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n-Butane conversion on sulfated zirconia: *in situ* ^{13}C MAS NMR monitoring of the kinetics of the ^{13}C-label scrambling and isomerization

A.G. Stepanov[a,*], M.V. Luzgin[a], S.S. Arzumanov[a], W. Wang[b], M. Hunger[b], and D. Freude[c,*]

[a]*Boreskov Institute of Catalysis, prosp. Akad. Lavrentieva 5, Novosibirsk, 630090 Russia*
[b]*Institute of Chemical Technology, University of Stuttgart, 70550 Stuttgart, Germany*
[c]*Abteilung Grenzflächenphysik, Universität Leipzig, Linnéstraße 5, 04103 Leipzig, Germany*

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The kinetics of the conversion of ^{13}C-labeled *n*-butane adsorbed on sulfated zirconia (SZ) were monitored by *in situ* ^{13}C MAS NMR spectroscopy. Rate constants of *n*- to isobutane isomerization and of the ^{13}C-isotope scrambling from the primary to the secondary carbon atoms in *n*-butane were determined. The monomolecular scrambling of the ^{13}C-label in adsorbed *n*-butane has an activation energy of 17 ± 3 kcal mol^{-1} and occurs faster than the bimolecular process of *n*-butane isomerization which has an activation energy of 15.1 ± 0.2 kcal mol^{-1}. The transfer of the selective ^{13}C-label from the primary to the secondary carbon atom in the adsorbed *n*-butane seems to consist of two reaction steps: (i) a hydride abstraction by SZ leading to the formation of *sec*-butyl cations and (ii) a label scrambling in the *sec*-butyl cations. This two-step process with the formation of *sec*-butyl cations as intermediate increases the apparent activation energy for the ^{13}C-label scrambling, which is almost twice as large compared with the activation energy for carbon scrambling of *sec*-butyl cations in a superacidic solution.

KEY WORDS: hydrogen exchange; sulfated zirconia; ^{13}C MAS NMR; *n*-butane conversion.

1. Introduction

The skeletal isomerization of alkanes plays an important role in industrial processes of petrochemistry as well as in fundamental studies of catalysis by solid superacids. Sulfated zirconia is a promising catalyst for the isomerization of linear alkanes, in order to produce high-octane-number clean fuels [1,2]. Two different mechanisms have been suggested for the isomerization of alkanes on SZ, one monomolecular [3,4] and the other bimolecular [4–6]. Recently published investigations of the ^{13}C-label distribution in the reaction product isobutane [7,8] confirmed earlier suggestions [4–6] that a bimolecular reaction mechanism is realized for the conversion of *n*-butane on pure sulfated zirconia. On the contrary, for Pt–SZ catalysts and in the presence of H_2, a monomolecular mechanism was proposed [3,7,9]. By means of *in situ* NMR monitoring of the isomerization of ^{13}C-labeled *n*-butane ([1−^{13}C]-*n*-butane) on sulfated zirconia we observed a ^{13}C-label scrambling in the initial *n*-butane [8] in agreement with Adeeva *et al.* [6] who applied GC–MS. This label scrambling shows the alkane activation on solid acids. NMR monitoring of the kinetics of the ^{13}C-label scrambling were performed in the present study, in order to clarify the mechanism of the alkane activation on sulfated zirconia and the nature of the intermediates or transition states providing the scrambling of the skeletal carbon atoms.

2. Experimental section

2.1. Preparation of the samples

A sample of sulfated zirconia (SZ) consisting of the low temperature tetragonal phase with a surface area of 60 m^2 g^{-1} and 9.9 wt% of SO_3 was synthesized according to the procedure described elsewhere [10]. ^{1}H MAS NMR spectroscopy gave a concentration of Brønsted acid sites of 50 μmol g^{-1} by comparing the intensity of the signal at 6.2 ppm due to acid sites with that of adsorbed propane as an internal standard. The SZ sample (90 mg), filled in a glass insert, was calcined at 873 K in air and at 673 K under vacuum ($p \leq 10^{-3}$ Pa) for 2 h. Subsequently, [1−^{13}C]-*n*-butane (300 μmol g^{-1}) was adsorbed on SZ under vacuum and at the temperature of liquid nitrogen. After sealing the glass insert filled with the loaded SZ, the sample was kept at liquid nitrogen temperature. For the measurement of *n*-butane conversion the sample was taken from the liquid nitrogen, placed in the NMR probe, which was preheated to the temperature at which the reaction was studied (291–323 K).

