

Kinetics of H/D Exchange for *n*-Butane on Zeolite H-ZSM-5 Studied with ^1H MAS NMR In Situ

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The kinetics of hydrogen (H/D) exchange between Brønsted acid sites of zeolite H-ZSM-5 and deuterated *n*-butanes (*n*-butane- d_{10} and *n*-butane-1,1,1,4,4,4- d_6) has been monitored by ^1H magic-angle spinning (MAS) NMR spectroscopy in situ within the temperature range of 423–448 K. The initial part of the kinetics is defined mainly by the hydrogen exchange, whereas the final part is strongly influenced by the chemical transformation of the alkane. Analysis of the initial part has been performed on the basis of consecutive, parallel, and cyclic kinetic schemes of the H/D exchange. It has been found that both the methyl and methylene groups of *n*-butane are directly involved in the exchange with acidic SiOHAl groups of the zeolite. No intramolecular hydrogen exchange between the methyl and the methylene groups of the adsorbed *n*-butane has been detected. Similar rates of the direct exchange of either the methyl or methylene group with acidic SiOHAl groups and the apparent activation energy of 108 kJ mol⁻¹ are rationalized in terms of the carbonium ion mechanism of the exchange with the involvement of a pentacoordinated carbon atom in a transition state.

1. Introduction

A simple reaction of hydrogen (H/D) exchange between small alkanes and solid acid catalysts provides the pathway for understanding the alkane C–H bond activation by the catalyst active sites.¹ No wonder that many efforts with both theoretical and experimental methods were made to clarify the peculiarities of mechanisms of the H/D exchange for linear and branched alkanes.^{2–26}

While there is not any alternative to the carbonium ion mechanism of the exchange for methane^{2,3} and ethane⁶ with Brønsted acid sites, propane can be alternatively involved in the exchange with either the carbonium¹⁸ or carbenium ion¹⁷ intermediate or transition state. Regioselectivity into the methyl groups and low activation energy (~ 50 kJ mol⁻¹) of the exchange for isobutane have been formerly rationalized in terms of involvement of carbenium ion intermediates.^{5,13} Later on, a direct exchange for isobutane was claimed,^{21,22} despite inconsistency of the theoretical estimations of the activation energy for the direct exchange among different research groups.^{20,22,26}

For *n*-butane, a priori a direct H/D exchange for both the methyl and methylene groups of the linear alkane was assumed, and the regioselectivity of the exchange into either CH₃ or CH₂ groups was not analyzed.^{4,8} However, the analysis of regioselectivity of H/D exchange, which is sometimes observed for C₃ and C₄ alkanes,^{5,13,17,23} can be crucial for clarifying the peculiarities of alkane activation by the solid acid catalysts and establishing the mechanism of the exchange.

^1H magic-angle spinning (MAS) NMR can discriminate between different hydrocarbon fragments (e.g., CH₃ and CH₂ groups) of an alkane molecule in the adsorbed state at the temperature of reaction.^{9,13,17,18} Therefore, in situ ^1H MAS NMR

monitoring of the H/D exchange reaction allows the identification of the regioselectivity of the exchange and can differentiate among various possible mechanisms of the exchange, if carbonium or carbonium ions as intermediates or transition states are involved.^{9,13,18,23}

In this paper, we focus on the analysis of the peculiarities of the kinetics of H/D exchange for different hydrocarbon fragments of *n*-butane molecule by ^1H MAS NMR spectroscopy in situ in order to gain insight into the mechanism of the exchange for this linear alkane on acidic zeolite H-ZSM-5.

2. Experimental Section

2.1. Materials and Sample Preparation. The template-free synthesized ammonium form of zeolite ZSM-5 purchased from Tricat Zeolites was converted into H-form by the procedure described in ref 27. ^{29}Si MAS NMR analysis²⁸ revealed the Si/Al ratio to be equal to 13.2. ^{27}Al MAS NMR has shown the absence of either extra framework aluminum atoms or hexacoordinated aluminum atoms. The quantity of the acidic SiOHAl groups of 1200 $\mu\text{mol g}^{-1}$, estimated with the use of an adsorbed internal reference (benzene), was in a good accordance with the expected quantity based on the found Si/Al ratio.

