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Feature Article

Consequence of heterogeneity of active sites for reactivity mechanism of *n*-butane isomerization over SO_4^{2-}/ZrO_2-Al_2O_3 catalyst

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ABSTRACT

The relationship between the heterogeneity of active sites and isomerization mechanism of *n*-butane over alumina-promoted sulfated zirconia (SZA) was elucidated by two series of catalysts with different surface properties. The incomplete removal of coke deposition leads to a decrease in overall activity without the reduction of the rate of isobutane formation. Subjecting the fresh SZA catalyst to the thermal treatment at 650 °C causes a striking decrease in activity, resulting from the decrease in the superacidity and oxidizability of the catalyst. While the thermal treatment at 600 °C only selectively suppresses the side reactions. It is found that the peaks in NH3-TPD profiles at 500–700 °C are caused by a redox reaction between strongly adsorbed ammonia and superacid sites by in situ NH3-TPD-MS measurements. Thus, this peak reflects the strength of superacidity and oxidizability. At the beginning of the reaction, the effective oxidative and protonative activation routes result in the higher concentration of intermediates, which facilitates the "dimerization-isomerization-cracking" reactions. The incomplete removal of coke and the appropriate decrease in the density of sulfate species on the surface selectively promoted the monomolecular pathway.

1. Introduction

Over the past 30 years, the sulfated zirconia (SZ) has been extensively investigated and holds considerable promise for being the next generation of catalyst for alkane isomerization due to its environmental friendliness compared with the chlorinated alumina based catalysts, which suffer from continuous chlorine loss during reaction. Although the SZ catalyst exhibits high catalytic activity of *n*-butane isomerization and selectivity to isobutane at low reaction temperature, the rapid deactivation limits its application. The prerequisite for solving this problem is to shed light on the correlation between the reactivity mechanism and the changes of the active sites in the course of the reaction. Despite many attempts have focused on this [1–9], no direct evidence or consistent understanding has been reached.

The prevalence of monomolecular or bimolecular reaction pathway of *n*-butane isomerization has been intensely discussed in the open literature [10–18]. The monomolecular pathway is highly selective to isobutane with a higher energetic requirement because of the difficulty in the formation of the classical cyclopropane ring structure. In contrast to the monomolecular pathway, the bimolecular pathway involves the formation of C_8 intermediates from two unsaturated C_4 entities, skeletal isomerization of the C_8 intermediates (methyl transfer and rearrangement), β-scission of the isomerized C_8 intermediates, and further saturation of cracked products [11,13]. The bimolecular pathway is energetically favorable but not selective to isobutane.

Although the heterogeneity of active sites on the sulfated zirconia has been proposed by several researchers, no general consensus on the intrinsic mechanism between the heterogeneity and isomerization pathway of *n*-butane has been reached. Kim et al. [19] suggested that the active sites on the sulfated zirconia were distributed within a range of average site activity. Specifically, the significant initial decrease in isomerization activity was mainly caused by the loss of the more active sites, while the less active sites were responsible for *n*-butane conversion at higher time on stream of reaction. Kuba and Knözinger [20] identified two different types of sulfate species using a time-resolved *in situ* Raman spectrometer and found that both of them were active for the high initial activity. They observed that one type of initially present sulfate species was eroded during the reaction with a quick deposition of coke in the first few minutes and ascribed this to the reduction of the sulfate species to H_2S despite lack of direct evidence. Later, Li et al. [21] confirmed that at least two types of sulfate species existed on the surface of sulfate zirconia. Approximately 40% of sulfate species could be removed by washing with water and these labile were related to the oxidizability of the catalyst. Our latest study showed that the sulfation treatment of amorphous zirconium hydroxide provided two kinds of active sites, superacid sites and reducible sulfate sites, which

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independently co-existed on the catalyst surface and played a synergistic effect in isomerization activity of *n*-butane [22]. Our results showed that about 25% of the sulfate species were contributed to the superacid sites, which was compatible with the values reported by Li and Gonzalez [23].

In summary, there is little known about the mechanistic details of the nature of the heterogeneity of the active sites on alumina sulfated zirconia (SZA) surface and its impacts on the reaction pathway of *n*-butane isomerization, which will be solved in this paper. For the first time, we found that both the appropriate thermal treatment of fresh catalysts and the incomplete removal of coke deposition on the deactivated catalysts at low regeneration temperature improve the selectivity to isomerization without decreasing the yield of isobutane. The evolutions of heterogeneous active sites during different thermal treatment conditions and regeneration conditions were characterized by XRD, nitrogen adsorption-desorption, NH_3-TPD, and TPD-MS, from which the structure-activity correlation of SZA catalyst was elucidated and the inconsistencies in literature are resolved.

2. Experimental

2.1. Catalyst preparation

The synthesis of the zirconium-alumina hydroxide was the same as in our previous study [24]. The synthesized zirconium-alumina hydroxide was sulfated with 0.5 M sulfuric acid solution for 0.5 h. After filtration and drying at 110 °C, the fresh catalyst was obtained by calcining the sulfated zirconium-alumina at 650 °C in a muffle furnace for 2 h, designated as SZA. Subsequently, a series of SZA catalysts with different surface properties and catalytic performances were obtained by thermal treatment of fresh SZA samples with different temperatures and times. The obtained catalysts are designed as SZAx-yh, where "x" and "y" are the temperature and time for thermal treatment.