2.2. NMR analysis

The reaction products of the conversion of *n*-butane on SZ in a sealed glass batch reactor were analyzed *in situ* by ^{13}C MAS NMR spectroscopy. ^{13}C NMR spectra were recorded with high-power proton decoupling and magic-angle spinning (MAS) at a resonance frequency of 100.613 MHz on a Bruker MSL-400

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[*] To whom correspondence should be addressed.
E-mail: a.g.stepanov@catalysis.nsk.su, freude@uni-leipzig.de

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spectrometer at temperatures of 291–323 K. The ^{13}C spins were excited with pulses of a flip angle of 45° corresponding to a pulse length of 2.5 μs, and with a repetition time of 3–4 s thus avoiding relaxation effects by T_1. The sample spinning rate was 2–3 kHz and 40–100 scans were collected for each spectrum. The chemical shifts of the ^{13}C nuclei in the adsorbed organic species were determined with respect to TMS as the external reference with accuracy ±0.5 ppm. The accuracy of relative line positions was 0.10–0.15 ppm. [1−^{13}C]-*n*-butane with one ^{13}C-labeled methyl group was prepared from [1−^{13}C]-ethanol (^{13}C-isotopic enrichment of 99%) *via* a six-step process.

3. Results and discussion

Figure 1 shows the variation of the ^{13}C MAS NMR spectrum of [1−^{13}C]-*n*-butane adsorbed on SZ as a function of the heating time at the reaction temperature of 313 K. The first spectrum recorded at this temperature within 10 min shows a strong signal at 14.7 ppm due to the ^{13}C-labeled methyl groups of *n*-butane. The intensity of this signal decreases while another signal at 26.0 ppm increases. The signal at 26.0 ppm can be explained as a superposition of two signals due to ^{13}C-labeled CH_3 and CH species in isobutane. Simultaneously, the intensity of the signal due to the CH_2 groups of *n*-butane at 27.0 ppm increases, passes a maximum after a time of 100 min and, subsequently, decreases. This variation of the intensity of the signal at 27.0 ppm as a function of time indicates that the ^{13}C-label transfers from the methyl group into the methylene group of the adsorbed *n*-butane. Thus, two parallel reactions of *n*-butane adsorbed on SZ occur, i.e., isomerization and a label scrambling.

In figure 2, the relative intensities of the ^{13}C MAS NMR signals of the ^{13}C-labels in [1−^{13}C]-*n*-butane (14.7 ppm), [2−^{13}C]-*n*-butane (27.0 ppm), and isobutane (26.0 ppm) adsorbed on sulfated zirconia are plotted. The spectra were recorded as a function of time at temperatures of 291–323 K. The conversion of [1−^{13}C]-*n*-butane on SZ can be described by the pathways shown in scheme 1. Here, A and B denote [1−^{13}C]-*n*-butane and [2−^{13}C]-*n*-butane, respectively, and C denotes a double ^{13}C-labeled isobutane [8].

Assuming that all the stages correspond to the first-order kinetics, the system of kinetic equations, equation (1), defines the variation of the ^{13}C-labels as a function of time. For *A*, *B*, and *C* denoting the quantities of [1−^{13}C]-*n*-butane, [2−^{13}C]-*n*-butane, and isobutane molecules adsorbed on SZ, respectively, we have [11]:

$$\begin{aligned}\frac{\mathrm{d}A}{\mathrm{d}t} &= -(k_1+k_2)A + k_1B + k_3C,\\ \frac{\mathrm{d}B}{\mathrm{d}t} &= k_1A - (k_1+k_2)B + k_3C,\\ \frac{\mathrm{d}C}{\mathrm{d}t} &= k_2A + k_2B - 2k_3C.\end{aligned} \tag{1}$$

The solution of the system of three differential equations is given in equation (2):

$$\begin{aligned}A(t) &= \frac{k_3a}{2k_3+k_2} + \frac{k_2a}{2(2k_3+k_2)}\exp[-(2k_3+k_2)t]\\ &\quad + \frac{a}{2}\exp[-(2k_1+k_2)t],\\ B(t) &= \frac{k_3a}{2k_3+k_2} + \frac{k_2a}{2(2k_3+k_2)}\exp[-(2k_3+k_2)t]\\ &\quad - \frac{a}{2}\exp[-(2k_1+k_2)t],\\ C(t) &= \frac{k_2a}{2k_3+k_2} - \frac{k_2a}{2k_3+k_2}\exp[-(2k_3+k_2)t].\end{aligned} \tag{2}$$

