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Mechanism Studies of the Conversion of ^{13}C-Labeled *n*-Butane on Zeolite H-ZSM-5 by Using ^{13}C Magic Angle Spinning NMR Spectroscopy and GC–MS Analysis

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Abstract: By using ^{13}C MAS NMR spectroscopy (MAS = magic angle spinning), the conversion of selectively ^{13}C-labeled *n*-butane on zeolite H-ZSM-5 at 430–470 K has been demonstrated to proceed through two pathways: 1) scrambling of the selective ^{13}C-label in the *n*-butane molecule, and 2) oligomerization–cracking and conjunct polymerization. The latter processes (2) produce isobutane and propane simultaneously with alkyl-substituted cyclopentenyl cations and condensed aromatic compounds. In situ ^{13}C MAS NMR and complementary ex situ GC–MS data provided evidence for a monomolecular mechanism of the ^{13}C-label scrambling, whereas both isobutane and propane are formed through intermolecular pathways. According to ^{13}C MAS NMR kinetic measurements, both pathways proceed with nearly the same activation energies (E_a = 75 kJ mol^{-1} for the scrambling and 71 kJ mol^{-1} for isobutane and propane formation). This can be rationalized by considering the intermolecular hydride transfer between a primarily initiated carbenium ion and *n*-butane as being the rate-determining stage of the *n*-butane conversion on zeolite H-ZSM-5.

Keywords: butane · GC–MS analysis · NMR spectroscopy · reaction mechanisms · zeolites

Introduction

The studies of the mechanisms of catalytic hydrocarbon conversion provide support for the development of new processes as well as for the improvement of existing hydrocarbon processing methods. Among the reactions that are of high industrial importance for petroleum refining and petrochemistry, one should mention the processes of alkane isomerization, alkylation, and cracking.[1] Over the last 10 years or so, much attention has been paid to the investigation of the mechanisms of such reactions on solid acid catalysts.[2–11] Several approaches have been used to ascertain the mechanisms of alkane activation and transformation on solid acid catalysts. The general procedure consists of kinetic studies aimed at the determination of both the reaction product distribution, which is depends on the conversion, and the reaction orders of the reactants.[2,4–7,10] Such studies allow one to distinguish between the primary and secondary processes of alkane activation and to make a preliminary conclusion about the character (intra- or intermolecular) of their mechanism.

Another approach to the discrimination between mono- (intra) and bi- (inter) molecular mechanisms of hydrocarbon conversion on solid catalysts, which provides more direct information about the reaction mechanism, uses ^{13}C-labeled reactants, both for monitoring the redistribution of a number of ^{13}C labels per molecule by GC–MS analysis[3,6,9,10,12–14] and for following the migration of the selective ^{13}C labels during the reaction by means of solid-state ^{13}C NMR spectroscopy.[15–17] In some cases, only integrated studies using complementary techniques (e.g., the combined

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use of both GC–MS analysis and NMR spectroscopy) provided insight into the reaction mechanism.[17]

The next point concerning the mechanism of alkane transformation on solid acid catalysts that should be addressed, the nature of the initial intermediate formed from alkane activation, is still under discussion,[8,18] despite the general agreement on the carbenium-type nature of the reaction intermediates.[1] The alkane activation on the solid acid catalysts is known to be the initial step of at least three processes: 1) The carbon scrambling, which can be observed with selectively ^{13}C-enriched reactants.[15,17,19] The scrambling usually precedes a chemical transformation of the alkane. 2) The isomerization of *n*-alkanes to isoalkanes. 3) Cracking of alkanes into smaller paraffins and olefins. Among the above processes, the ^{13}C-label scrambling is of particular interest, as it is indicative of activation without a chemical transformation of the alkane. Therefore, characterization of the ^{13}C-label scrambling offers an approach towards clarifying the mechanism for the initial stage of alkane activation. In this respect, one can expect that monitoring the kinetics of both the label scrambling in small alkanes and the alkane conversion towards isomerization and cracking would provide valuable information about the mechanism of the alkane activation and conversion.

In this work, we performed integrated studies on the mechanisms and kinetics of the *n*-butane conversion on zeolite H-ZSM-5, using both in situ ^{13}C MAS NMR spectroscopy (MAS = magic angle spinning) and GC–MS analysis as a complementary technique for the identification of the reaction products and their isotopic composition.

Results

In situ ^{13}C MAS NMR spectroscopy of the products of *n*-butane conversion: In the presence of zeolite H-ZSM-5, *n*-butane undergoes an isomerization reaction to isobutane[20,21] and a cracking reaction.[2] The latter dominates at high temperatures of approximately 523–773 K. The ^{13}C-label scrambling in hydrocarbons on solid catalysts is not accessible by any in situ technique except ^{13}C NMR spectroscopy. The ^{13}C-label scrambling in *n*-butane adsorbed onto Pt/H-theta-1 zeolite has been already observed,[15] however systematic studies of this phenomena for any zeolite catalyst, including the kinetic measurements, have never been performed before.

Figure 1 shows the ^{13}C MAS NMR spectra of the reaction products formed at 470 K from *n*-butane on H-ZSM-5. Note that *n*-butane has been initially selectively ^{13}C-labeled on only one of the methyl groups ([1-^{13}C]*n*-butane); therefore, only the ^{13}CH$_3$ group of the initial *n*-butane as well as the carbon atoms in the reaction products, in which the ^{13}C label migrates in the course of the reaction, could be observed in the spectra. Accordingly, besides the signal due to the ^{13}C-labeled CH$_3$ group of the initial *n*-butane at $\delta = 14.5$ ppm, only one weak signal can be identified in the spectrum recorded after 20 min of the reaction at 470 K (Figure 1a).

