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A comprehensive mechanistic pathway for n-butane isomerization on sulfated zirconia

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Abstract

This paper proposes a comprehensive mechanistic model for n-butane isomerization on sulfated zirconia (SZ) that accounts for the apparent contradictory results reported in the literature. The use of nonspecific olefins as molecular probes in n-butane isomerization has played a central role leading to this mechanistic proposal. The contradictory results in the literature have led various authors to conclude that the reaction occurs via a bimolecular mechanism, while others have suggested that a monomolecular pathway is dominant. The presence of butene is well known to lead to increased isobutane formation, suggesting a predominantly bimolecular route. However, we recently showed that the addition of other olefins (ethylene, propylene, isobutene, and 1-pentene) also promotes the reaction rate and modifies the induction period. These results indicate that not only C_4 olefins, but also any olefin with the ability to form carbenium ion species on the catalyst surface, can promote catalytic activity. Taking into account our latest experimental evidence, a reaction mechanism is proposed involving a *bimolecular pathway* with the characteristics of a *monomolecular pathway* (dual-nature mechanism) using "olefin-modified sites" as the main centers of reaction. The major observations made for the isomerization of n-butane (i.e., isotopic scrambling, nonspecific olefin activity promotion, high isobutane selectivity, and catalyst deactivation) are discussed in light of the proposed molecular pathway, and the seeming duality of the mechanism is addressed.

Keywords: Sulfated zirconia; n-Butane isomerization; Olefin addition; Mechanism of reaction

1. Introduction

The skeletal isomerization of n-alkanes plays an important role in the production of branched, high-octane hydrocarbons as a replacement for traditional tetra-ethyl lead additives. Sulfated zirconia (SZ) has gained much attention for the isomerization of n-butane because it exhibits high activity and selectivity toward isobutane even at low temperatures [1–3]. Initially, this was suggested to be related to the strong acidity of SZs, similar to that found for zeolites such as HY [1,4], but it has been shown that this is not the case. Zeolites, for instance, require much higher temperatures to achieve similar conversions [5,6]. It is possible that the catalytic ability of SZ for n-butane isomerization is related to its capacity to promote redox reactions of hydrocarbons (oxidative dehydrogenation), as some authors have recently suggested [7–10].

There is still much controversy about the mechanistic pathway operating for n-butane isomerization on SZ. Several researchers have suggested that the reaction proceeds through a monomolecular mechanism involving formation of a protonated cyclopropane ring on unpromoted SZ [2,11,12] and on Pt-SZ in the presence of H_2 [13–15]. The monomolecular pathway can satisfactorily explain the high selectivity toward isobutane, especially for short time on stream (TOS) and low conversion [2,12].

The other mechanism for n-butane isomerization on SZ suggested by numerous researchers is the bimolecular mechanism [16–23]. The bimolecular pathway is considered to occur via the formation of butene, which subsequently oligomerizes with adsorbed $C_4{}^+$ carbenium ions to produce $C_8{}^+$ oligomeric species. Under this hypothesis, it is assumed that a $C_8{}^+$ species undergoes isomerization and β-cleavage, leading to mainly isobutane and some disproportionation products. To date, however, just how the isomerization step of the $C_8{}^+$ oligomer oc-

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curs and how it leads mainly to isobutane have not been clearly explained in the literature.

The hypothesized bimolecular mechanism is supported especially by two facts: (1) the observation of disproportionation products, such as propane and pentanes, and (2) substantial isotopic scrambling for the reaction using 1,4-^{13}C *n*-butane, with the isobutane product containing an isotopic distribution between 0 and 4 ^{13}C atoms [17,20,24,25], which cannot be explained solely by a monomolecular route. In addition to these two important observations, recent experimental results have shown that the initial formation rate of isobutane is dramatically enhanced by olefins introduced at low concentrations in the reactant stream [16,21–23]. The activity-promoting effect of olefins occurs even when the added olefin is not butene, pointing to a nonspecific olefin rate enhancement for isobutane formation [23]. In addition, excess isobutane molecules are formed from each olefin molecule added [16,21,23], suggesting that active sites formed by olefin addition last for multiple turnovers. This evidence has led us to conclude that active sites probably can be best described as olefin-modified sites [21,23]. From our standpoint, this observation supports a bimolecular pathway requiring butene oligomerization before isomerization. A bimolecular pathway is also largely supported by the presence of an induction period, which has been hypothesized to result from the formation and accumulation of olefinic intermediates on the surface before isomerization [26].