n-Butane- d_{10} (99% D) and *n*-butane-1,1,1,4,4,4- d_6 (99% D) (*n*-butane- d_6) were purchased from Aldrich Chemical Co. Inc. The purity of both reagents was checked by gas chromatography mass spectrometry (GC-MS). No impurities higher than the detection threshold (20 ppm) were observed for *n*-butane- d_{10} . It has been found that *n*-butane- d_6 contains 2.0% ethane and 0.6% propane, with both impurities being deuterated. No olefin impurities higher than the detection threshold (20 ppm) were detected. However, the analysis of kinetics of the H/D exchange with *n*-butane- d_6 has shown that there should be a trace quantity of olefin present in this alkane, affecting the kinetics of the exchange (vide infra). So, we additionally purified *n*-butane- d_6 and *n*-butane- d_{10} from the possible admixed olefins by several cycles of adsorption/desorption (at 343–373 K) on zeolite

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TABLE 1: Exchange Reactions Used for Simulating the Kinetics of the H/D Exchange for *n*-Butane on H-ZSM-5

reaction number	exchange reaction	equilibrium constant K_{eq}	rate constant k
1	$CD_3 + OH \rightleftharpoons CD_2H + OD$	3	k_{CH_3}
2	$CD_2H + OH \rightleftharpoons CDH_2 + OD$	1	k_{CH_3}
3	$CDH_2 + OH \rightleftharpoons CH_3 + OD$	1/3	k_{CH_3}
4	$CD_2 + OH \rightleftharpoons CDH + OD$	2	k_{CH_2}
5	$CDH + OH \rightleftharpoons CH_2 + OD$	1/2	k_{CH_2}
6	$CD_2H + CD_2 \rightleftharpoons CDH + CD_3$	2/3	k_{intra}
7	$CDH_2 + CD_2 \rightleftharpoons CH_2 + CD_3$	1/3	k_{intra}
8	$CH_3 + CD_2 \rightleftharpoons CH_2 + CD_2H$	3	k_{intra}
9	$CD_2H + CDH \rightleftharpoons CH_2 + CD_3$	1/6	k_{intra}
10	$CDH_2 + CDH \rightleftharpoons CH_2 + CD_2H$	1/2	k_{intra}
11	$CH_3 + CDH \rightleftharpoons CH_2 + CDH_2$	3/2	k_{intra}
12	$CDH_2 + CD_2 \rightleftharpoons CDH + CD_2H$	2	k_{intra}
13	$CH_3 + CD_2 \rightleftharpoons CDH + CDH_2$	6	k_{intra}

mordenite (H-MOR) activated under vacuum, similar to the case of the studied zeolite H-ZSM-5.

The samples for NMR measurements were prepared by heating 60 mg of the zeolite sample in glass tubes of 5.5 mm outer diameter, which fit the internal diameter of the NMR rotor. For activation of the zeolite, the temperature was increased at the rate of 10 K h⁻¹ under vacuum starting from room temperature. The samples were further maintained at 673 K for 24 h under vacuum (less than 10⁻² Pa). The loading was further performed at room temperature with 2 molecules per unit cell (ca. 300 μmol g⁻¹) of *n*-butane, and the sample was further sealed off (12 mm length of the glass tube).

2.2. NMR Measurements. ¹H MAS NMR measurements were performed on a Bruker Avance 400 spectrometer at 423–448 K and a rotation frequency of 3 kHz for the 7 mm rotor with the inserted sealed glass tube. ¹H NMR spectra were recorded by using a Hahn-echo pulse sequence (π/2-τ-π-τ-acquisition), where τ equals to one rotor period (333 μs). The duration of the excitation pulse (π/2) was 4.5 μs. Twenty-four scans were accumulated with a 4–6 s recycle delay. The time interval for successive recorded spectra during the kinetics measurements ranged from 5 to 30 min in dependence of temperature and the rate of the protium transfer from the zeolite SiOHAl groups to the deuterated alkane molecules. The accuracy of determination of the relative line position with respect to the external standard tetramethylsilane (TMS) was 0.02 ppm.

The sample temperature was controlled by the Bruker BVT-1000 variable-temperature unit. The calibration of the temperature of the sample inside the rotor was made with an accuracy of ±2 K by means of lead nitrate as ²⁰⁷Pb MAS NMR chemical shift thermometer.²⁹

2.3. Kinetics Modeling. The initial parts of the kinetic curves, which corresponded mainly to the H/D exchange, were used for the analysis, since the obtained kinetic curves exhibited a rather complicated form (vide infra). They have been simulated on the basis of the reactions shown in Table 1. The reactions describe a consecutive hydrogen exchange of the methyl and methylene groups of *n*-butane with protons of acidic groups of the zeolite (reactions 1–5 in Table 1) as well as the intramolecular hydrogen scrambling between CH₂ and CH₃ groups of *n*-butane (reactions 6–13 in Table 1). The rate constants were supposed to be equal for reactions of the same type; that is, 13 reactions from Table 1 were characterized by three rate constants (k_{CH_3} , k_{CH_2} , k_{intra}). The equilibrium constants take into account the statistical factors which are caused by a particular distribution of hydrogen isotopes. The concentration of protium in all reagents and products, that is, in the methyl groups (CH₃D_{3-*k*}), the methylene groups (CH₂D_{2-*l*}), and hydroxyl groups (OH and