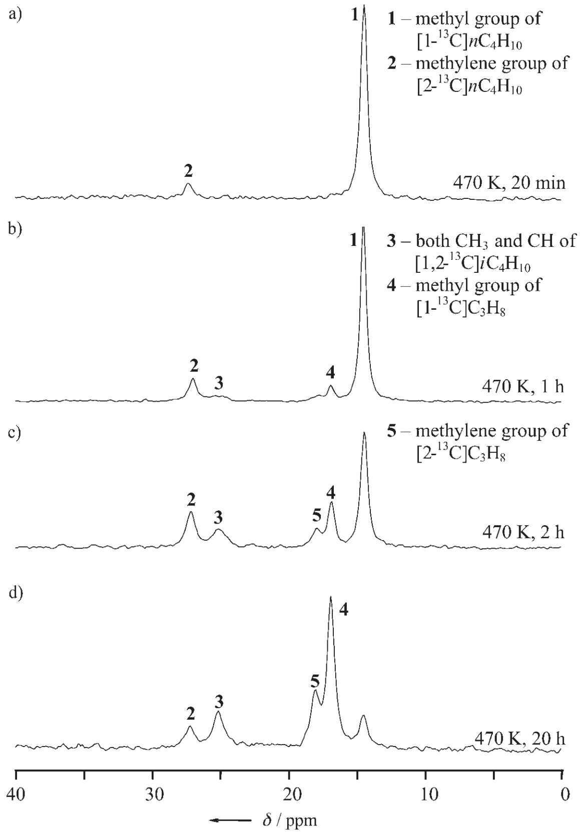


Figure 1. ^{13}C MAS NMR spectra of the products formed by the conversion of [1-^{13}C]nC_4H_{10} on zeolite H-ZSM-5 at 470 K after reaction times of a) 20 min, b) 1 h, c) 2 h, and d) 20 h.

This signal at $\delta = 27.2$ ppm is indicative of the formation of [2-^{13}C]*n*-butane, that is, the migration of the ^{13}C label from the methyl group of *n*-butane to its methylene group. This is the first and fastest process of the [1-^{13}C]*n*-butane transformation on zeolite H-ZSM-5. Further heating of the sample resulted in the appearance of signals caused by the other products (Figure 1b, c). The signal at $\delta = 25.1$ ppm belongs to ^{13}C-labeled isobutane. Both the CH$_3$ and CH groups are responsible for the appearance of this signal. The resonances at $\delta = 16.9$ and 18.0 ppm belong to the methyl and methylene groups of propane, respectively.[14,16] The intensities of the propane and isobutane signals increase with the reaction time. Propane is the main product at the end of the reaction (Figure 1d).

It is important to note that methane and ethane are not detected among the reaction products and the mainly observed products appear to be isobutane and propane. This allows one to assume that the oligomerization-cracking mechanism,[22] rather than the protonation-cracking mechanism of Haag and Dessau,[23,24] occurs for light-alkane conversion under the conditions of our experiment. The oligomerization–cracking also implies the formation of oligomeric products and coke on the catalyst surface, leading to catalyst deactivation. The aromatic nature of the deactivating species formed under alkane conversion on acidic zeolites at higher temperatures (≥773 K) has been established by using solid-state ^{13}C NMR spectroscopy.[25,26] Based on results from IR spectroscopic studies, Trombetta et al. proposed the formation of polyisobutene species at the surface of H-ZSM-5 under the alkane conversion at temperatures ≥573 K.[11] However, according to unambiguous data obtained by using ^{13}C solid-state NMR spectroscopy, alkene oligomers should undergo further transformation into alkyl-substituted cyclopentenyl cations (CPC) on zeolites, even at lower temperatures.[14,27,28] Thus, the nature of the adsorbed products responsible for zeolite deactivation during alkane conversion on acidic zeolite needs further clarification.

To clarify the nature of the oligomeric species formed with propane and isobutane on the zeolite, the ^{13}C MAS NMR spectrum with cross polarization (CP) to emphasize the resonances caused by the expected immobile oligomeric species was recorded for the reaction products (Figure 2).

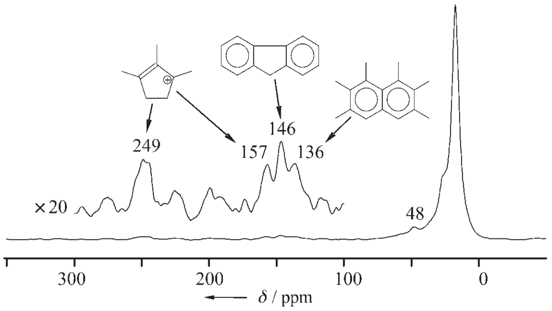
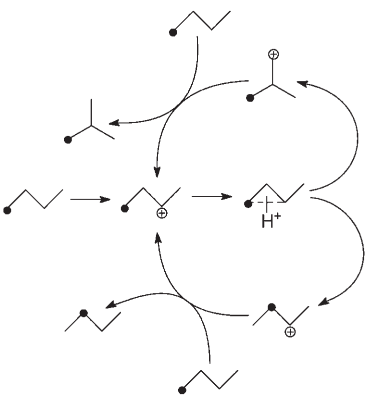


Figure 2. ^{13}C CP/MAS NMR spectrum of the products formed by the conversion of $[1\text{-}^{13}C]nC_4H_{10}$ on zeolite H-ZSM-5 after 20 h of the reaction at 470 K.

