

In situ monitoring of *n*-butene conversion on H-ferrierite by ^1H , ^2H , and ^{13}C MAS NMR: kinetics of a double-bond-shift reaction, hydrogen exchange, and the ^{13}C -label scrambling

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Abstract

Kinetics of a double-bond-shift reaction, hydrogen exchange, and ^{13}C -label scrambling were monitored in situ by ^2H , ^1H , and ^{13}C MAS NMR for *n*-but-1-ene adsorbed on the zeolite ferrierite under batch reactor conditions at 290–373 K. A double-bond-shift reaction, the fastest among the three reactions studied, can be monitored provided that 97% of Brønsted acid sites are substituted by Na cations. The activation energy for this reaction was found to be $9.8 \text{ kcal mol}^{-1}$. Hydrogen exchange with protons from the zeolite is observed for both methene and methyl groups of *n*-but-2-ene, formed from the initial *n*-but-1-ene. The terminal olefinic $=\text{CH}_2$ group of *n*-but-1-ene is involved in the exchange, providing the pathway for the exchange into the methyl group of the *n*-but-2-ene, mainly observed in the spectrum in accordance with thermodynamic equilibrium between *n*-but-1-ene and *n*-but-2-ene. This offers similar apparent activation energies of about 7 kcal mol^{-1} for the exchange into methene and methyl groups of *n*-but-2-ene. The ^{13}C -label scrambling in *n*-but-2-ene is indicative of *sec*-butyl cation formation from the olefin in the zeolite framework, which can be formed as a small quantity of transient species not detectable by NMR but providing the label scrambling. The apparent activation energy for the ^{13}C -label scrambling was found to be $21 \pm 2 \text{ kcal mol}^{-1}$, which is three times higher compared with the activation energy for the label scrambling in *sec*-butyl cation in a superacidic solution.

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1. Introduction

Hydrocarbon activation and transformation in the specific pore or channel system of acidic zeolites are prime examples of heterogeneously catalyzed reactions. Solid-state NMR is capable of characterizing both zeolite acid sites and adsorbed hydrocarbons and has therefore become an indispensable spectroscopic technique for in situ monitoring of

hydrocarbon activation and transformation on acidic zeolites.

Zeolite H-FER, the hydrogen form of ferrierite [1], represents a high-efficiency catalyst for the isomerization of *n*-butene into isobutene [2,3]. Its high selectivity and stability in the isomerization of *n*-butene to isobutene [2,3] seems to be due to the specific two-dimensional channel system of the zeolite pores (ten-membered ring $5.4 \times 4.2 \text{ \AA}$, and eight-membered ring $4.8 \times 3.5 \text{ \AA}$ [1]). Ferrierite is superior to the zeolite ZSM-5 [4], possessing a similar acidity but a channel system with larger pores ($\sim 5.5 \text{ \AA}$ in diameter [5]).

Because of the narrow pores of ferrierite, *n*-butene does not oligomerize rapidly at low temperatures [6,7], in con-

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trast to ZSM-5, where oligomerization occurs readily under similar conditions [6,8]. The ^{13}C -label scrambling in the adsorbed *n*-butene [7] shows the olefin activation, and kinetic measurements of the scrambling provide valuable information on the mechanism of olefin activation. In this paper we focus on in situ kinetic measurements by ^1H , ^2H , and ^{13}C MAS NMR of hydrogen exchange, a double-bond-shift reaction, and ^{13}C -label scrambling in *n*-butene adsorbed to H-FER with the aim of clarifying the mechanism of olefin activation.

2. Experimental

2.1. Materials

The sodium form of zeolite ferrierite ($\text{Si}/\text{Al} = 47$) was prepared by Prof. Dr. W. Schwieger by the procedure described in Ref. [9]. Two samples were prepared by conversion of the Na form into the H form. The compositions $\text{H}_{0.02}\text{Na}_{0.73}\text{Al}_{0.75}\text{Si}_{35.25}\text{O}_{72}$ (sample H-FER1) and $\text{H}_{0.47}\text{Na}_{0.28}\text{Al}_{0.75}\text{Si}_{35.25}\text{O}_{72}$ (sample H-FER2) were obtained by chemical analysis. Sample H-FER1, with a very small concentration of Brønsted acid sites, was used for the study of a double-bond-shift reaction, and sample H-FER2, with a higher concentration of Brønsted acid sites, was used for the study of H/D exchange and ^{13}C -label scrambling. $[2\text{-}^{13}\text{C}]\text{-}n\text{-But-1-ene}$, with the ^{13}C isotope (99% ^{13}C isotope enrichment) at the inner olefinic $=\text{CH}$ -group, and fully deuterated *n*-but-1-ene- d_8 (98% ^2H isotope enrichment), purchased from MSD Isotopes Inc., were used without further purification.

2.2. Preparation of the samples

The samples were calcined at 673 K for 2 h in air and for 2 h under vacuum (10^{-3} Pa). Then *n*-but-1-ene (about 300 $\mu\text{mol/g}$ H-FER) was adsorbed under vacuum by cooling of the sample with liquid nitrogen. This loading corresponds to about one olefin molecule per aluminum atom in the ferrierite framework or 1.4 molecules per bridging OH group for H-FER2 and 33 molecules per bridging OH group for H-FER1. After the glass tube was sealed, the samples were kept at liquid-nitrogen temperature. Before the measurements, the sample was taken from the liquid nitrogen and transferred to the NMR probe, which was preheated to a well-defined temperature (290–373 K). The first ^2H (^1H) and ^{13}C MAS NMR spectra were recorded within 5 min and 10–20 min, respectively, after the temperature was increased from liquid-nitrogen temperature to the desired temperature.