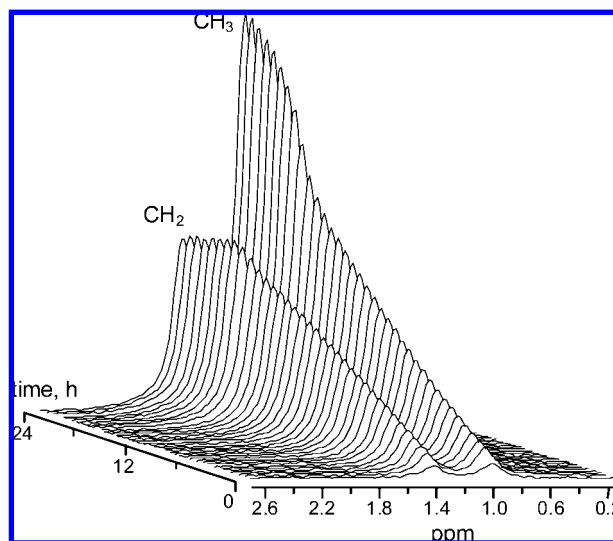


Figure 1. Stack plot of ¹H MAS NMR spectra of *n*-butane-*d*₁₀ adsorbed on H-ZSM-5. *T* = 438 K. The first spectrum (bottom) was recorded 20 min and the last one (top) 24 h after the reaction start. Time interval for two successive spectra is 40 min.

OD), was calculated by the Runge–Kutta integration method.³⁰ The details of the kinetics modeling can be found in refs 18 and 25.

3. Results and Discussion

Figure 1 shows a stack plot of ¹H MAS NMR spectra of *n*-butane-*d*₁₀ adsorbed on H-ZSM-5 in dependence on the reaction time. The intensities of two signals from CH₃ (1.0 ppm) and CH₂ groups (1.4 ppm) of *n*-butane slowly increase with time for the first 20 h of the reaction of the H/D exchange due to transfer of protium from the zeolite SiOHAl groups to both the methyl and methylene groups of the alkane. Simultaneously, the broad signal from the SiOHAl groups of the zeolite at ~4.5 ppm loses its intensity (not shown). The behavior of signals of CH₃ and CH₂ groups with time significantly changes ~20 h after the reaction start: a drastic increase of the signal intensity is observed for the methyl groups, whereas the intensity of the methylene groups decreases.

For the reaction of the H/D exchange between *n*-butane-*d*₁₀ and SiOHAl groups, the expected ratio between the intensities of the methyl and methylene groups in *n*-butane should be 3:2 at the end of the reaction (the condition of equilibrated distribution of protium among the acidic OH groups and the alkane). However, the final ratio between the intensities of the methyl and methylene groups was found to be 2.0–2.4 (see Figure 2). This is essentially different from the expected equilibrium value of 3:2.

n-Butane is known to undergo oligomerization-cracking, dehydrogenation, and isomerization on zeolite H-ZSM-5.^{4,8,31–33} Isobutane and propane are the main products under the conditions of a closed batch reactor.³⁴ The formation of the products of *n*-butane chemical transformation, propane and isobutane, implies that the amount of the methyl groups should increase at the expense of the methylene groups. Moreover, the formed isobutane is easily involved in the H/D exchange even at 323 K.¹³ The fast H/D exchange of the methyl groups of the formed deuterated isobutane (exhibiting a similar chemical shift at 1.0 ppm as that for CH₃ of *n*-butane) can reasonably rationalize a sharp growth of intensity of the signal at 1.0 ppm after 20 h of the reaction duration. The sharp increase of the intensity of the