Five broad signals can be observed in this spectrum. The three signals occurring at $\delta = 249$, 157, and 48 ppm belong to alkyl-substituted cyclopentenyl cations (CPC), that is, the C^+ center, the $-C=$ group, and CH_3 substituents, respectively.[29] The other two signals at $\delta = 146$ and 136 ppm are assigned to condensed aromatic compounds.[30] Admittedly, we assign the signal at $\delta = 136$ ppm to naphthalenic and/or anthracenic compounds, whereas the signal at $\delta = 146$ ppm could be due to fluorenic and/or biphenylic species.[30] Thus, two processes occur during the *n*-butane conversion on zeolite H-ZSM-5: 1) the scrambling of the ^{13}C label in the *n*-butane molecule, and 2) the formation of isobutane and propane with the simultaneous formation of CPC and condensed aromatic compounds. Cyclopentenyl cations and condensed aromatic compounds are the adsorbed species that could deactivate the catalyst.

A transfer of the selective ^{13}C label from the CH_3 to CH_2 group of *n*-butane, as well as the formation of isobutane, may be rationalized in terms of a rearrangement of the *sec*-butyl cation formed from the initial *n*-butane, presumably by an intermolecular hydride-transfer reaction. Protonated methylcyclopropane as an intermediate or a transition state[31,32] can provide these reactions. Either $[2\text{-}^{13}C]n$-butane or $[1\text{-}^{13}C]$isobutane could be finally formed from $[1\text{-}^{13}C]n$-butane depending on the particular C−C bond cleavage in the methylcyclopropane ring (Scheme 1). The formation of isobutane through the monomolecular pathway shown in Scheme 1 should be energetically unfavorable, because the opening of the protonated methylcyclopropane ring in the case of *n*-butane isomerization would lead to a primary carbenium ion, which possesses a much higher energy in comparison with the secondary carbenium ion.[33] Indeed, as has been demonstrated for the case of the *n*-butane conversion on sulfated zirconia (SZ), the formation of isobutane proceeds through a bimolecular pathway, whereas the ^{13}C-label scrambling in *n*-butane on SZ represents a monomolecular process.[17] For the *n*-butane→isobutane isomerization on acidic zeolites, only indirect arguments based on the product distribution were obtained in favor of an intermolecular mechanism of this process (see, for example, ref. [21]). Derouane et al. argued for a monomolecular mechanism of *n*-butane isomerization on Pt/H-theta-1 zeolite.[15] However, the intramolecular pathway of *n*-butane isomerization, which is typical for Pt-promoted solid acid catalysts, is usually turned into the intermolecular pathway with unpromoted acid catalysts.[13,34]



Scheme 1. Possible pathways of the ^{13}C-label scrambling in *n*-butane and the isomerization to isobutane on zeolite H-ZSM-5 through a monomolecular mechanism. Symbol ● denotes the ^{13}C-labeled carbon atom.

Ex situ GC–MS analysis of the reaction products: To clarify the pathway (intra- or intermolecular) of the ^{13}C-label scrambling in *n*-butane, as well as the formation of isobutane and propane from *n*-butane, we have analyzed the products of the conversion of $[1\text{-}^{13}C]n$-butane on H-ZSM-5 by using GC–MS. The GC–MS analysis was performed after extracting the products from the catalyst with Et_2O. The sample for the GC–MS analysis corresponded to that exhibiting the ^{13}C MAS NMR spectrum after a reaction time of 120 min at 470 K (Figure 1c).

Figure 3 shows the mass spectra (the molecular ion region) of *n*-butane, isobutane, and propane extracted from zeolite H-ZSM-5 compared with mass spectra of unlabeled alkanes. The mass spectrum of *n*-butane released from the catalyst (Figure 3b) agrees with that obtained from the *n*-

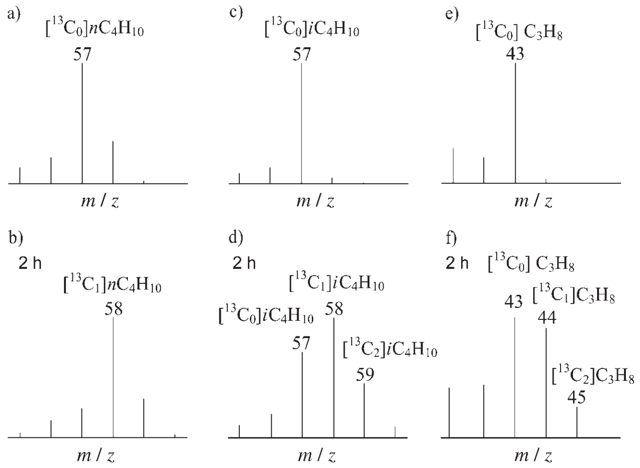
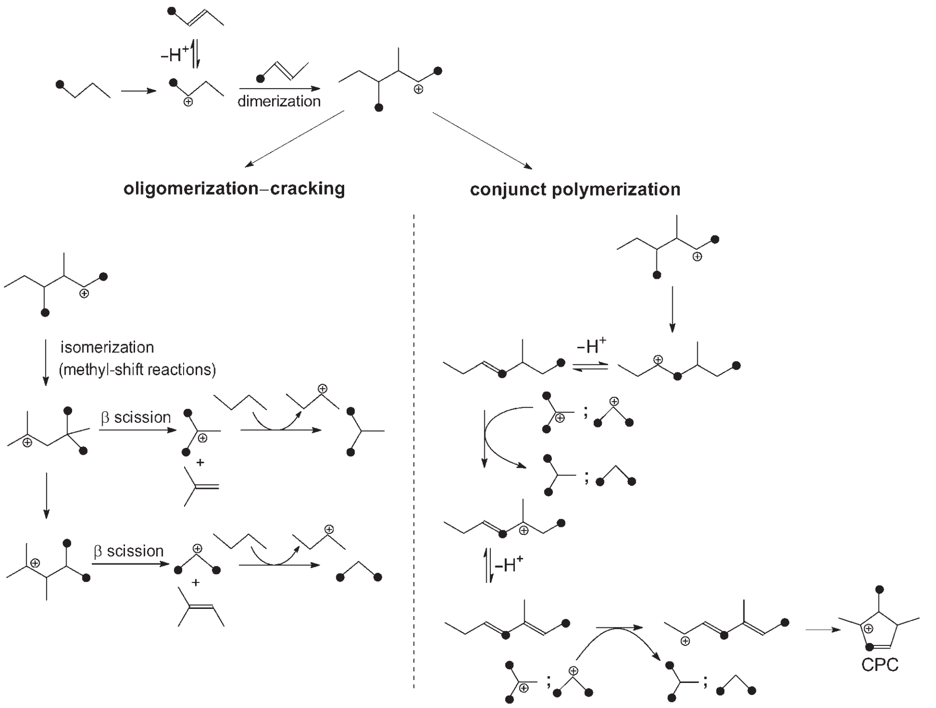