2.3. NMR analysis

The reaction products were analyzed in sealed glass tubes. ^1H , ^2H , and ^{13}C MAS NMR spectra with high-power proton decoupling were recorded at 400.13, 61.432, and

100.613 MHz, respectively, on a Bruker MSL-400 spectrometer. ^{13}C CP/MAS NMR experiments were performed by cross-polarization with a high-power proton decoupling field corresponding to a 5.0- μs pulse length for the $\pi/2$ pulse, a contact time of 5 ms, and a recycle delay of 3 s. The spinning rates were 2.7–4.5 kHz. We collected sixteen scans with a repetition time of 3 s for each ^2H NMR spectrum, 100 scans with a repetition time of 2 s for each ^1H spectrum, and 100 scans with a repetition time of 3 s for each ^{13}C NMR spectrum. Chemical shifts were adjusted to TMS with an accuracy ± 0.2 ppm with the use of an external reference sample.

3. Results and discussion

3.1. A double-bond-shift reaction

n-But-1-ene **1** readily undergoes a double-bond-shift reaction when it is adsorbed to H-FER [6,7,10,11]. ^{13}C and ^1H MAS NMR spectra of *n*-but-1-ene adsorbed on H-FER2 were measured within 5–10 min after the sample was warmed from liquid nitrogen to room temperature. They show a complete transformation of *n*-but-1-ene **1** into *n*-but-2-ene **2**. When H-FER1 is used instead of H-FER2, the double-bond-shift reaction becomes slow enough and it is possible to follow the kinetics of this reaction in situ with fully deuterated *n*-but-1-ene- d_8 by ^2H MAS NMR.

Fig. 1 shows the time dependence of ^2H MAS NMR spectra of deuterated *n*-but-1-ene- d_8 **1** adsorbed on H-FER1. The signals at 1.0, 2.0, 5.0, and 5.9 ppm correspond to CD_3 , CD_2 , $=\text{CD}_2$, and $-\text{CD}=\text{}$ groups of **1**, respectively. In the course of the reaction all the signals from **1** decrease in intensity, whereas the signal at 1.7 ppm from the methyl groups of *n*-but-2-ene- d_8 **2** increases. The growth of the expected signal at 5.6 ppm for $-\text{CD}=\text{}$ groups of the adsorbed **2** is not so

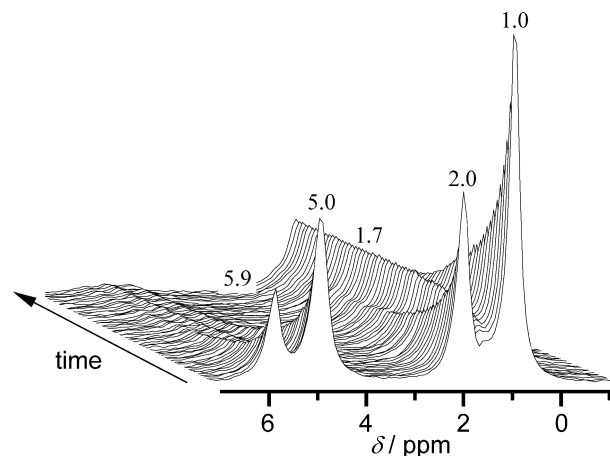


Fig. 1. ^2H MAS NMR spectra of *n*-but-1-ene- d_8 adsorbed on H-FER1 measured at 333 K. The first spectrum (bottom) was recorded 5 min and the last 18.5 h after increasing the temperature from liquid nitrogen to 333 K. The time interval between subsequent spectra 1–18 and 18–59 was 12 min and 22 min, respectively.

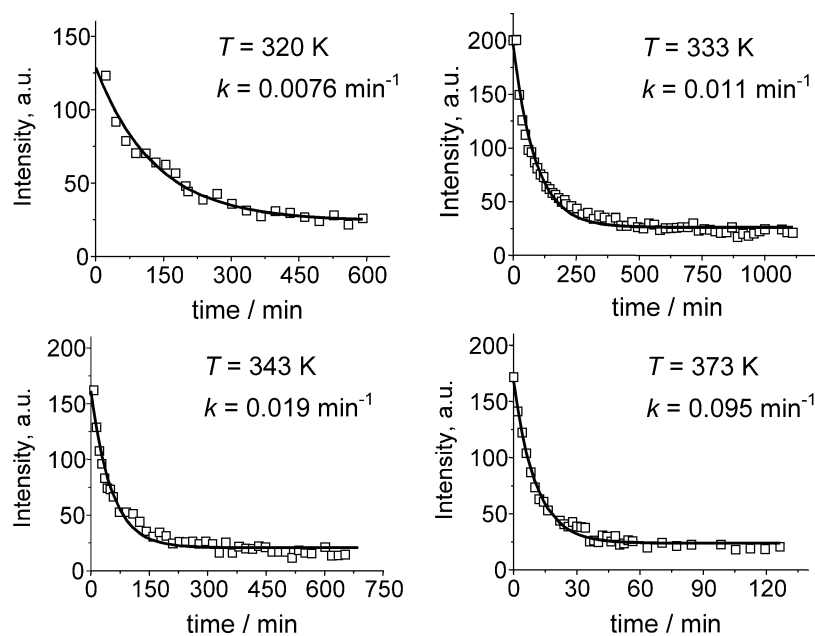


Fig. 2. Kinetics of a double-bond-shift reaction of *n*-but-1-ene-*d*₈ to *n*-but-2-ene-*d*₈ on H-FER1. Solid lines represent the fits to the experimental points by using Eq. (1) with the rate constants *k*, indicated nearby each kinetics. Four of six measured kinetics are shown.