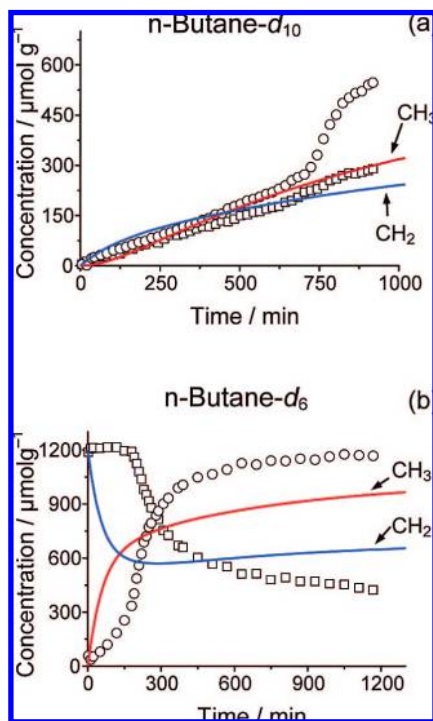


Figure 2. Simulation (solid curves) of the experimental kinetics of the H/D exchange for the methyl (○) and the methylene (□) groups of butane-*d*₁₀ (a) and butane-*d*₆ (b) on H-ZSM-5 in accordance to the consecutive kinetic scheme. *T* = 443 K. Rate constants are $k_{\text{CH}_2} = 1.17 \times 10^{-7} \text{ g } \mu\text{mol}^{-1} \text{ min}^{-1}$ and $k_{\text{intra}} = 1 \times 10^{-5} \text{ g } \mu\text{mol}^{-1} \text{ min}^{-1}$.

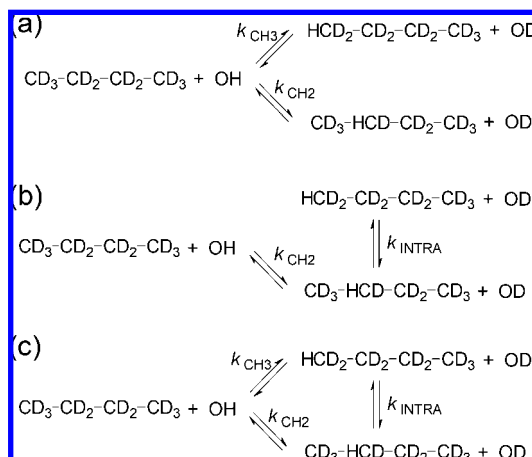
methyl groups only after 20 h of the reaction obviously indicates a prolonged induction period for the process of *n*-butane chemical transformation by oligomerization-cracking within the temperature range of 423–448 K. A prolonged induction period provides a confirmation for the presence of only a very small amount of admixed olefins in the used deuterated butanes, which could initiate a chemical conversion of *n*-butane.^{35,36} The presence of an induction period for *n*-butane chemical conversion was also confirmed by ¹³C MAS NMR measurements. Hydrocarbons other than initial deuterated *n*-butanes were not observed until the end of the induction period, which has a similar duration to that found from the kinetics of hydrogen exchange. Isobutane and propane were found by ¹³C MAS NMR as the main products of *n*-butane oligomerization-cracking, while isopentane and aromatics were formed in essentially less amounts, similar to the earlier findings for ¹³C-labeled *n*-butane.³⁴ Following the induction period, the degree of *n*-butane chemical conversion was estimated to be 30–75% depending on the final points of kinetics at different temperatures.

So, the kinetics of H/D exchange for *n*-butane consists of two parts. During the initial 20 h of the reaction (*n*-butane-*d*₁₀ at 438 K), the kinetics is defined mainly by H/D exchange between the alkane and the zeolite acidic OH groups, with the contribution from the chemical transformation being negligible. After 20 h of the reaction, an essential contribution to kinetics is provided by the H/D exchange of the products of *n*-butane-*d*₁₀ chemical conversion (mainly, isobutane).^{13,34} The exchange with another product of *n*-butane conversion, propane, is extremely slow at 423–448 K.^{9,37}

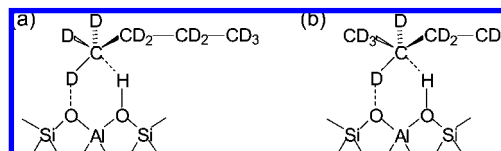
3.1. Analysis of Kinetic Schemes for the H/D Exchange.

The analysis of initial part of the kinetics, which corresponds to the H/D exchange of *n*-butane with the zeolite SiOHAl groups, has been performed within the frames of parallel, cyclic, and consecutive schemes of the exchange (Scheme 1). The

SCHEME 1: Parallel (a), Consecutive (b), and Cyclic (c) Schemes for the Possible Mechanisms of the H/D Exchange for *n*-Butane on H-ZSM-5 Zeolite



