Carbenium ion properties of octene-1 adsorbed on zeolite H-ZSM-5

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It is shown that octene-1 adsorbed on zeolite H-ZSM-5 at ambient temperature exhibits carbenium ion properties. Namely: (1) According to ^2H NMR, the proton of the acidic $\equiv Al-OH-Si\equiv$ group of the zeolite is transferred into the $CH_2=$ group of the octene-1 molecule. (2) According to ^{13}C NMR the ^{13}C label inserted into the terminal $CH_2=$ group of the octene-1 molecule is scrambled over its hydrocarbon skeleton. Thermodynamic and kinetic parameters for carbon scrambling are measured within the temperature range 290–343 K. The zeolite framework is shown to favour the formation of the linear rather than branched carbenium ion.

Keywords: Octene-1; H-ZSM-5 zeolite; ^{13}C carbon scrambling; carbenium ion; ^{13}C CP/MAS NMR; ^2H NMR.

1. Introduction

It is generally accepted that at ambient temperatures oligomerization of small olefins (ethylene, propylene, etc.) on acidic form (H-form) zeolites results in formation of long chain paraffinic species [1–6]. This conclusion is based on the following observations. First, IR spectra of oligomeric species that are formed at low temperature (300 K) and trapped inside the zeolite pores usually exhibit no characteristic bands for C=C stretch [1]. Second, their ^{13}C NMR spectra do not show the signals at 110–140 ppm, which are typical for the C=C moiety [2,4,5].

One needs an additional source of hydrogen to "hydrogenate" the long chain olefins into paraffins. Therefore, hydrogen deficient aromatics or coke should also be formed upon olefin oligomerization into paraffins. However, neither aromatics nor coke are formed in noticeable amounts at 300 K [7]. Thus, further studies are needed to clarify what products are actually formed in the pores of H-form zeolites during olefin oligomerization.

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Octene-1 may be one of the final products of the low temperature oligomerization of small olefins [8]. Therefore, in this work we have tried to elucidate with ^{13}C CP/MAS and ^{2}H solid state NMR in what form octene-1 is adsorbed on H-ZSM-5 zeolite. In our ^{13}C NMR studies we used both octene-1 with the natural ^{13}C isotope abundance, and octene-1 selectivity labelled with ^{13}C in the terminal $CH_2=$ group, i.e. octene-1-^{13}C. ^{13}C and ^{2}H NMR data show that octene-1 adsorbed on H-ZSM-5 at 296 K exhibits carbenium ion properties.

2. Experimental

Octene-1-^{13}C used in our ^{13}C NMR studies was 81.9% enriched with ^{13}C in the $CH_2=$ group. It contained 20% of octene-2 as the admixture that was 81.9% enriched with ^{13}C in the terminal CH_3 group adjacent to the $-CH=CH-$ fragment.

Approximately 0.1 g of H-ZSM-5 zeolite (Si/Al = 44 or 54) was placed into the glass tube, which could be tightly packed into the 7 mm zirconia NMR rotor. Prior to use the tube was sealed to the vacuum line and the zeolite sample was activated under vacuum for 3–4 h at 450°C. After cooling the zeolite to ambient temperature (290–300 K), 300–400 μmol/g octene-1-^{13}C (or octene-1 with the natural ^{13}C abundance) was freezed on it. Subsequently, still retaining the glass tube in liquid nitrogen, we sealed it off. The sealed tube was kept in liquid nitrogen until NMR measurements were started. To record ^{13}C NMR spectra, the tube was removed from liquid nitrogen, transferred into the MAS rotor, and accumulation of the ^{13}C NMR signal at 290–343 K was started.

^{13}C NMR spectra with magic angle spinning (MAS) and high power proton decoupling, and with or without cross-polarization (CP) were recorded at 100.613 MHz using a Bruker MSL-400 spectrometer. The following conditions were used for the CP experiment: the proton high power decoupling field was 12 G (4.9 μs 90° ^{1}H pulse), contact time 5 ms at Hartmann–Hahn matching conditions 51 kHz, delay time between scans 3 s, spinning rate 2.4–2.6 kHz. The number of scans was 100–3600. One-pulse excitation spectra with high power decoupling were recorded using a 45° pulse of 2.5 μs length and repetition time 15 s. Relaxation times T_1 for ^{13}C carbon signals of adsorbed octene-1 were in the interval 1.0–2.8 s. Chemical shifts were referenced using TMS as the external standard with accuracy ±0.5 ppm. The precision in defining the relative signal position in one spectrum was 0.1–0.15 ppm. The temperature of the samples was controlled with a BVT-1000 variable-temperature unit with ±1 K precision.