Figure 3. Mass spectra of *n*-butane (a, b), isobutane (c, d), and propane (e, f) formed by the conversion of $[1\text{-}^{13}C_1]nC_4H_{10}$ on zeolite H-ZSM-5 and extracted from the catalyst with Et_2O: a) the unlabeled nC_4H_{10} ($[^{13}C_0]nC_4H_{10}$) reference; b) *n*-butane extracted after 2 h of the reaction at 470 K; c) the unlabeled iC_4H_{10} ($[^{13}C_0]iC_4H_{10}$) reference; d) isobutane extracted after 2 h of the reaction at 470 K; e) the unlabeled C_3H_8 ($[^{13}C_0]C_3H_8$) reference; f) propane extracted after 2 h of the reaction at 470 K.

butane reference (Figure 3a), but is shifted by $m/z=1$ to higher m/z ratios. *n*-Butane extracted from the catalyst contained only single ^{13}C-labeled molecules. $C_4H_9^+$ ions with $m/z=58$, generated from $[^{13}C_1]nC_4H_{10}$, were the only species observed in the mass spectrum (see Figure 3b). On the other hand, based on the ^{13}C MAS NMR spectroscopy results, these *n*-butane molecules, analyzed after 2 h of the reaction, contain the ^{13}C labels at either the CH_3 or CH_2 positions. This means that the scrambling of the ^{13}C label in *n*-butane adsorbed onto H-ZSM-5 proceeds without changing the number of ^{13}C labels per molecule. This finding hints to the monomolecular mechanism of the ^{13}C-label scrambling. The observation of the ^{13}C-label scrambling in *n*-butane (adsorbed onto H-ZSM-5) through an intramolecular mechanism is indicative of the formation of a *sec*-butyl cation providing the label scrambling (Scheme 1), similar to the process in superacidic solutions.[31,32] Indeed, there is no alternative mechanism for the ^{13}C-label scrambling in alkanes or olefins so far, besides the scrambling in the carbenium ions formed from either alkanes or olefins.[35–37]



Scheme 2. Oligomerization–cracking and conjunct polymerization of *n*-butane on zeolite H-ZSM-5. The scheme rationalizes the formation of the double-labeled isobutane and propane molecules from the single-labeled *n*-butane. Symbol ● denotes the ^{13}C-labeled carbon atom.

The comparison of the mass spectrum of isobutane formed from $[1\text{-}^{13}C]n$-butane (Figure 3d) with that of unlabeled isobutane (Figure 3c) leads to the conclusion that, in addition to single-labeled isobutane ($[^{13}C_1]iC_4H_{10}$), both unlabeled ($[^{13}C_0]iC_4H_{10}$) and double-labeled ($[^{13}C_2]iC_4H_{10}$) molecules are generated. Indeed, according to their m/z ratio, the peaks with $m/z=57$, 58, and 59 correspond to $C_4H_9^+$ ions formed from $[^{13}C_0]iC_4H_{10}$, $[^{13}C_1]iC_4H_{10}$, and $[^{13}C_2]iC_4H_{10}$, respectively.

Analogously to isobutane, propane formed on zeolite H-ZSM-5 is identified in the mass-spectrum as the $C_3H_7^+$ ion and consists of unlabeled ($[^{13}C_0]C_3H_8$, $m/z=43$), single-labeled ($[^{13}C_1]C_3H_8$, $m/z=44$), and double-labeled ($[^{13}C_2]C_3H_8$, $m/z=45$) molecules (cf. Figure 3f and e). The formation of the double-labeled and unlabeled alkanes from the single-labeled *n*-butane can be rationalized only in terms of an intermolecular pathway of the *n*-butane conversion, including a dimerization step. This pathway provides the possibility for the incorporation of two ^{13}C labels into the hydrocarbon fragment, which could be a precursor of alkanes formed by β-scission and hydride-transfer reactions (Scheme 2). Unlabeled alkanes can be formed in a similar way from hydrocarbon precursors containing no labeled fragments. Thus, the present results confirm the earlier suggestion of an intermolecular mechanism for isobutane formation from *n*-butane on zeolite H-ZSM-5.[21]

The formation of isobutane, propane, and hydrogen-deficient species, such as cyclopentenyl cations and condensed aromatic compounds, from *n*-butane on zeolite H-ZSM-5 can be rationalized in terms of two processes: oligomerization–cracking and conjunct polymerization,[38–40] as depicted in Scheme 2. These processes involve a variety of stages including dimerization (oligomerization) of carbenium ions with equilibrated alkenes, isomerization of the dimer, β scission, hydride transfer from alkanes and oligomeric olefins (and, afterward, from dienes) to carbenium ions, and cyclization. The steps of the β scission in the oligomerization-cracking process led to a mixture of propane and isobutane. The olefins that are formed by this process are further involved in oligomerization steps, giving rise again to the alkanes and olefins.