pronounced because of its small intensity and large width. This transformation of the ²H NMR spectrum of **1** indicates that a double-bond-shift reaction occurs on H-FER1. In conclusion, a double-bond-shift reaction can be monitored in situ by NMR in the temperature range 300–373 K, since this transformation is slowed down in the zeolite H-FER1 compared with H-FER2 by the replacement of most of the Brønsted sites by Na cations.

The rate constant *k* of the *n*-but-1-ene to *n*-but-2-ene transformation can be determined by the evaluation of the time-dependent intensity of the ²H MAS NMR signal of the methyl group of **1**. Assuming first-order reaction kinetics and irreversibility of the reaction, we have

$$I_t^{\text{CH}_3} = I_0^{\text{CH}_3} \exp(-kt), \quad (1)$$

where $I_t^{\text{CH}_3}$ and $I_0^{\text{CH}_3}$ are the integral intensities of the methyl group of **1** at the reaction time *t* and at *t* = 0, respectively.

The temperature dependence of the rate constants (see Fig. 2) gives the Arrhenius plot shown in Fig. 3. The activation energy obtained for the double-bond-shift reaction is $9.8 \pm 1.1 \text{ kcal mol}^{-1}$.

Kondo et al. [12] have shown that a double-bond-shift reaction of **1** to **2** on H-ZSM-5 is a more facile process compared with the H/D exchange between but-1-ene and OH groups of the zeolite. At low temperatures (< 230 K) it proceeds in the absence of proton transfer from the acidic OH groups of the zeolite. In contrast, the H/D exchange requires a proton transfer to form the protonated intermediate, either alkoxy species or carbenium ion. Nevertheless, the acidic OH groups are the active sites for the *n*-but-1-ene to *n*-but-2-ene isomerization. A double-bond-shift reaction could not be observed on the Na forms of both ZSM-5 [8]

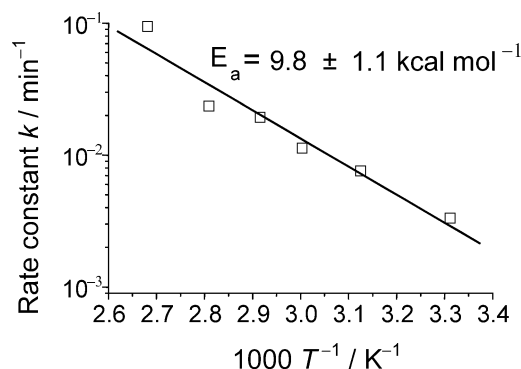


Fig. 3. Arrhenius plot for a double-bond-shift reaction of *n*-but-1-ene-*d*₈ to *n*-but-2-ene-*d*₈ on H-FER1.

and ferrierite [6,7,10,11]. A double-bond-shift reaction proceeds slowly with H-FER1, which contains a relatively small fraction of acidic OH groups, and fast with H-FER2, on which the reaction goes to completion within a few minutes at 300 K. A comparison of H-FER1 with Na-ZSM-5 and Na-FER shows that the small concentration (3 mol% of acidic OH groups with respect to aluminum atoms) of acidic OH groups left in FER1 performs a double-bond-shift reaction, whereas sodium cations should not be involved.

Diffusion of the reactant molecule to the catalytically active Brønsted acid sites should not be a rate-limiting process for a double-bond shift reaction with H-FER1, since the diffusion of small molecules like the studied olefins or alcohols is a fast process that takes place in minutes for a crystal size of $9 \times 40 \times 210 \mu\text{m}$ [13]. This is fast compared with the observed *n*-but-1-ene transformation (see Fig. 2).

Kondo et al. [12] obtained an activation energy of $11.7 \pm 1 \text{ kcal mol}^{-1}$ for H-ZSM-5. Our value of $9.8 \pm$

1.1 kcal mol⁻¹ for H-FER1 is not significantly different. Therefore, we can suppose that a double-bond-shift reaction on H-FER proceeds as proposed by Kondo et al. [12] without proton transfer from the acidic OH groups of the zeolite to the olefin molecules. At higher temperatures (> 230 K) the double-bond-shift reaction proceeds simultaneously with the H/D exchange reaction [12]. This means that the classical carbenium ion mechanism may also contribute to double-bond migration at these temperatures. Thus, in the higher temperature region (303–373 K) of this study it is not possible to distinguish between the classical mechanism and the mechanism proposed by Kondo et al. [12].