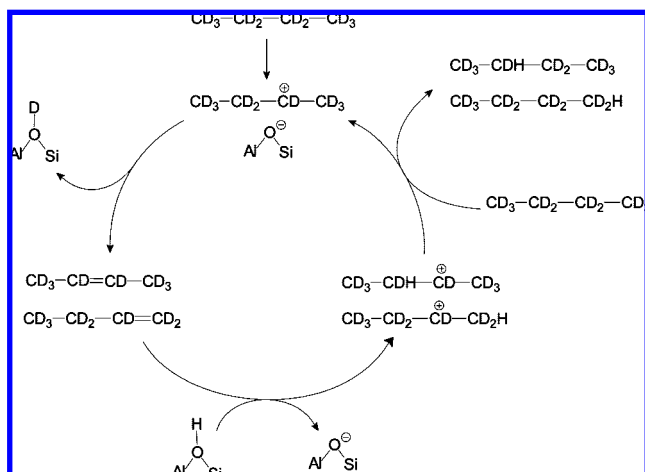
SCHEME 2: Transition States for the Direct H/D Exchange between the CD₃ Groups (a) and the CD₂ Groups (b) of *n*-Butane-*d*₁₀ and SiOHAl Sites of H-ZSM-5 by the Carbonium Ion Mechanism



temperature dependence of experimental kinetics, which offered the activation energies for the H/D exchange, was investigated in a rather narrow temperature range of 423–448 K, because the contribution from the chemical conversion to the experimental kinetics was negligible only at temperatures below 448 K.

The parallel scheme enables an exchange of both the methyl and methylene groups of *n*-butane with involvement of carbonium or carbenium ion mechanisms. The carbonium ion mechanism implies that both the methyl and the methylene groups are directly involved in the exchange with the acidic OH groups through the intermediate formation of pentacoordinated carbon atoms in a transition state as shown in Scheme 2. The carbenium ion mechanism implies the intermediate formation of the *sec*-butyl cation from *n*-butane, its subsequent deprotonation to form *n*-butene-1 and *n*-butene-2, and further reprotonation of the butenes to give again *sec*-butyl cation, enriched with protium in the methyl and methylene groups (Scheme 3). Only fast interconversion of the intermediate butenes involving acidic OH groups³⁸ or fast hydrogen scrambling via a protonated cyclopropane in protium enriched butyl cation³⁹ can provide a transfer of the protium from the acidic OH groups of the zeolite into both the methyl and methylene groups of deuterated *n*-butane.

The consecutive scheme describes a carbenium ion mechanism, for which a thermodynamically more stable *n*-butene-2⁴⁰ is preferentially formed following the *sec*-butyl cation deprotonation. A further reprotonation of the *n*-butene-2 enriches the methylene groups of the *sec*-butyl cation with protium. This should provide a regioselective exchange⁵ into the methylene group of *n*-butane by hydride ion transfer reaction with *n*-butane-*d*₁₀ (Scheme 3). However, an additional possible stage of hydrogen atom scrambling in the butyl cation offers a transfer of protium also into the methyl groups. So both the methyl and the methylene groups could be involved in the exchange.

SCHEME 3: Catalytic Cycle Which Could Provide a Carbenium Ion Mechanism of the H/D Exchange for *n*-Butane-*d*₁₀ on Acidic Zeolite

TABLE 2: Duration of the Induction Period τ_{ind} for the Chemical Transformation of *n*-Butane-*d*₁₀ and *n*-Butane-*d*₆ on H-ZSM-5

<i>T</i> (K)	τ_{ind} (min)	
	<i>n</i> -butane- <i>d</i> ₁₀	<i>n</i> -butane- <i>d</i> ₆
423	4200	1380
428	3140	520
433	1690	
438	1070	325
443	740	170
448	340	

The cyclic kinetic scheme implies the existence of an additional stage of intramolecular exchange between the methyl and methylene groups for the carbonium ion mechanism. This intramolecular transfer of hydrogen atoms can be realized with an intermediate formation of *sec*-butyl cations, in which the hydrogen atom scrambling occurs.

Consecutive Scheme of Exchange. Figure 2 shows experimental results and kinetics simulations on the basis of the consecutive scheme of the exchange. Reactions 4–13 from Table 1 were taken into account for simulations. It can be seen from Figure 2 that simulated curves correspond fairly satisfactorily to experimental kinetics for *n*-butane-*d*₁₀, when $k_{\text{intra}} = 85 \times k_{\text{CH}_2}$, that is, when intramolecular exchange is essentially faster than the exchange of the acidic OH groups with methylene groups. For *n*-butane-*d*₆, fast intramolecular exchange should provide a fast decrease of the intensity of the signal from the methylene (CH₂) groups (Figure 2b). However, the experimental kinetics show that, for the first 170 min of the reaction, when only the H/D exchange takes place (Table 2), the intensity of the methylene groups decreases only faintly. This does not support the existence of the stage of fast intramolecular exchange. So, the exchange cannot be rationalized in the frame of the consecutive scheme.