^{2}H NMR spectra were recorded at 61.42 MHz using experimental conditions similar to those, described in ref. [8].

3. Results

The ^{13}C CP/MAS NMR spectrum of octene-1 with the natural ^{13}C abundance adsorbed on H-ZSM-5, is given in fig. 1. It is seen that only the signals in the region of paraffinic hydrocarbons (10–40 ppm) are observed, namely, at 14.3 ppm from the terminal CH_3 group, at 24.9 ppm from the CH_2 group which is next to the CH_3 group, and at 30–33 ppm from the rest CH_2 groups [9]. The signals from the $CH_2{=}CH{-}$ moiety at 114 and 139 ppm [9] are not detected. Note, that upon adsorption at 296 K the conversion of octene-1 to other hydrocarbons occurs. As seen from fig. 1, a small signal at 40 ppm appears, which is different from the signals of the initial octene-1 [9]. This can be related to isomerization of the octene-1 hydrocarbon skeleton to some limited extent. An appearance of other small signals at 17–25 ppm in the ^{13}C MAS NMR spectrum recorded without CP (vide infra, fig. 2) should also be related to isomerization. The assignment of the main NMR signals (including both ^{13}C and ^{2}H NMR) for octene-1 and H-ZSM-5 zeolite is summarized in table 1.

It is conventional to ascribe the observed signals to paraffinic species, formed inside the zeolite framework after octene-1 adsorption [2,4–6]. The fact that positions of the signals at 14–33 ppm for the adsorbed octene-1 (fig. 1) coincide with those for liquid octene-1 or *n*-octane [9], when taken together with the absence of the ^{13}C NMR signals from the $CH_2{=}CH{-}$ moiety, seems to support the suggestion that linear paraffinic species are formed. To verify octene-1 transformation into *n*-octane, we recorded its one-pulse excitation ^{13}C NMR spectrum (without CP) with the aim of quantitative assessment of signal areas for various peaks. Experimental and simulated spectra are shown in figs. 2A and 2B. The same three groups of signals as those in the CP/MAS spectrum of fig. 1 dominate in the spectrum of

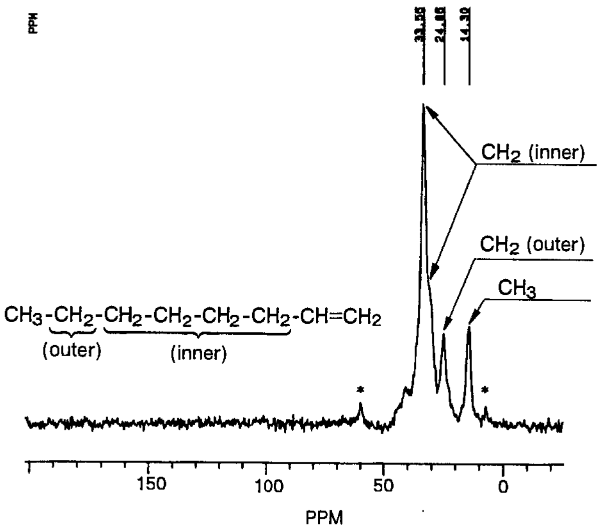


Fig. 1. ^{13}C CP/MAS NMR spectrum of octene-1 (natural ^{13}C abundance) adsorbed (428 μmol/g) on H-ZSM-5 (Si/Al= 44), recorded at 296 K. 3600 scans have been collected with repetition time 3 s. Asterisks (*) denote spinning side bands.