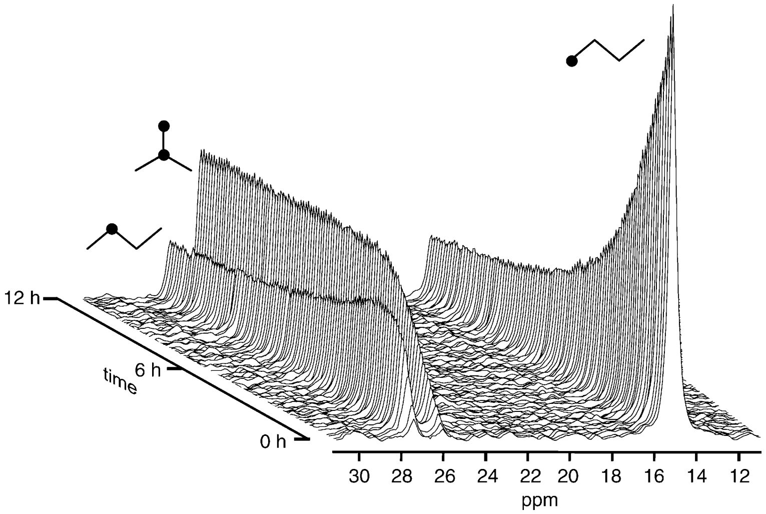


Figure 1. Stacked plot of the ^{13}C MAS NMR spectra of [1−^{13}C]-*n*-butane adsorbed on sulfated zirconia recorded at 313 K after different heating times. The first spectrum (bottom) was recorded 10 min and the last 12 h after *n*-butane adsorption and the start of the heating. The time between subsequent spectra was 10 min.

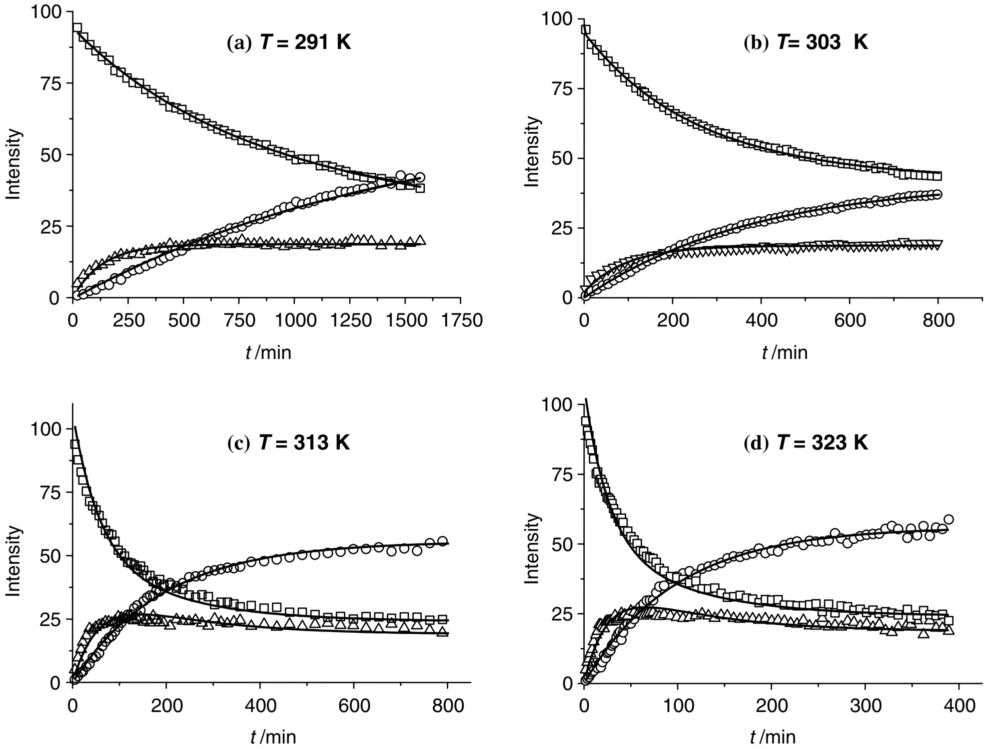


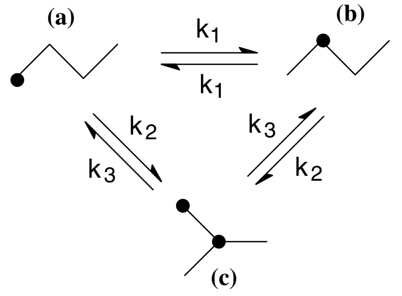
Figure 2. Relative ^{13}C MAS NMR intensities of the ^{13}C-labels in [1−^{13}C]-*n*-butane at 14.7 ppm (□), [2−^{13}C]-*n*-butane at 27.0 ppm (Δ), and isobutane at 26.0 ppm (○), adsorbed on sulfated zirconia. The spectra were recorded as a function of time at temperatures of 291 K (a), 303 K (b), 313 K (c), and 323 K (d). The solid lines represent fits of the experimentally obtained curves *via* equations (2) with the rate constants given in table 1.