Parallel Scheme of Exchange. Similar to the analysis of the consecutive scheme, only the starting regions of the kinetic curves during the induction period for chemical conversion (Table 2), which describe mainly the H/D exchange of *n*-butane with the zeolite acidic OH groups, were simulated based on reactions 1–5 from Table 1. The simulated curves in Figures 3 and 4 are in good agreement with the experimental kinetics for both *n*-butane-*d*₁₀ and *n*-butane-*d*₆. We obtain approximately equal rate constants k_{CH_3} and k_{CH_2} for variously deuterated

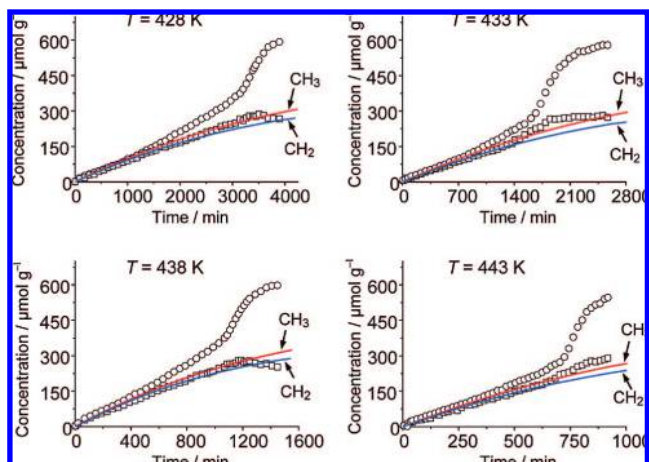
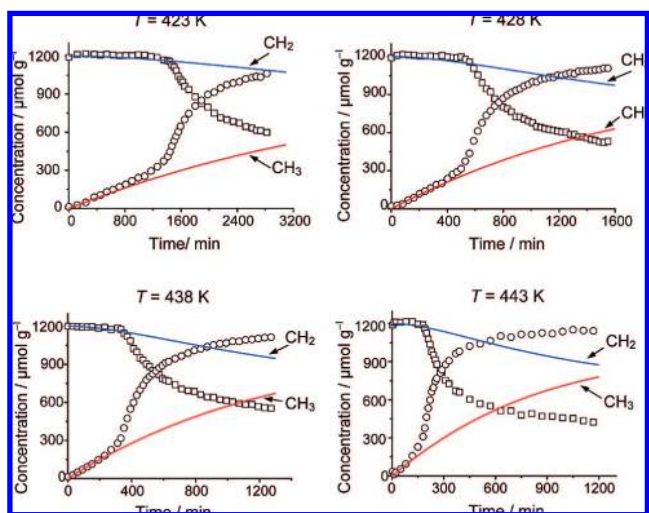

Figure 3. Simulations (solid curves) of the experimental kinetics of the H/D exchange for the methyl (O) and methylene (□) groups of *n*-butane-*d*₁₀ on H-ZSM-5 in accordance to the parallel kinetic scheme. The rate constants, which correspond to the solid curves, are given in Table 3.

Figure 4. Simulation (solid curves) of the experimental kinetics of the H/D exchange for the methyl (O) and the methylene (□) groups of *n*-butane-*d*₆ on H-ZSM-5 in accordance to the parallel kinetic scheme. The rate constants, which correspond to the solid curves, are shown in Table 3.

TABLE 3: Rate constants of the H/D exchange for the methyl and methylene groups of *n*-butane-*d*₁₀ and *n*-butane-*d*₆ on H-ZSM-5, based on the parallel scheme of the exchange.

<i>T</i> (K)	<i>n</i> -butane- <i>d</i> ₁₀		<i>n</i> -butane- <i>d</i> ₆	
	$k_{\text{CH}_3}^a$	$k_{\text{CH}_2}^a$	$k_{\text{CH}_3}^a$	$k_{\text{CH}_2}^a$
423	1.4	1.3	3.0	2.7
428	1.5	1.4	8.0	8.0
433	2.1	1.9		
438	2.6	2.6	11.0	11.0
443	5.0	4.7	16.0	16.0
448	6.6	6.2		

^a $\times 10^7$, g $\mu\text{mol}^{-1} \text{min}^{-1}$.

n-butanes (Table 3). This means that there is a consistency of the kinetics of the exchange for two differently deuterated *n*-butanes within the frame of the parallel scheme of the exchange. The apparent activation energy (E_a) for the exchange was estimated from the Arrhenius plot to be about 108 kJ mol^{−1} for both the methyl and the methylene groups of *n*-butane-*d*₁₀

