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Isomerization of *n*-butane over sulfated zirconia catalyst under supercritical conditions

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Abstract

Heterogeneous catalytic processes in supercritical fluids offer environmentally benign alternatives to current catalyst technologies. In the case of isomerization of light alkanes over solid acid catalysts at atmospheric pressure, the catalysts deactivate rapidly due to coke formation on the catalyst surface. To solve this problem, we studied the isomerization of *n*-butane over sulfated zirconia in a *n*-butane supercritical condition of reactant and products. Under the supercritical condition, no significant deactivation was observed, and the steady state activity was maintained. Furthermore, the active sites of sulfated zirconia were characterized by FT-IR spectroscopy: it was found that Lewis acid sites on sulfated zirconia play an important role in the isomerization of *n*-butane.

Keywords: Isomerization of *n*-butane; Isomerization of light alkane; Supercritical fluid; Sulfated zirconia

1. Introduction

With the recent enactment and phasing-in of regulations regarding the elimination of certain gasoline components, such as benzene, aromatics, and olefins [1,2], there has been a great demand for both clean and high-octane gasoline components. Thus, *i*-butane is becoming an important compound as a feedstock for the alkylate gasoline, MTBE and ETBE. There are several reports that sulfated oxide catalysts can isomerize *n*-butane to *iso*-butane even at room temperature. Sulfated zirconia, in particular, is known as a solid super acid and is a potential effective catalyst of the isomerization [3–16]. However, it is also known that strong acidity causes a rapid deactivation during isomerization of alkanes. Many published data have suggested various reasons for the deactivation [17–20], but the prevailing theory is the coke formation on the catalyst surface [18–26]. Therefore, reduction of the coke formation during the reaction is the most important issue for a satisfactory isomerization reaction.

Supercritical fluids have been widely studied as extraction media. Such a fluid behaves both as a liquid exhibiting high solubility and as a gas exhibiting sensitive density changes with the pressure and the temperature. Such properties lead to its unique characteristics of low viscosity and high diffusibility. These characteristics promote penetration into porous materials and material diffusion. Solubility of materials depends not only on the characters of molecules but also on the distance between each pair of molecules; therefore, the density also plays an important role in the material solubility. Supercritical fluids have high density; such density can be easily controlled by the pressure and the temperature, i.e. solubility can be controlled [27]. We have previously reported our findings regarding solid acid-catalyzed alkylation of *i*-butane with 1-butene under supercritical conditions; we found that coke formation on the solid acid catalysts was reduced and that the deactivation could be reduced under supercritical conditions [28].

We have applied a supercritical fluid to minimize the deactivation rate and to achieve stable activity on solid acid-catalyzed isomerization. We expect that the supercritical fluids would extract the coke precursors from the catalyst surface effectively, and that the initial catalytic activity would be maintained.

In this work, we have studied isomerization of *n*-butane to *iso*-butane over sulfated zirconia under supercritical con-

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ditions of reactants and products to investigate the influence of reaction conditions on the catalyst activity. We also characterized the acidic nature of sulfated zirconia by using FT-IR spectroscopy.

2. Experimental

2.1. Catalyst preparation

SO_4^{2-}/ZrO_2 (labeled as SZ) samples were prepared from zirconium hydroxide (Daiichi Kigenso Kagaku Kougyo, grade: RSD). Zirconium hydroxide was impregnated with $(NH_4)_2SO_4$ aqueous solution and stirred overnight at 333 K. The solid catalyst obtained was dried at 373 K for 12 h. The sulfur content ratio of samples was adjusted at 4.0 wt.%. Dried samples were calcined in situ prior to the reaction, as described in Section 2.3.