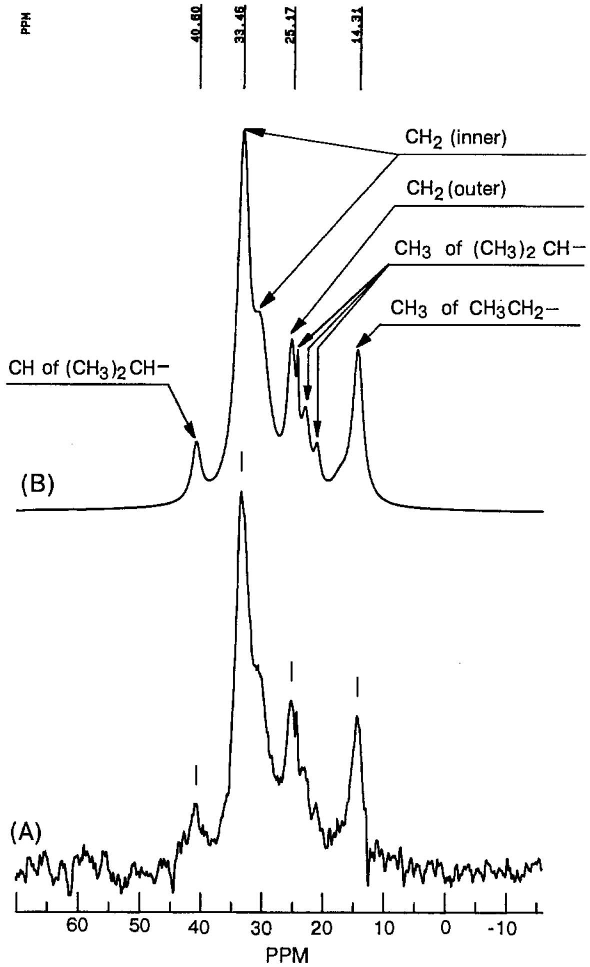


Fig. 2. ^{13}C MAS NMR spectrum of octene-1 with natural ^{13}C abundance adsorbed (316 μmol/g) on H-ZSM-5 (Si/Al = 44), recorded without CP at 296 K (2680 scans, 15 s repetition time). (A) Experimental spectrum; (B) simulation of the experimental spectrum to make quantitative assessment of signal areas.

fig. 2. Weaker signals at 17–25 and 40 ppm that are resolved much better in the spectrum of fig. 2 than in the spectrum of fig. 1, on the ground of their chemical shifts [10] can be attributed, respectively, to the CH_3 groups and CH group of the branched terminal $(CH_3)_2CH$ fragments formed upon isomerization of the skeleton of octene-1.

For *n*-octane the ratio between the terminal CH_3 and various CH_2 groups is CH_3 : CH_2(outer) : (CH_2)(inner) = 1 : 1 : 2. Integral peak areas for the three dominating signals in the experimental spectrum (fig. 2A) show the following ratios: CH_3 : CH_2(outer) : (CH_2)(inner) = 1 : 1 : 4 (see also table 1). These ratios are not in favour of *n*-octane formation. They suggest that in the adsorbed octene-1 two of

Table 1
Assignment of the main NMR signals for octene-1 adsorbed on H-ZSM-5

^{13}C NMR

liquid octene-1

functional groups	CH_3	$-CH_2-$ (outer)	$-(CH_2)_4-$ (inner)	$-CH=$	$CH_2=$
chemical shift (ppm)	14.3	23.2	29.5–34.4	138.9	114.4
signal intensity	1	1	4	1	1

adsorbed octene-1

functional groups	CH_3	$-CH_2-$ (outer)	$-(CH_2)_4-$ (inner)	$-CH=$	$CH_2=$
chemical shift (ppm)	14.3	24.9	30–33	the signals are not observed	
signal intensity	1	1	4	–	–

liquid n-octane

functional groups	CH_3	$-CH_2-$ (outer)	$-(CH_2)_2-$ (inner)
chemical shift (ppm)	13.9	23.0	32.4; 29.7
signal intensity	1	1	2

^{2}H NMR

D-ZSM-5 zeolite

functional groups	$\equiv Al-OD-Si\equiv$
quadrupole splitting (kHz)	176

D-ZSM-5 + octene-1

functional groups	$\equiv Al-OD-Si\equiv$	$\equiv Si-OD$	CH_2D-	$-CHD-$
quadrupole splitting (kHz)	–	186	38	123

the eight carbon atoms are not "visible" in the ^{13}C NMR spectrum. Indeed, as we have mentioned above, the signals at 114 and 139 ppm for the olefinic moiety (table 1) are not observed. Note, that the ratio between linear (the signal at 14.3 ppm [10]) and branched (the signals at 17–25 ppm [10]) terminal fragments, i.e. CH_3(linear) : $(CH_3)_2CH$(branched), is 3.7 : 1. This indicates that at 296 K ca. 20% of octene-1 isomerizes after adsorption on zeolite to form branched hydrocarbon species.