Isopropyl and *tert*-butyl cations formed by β scission in the oligomerization-cracking process can abstract hydride ions not only from the initial *n*-butane, but also from the formed oligomers. This results in more hydrogen-deficient dienes and trienes, as well as alkanes. Trienes are further protonated and cyclized on the acidic zeolite. This intermolecular process, which is called conjunct polymerization,[38–40] gives rise to the stable CPC and an additional amount of propane and isobutane after a long reaction time. Conjunct polymerization provides a method for the formation of both the alkanes with two ^{13}C labels and ^{13}C-multilabeled CPC. The CPC only becomes detectable in the ^{13}C NMR spectra because of the ^{13}C labeling; otherwise, the ^{13}C CP/MAS NMR analysis would not be sensitive enough to detect the CPC, which forms in an extremely small concentration on the zeolite surface under the conditions of our experiment. The CPC species formed are converted further into condensed aromatic compounds.[41]

It should be noted in advance that the initial formation of the carbenium ion presented in Schemes 1 and 2 can occur by several ways on zeolite H-ZSM-5; these ways will be discussed later (see the Discussion section).

The product distribution for the *n*-butane conversion on zeolite H-ZSM-5, which is revealed by ^{13}C MAS NMR spectroscopy, appears to be similar to that typically observed earlier for conjunct polymerization of olefins and alkanes in concentrated sulfuric acid,[38–40] for olefins and alcohols on acidic zeolites,[14,27,42] as well as for *n*-pentane and *n*-butane conversion on sulfated zirconia.[16,17]

It should be emphasized that isobutane (as well as propane) is produced in the course of all stages of the conjunct-polymerization process rather than only through the pure oligomerization-cracking process (Scheme 2) observed earlier (e.g., for the *n*-butane isomerization on SZ).[17] Indeed, contrary to the *n*-butane isomerization on sulfated zirconia,[17,43] even in the initial period of the reaction, we do not observe the selective formation of isobutane; propane and isobutane appear simultaneously in the spectra (see Figures 1 and 4).

Kinetics of the *n*-butane conversion: To further clarify the mechanism of the *n*-butane activation and transformation on H-ZSM-5, we have monitored the kinetics of both the ^{13}C-label scrambling and the conversion of *n*-butane to isobutane and propane by using ^{13}C MAS NMR spectroscopy. Figure 4 shows the variation of the intensities of the ^{13}C MAS NMR signals of [1-^{13}C]*n*-butane, [2-^{13}C]*n*-butane, isobutane, and propane on zeolite H-ZSM-5 as a function of the reaction time. For a quantitative description of the observed kinetics, a simplified kinetic scheme was used (Scheme 3). This scheme includes only the initial *n*-butane and the main final reaction products, it does not reflect the detailed mechanism of the reaction suggested in Scheme 2, but allows us to derive the kinetic

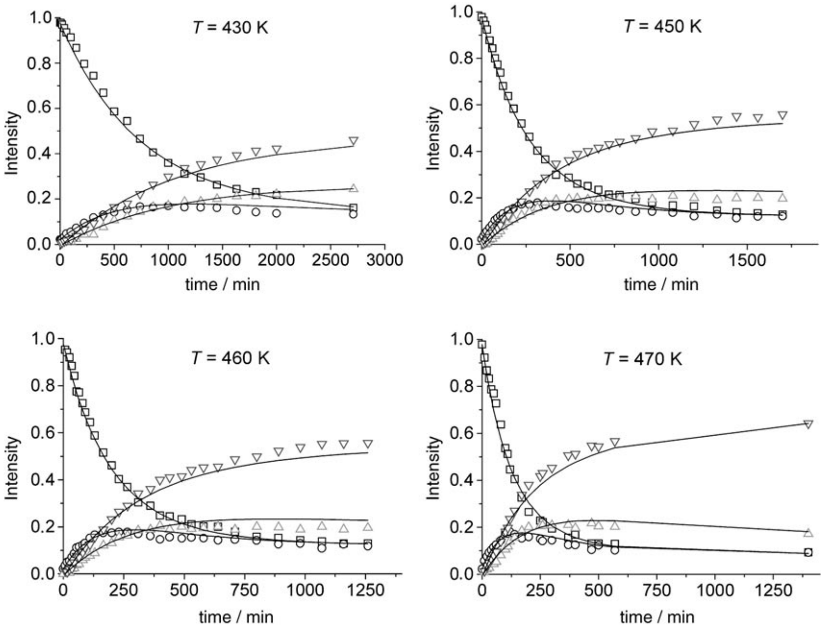
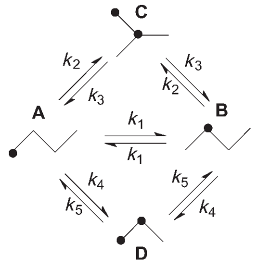


Figure 4. ^{13}C MAS NMR intensities of the signals of the initial *n*-butane and its conversion products formed on zeolite H-ZSM-5, plotted as a function of the reaction time: □, [1-^{13}C]*n*-butane (the signal at $\delta=14.5$ ppm); ○, [2-^{13}C]*n*-butane (the signal at $\delta=27.2$ ppm); △, isobutane (the signal at $\delta=25.1$ ppm); ▽, propane (the signals at $\delta=16.9$ and 18 ppm). The solid curves represent the fits of the experimental curves using the solution to Equations (1)–(4) with the rate constants given in Table 1.