Nevertheless, some authors have suggested that *n*-butane isomerization does not proceed through a bimolecular route exclusively. Matsuhashi et al. [2] concluded that *n*-butane isomerization occurs through a monomolecular pathway in the early stages of reaction before becoming a bimolecular pathway at long TOS. Li et al. [12] also proposed that the monomolecular isomerization pathway occurs at very low *n*-butane conversions, resulting in 100% isobutane selectivity. As conversion increases, the contributions from a bimolecular route become important, yielding disproportionation products.

Various studies have found that the reaction mechanism is dependent on reaction temperatures. According to Tran et al. [5], a diluting gas such as H_2 considerably decreases the formation rate of isobutane at low temperatures (150 and 200 °C), whereas there is no impact at 250 °C. This was taken as an indication that a bimolecular pathway is more pronounced at low temperatures, as was also suggested by a study using double-labeled ^{13}C butane by Echizen et al. [27], who found an increase in the monomolecular pathway for *n*-butane isomerization with increasing reaction temperature.

The work presented here is a continuation of our research on the effect of nonspecific olefin addition on the catalytic activity of SZ for *n*-butane isomerization and its relationship to the reaction mechanism. As reported previously, olefins, such as propylene, 1-butene, and 1-pentene, have a substantial impact on the induction period of *n*-butane isomerization on SZ in an indistinguishable way [23]. The main conclusion from that work was that olefin-modified sites, rather than purely Brønsted or Lewis acid sites themselves, may be at the center of catalytic activity for *n*-butane isomerization. The present work expands on the range of olefins that can affect the isomerization activity of SZ, including ethylene and isobutene. Conclusions based on these results lead us to a proposed mechanism exhibiting a duality between monomolecular and bimolecular routes that substantiates all of the major facts observed for *n*-butane isomerization. Thus, the issues of high selectivity, presence of disproportionation products, isotopic scrambling, catalyst deactivation, and the effect of nonspecific olefin addition on reaction activity can all be addressed within the context of our mechanistic proposal.

2. Experimental

2.1. Catalyst preparation and characterization

The SZ catalyst was prepared by calcining the sulfate-doped zirconium hydroxide [$Zr(OH)_4$] precursor [MEI (XZO 1249/01, Flemington, NJ)] at 600 °C under static air for 2 h. The BET surface area of the calcined SZ catalyst was determined using N_2 adsorption with a Micromeritics ASAP 2010 (Norcross, GA). The sulfur content was determined by Galbraith Laboratories (Knoxville, TN). The crystallinity of the calcined catalyst was studied using a Philips X'Pert X-ray diffractometer using monochromatized Cu-K_α radiation and a Ni filter, operating at 40 kV and 30 mA.

2.2. n-Butane isomerization

A quartz microreactor (8 mm i.d.) was used in this study. The reaction was carried out with a maximum conversion of <6% to operate under differential conditions. Before reaction, 0.2 g of the SZ catalyst was pretreated in situ at 315 °C under 30 cc/min of dry air (National Specialty Gases, Zero Grade) for 4 h. Then the reactor was cooled to the reaction temperature of 100 °C under air and flushed with He (National Specialty Gases, UHP) for 30 min. The total flow rate of the reactant stream was 60 cc/min (STP), consisting of 30 cc/min of 5% $n\text{-}C_4 + 1\%$ Ar in a balance of He (National Specialty Gases). The reaction pressure was kept constant at 1.5 atm. The flow of pure He was adjusted to maintain a constant flow rate of *n*-butane when olefin [1% of $C_2^=$, $C_3^=$, 1-$C_4^=$, iso$C_4^=$ or 1-$C_5^=$ in He (National Specialty Gases, UHP)] was added to the feed stream. Any olefin impurities from the *n*-butane cylinder were removed using a trap containing 10 g of H-mordenite held at room temperature. The impurities remaining in the *n*-butane feed were 2 ppm propane and 7 ppm isobutane.

In this study, various olefins ($C_2^=$, $C_3^=$, 1-$C_4^=$, iso-$C_4^=$, and 1-$C_5^=$) were added to the reaction stream to measure their effect on SZ activity. Ethylene was added to the reaction at the lowest olefin/paraffin (O/P) ratio of 0.003 due to the strong catalyst activation-deactivation response to this olefin, while isobutene was continuously added at 0.009. Other olefins ($C_3^=$, 1-$C_4^=$, or 1-$C_5^=$) were added at various O/P ratios (0.003–0.015). Reactions were carried out at 100 °C, where reaction rates were not affected by either mass or heat transfer limitations.

Reaction samples were collected using a 34-port VICI autosampling valve that could obtain up to 16 product samples to