Here $a = A(0)$ is a normalization constant that corresponds to the quantity of adsorbed [1−^{13}C]-*n*-butane or the initial intensity of the signal 14.7 ppm at the reaction time $t = 0$. The curves of the relative ^{13}C MAS NMR intensities of the ^{13}C-labels, shown in figure 2, were fitted according to equation (2) and with the rate constants given in table 1.

The Gibbs potential, Δ_rG, and the reaction enthalpy, Δ_rH, of the isomerization of *n*- to isobutane were estimated *via* the temperature dependence of the equilibrium constant $K = k_2/k_3$ and found to be (−0.7 ± 0.6) kcal mol^{-1} and (−2.9 ± 0.6) kcal mol^{-1}, respectively. This is in a good agreement with literature data for this reaction ($\Delta_rG^{298} = -0.9$ kcal mol^{-1}nd $\Delta_rH^{298} = -2.3$ kcal mol^{-1}12]). The agreement confirms the validity of scheme 1 for the description of the conversion of *n*-butane on SZ.

Considering the experimental data obtained in the present work, the ^{13}C-label scrambling rate in *n*-butane is higher than the rate of isomerization. Brouwer [13] found that the ^{13}C-label scrambling in *n*-butane is an essentially more facile process than its isomerization to isobutane in liquid superacids (HF–SbF$_5$). Scrambling occurred with a rate similar to that of the isomerization of *n*-pentane and *n*-hexane, while *n*-butane did not isomerize to isobutane at all.

This was explained by the necessity of the formation of a primary carbenium ion acting as an intermediate or a transition state. The formation of this primary carbenium ion is characterized by a higher energy barrier



Scheme 1. (Black dots in the scheme denote the ^{13}C label).

Table 1

Rate constants for the ^{13}C-label scrambling (k_1) in *n*-butane and the isomerization of *n*- to isobutane (k_2) and *iso*- to *n*-butane (k_3) on sulfated zirconia, derived from *in situ* ^{13}C MAS NMR investigations of the reaction kinetics under the conditions of a batch reactor

Temperature, K	k_1×10^3 min^{-1}	k_2×10^3 min^{-1}	k_3×10^3 min^{-1}
291	1.04 ± 0.06	0.43 ± 0.02	0.11 ± 0.03
303	1.7 ± 0.15	1.3 ± 0.1	0.41 ± 0.05
313	7.6 ± 0.4	2.9 ± 0.1	1.2 ± 0.1
323	17.0 ± 1.5	5.6 ± 0.2	2.3 ± 0.3

than the formation of a secondary carbenium ion, which is necessary for the ^{13}C-label scrambling in *n*-butane or isomerization of *n*-pentane. At the same time, the isomerization of *n*- to isobutane and the ^{13}C-label scrambling in these compounds have been found to proceed at the same rates in the presence of a promoted aluminum bromide catalyst [14]. A possible explanation of the different kinetics in HF–SbF$_5$ and on aluminum halide catalysts is that an intramolecular reaction mechanism is involved in the former case and a bimolecular reaction mechanism is realized in the latter case [13].

In the present experiments on SZ, the higher rate constant for the ^{13}C-label scrambling compared to that for isomerization can be explained in a similar way as for superacidic solutions. The necessity to form a high-energetic primary isobutyl cation as intermediate or transition state during the isomerization of *n*- to isobutane *via* a monomolecular mechanism provides a possible explanation for the low rate constant in comparison with the ^{13}C-label scrambling in the initial *n*-butane [13]. However, it was unequivocally demonstrated in several studies that *n*-butane isomerizes on SZ *via* a bimolecular mechanism [6–8]. This implies that on SZ the monomolecular label scrambling in *n*-butane is faster than the bimolecular isomerization of *n*- to isobutane.

Figure 3 shows how the apparent activation energies were determined from an Arrhenius plot of the rate constants at various reaction temperatures. The activation energy for the isomerization of *n*- to isobutane of 15.1 kcal mol^{-1}s in good agreement with the value of $E_a = 14.0$ kcal mol^{-1} published earlier for the bimolecular mechanism [15,16]. Matsuhashi *et al.* [4] have estimated an activation energy of 13.0 kcal mol^{-1} in the induction period of the isomerization of *n*- to isobutane, i.e., before products of an *n*-butane disproportionation (propane and pentanes) appear. Therefore, they assigned this value to the activation energy of the monomolecular isomerization of *n*-butane. However, isobutane was the only reaction product after 1 h reaction at 293 K, and an analysis of the ^{13}C-label distribution in isobutane indicated the presence of two ^{13}C-labels in the isobutane molecule which is formed by the conversion of single ^{13}C-labeled *n*-butane [8]. This implies that the activation energy estimated by Matsuhashi *et al.* [4] corresponds to the bimolecular isomerization of *n*-butane. The apparent activation energy expected for the monomolecular isomerization of *n*- to isobutane is about 30 kcal mol^{-1}17].