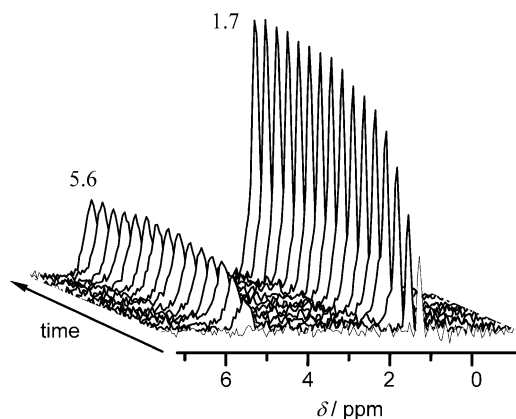


Fig. 4. Stack plot of the ¹H MAS NMR spectra at 360 K of *n*-but-1-ene-*d*₈ adsorbed on H-FER2. The first spectrum (bottom) was recorded 4 min and the last 65 min after increasing the temperature from liquid nitrogen to 360 K. The time interval between subsequent spectra was 4 min. The first spectrum corresponds to *n*-but-2-ene-*d*₈, which has been rapidly formed from *n*-but-1-ene-*d*₈ within the time interval, before the first spectrum is recorded.

3.2. H/D isotope exchange

Hydrogen exchange transfers ¹H nuclei from the acidic hydroxyl groups of the zeolite to the initially deuterated butene molecules. ¹H MAS NMR spectra of *n*-but-2-ene-*d*₈ 2 formed from *n*-but-1-ene-*d*₈ 1 on H-FER2 and recorded within 4 min after adsorption show weak signals at 1.7 and 5.6 ppm (Fig. 4) due to methyl and methene groups of butene 2, which increase with time. The ratio between the intensities of the CH₃ and CH groups in the final spectrum is 3:1. This ratio indicates that both methyl and methene groups are involved in the hydrogen/deuterium exchange.

The kinetics of hydrogen exchange can be described by the following equation:

$$I_t = (I_\infty - I_0)[1 - \exp(-k_1 t)] + I_0, \quad (2)$$

where I_t and I_∞ are the integral intensities of the signals from CH_{*n*} (*n* = 1 or 3) groups in the ¹H MAS NMR spectrum of *n*-but-2-ene at the observation times *t* and *t* = ∞ (equilibrium). I_0 is the parameter that describes nonzero intensity at *t* = 0 (vide infra) and k_1 is the rate constant, which is identified with the rate for H/D exchange [14].

Fig. 5 shows that the rate constants k_1 for the H/D exchange are different for methyl and methene groups; the exchange into the methene group proceeds notably faster. However, the activation energies for hydrogen exchange (see Fig. 6) are similar and close to the value of 7.4 kcal mol⁻¹, which was estimated by IR spectroscopy for the reaction on zeolite ZSM-5 [12].

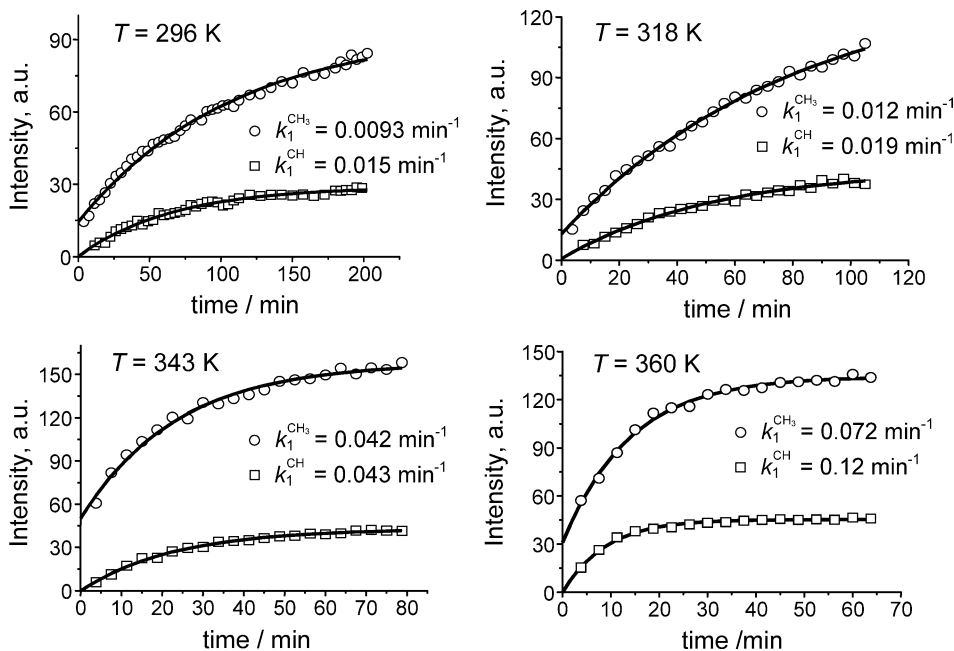


Fig. 5. Kinetics of proton transfer from the acidic OH groups of zeolite H-FER2 to the methyl (○) and methene (□) groups of *n*-but-2-ene-*d*₈. Solid lines represent the fits using Eq. (2) with the rate constants k_1 , indicated nearby each kinetics.