Scheme 3. A simplified kinetic scheme suggested for the conversion of *n*-butane on zeolite H-ZSM-5. Symbol ● denotes the ^{13}C-labeled carbon atoms.

parameters of the reaction. **A** and **B** in Scheme 3 denote [1-^{13}C]*n*-butane and [2-^{13}C]*n*-butane, respectively. **C** is a double-labeled isobutane molecule and **D** is a double-labeled propane molecule. Both propane and isobutane are considered to be formed in parallel by the conjunct-polymerization process. There is no direct conversion of isobutane to propane. At the end of the reaction, the signals of *n*-butane do not disappear. This implies that *n*-butane can also be a product of the conjunct-polymerization process, similar to isobutane and propane. To emphasize the apparent equilibrium of *n*-butane with propane and isobutane, the rate constants k_3 and k_5 of imaginary reversible processes were introduced to the kinetic scheme.

Although the formation of isobutane and propane represents an intermolecular reaction, we assume for simplicity, first-order kinetic equations for the description of all the reaction steps. The following system of kinetic equations [Eqs. (1)–(4)] can be used to describe the scheme of chemical reactions and to show the dependence of the intensities (I) of the signals of **A**, **B**, **C**, and **D** as a function of the reaction time:

$$\frac{dI_{\mathrm{A}}}{dt} = -(k_1 + k_2 + k_4)I_{\mathrm{A}} + k_1 I_{\mathrm{B}} + k_3 I_{\mathrm{C}} + k_5 I_{\mathrm{D}} \tag{1}$$

$$\frac{dI_{\mathrm{B}}}{dt} = k_1 I_{\mathrm{A}} - (k_1 + k_2 + k_4)I_{\mathrm{B}} + k_3 I_{\mathrm{C}} + k_5 I_{\mathrm{D}} \tag{2}$$

$$\frac{dI_{\mathrm{C}}}{dt} = k_2 I_{\mathrm{A}} + k_2 I_{\mathrm{B}} - 2k_3 I_{\mathrm{C}} \tag{3}$$

$$\frac{dI_{\mathrm{D}}}{dt} = k_4 I_{\mathrm{A}} + k_4 I_{\mathrm{B}} - 2k_5 I_{\mathrm{D}} \tag{4}$$

The solution to these equations requires the use of the conservation equation [Eq. (5)]:

$$\mathbf{A} + \mathbf{B} + \mathbf{C} + \mathbf{D} = A_0 \tag{5}$$

in which A_0 corresponds to the initial concentration of all ^{13}C labels. This conservation should be fulfilled at any time of the reaction. We assume that the conservation [Eq. (5)] really does occur, because the loss of the total intensity of the ^{13}C spectrum (propane+butanes) due to the formation of CPC and aromatic compounds, detectable only by ^{13}C CP/MAS NMR spectroscopy, did not exceed 10% even at the end of the reaction. Therefore, we have used the ^{13}C MAS NMR intensities, normalized to the integrated intensity of the first recorded spectrum, for fitting the experimental kinetics and for deriving the apparent rate constants.

Table 1. Apparent rate constants of the ^{13}C-label scrambling (k_1) of *n*-butane and of the formation of isobutane (k_2) and propane (k_4) on zeolite H-ZSM-5, derived from ^{13}C MAS NMR monitoring the reaction kinetics under batch conditions.

Temperature [K]	$k_1 \times 10^3$ [min^{-1}]	$k_2 \times 10^3$ [min^{-1}]	$k_4 \times 10^3$ [min^{-1}]
430	0.45	0.27	0.44
450	1.4	0.8	1.2
460	1.9	1.0	1.6
470	2.9	1.6	2.6

The experimental curves describing the behavior of the ^{13}C MAS NMR intensities of species **A**, **B**, **C**, and **D** with time, were fitted according to the solutions to Equations (1)–(4) and using the values of the apparent rate constants given in Table 1. The apparent activation energies were determined by using Arrhenius plots of the found rate constants against the reaction temperature, as shown in Figure 5. The obtained kinetic data indicate that the ^{13}C-label scrambling in *n*-butane is performed with activation energy of approximately 75 kJ mol^{-1} (E_1, Figure 5), which is in good agreement with the value of $E_a = 71$ kJ mol^{-1} determined for the monomolecular ^{13}C-label scrambling in *n*-butane adsorbed onto sulfated zirconia.[44] The activation energy value of approximately 71 kJ mol^{-1} (E_2, Figure 5) obtained for the isobutane formation is rather close to the activation energy value of 58–63 kJ mol^{-1} reported earlier for the isobutane formation by a bimolecular reaction mechanism on solid acid catalysts.[20,44,45] The apparent activation energy of approximately 71 kJ mol^{-1} (E_4, Figure 5) observed for the propane formation is much lower in comparison with the value determined for the propane formation from *n*-butane on zeolite H-ZSM-5 ($E_a = 133$ kJ mol^{-1}) at higher temperatures ($T > 700$ K).[2]

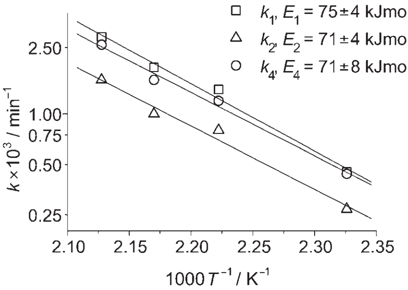


Figure 5. Arrhenius plot of the rate constants (k) given in Table 1 for the ^{13}C-label scrambling in *n*-butane (□) and the formation of isobutane (△) and propane (○) on zeolite H-ZSM-5.