2.2. Catalyst characterization

In order to study the acidity of the catalyst, we measured IR. A vacuum-tight IR cell with KBr windows was designed to fit an infrared spectrometer (Shimadzu, FT-IR-8200PC) and was attached to a vacuum system (10^{-4} Pa). The cell was arranged such that sample wafer (0.01 g cm^{-2}) could be set down into slots between the KBr windows, and pulled upward by a magnet into the heated part. The samples were calcined in situ for 5 h at various temperatures, followed by with evacuation for 30 min at the same temperatures. We also obtained the IR spectra with pyridine adsorption. The samples were cooled down to 373 K and were exposed to 670 Pa (5 Torr) of pyridine for 0.5. After evacuation for 0.5 h, the temperature was raised and IR spectra were taken at the corresponding temperatures. In order to study the crystal structures of SZ, we obtained XRD patterns of calcined SZ on an X-ray diffractometer (Rigaku, RINT2100V/P) with Cu Kα (λ = 0.15418 nm). To determine the specific surface area of the catalysts, we performed nitrogen adsorption measurements at 77 K on an automatic gas adsorption apparatus (BEL JAPAN, BELSORP 28SA). As pretreatment, 0.3 g of sample was placed in a Pyrex tube and evacuated at 573 K over night. The specific surface area was obtained by the BET method. Catalysts after reactions were analyzed by thermogravimetry on a TG-DTA (Rigaku, Thermoplus TG8120) equipped with a thermocouple consisting of Pt–Pt 13% Rh under air. A heating rate was 10 K min^{-1}.

2.3. Isomerization of n-butane

Isomerization of *n*-butane was carried out in a fixed-bed continuous flow reactor. The detailed reactor flow has been described in our previous paper [28]. The critical point of *n*-butane is at 425 K and 3.8 MPa [29]. The conditions of the reactions were as follows: reaction temperature, 388–588 K; reaction pressure, 0.1–6.0 MPa; the weight of the catalyst, 1.0 g; the feed rate of liquid *n*-butane (Takachiyo Chemical Industrial, Pure 99.0%), 0.25 ml min^{-1}. Prior to the reaction, the catalysts were pelletized, crushed to 30–50 mesh, and calcined in situ at 673–973 K for 5 h under O_2 flow, then cooled down to the reaction temperature, and purged with He for 1 h. The product gas was analyzed by using an on-line TCD gas chromatograph (Shimadzu, GC-8A IT) equipped with a stainless column (GL Sciences, VZ-9, 6 m).

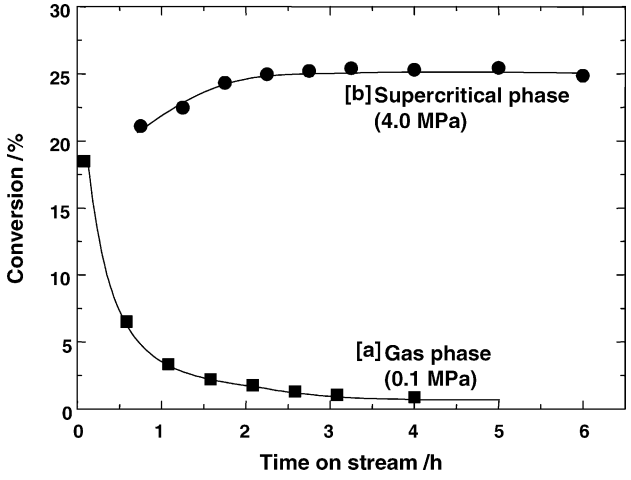

Fig. 1. Catalytic activity of isomerization of *n*-butane over SO_4^{2-}/ZrO_2 (SZ) as a function of time on stream. Reaction conditions: reaction temperature, 488 K; reaction pressure, (a) 0.1 MPa, (b) 4.0 MPa; catalyst, SZ calcined at 773 K; W/F, 6.0 g h mol^{-1}.

3. Results and discussion

We studied the isomerization of *n*-butane at various conditions to verify the effect of the supercritical conditions. The conversion profiles are also shown as a function of time on stream under the condition of the gas-phase (0.1 MPa) and the supercritical condition (4.0 MPa) in Fig. 1. Under the gas-phase reaction (Fig. 1(a)), although initial catalytic activity was relatively high, rapid deactivation occurred and no activity was observed after 3 h time on stream. In the case of Fig. 1(b) (4.0 MPa), coke may have formed in the earlier stage before the supercritical conditions were established. However, as the supercritical condition was established, the supercritical fluid started to wash out coke precursors, resulting the increase of the conversion from 20 up to 25% followed by the stable activity. The lower initial catalytic activity of the reaction under the supercritical condition is due to the time required for establishing supercritical condition, and thus forming the coke precursor on the catalyst surface. The coke precursor is partly diffused into the reaction fluid after supercritical conditions are established.

The influences of the reaction pressure on conversion, selectivity, and deactivation rate of the isomerization at 488 K are summarized in Fig. 2 (the reactions at the pressure above 3.8 MPa were supercritical phase). Selectivity was