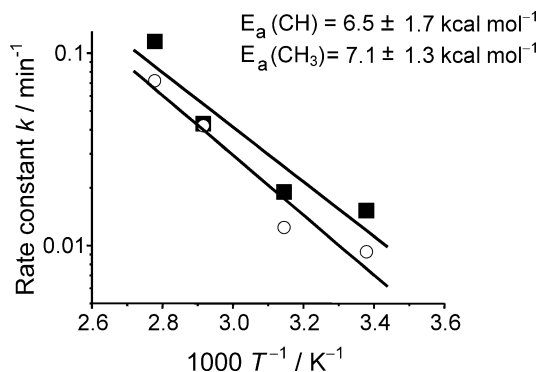
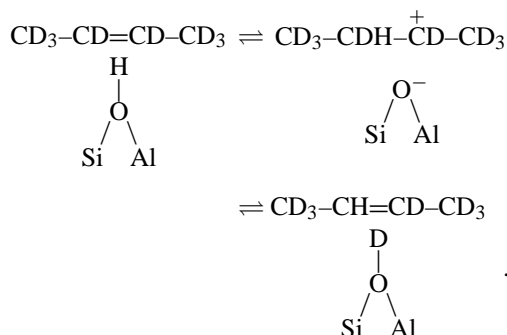


Fig. 6. Arrhenius plot for the H/D exchange for methyl (○) and methene (■) groups of *n*-but-2-ene-*d*₈ on H-FER2.

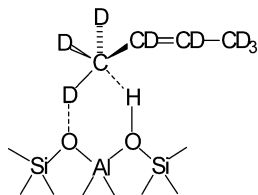
It is reasonable to assume that the exchange into the methene groups occurs via a formation of carbenium ion (or alkoxy species) as an intermediate:



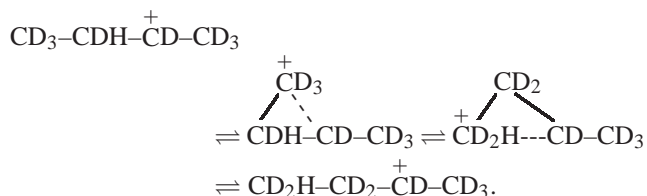
Methyl groups are not involved in the exchange by this mechanism.

For hydrogen exchange between acidic OH of the zeolite and the methyl groups of **2** we discuss three mechanisms.

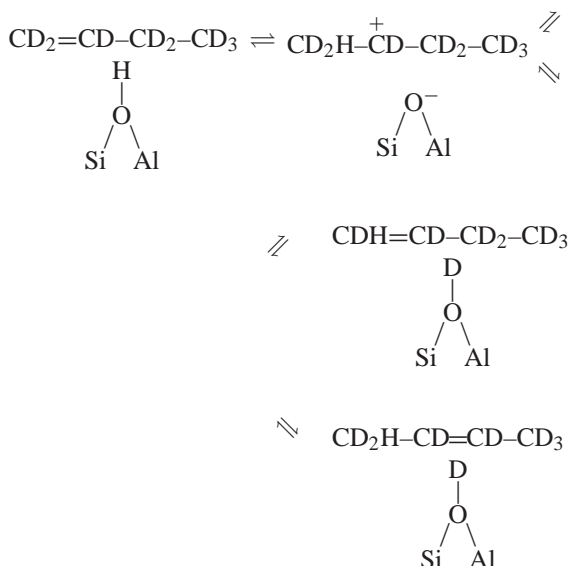
1. Methyl groups can exchange with OH groups directly through the formation of a pentacoordinated transition state with the exchanging hydrogen atoms at a half-way position between the carbon of the methyl group and the zeolitic oxygen atoms. This was suggested in theoretical considerations of the exchange in alkanes [15] and in experimental studies by NMR [16] and IR [17,18]:



2. Protium transfers from the methene group, primarily involved in the exchange, into the methyl group via the formation of a protonated cyclopropane intermediate:



3. Protium transfers into the methyl group by the mechanism of interconversions of **1** and **2**. The equilibrium between two isomers provides a transfer of protium into the methyl group of *n*-but-2-ene, which is mainly observed in the ¹H MAS NMR spectra:



The analysis of the NMR data favors mechanism 3. It seems that mechanism 1 is realized only at higher temperatures for alkanes ($T > 423$ K), with an apparent activation energy for this process greater than 20–25 kcal mol⁻¹ [16–18]. Mechanism 2 requires protium transfer into the deuterated methyl group in *sec*-butyl cation formed from *n*-but-2-ene by cyclization to a protonated methylcyclopropane intermediate, followed by proton scrambling rearrangement and reopening to *sec*-butyl cation. Protons and carbons should scramble simultaneously in a common methylcyclopropane intermediate. It would be expected in this case that the protons scramble more rapidly than the carbons, but proton scrambling and ¹³C-label scrambling occur with the same activation energy as for *sec*-butyl cation in a superacid [19,20]. However, the experiment shows that the rate of the H/D exchange into the methyl group is one order of magnitude higher compared with the ¹³C-label scrambling at 296–333 K (see the rate constants in Figs. 5 and 9). The rates of H/D exchange and ¹³C-label scrambling become comparable at 343 K, but the activation energy for the ¹³C-label scrambling is three times higher (vide infra) compared with that for hydrogen exchange. This implies different intermediates for ¹³C label scrambling and protium transfer to the deuterated methyl groups in butene **2**. Thus we conclude that intermediacy of protonated methylcyclopropane, providing the carbon scrambling in butene **2**, is not the main route for the protium transfer from the methene group into the deuterated methyl group.