3.1. CARBON SCRAMBLING IN ADSORBED OCTENE-1

To follow the fate of the non-observed $CH_2=CH-$ fragment of octene-1 inside H-ZSM-5, octene-1 enriched with ^{13}C in the $CH_2=$ group ($^*CH_2=$) (see its ^{13}C

NMR spectrum, fig. 3) was adsorbed on the zeolite. Fig. 4A shows that 10 min after the adsorption, the expected most intense signal of the labelled $^*CH_2=$ group near 114 ppm in fact is not observed (compare fig. 4A and fig. 3). Instead, the intense signal appears at 14.3 ppm, i.e. where the signal from the CH_3 group of the unlabelled octene-1 is located (fig. 1). This clearly indicates that the $^*CH_2=$ group of octene-1-^{13}C transforms into the $^*CH_3$ group. Further, the intensity of the signal at 14.3 ppm decreases with time, while the intensity of the signals at 30–33 ppm, which were earlier assigned to CH_2 (inner) groups (see figs. 1, 2 and table 1), increases. Note, that the signals at 12.7 and 17.9 ppm from the labelled $^*CH_3$ groups of cis and trans isomers of the octene-2 admixture [9], are also not observed. These facts mean that: (1) the initially labelled $^*CH_2=$ group transforms into $^*CH_3$ in octene-1 or in some other hydrocarbon with linear skeleton, and (2) the so formed $^*CH_3$ group, as well as that of the octene-2 admixture, transforms further into the $^*CH_2$ groups of hydrocarbon species with mainly linear skeletons. The ratio between the intensities of various signals in the spectrum of the adsorbed labelled octene-1 changes with time (fig. 4) to that observed for octene-1 with nat-

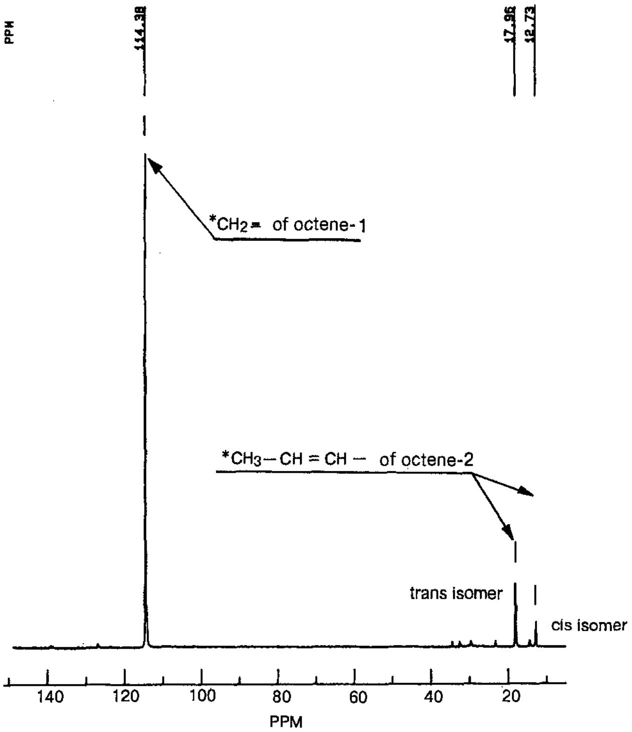


Fig. 3. High resolution ^{13}C NMR spectrum at 296 K of liquid octene-1, enriched with ^{13}C (81.9%) in the $^*CH_2=CH-$ group. The main signal at 114.4 ppm from the labelled $^*CH_2=$ group is preferentially observed. The signals at 12.7 and 17.9 ppm belong to admixed octene-2, labelled in the CH_3 group of the $^*CH_3-CH=CH-$ fragment (cis and trans isomers, respectively).

