as room temperature [3]. For this reason a large number of research works were focused on this catalyst and many reviews are available [4–11]. Nevertheless, it was usually observed that sulfated zirconia showed rapid deactivation during catalytic reactions. When some promoters such as Fe, Mn, Ni and Cr were introduced into sulfated zirconia [12–17], it was found that these promoters significantly increased catalytic activity on *n*-butane isomerization at low temperature. However, rapid deactivation was still observed [18–20] and the marked promoting effect disappeared if the reaction was performed at high temperature (523 K) in the presence of hydrogen [21,22].

Recently, Gao et al. [21] firstly reported that sulfated zirconia promoted by a little amount of Al exhibited excellent catalytic activity and also improved resistance to deactivation at high temperature (523 K) for *n*-butane isomerization in the presence of hydrogen. This remarkable promoting effect was most likely attributed to a different distribution in the acid

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sites strength [21–23]. Since then, many contributions on Al-promoted sulfated zirconia (SZA) have been published [24–29], which confirmed that the introduction of a small amount of Al could improve catalytic activity and stability of sulfated zirconia for *n*-butane isomerization in the presence of hydrogen. It has been noted that SZA with 3 mol % Al_2O_3 content prepared under calcination at 923 K for 3 h exhibited excellent catalytic activity and reduced deactivation. However, the concrete preparative procedures reported for SZA were different, depending on the authors. Up to now, no study is available on the influence of synthesis parameters for SZA on catalytic activity of *n*-butane isomerization in the presence of hydrogen.

On the other hand, it is well known that catalysis is a surface phenomenon. Generally, a larger surface area is required to reach a higher catalytic activity. Since conventional sulfated zirconia has a relatively small surface area, many methods have been attempted to improve its surface area [30–45]. For example, sulfated zirconia was supported on silica materials and alumina materials with high surface area [30–36]. Mesostructured sulfated zirconia were synthesized using various templates [37–40], or by alcoholthermal route [41]. Nanosized [42–44] and macroporous [45] sulfated zirconia were also prepared. More recently, mesostructured Al-promoted sulfated zirconia with high surface area has also been synthesized using various templates [46,47].

In the present work, we underline the importance of synthesis parameters for Al-promoted sulfated zirconia on the catalytic activity in *n*-butane isomerization in the presence of hydrogen. Interestingly, Al-promoted sulfated zirconia with a high surface area (174 m^2/g) can be obtained by properly adjusting synthesis parameters under hydrothermal condition at 373 K. The relationship between surface area, Brønsted acid sites, sulfur species and catalytic activity is discussed.

2. Experimental

2.1. Catalyst preparation

0.02 mol $ZrOCl_2{\cdot}8H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$ (3 mol % Al_2O_3) were dissolved in water. A calculated amount of 26% ammonia solution dependent on the molar ratio of OH^-:Zr was added dropwise into the above solution at a rate of 0.5 ml/min. The obtained solution with precipitate was closed in a vessel and stirred for 1 h at room temperature. For conventional Al-promoted sulfated zirconia (SZA), the solution with precipitate was either directly filtered or filtered after ageing at room temperature for 24 h; for hydrothermal Al-promoted sulfated zirconia (HSZA), the solution with precipitate was kept at 373 K for 24 h or 48 h or 96 h. The obtained precipitate was washed with distilled water until the disappearance of chloride ions ($AgNO_3$ test), dried at 383 K for 24 h and powdered to below 50 mesh. Sulfation procedure was carried out by impregnation method with 0.5 M H_2SO_4 solution (15 ml/g) under continuous stirring at room temperature for 1 h. The sulfated $Al(OH)_3$–$Zr(OH)_4$ was filtered without washing, dried again at 383 K and calcined at 923 K for 3 h. For SZA, the samples are designated as SZA-*X*-*Y*: *X* stands for molar ratio of OH^-:Zr, *Y* stands for ageing time (h); for HSZA, the samples are designated as HSZA-*X*-*Y*: *X* stands for molar ratio of OH^-:Zr, *Y* stands for synthesis time under hydrothermal condition (h). It needs to be referred that zirconium concentration was usually 0.4 M unless otherwise stated.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Siemens D5000 diffractometer (45 kV, 40 mA) using nickel-filtered Cu Kα radiation with wavelength of $\lambda = 1.5406$ Å. The crystallite size of tetragonal phase was determined from the characteristic peak ($2\theta = 30.4^\circ$ for the (1 1 1) reflection) using the Debye–Scherrer equation: $D = K\lambda/\beta \cos\theta$, where $K = 0.9$, D represents crystallite size, λ represents the wavelength of Cu Kα radiation, and β represents the corrected half width of the diffraction peak. Nitrogen adsorption isotherms were obtained at 77 K on a Micromeritics Tristar Gas Sorption and Porosimetry system. Samples were normally prepared for measurement after degassing at 423 K under vacuum until a final pressure of 1×10^{-3} Torr was reached. Thermogravimetric analysis (TGA) was carried out on a SETARAM with a heating rate of 15 K/min from room temperature to 1473 K. The sample was mounted horizontally and purged with synthetic air (50 mL/min). The sulfate content was calculated based on the weight loss from 923 to 1473 K. The weight loss corresponded to the content of SO_3. The sulfate content, i.e. SO_4^{2-} content, would be 1.2 times the weight loss. The detailed interpretation has been shown in the reported reference [33].

2.3. Titration of Brønsted acid sites by H/D exchange

Deuteration of the catalyst was performed in an all-glass grease-free flow system as described earlier [26]. The catalyst was first activated in dry air at 723 K for 2 h to eliminate organic contamination and desorb moisture. Then it was pre-treated in dry N_2 at the same temperature for an additional 1 h. The temperature was lowered to 473 K for deuteration. The catalyst deuteration was performed by sweeping D_2O with N_2 (40 ml min^{-1}, ca. 3 mol % D_2O in N_2) for 1 h. Excess D_2O was then removed by flushing the catalyst at 473 K with dry N_2 for 0.5 h.

The above deuterated catalyst (0.5 g) was contacted at 473 K for 1 h with N_2 (40 ml min^{-1}, ca. 3 mol % H_2O in N_2) bubbled through a U tube containing distilled H_2O at room temperature. Excess water was then removed by flushing the catalyst at 473 K for 0.5 h with dry N_2. During the H/D exchange and flushing, the partially exchanged water (H_2O/HDO/D_2O mixture, named H*x*OD*y*) was collected in a cold trap (the mixture of ethanol and liquid nitrogen). An excess