Protium transfer into the methyl group can be reasonably rationalized by mechanism 3. At first, butene **1** converts rapidly to butene **2** via a fast double-bond-shift reaction. This process brings protium from the zeolite OH group

into the deuterated methyl group of butene **2**, if the carbenium ion mechanism for a double-bond-shift reaction is realized. In the equilibrium established between butene **1** and butene **2**, the latter represents a prevailing species. The expected equilibrium constant $1 \leftrightarrow 2$ is equal to 22 at 300 K [21]. However, fast interconversion of **1** and **2** brings the protium isotope into the deuterated methyl group of butene **2**. Similar apparent activation energies for the transfer into methyl and methene groups of **2** may imply similar activation energies for the transfer into the inner $-\text{CD}=\text{}$ group of butene **2** and the terminal $=\text{CD}_2$ group of butene **1**. Simultaneously, faster transfer into the methene group of **2** compared with its methyl group implies faster transfer into the $-\text{CD}=\text{}$ group of butene **2** compared with the $=\text{CD}_2$ group of butene **1**.

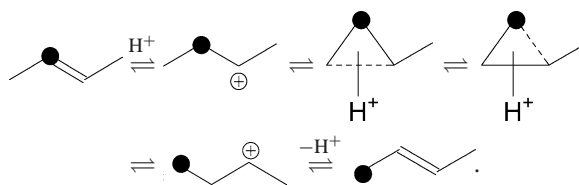
It should be noted that a preferential H/D exchange in the methyl group of butene **2** is observed at a very short reaction time (see Figs. 4 and 5). Eq. (2) contains the initial intensity I_0 , which was found to be almost zero for all kinetics of H/D exchange in the CH groups of butene **2**. At the same time I_0 appreciably exceeds zero for all kinetics of H/D exchange in the CH_3 groups (see Fig. 5). The nonzero value of I_0 for the CH_3 groups indicates that the methyl group of butene **2** has already derived protons from the zeolite during the first moment of our NMR monitoring of the H/D exchange in butene **2** (see the first spectrum in Fig. 4), whereas the methene group of butene **2** has not. This implies that the fast double-bond-shift reaction of butene **1** into butene **2** on H-FER2 at temperatures as high as 296 K is accompanied by the protium transfer from the OH group of the zeolite into the $=\text{CD}_2$ group of butene **1** and then to the methyl group of butene **2**, resulting in fast initial growth of the signal from the methyl protons of **2**. This indicates that the double-bond-shift reaction proceeds via the classical protonation/deprotonation scheme for the studied temperature range, rather than via the mechanism suggested by Kondo et al. [12] for the reaction at lower temperatures.

3.3. ^{13}C -label scrambling

The ^{13}C -label scrambling has been shown to occur for *n*-but-2-ene on ferrierite at low temperatures (300–373 K), and it is not accompanied by the olefin skeletal isomerization into isobutene [7]. The appearance with time of the signal at 126 ppm from the inner $-\text{CH}=\text{}$ group of butene **2** upon adsorption of butene **1**, labeled with ^{13}C isotope in the terminal $=\text{CH}_2$ group, was indicative of the label scrambling (see Fig. 1 of Ref. [7]). The same conclusion is valid for butene **1**, labeled in the $-\text{CH}=\text{}$ group. In this case the signals from the methyl groups of *trans* and *cis* butenes **2** appear in the spectrum with time (Figs. 7 and 8).

^{13}C -label scrambling is usually observed for carbenium ions generated in superacids from alkane or olefins [19,22]. The scrambling occurs in the formed carbenium ion through formation of the protonated cyclopropane in-

termediate (or transition state) [19,23,24] according to the following scheme:



The symbol (●) denotes the ^{13}C label in this scheme.

Label scrambling should occur in the formed carbenium ion [19,23,24]. This implies that the label scrambling proves the generation of *sec*-butyl carbenium ions on acidic ferrierite. But they were not detected by solid-state NMR. Therefore, the carbenium ion formed in the zeolite should have a very short lifetime or a relatively small concentration. It is worth noting here that alkoxy species, as an alternative to carbenium ion but a more stable intermediate, is not detected for butene **2** on H-FER2 as well. Alkoxy species would give rise to a signal at 70–80 ppm [25,26] in Fig. 7.

Figs. 7 and 8 show variation with time of the ^{13}C CP/MAS NMR spectrum obtained after $[2-^{13}\text{C}]\text{-}n\text{-but-1-ene}$ adsorption on H-FER2. A rapid conversion of $[2-^{13}\text{C}]\text{-}n\text{-but-1-ene}$ **1** into $[2-^{13}\text{C}]\text{-}n\text{-but-2-ene}$ **2** by a double-bond-shift reaction takes place. The spectrum recorded within the first 17 min exhibits only the signal from the ^{13}C labeled $-\text{CH}=\text{}$ group of **2** at 126 ppm (Fig. 7a). The increase in the intensities of the methyl groups at 13 and 17 ppm (Figs. 7b and 8) points to the transfer of the ^{13}C label from the $-\text{CH}=\text{}$ group of butene **2** into the methyl groups of *cis*- and *trans*-butenes **2**, respectively. The spectrum in Fig. 7b and the top spectra in Fig. 8 correspond to the complete scrambling of ^{13}C -label over the molecule of butene **2**, which is observed after 20 h at 323 K.