2.2. Catalytic activity tests

n-Butane isomerization tests were carried out in a fixed-bed microreactor (12 mm i.d) at 200 °C under atmospheric pressure, with 1.0 g of the catalyst (80–180 mesh) loaded into the reactor. Prior to the reaction, the catalysts were activated in flowing air at 350 °C for 30 min. Afterwards, the catalysts were cooled down to 200 °C and *n*-butane was fed into the reactor with H_2 as diluent gas (H_2:C_4^0 = 0.6:1). The WHSV for all tests was 2.38 h^{-1}. The compositions of feeds and products were analyzed by a Bruker 450 Gas Chromatogram equipped with a FID detector. The *n*-butane (Keyuan Gas Co., Ltd.) was purified with a trap containing 30 H-Y zeolite to remove any olefin impurities present in the feed, after which, the concentration of residual butene in the feed was below the detection limit of the GC (0.001%). For the regenerability investigation, the deactivated catalysts after 0.5 h of reaction were purged with N_2 for 30 min at 200 °C, and then regenerated in a flow of air at different temperatures for 2 h. Subsequently, the reaction was restarted at 200 °C.

2.3. Catalyst characterization

The phase transformation of the catalyst after different thermal treatment was identified by 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° at a speed of 10°/min. To determine the Brunauer–Emmett–Teller (BET) specific surface area and pore properties of catalysts, the nitrogen adsorption-desorption measurements were carried out on a Quadrasorb SI instrument at −196 °C. Prior to the measurements, the samples were evacuated at 350 °C for 4 h at 5.3×10^{-4} kPa for the complete removal of the adsorbed moisture. The B/L sites ration was determined by pyridine adsorption FTIR experiments. Prior to the adsorption of pyridine, the samples were preheated at 120 °C for 12 h to remove undesired physisorbed water or other impurities. The pyridine was adsorbed at room temperature (about 20 °C) for 2 h. Prior to the measurement, the samples were evacuated at 120 °C and 1.0×10^{-3} kPa for 4 h and then cooled to room temperature to record the spectrum. To determine the B/L ratio, the values of the integrated molar absorption coefficients used to determine the B/L ratio were 1.67 cm/μmol for the 1545 cm^{-1} band characteristic of pyridine on a Brønsted acid site and 2.22 cm/μmol for the 1455 cm^{-1} band of pyridine on a Lewis acid site [25]. The carbon and sulfur content of catalysts was determined by a high-frequency infrared carbon sulfur analyzer (HX-HW8B).

An in situ temperature-programmed oxidation mass spectrometer (TPO-MS) was employed to investigate the evolution of surface species from the deactivated SZA surface under an air flow. About 0.5 g catalyst was loaded and the reaction was carried out under the same reaction conditions as described in section 2.2. Afterward, the catalyst sample was flushed in a flow of Ar at 200 °C for 30 min, then the TPO of deactivated sample was conducted under a flow of air at a heating rate of 10 °C/min. The effluent was analyzed by an on line Hiden quadrupole mass spectrometer. The mass numbers (*m/e*) 41, 43, and 44 were used for butene, butane, and CO_2, respectively.

The acidity and oxidizability of samples were measured by NH_3-TPD equipped with a thermal conductivity detector (TCD). About 0.1 g of sample (20–40 mesh) was pretreated at 500 °C for 30 min under flowing He atmosphere. Then, the sample was cooled down to 50 °C and saturated with ammonia. After flushing the physical adsorbed ammonia at 50 °C for 1 h, the sample was heated to 900 °C at a rate of 10 °C/min in He flow. To clarify the assignments of the peaks in NH_3-TPD measurements, the above mentioned on line MS was also employed and the mass numbers (*m/e*) 17 and 28 were used for NH_3 and N_2.

3. Results and discussion

3.1. Effects of the regeneration temperature

As shown in Fig. 1a and b, although the overall rates of *n*-butane conversion and isobutane formation were both decreased with time on stream in the reaction, the decline rate of isobutane formation was much slower than that of *n*-butane conversion, indicating the rapid increase in the selectivity to isobutane. It is generally recognized that the main by-products, propane and pentane, were formed by disproportionation of *n*-butane via a "dimerization-cracking" mechanism. The molar ratio between propane and pentane, however, was much greater than 1 in the first few minutes of reaction, and decreased to 1 quickly with time on stream (Fig. 1d). Considering the fact that the formation of methane was negligible compared with propane, this unequimolar ratio of propane/pentane indicates that a secondary dimerization reaction occurs between unsaturated C_5 and C_4 species. Different with the evolution of the rate of *n*-butane conversion, it clearly appears that the isobutane acts as intermediates of the reaction, gonging through a maximum characteristic of successive reaction at the beginning of the reaction. In the primary bimolecular reactions, the β-scission of isomerized C_8 intermediates produces unsaturated C_3-C_5 species, among which, the isopropyl carbenium ions are more unsteady than C_4 and C_5 ions and easily desorb from the surface as propane. The formed C_4 and C_5 intermediates are more readily dimerized to C_9 intermediates. After skeletal isomerization and β-scission of C_9 intermediates, the excessive propane was formed (Scheme 1). That is the reason for the higher rate of propane formation and the lower rate of isobutane formation at initial 1 min of reaction. Thus, we suggest that the selectivity to isobutane reflects the probability for the bimolecular reactions, and the propane/pentane molar ratio represents the degree of the secondary reactions.

The catalytic behavior of regenerated SZA catalyst is strongly dependent on the regeneration temperature. As shown in Fig. 1, the global catalytic behaviors of deactivated catalyst can be completely recovered

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