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Mechanism of butane skeletal isomerization on sulfated zirconia

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Abstract

A kinetic model of the skeletal isomerization of *n*-butane and isobutane on sulfated zirconia in the absence of Pt is presented. The skeletal isomerization of butane on sulfated zirconia has been shown to be initiated by oxidative dehydrogenation of the alkane. This is followed by the formation of alkoxy groups/carbenium ions at the surface, induced by strong Brønsted acid sites. The isomerization of the *sec*-butyl carbenium ion occurs mono-molecularly, as suggested by the 100% selectivity for isomerization extrapolated to zero conversion. With increasing conversion, the selectivity decreased linearly, leading to propane and pentanes up to 40% of conversion. The lower selectivity for isomerization is qualitatively explained by reactions of isobutene present in small concentrations in the reactor at higher conversions. Transient experiments show conclusively that the isomerization of the carbenium ion and not the hydride transfer from the alkane to the carbenium ion is the rate-determining step.

Keywords: Sulfated zirconia; Butane; Isomerization; Kinetics; Hydride transfer; Chain propagation; Activation energy

1. Introduction

Sulfated zirconia and other sulfated metal oxides are of interest because of their unique activity for skeletal isomerization of short alkanes at low temperatures [1,2]. In recent years the kinetics of butane isomerization on sulfated zirconia has been studied frequently [3–7], and the results have been reviewed [8]. However, the marked differences in *n*-butane and isobutane isomerization reactions indicate that the conclusions reached for a narrow set of conditions may not be generalized.

An induction period is observed, when butane is isomerized on sulfated zirconia at low temperature, which is assumed to be due to the accumulation of carbenium ion species on the surface [9,10]. The presence of butenes shortened the induction period significantly [11], which is rationalized by the easier formation of carbenium ions by protonation. The importance of carbenium ions during alkane skeletal isomerization on sulfated zirconia has also been indicated by the negative effect of CO (formation of oxocarbenium ion) [9,12]. Quantum chemical studies have contributed significantly to the understanding of the state of these carbenium ions and their conversion [13].

Intermolecular (bimolecular, involving a *sec*- or *tert*-octylcarbenium ion) and intramolecular (monomolecular) routes [14–21] have been proposed for butane isomerization on solid acids. The intramolecular isomerization of a butyl carbenium ion requires the formation of a primary carbenium ion, which is characterized by a high-energy barrier in the gas phase. Therefore, the intermolecular mechanism was speculated to be the preferred route, as it involves only the formation of secondary carbenium ions, followed by cracking and the subsequent hydride transfer/desorption step. In this context, it should be noted that the kinetics of *n*-butane isomerization was analyzed previously with the assumption that dimerization and cracking are involved [3]. The high isobutane selectivity (90–92%) during *n*-butane isomeriza-

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tion was explained by the different stability and reactivity of the C_8 isomers, and the low reaction rate of isobutane was ascribed to the steric hindrance of two *tert*-butyl groups forming the C_8 intermediate.

n-Butane isomerization carried out in the presence of hydrogen showed a reaction order for *n*-butane above 1 [4]. Therefore, the intermolecular mechanism was concluded to dominate under these conditions. The opposite conclusion was reached by Garin et al., who used mono ^{13}C-labeled *n*-butane under similar reaction conditions [16]. However, in most of the experimental works dealing with isomerization of ^{13}C-labeled *n*-butane on promoted and unpromoted sulfated zirconia at low temperature, an extensive isotopic scrambling was observed. These results were used as evidence for an exclusive or prevailing bimolecular route [4,15,18,20,22]. It should be noted that in all of these papers either the concentration of olefins in butane was not specified and/or a purification step was not documented. In addition, the reported conversion at which the reaction mixture was analyzed for isotopic scrambling was much higher than that corresponding to differential conditions (for example, 40% in Ref. [15] and 10% in Ref. [18]). It is important to note that the results of Garin (in favor of a monomolecular mechanism) were critically reinterpreted by Adeeva et al. [8], who stated that the absence of isotope scrambling does not prove the mechanism to be intramolecular.