Discussion

Both the ^{13}C-label scrambling in the *n*-butane molecule and the conversion of *n*-butane into propane and isobutane through oligomerization–cracking and conjunct polymerization require the initial formation of a carbenium ion from the alkane. For acidic zeolite H-ZSM-5, the carbenium ions can be created in three ways: 1) dehydrogenation of carbonium ions formed from an alkane by its protonation with a Brönsted acid site, 2) protonation of the small quantity of admixed olefins, and 3) hydride abstraction from an alkane with the aid of a Lewis acid site. We cannot rule out any of these three possibilities for the initial carbenium ion formation.

Indeed, despite the earlier postulated possibility of protonation of the alkanes by Brönsted acid sites and further carbenium ion formation through a dehydrogenation/cracking process only at temperatures above 700 K,[23] the possibility of alkane protonation and a dehydrogenation/cracking reaction at temperatures as low as 423 K has been demonstrated by the reaction of propane and isobutane with carbon monoxide on H-ZSM-5 in a microreactor under static conditions.[46] So, under the conditions of our experiment, a small quantity of the initial cation can be formed by way of *n*-butane protonation and dihydrogen evolution. The quantity of the evolved dihydrogen is apparently too small to be detectable with ^{1}H MAS NMR spectroscopy.

A probable admixture of any olefin in [1-^{13}C]*n*-butane used for the reaction can also initiate the formation of the carbenium ions. A cation formed by protonation of an olefin using Brönsted acid sites can further abstract a hydride ion from [1-^{13}C]*n*-butane, offering the *sec*-butyl cation, which becomes further involved in the scrambling and dimerization reaction.

The third possibility for the initial carbenium ion formation from *n*-butane might be a hydride abstraction by the Lewis acid sites of the zeolite catalyst. A small fraction of Lewis acid sites should exist in the zeolite, as found from the ^{27}Al MAS NMR of the zeolite sample which showed the presence of extra-framework aluminum (octahedral) species with the amount not exceeding 0.5 % of the total aluminum content (tetrahedral + octahedral). Lewis acid sites can be generated from octahedral aluminum[47–50] during the calcination procedure. We consider this possibility less probable. Indeed, the cation generated by this mechanism can provide the ^{13}C-label scrambling in *n*-butane, but it is not able to progress to oligomerization–cracking. The stage of the cation dimerization cannot be realized by its interaction with the equilibrated olefin, in so far as there are no generated active sites in the zeolite that could provide cation deprotonation and offer an olefin. Thus, of the three possibilities for cation generation, the third one is considered to be least probable.

The similarity of the apparent activation barriers of both the ^{13}C-label scrambling and the formation of isobutane and propane observed for the *n*-butane conversion on H-ZSM-5 at 430–470 K, allows one to assume that all these processes proceed with a common rate-determining step. The rate-determining step seems to be the intermolecular hydride transfer between the initial *n*-butane and the primarily initiated carbenium ion. Indeed, the activation energy of the hydride-transfer reaction of alkanes can be as high as 75 kJ mol^{-1} for this reaction both in superacidic solutions[31] and on solid acid catalysts,[51] which is close to the activation barriers observed in this study.

The hydride-transfer reaction provides *sec*-butyl cations, which are common intermediates for both monomolecular ^{13}C-label scrambling (Scheme 1) and the formation of isobutane and propane through intermolecular oligomerization-cracking and conjunct-polymerization processes (Scheme 2).

The rate-determining role of the hydride transfer from the alkane could account for the higher activation energy of 75 kJ mol^{-1} for the ^{13}C-label scrambling in *n*-butane on zeolite H-ZSM-5 in comparison with that of the ^{13}C-label scrambling in the *sec*-butyl cation in superacidic solution, which was found to be only 31 kJ mol^{-1}.[35] One can not exclude either the possibility that both the hydride-transfer reaction and the carbon scrambling in the *sec*-butyl cation contribute to the apparent activation energy of the ^{13}C-label scrambling in *n*-butane on H-ZSM-5. In ref. [52] it was estimated that the true activation energy of the label scrambling (E_a^{scr}) in the *sec*-butyl cation on zeolite catalysts could be about 105 kJ mol^{-1}. A possible energy diagram for this reaction path, which can be suggested in the case of the ^{13}C-label scrambling, is presented in Figure 6. It includes the adsorption of *n*-butane onto zeolite H-ZSM-5 ($\Delta H_{ads} \approx 62$ kJ mol^{-1}[53]), the hydride transfer ($E_a^{ht} = 63$ kJ mol^{-1}[54]), as well as the ^{13}C-label scrambling in the *sec*-butyl cation.[52] This reaction pathway seems to account for the values of the apparent activation energy of 75 kJ mol^{-1} for the ^{13}C-label scrambling observed in the present study. However, further theoretical investigations are needed to rationalize the high value of the activation energy for the carbon scrambling in the *sec*-butyl cation on zeolite catalysts in comparison with superacidic solutions.