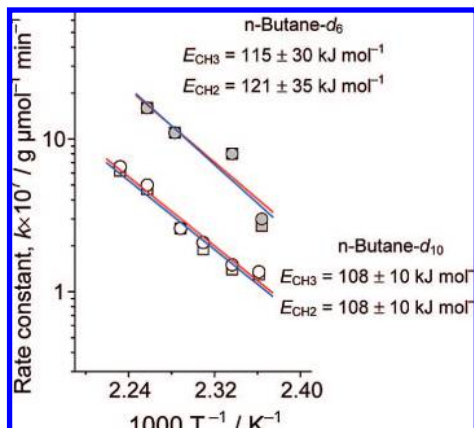


Figure 5. Arrhenius plots of the H/D exchange for the methyl (empty circle, gray filled circle) and methylene (empty square, gray filled square) groups of *n*-butane-*d*₁₀ and *n*-butane-*d*₆ on H-ZSM-5. Rate constants were determined based on the parallel scheme of the exchange.

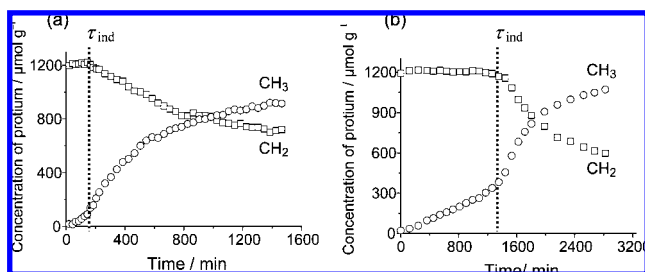


Figure 6. Kinetic curves of the H/D exchange for the methyl (○) and methylene groups (□) of *n*-butane-*d*₆ on H-ZSM-5 at 423 K before (a) and after (b) purification from admixed olefins. The duration of induction period τ_{ind} is about 150 min for (a) and 1350 min for (b).

(Figure 5). Rate constants for *n*-butane-*d*₆ are higher compared to those for *n*-butane-*d*₁₀ (Table 3). However, the activation energy is similar to that of *n*-butane-*d*₁₀ (Figure 5). It is worth noting that the induction period for chemical conversion, τ_{ind} , which describes the H/D exchange between the methyl, the methylene groups, and the acidic OH groups, is notably shorter for *n*-butane-*d*₆ compared to that for *n*-butane-*d*₁₀ (Table 2). Different levels of minor impurities of olefins, which can be present in the initial reagents, can provide the difference in the duration of the observed induction period for chemical transformation.^{35,36} Indeed, it is seen from Figure 6 that additional purification of the purchased *n*-butane-*d*₆ from olefins extends the induction period τ_{ind} . The estimated concentration of olefin impurities in both *n*-butanes after their purification is less than 20 ppm. However, a possible difference in their concentration within this threshold of olefin impurities seems to influence the duration of the induction period. According to the observed duration of the induction period, the quantity of admixed olefins, left in the alkanes after their purification, seems to be higher for *n*-butane-*d*₆. The higher rate constants of hydrogen exchange for *n*-butane-*d*₆ could be rationalized by a more notable contribution of the chemical conversion to the kinetic curve of the hydrogen exchange.

The estimated values of activation energy, E_a , for the exchange are close to the activation energies obtained for the exchange in deuterated propane on H-ZSM-5.^{9,18,37} Similar values of E_a were also reported for the hydrogen exchange for other small alkanes with the reaction performance via the carbonium ion mechanism.^{2,3,6,10,11,19,24,41} The values of the activation energy for both the methyl and methylene groups of

n-butane, which are in good correspondence with theoretical estimations of E_a for primary and secondary carbons of this linear alkane,^{19,24} provide a confirmation that the hydrogen exchange occurs by the mechanism with involvement of the pentacoordinated carbonium ion in the transition state. Essentially lower values of apparent activation energy (50–54 kJ mol^{−1}) were found earlier for the carbenium ion mechanism of the exchange for isobutane on H-ZSM-5¹³ or propane on sulfated zirconia.¹⁷

It is worth noting that, possessing similar activation energies with propane,^{9,18,37} the exchange occurs faster in *n*-butane. It should be about five times faster for the methyl groups at 448 K; see ref 18. Moreover, *n*-butane exhibits equal rate constants for the methyl and methylene groups (see Table 3), whereas $k_{\text{CH}_3} \approx 1.5k_{\text{CH}_2}$ for propane.¹⁸ The case with propane finds its rationalization by the decisive contribution of the entropy factor into the exchange rate constant. Bučko et al.²⁴ have shown that the probability of the formation of an adsorption complex of propane with a Brønsted acid site via the methylene group is about 17 times lower than that via a methyl group. The equal rate constants for the methyl and methylene groups of *n*-butane indicate that there is no preference in the formation of the pentacoordinated carbonium ion transition state with either the methyl or the methylene group; entropic effects to k_{CH_3} and k_{CH_2} of *n*-butane should be identical.