The complete absence of disproportionation products, propane and pentanes, at least in the early stages of *n*-butane isomerization on sulfated zirconia [14] or other acid solid catalysts [21], has been interpreted as evidence for a monomolecular mechanism. However, results of Luzgin et al. suggested that at lower conversions intermolecular pathways to isobutane are conceivable. In this context it should be noted that the cracking products of branched octanes on sulfated zirconia at 373 K do not lead exclusively to isobutene, and hence octylcarbenium ions were concluded not to be the main intermediates of butane isomerization [23].

In summary, the experiments reported here do not allow us to unequivocally decide the pathways along which *n*-butane skeletal isomerization proceeds. This is among other factors to be ascribed to impure feeds, which induce various reactions, including oligomerization and deactivation. After having demonstrated that the initiation step consists of the oxidative dehydrogenation of *n*-butane [10], here the propagation step of the butane skeletal reaction on sulfated zirconia at 373 K is addressed.

2. Experimental

2.1. Catalyst preparation

Sulfate-doped zirconium hydroxide was obtained from Magnesium Electron, Inc. (batch number XZO 1077/01). The as-received sample was heated to 873 K with an increment of 10 K/min and maintained at the final temperature for 3 h in static air to form sulfated zirconia with a concentration 0.053 mmol/g of Brønsted acid sites. The resulting catalyst was kept in a desiccator and was activated in situ as described below before the kinetic studies.

2.2. Adsorption isotherms and differential heats of adsorption

The adsorption isotherms were measured in a SETARAM TG-DSC 111 instrument. Approximately 15 mg of pellets was charged into the quartz crucible used in the TG-DSC system. The sample was activated by heating to 673 K with an increment of 10 K/min and maintained at 673 K for 2 h in vacuum ($p < 10^{-6}$ mbar). After activation, the temperature was stabilized at 373 K. *n*-Butane and isobutane were introduced into the closed system in small doses and allowed to equilibrate with the sulfated zirconia until no further mass increase was observed. The butane pulses were repeated until the pressure reached 300 mbar. The differential heats of *n*-butane and isobutane adsorption were determined at 308 K.

2.3. Butane isomerization

Isomerization of *n*-butane (99.5%, Messer) and isobutane (99.95%, Messer) was carried out in a quartz micro tube reactor (8 mm i.d.) at atmospheric pressure under differential conditions (conversion $< 0.5\%$). Sulfated zirconia pellets (355–710 µm) (0.2 or 0.5 g for *n*-butane or isobutane, respectively) were loaded into the reactor and activated in situ at 673 K for 2 h in He flow (10 ml/min). The catalyst was cooled to 373 K, and the reactant mixture (various *n*- and isobutane partial pressures in He, total flow of 20 ml/min) was passed through the catalyst bed. Butane was passed through an olefin trap containing activated zeolite H-Y (20 g), before it was mixed with He. The butene concentration in the resulting gas was below the detection limit (i.e., < 1 ppm). The reaction products were analyzed with an on-line HP 5890 gas chromatograph (GC) equipped with a capillary column (Plot Al_2O_3, 50 m × 0.32 mm × 0.52 mm) connected to a flame ionization detector (FID).

In order to investigate the catalytic activity and selectivity of sulfated zirconia for *n*-butane (5% *n*-butane in He) at high conversion, 1.5 g of sulfated zirconia was loaded into the reactor, and reactant flow rates between 0.5 and 2 ml/min were applied.

2.4. Transient kinetic analysis

A concentration transient study during *n*-butane isomerization at 373 K (0.2 g of sulfated zirconia, 20 ml/min of 5% *n*-butane in He) on sulfated zirconia was performed after 5 h TOS (time on stream), when stable activity was observed. The feed was changed in a step function from 5 vol% *n*-butane to 2 vol% propane in He or pure He (20 ml/min). Samples of the effluent were collected with a VICI 32-port valve (16 loops) and analyzed by GC.