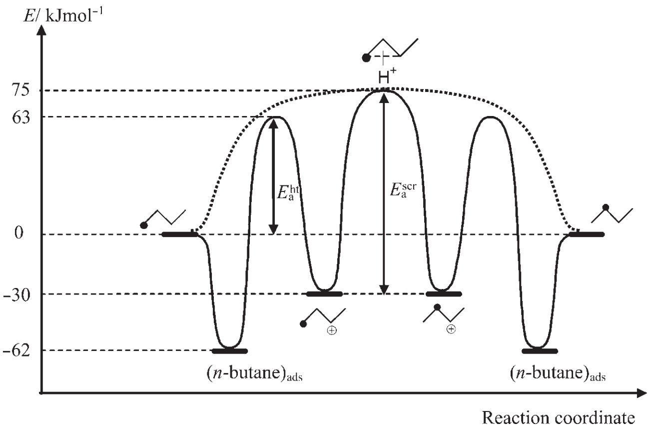


Figure 6. Energy diagram for the ^{13}C-label scrambling in *n*-butane adsorbed onto zeolite H-ZSM-5.

Conclusions

By using both ^{13}C MAS NMR spectroscopy and GC–MS analysis, the following conclusions on the conversion of *n*-butane, selectively labeled with a ^{13}C isotope on the CH_3 group, on zeolite H-ZSM-5 at 430–470 K have been drawn: The conversion of *n*-butane proceeds through two parallel processes—the ^{13}C-carbon atom scrambling in *n*-butane results in a migration of the selective ^{13}C label from the methyl group of *n*-butane to its methylene group, and the formation of isobutane and propane simultaneously with the generation of alkyl-substituted cyclopentenyl cations and condensed aromatic compounds. The distribution of the ^{13}C labels in propane, *n*-butane, and isobutane obtained from the mass spectra analyses of these products provide evidence that the scrambling of the ^{13}C label in *n*-butane represents a monomolecular reaction, whereas the formation of isobutane and propane proceeds through an intermolecular mechanism. The latter can be represented by two processes: oligomerization–cracking and conjunct polymerization. The close values of the apparent activation energies of the ^{13}C-label scrambling and the formation of isobutane and propane, determined by means of ^{13}C MAS NMR spectroscopy, indicate that the intermolecular hydride-transfer reaction between the primarily formed carbenium ion and *n*-butane can be a rate-determining step of the *n*-butane conversion on zeolite H-ZSM-5 in this temperature range.

Experimental Section

Materials: Zeolite H-ZSM-5 ($n_{Si}/n_{Al}=25$) was synthesized according to ref. [55] and characterized by using X-ray powder diffraction, chemical analysis, and ^{29}Si and ^{27}Al MAS NMR spectroscopy. *n*-Butane with a ^{13}C label on one of the methyl groups ([1-^{13}C]*n*-butane, 99 % ^{13}C isotope enrichment) was purchased from ISOTEC Inc. and was used without further purification. For the GC–MS analysis, propane, *n*-butane, and isobutane with purity higher than 99 % were purchased from Aldrich and were not purified further.

Preparation of the samples: A zeolite sample (16 mg) was placed into a glass cylindrical tube (3.0 mm outside diameter), then calcined at 673 K in air for 2 h, and further calcined under vacuum ($p \leq 10^{-3}$ Pa) for 2 h. Subsequently, [1-^{13}C]*n*-butane (400 μmol g^{-1}) was adsorbed onto the H-ZSM-5 sample under vacuum at the temperature of liquid nitrogen (ca. -195 °C). After this, the glass tube (length ca. 10 mm), containing *n*-butane adsorbed on the zeolite, was sealed. The dimensions of the sealed glass tube were chosen to fit in a 4 mm zirconia rotor for the NMR analysis. About 100 samples were prepared to follow the kinetics in the temperature range of 430–470 K, 20–30 samples being used at each temperature point. Each sample was heated for certain time durations at each definite reaction temperature to fit a time interval from a few minutes to 45 h.

NMR spectroscopy: The reaction products of the *n*-butane conversion on H-ZSM-5 were analyzed in the sealed glass tubes in situ by using ^{13}C MAS NMR spectroscopy. The ^{13}C NMR spectra, with high-power proton decoupling and magic angle spinning (MAS) and with or without cross-polarization (CP), were recorded at 100.613 MHz (magnetic field of 9 tesla) on a Bruker MSL-400 spectrometer at 296 K. The following conditions were used for the spectra recorded with CP: The proton high-power decoupling field was 11.7 G according to the length of the $\pi/2$ pulse of 5.0 μs. The contact time was 5 ms under the Hartmann–Hahn matching conditions of 50 kHz, and the delay time between the scans was 3 s. The ^{13}C MAS NMR spectra were recorded with single-pulse excitation with $\pi/4$ pulses of 2.5 μs duration, and a recycle delay of 3 s. The sample spinning rate was 3–7 kHz. 400–800 scans were collected for each ^{13}C MAS NMR spectrum and 25000 scans for each ^{13}C CP/MAS NMR spectrum. The ^{13}C chemical shifts (δ) of the adsorbed organic species were determined with respect to TMS as an external-shift standard with an accuracy of $\Delta\delta = \pm 0.5$ ppm.

GS–MS analysis: The reaction products formed by the conversion of [1-^{13}C]*n*-butane on zeolite H-ZSM-5 were extracted from the catalyst with Et$_2$O and analyzed by using a Varian CP-3800 gas chromatograph equipped with a PLOT fused silica capillary column (length = 30 m, inner diameter = 0.32 mm). The column was filled with CP-PoraPLOT Q-HT as the stationary phase forming a film 10 μm thick. The temperature program started at 308 K with a heating rate of 8 K min^{-1}. The detector was a mass spectrometer Varian Saturn 2000, which scanned from $m/z = 10$ to 650 with a cycle time of 0.5 s.

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