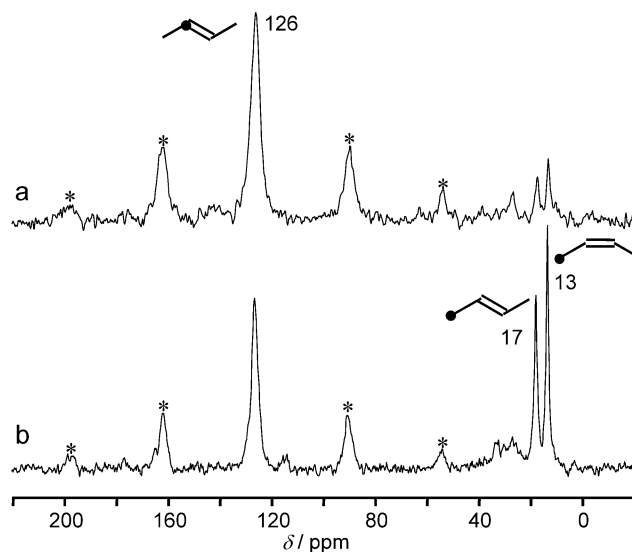


Fig. 7. ^{13}C CP/MAS NMR spectra obtained at 293 K after $[2-^{13}\text{C}]\text{-}n\text{-but-1-ene}$ adsorption on H-FER2. Spectra were recorded after 17 min (a) and 20 h (b) at 323 K. Asterisks (*) denote spinning side-bands.

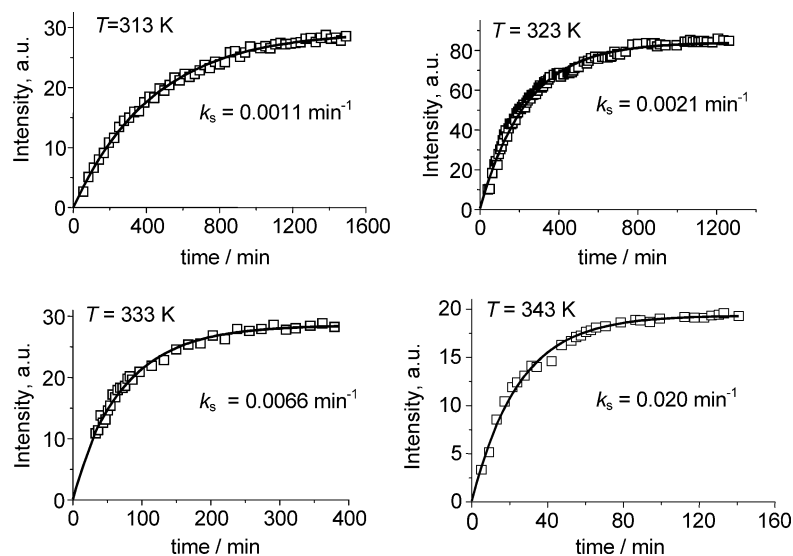


Fig. 9. Kinetics of the ^{13}C -label scrambling from the $-\text{CH}=\text{}$ group of $[2-^{13}\text{C}]n\text{-but-2-ene}$ into its methyl groups on zeolite H-FER2. Solid lines represent the fits using Eq. (3) with the rate constants k_s , indicated nearby each kinetics.

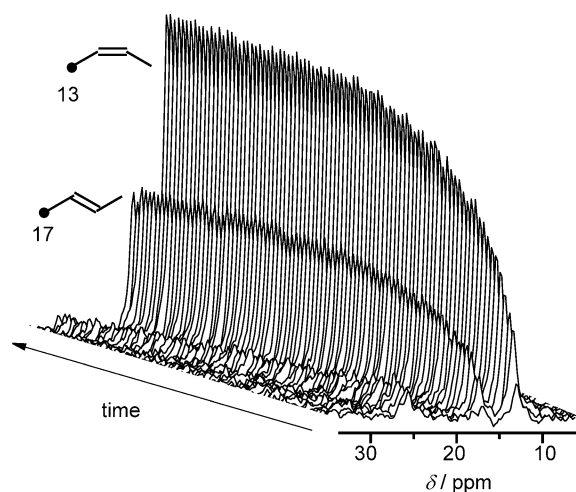


Fig. 8. Stack plot of the ^{13}C CP/MAS NMR spectra recorded at 323 K after $[2-^{13}\text{C}]n\text{-but-1-ene}$ adsorption on H-FER2. First (bottom) and last (top) spectra were recorded 17 min and 20.6 h, respectively, after the temperature jump from liquid nitrogen to 323 K. The time interval between subsequent spectra was 14 min. The first spectrum corresponds to $[2-^{13}\text{C}]n\text{-but-2-ene}$ **2**, rapidly formed from $[2-^{13}\text{C}]n\text{-but-1-ene}$ after increasing the temperature to 323 K.

The ^{13}C -label scrambling in $n\text{-but-2-ene}$ can be described by the scheme



Here **A** and **B** correspond to $[2-^{13}\text{C}]n\text{-but-2-ene}$ and $[1-^{13}\text{C}]n\text{-but-2-ene}$, respectively. The kinetic equation is

$$B_t = B_\infty [1 - \exp(-2k_s t)], \quad (3)$$

where B_t and B_∞ are the integral intensities of the methyl groups of $[1-^{13}\text{C}]n\text{-but-2-enes}$ (both *cis* and *trans* isomers)

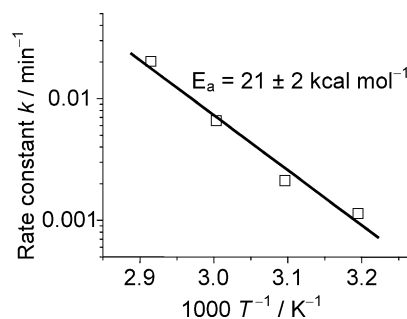


Fig. 10. Arrhenius plot for the ^{13}C -label scrambling in $n\text{-but-2-ene}$ on H-FER2.

at the reaction times t and $t = \infty$ (equilibrium) and k_s is the rate constant for the label scrambling.