Narbeshuber et al.^{8,42} have drawn similar conclusions about the mechanism of H/D exchange for *n*-butane on H-ZSM-5 zeolite. However, they reported a lower value of E_a for the H/D exchange (80–85 kJ mol^{−1}). The value of E_a reported in refs 8 and 42 was obtained from the analysis of the isotope transient response experiments (SSITR) under flow conditions and at much higher temperatures (673–823 K). They also determined the activation energy by in situ IR spectroscopy⁸ based on initial rates for the H/D exchange reaction, which were extremely fast under their conditions. A time threshold of ~15 s between two points in the experimental kinetics was too short, which could lead to an understatement of the activation energy value in the IR experiment. Thus, the different experimental conditions can account for the discrepancy of E_a in refs 8 and 42 with our values of activation energy.

Cyclic Scheme of Exchange. Reactions 1–13 from Table 1 were further used as the basis for simulating the kinetic curves based on the cyclic scheme. The simulation has shown that the contribution of intramolecular exchange cannot be reliably estimated by the analysis of the kinetics for fully deuterated *n*-butane-*d*₁₀. It was only possible to estimate the upper limit of the intramolecular rate constant k_{intra} , which did not exceed the rate constants k_{CH_3} or k_{CH_2} earlier found in the frame of the parallel scheme of the exchange, $k_{\text{intra}} \leq k_{\text{CH}_3} = k_{\text{CH}_2}$.

A contribution of intramolecular exchange could be better estimated from the analysis of the kinetics for *n*-butane-*d*₆. Figure 7a shows that the experimental kinetics can be described with $k_{\text{intra}} = 0$ and equal k_{CH_3} and k_{CH_2} . If $k_{\text{intra}} \neq 0$ and $k_{\text{intra}} \leq k_{\text{CH}_3} = k_{\text{CH}_2}$ as estimated for *n*-butane-*d*₁₀, the equilibration of protium concentrations between the methyl and methylene groups starts at the beginning of the reaction, with the intensity of the CH₂ groups fast decreasing (Figure 7b). This indicates that intramolecular hydrogen exchange between the methyl and methylene groups of *n*-butane does not take place. The cyclic scheme of the hydrogen exchange is not realized for *n*-butane on H-ZSM-5 zeolite.

4. Conclusion

In situ ¹H MAS NMR monitoring (423–448 K) of the transformation of deuterated *n*-butanes (*n*-butane-*d*₁₀ and *n*-butane-

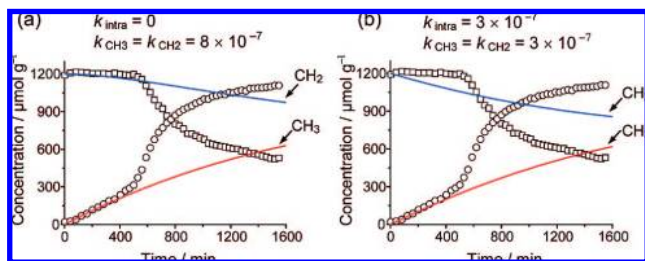


Figure 7. Simulation (solid curves) of the experimental kinetics of the H/D exchange for the methyl (○) and methylene (□) groups of butane- d_6 on H-ZSM-5 ($T = 428$ K) in accordance to the cyclic kinetic scheme. Values of the rate constants k_{CH_3} , k_{CH_2} , and k_{intra} are given in $g \mu mol^{-1} min^{-1}$.

1,1,1,4,4,4- d_6) on zeolite H-ZSM-5 allowed us to make the following conclusions on the peculiarities of the hydrogen H/D exchange for this alkane.

The hydrogen exchange of deuterated n -butanes at 423–448 K is complicated with increasing reaction time by chemical transformation of the alkane via isomerization and oligomerization-cracking reactions. The induction period of the chemical transformation of n -butane is sensitive to the admixture of olefins within their threshold of 20 ppm. The kinetics of the H/D exchange within the induction period for chemical conversion could be analyzed. The modeling of the kinetic curves with regard to different possible kinetic schemes of the H/D exchange allows us to conclude that both the methyl and methylene groups of n -butane are directly involved in the exchange with Brønsted acid sites of the zeolite. The intramolecular hydrogen exchange between the methyl and the methylene groups of n -butane does not take place. Similar rates of exchange into the methyl and methylene groups and the activation energy of 108 $kJ mol^{-1}$ presume the carbonium ion mechanism of the exchange involving a pentacoordinated carbon atom in the transition state.

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