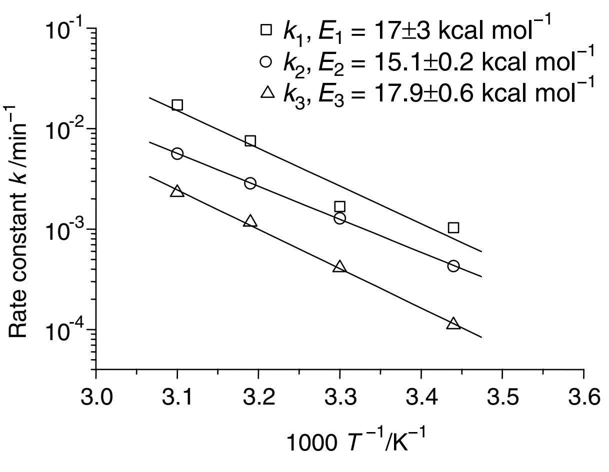


Figure 3. Arrhenius plot of the rate constants k of the ^{13}C-label scrambling in *n*-butane (□) and of the isomerization of *n*- to isobutane (○) and *iso*- to *n*-butane (Δ) on sulfated zirconia given in table 1.

The kinetic data obtained in the present work indicate that the ^{13}C-label scrambling in *n*-butane occurs with an activation energy of 17 kcal mol^{-1} (figure 3). This ^{13}C-label scrambling in *n*-butane adsorbed on SZ was shown to occur as an intramolecular process [6,8]. In superacidic solutions, the ^{13}C-label scrambling occurs in *sec*-butyl carbenium ions formed from *n*-butane *via* the formation of protonated cyclopropane as an intermediate or transition state. In this respect, the observation of the ^{13}C-label scrambling in *n*-butane adsorbed on SZ by a monomolecular mechanism is indicative of the formation of a *sec*-butyl carbenium ion as intermediate or transition state on SZ, similar to this process in superacidic solutions. Indeed, there is so far no alternative mechanism for the ^{13}C-label scrambling in alkanes or olefins, except for the scrambling in the carbenium ions formed from either alkane or olefin.

The activation energy of the ^{13}C-label scrambling in *sec*-butyl cation in superacidic solutions was found to be 7.5 kcal mol^{-1} [18]. A higher activation energy for the ^{13}C-label scrambling in *n*-butane adsorbed on SZ may imply that a stage of hydride abstraction from *n*-butane by SZ to form *sec*-butyl cation is responsible for the increase of the apparent activation energy of the scrambling. Indeed, the activation energy for the hydride abstraction reaction for alkanes in superacidic solutions may reach 17 kcal mol^{-1} [19]. Alternatively, both hydride abstraction with an activation energy of 13–14 kcal mol^{-1}, as in superacidic solutions[19,20], and the ^{13}C-label scrambling in *sec*-butyl cations may contribute to the apparent activation energy of 17 kcal mol^{-1} or the ^{13}C-label scrambling *n*-butane adsorbed on SZ.

4. Conclusions

The *in situ* ^{13}C MAS NMR monitoring of the kinetics of the conversion of ^{13}C-labeled *n*-butane adsorbed on sulfated zirconia allows the estimation of both the rate constants for isomerization of *n*- to isobutane and the ^{13}C-label scrambling in *n*-butane from primary to secondary carbon atoms. The monomolecular scrambling of the ^{13}C-label in adsorbed *n*-butane has an activation energy of 17 kcal mol^{-1} and occurs faster than the bimolecular process of *n*-butane isomerization which has an activation energy of 15.1 kcal mol^{-1}. The ^{13}C label scrambling in *n*-butane adsorbed on sulfated zirconia suggests the formation of *sec*-butyl cations as intermediates or transition states providing the label scrambling. Two successive stages of the reaction, namely a hydride abstraction by the sulfated zirconia leading to the formation of *sec*-butyl cations and the ^{13}C-label scrambling in the formed cations seem to control the apparent activation energy of the ^{13}C-label scrambling, which is more than twice as high as the activation energy for the carbon scrambling in *sec*-butyl cations in superacidic solutions.

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