The rate constants for the scrambling, k_s , derived from the fits to the experimental kinetics by Eq. (3) (see Fig. 9) indicate that the scrambling in the adsorbed butene **2** is a rather slow process. Indeed, it has been found that the time of half-conversion is about 20 min at the highest measured temperature of 343 K, and it is more than 5 h at 313 K.

The Arrhenius plot for k_s (Fig. 10) offers the apparent activation energy for the ^{13}C -label scrambling. Its value of $21 \pm 2 \text{ kcal mol}^{-1}$ is almost three times higher compared with that of the label scrambling in the *sec*-butyl cation in the liquid superacid [19]. The higher value of the activation energy may imply that both proton transfer from the acidic OH group of the zeolite to the olefin double bond and label scrambling in the formed *sec*-butyl cation contribute to the apparent activation energy for the ^{13}C -label scrambling in the adsorbed butene **2**.

The high value of activation energy (21 kcal mol^{-1}) for the label scrambling can be explained by an analysis of the energy profile. We take into account the heat of adsorption of the olefin in the zeolite to form π -complexes [27,28], the

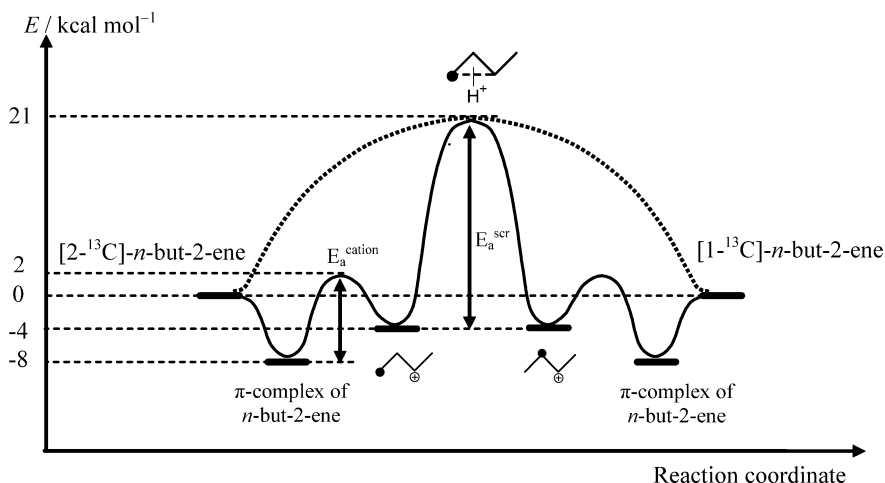


Fig. 11. Energy diagram for the *n*-but-2-ene ^{13}C -label scrambling in ferrierite.

theoretical finding by Teraishi [29] that local minima can be found for adsorbed carbenium ions about 3–5 kcal mol $^{-1}$ higher than that of the corresponding π -complexes, and the data by Boronat et al. [30] that the activation energy for the formation of carbenium ion from π -complexes E_a^{cation} can hardly exceed 10 kcal mol $^{-1}$. This gives the energy diagram depicted in Fig. 11.

It follows from this diagram that the true activation energy E_a^{scr} for the label scrambling in the cation adsorbed to zeolite should be about 25 kcal mol $^{-1}$. This value is essentially higher than that for the cation in a superacid. So, a protonation process is less likely to contribute notably to the apparent activation energy of the label scrambling.

Further theoretical considerations of the hydrocarbon conversion in zeolites are necessary to explain the high value of the observed activation energy for the label scrambling.

4. Conclusions

In situ ^2H , ^1H , and ^{13}C MAS NMR monitoring of the kinetics of a double-bond-shift reaction, hydrogen exchange, and the ^{13}C -label scrambling for *n*-but-1-ene adsorbed on ferrierite provides valuable information about olefin activation and transformation on this zeolite. A double-bond-shift reaction, the fastest among the three reactions studied, can be monitored by NMR under batch reactor conditions, provided that 97% of Brønsted acid sites are substituted by Na cations. Both methene and methyl groups of *n*-but-2-ene, rapidly formed from initial *n*-but-1-ene, are involved in hydrogen exchange. Involvement of the olefinic =CH $_2$ group of *n*-but-1-ene in the exchange, as well as the inner =CH-group of *n*-but-2-ene, and thermodynamic equilibrium between *n*-but-1-ene and *n*-but-2-ene provide similar apparent activation energies for the exchange into methene and methyl groups of *n*-but-2-ene. The ^{13}C -label scrambling in *n*-but-2-ene shows the *sec*-butyl cation formation in the zeolite framework. This cation may be formed as a small quantity of transient species that is not detectable by NMR. The

apparent activation energy for the ^{13}C -label scrambling in *n*-but-2-ene, which is measured for the formed cation, is three times higher compared with the activation energy for the label scrambling in *sec*-butyl cation in liquid superacid [19].

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