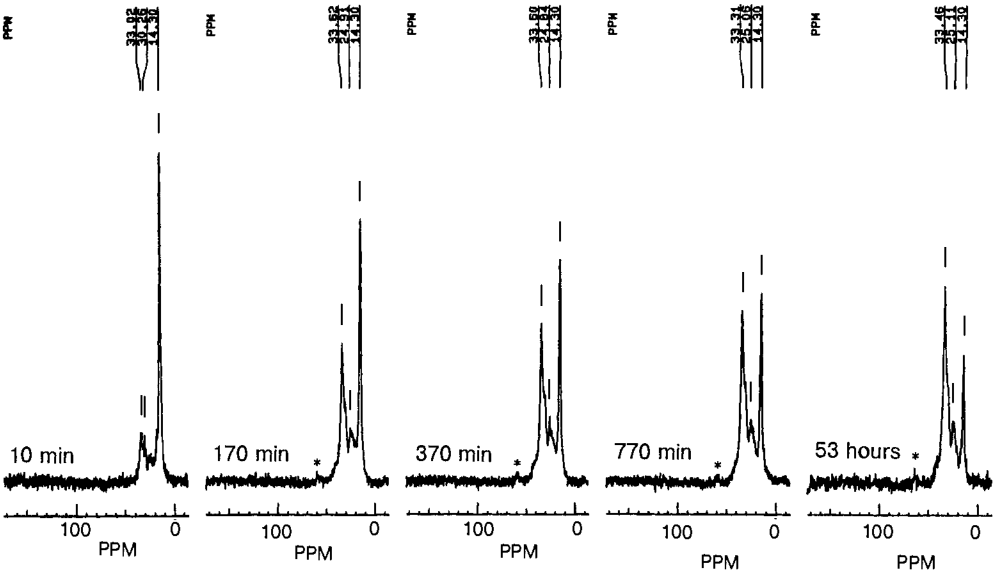


Fig. 4. The change with time of the ^{13}C CP/MAS NMR spectrum of octene-1-^{13}C (labelled with ^{13}C in the $^{*}CH_2=$ group) adsorbed (290 μmol/g) on zeolite H-ZSM-5 (Si/Al= 44). All the spectra were recorded at 290 K after preliminary retaining of the zeolite sample with adsorbed octene-1-^{13}C at 290 K for the period of time, which is indicated above each spectrum. 400 scans have been collected per spectrum. More than 20 spectra were recorded with 50 min interval, five of them are shown in the figure. Asterisks (*) denote spinning side bands.

ural ^{13}C abundance (fig. 1, table 1). This means that complete scrambling of the ^{13}C label over the hydrocarbon skeleton of the adsorbed octene-1-^{13}C occurs at room temperature.

Thus, the adsorption of octene-1 leads to formation of a species inside the H-ZSM-5 channels with a permanently rearranging hydrocarbon skeleton. These rearrangements scramble the ^{13}C label over the skeleton. Strong scrambling of carbon atoms is a characteristic feature of carbenium ions in liquids and solids [11–14]. Therefore, carbenium ions must be formed inside the H-ZSM-5 zeolite upon adsorption of octene-1.

The initial transformation of octene-1 upon its adsorption on H-ZSM-5 can be represented as follows:

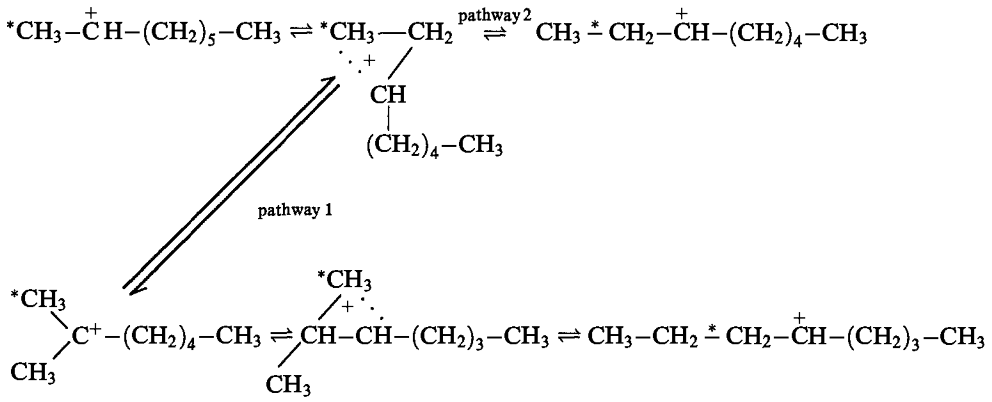
$$^{*}CH_2{=}\,CH{-}(CH_2)_5{-}CH_3 + \equiv Al{-}OH{-}Si\equiv \rightleftharpoons$$

$$^{*}CH_3{-}\overset{+}{C}H{-}(CH_2)_5{-}CH_3 + \equiv Al{-}O^{-}{-}Si\equiv$$

Scheme 1.

Further, via protonated cyclopropane intermediates [11] the ^{13}C label penetrates into the neighbouring CH_2 group and subsequently into more distant CH_2 groups (see scheme 2). Scheme 2 explains simultaneously both the scrambling of the ^{13}C

label over the hydrocarbon skeleton of adsorbed octene-1 (pathways 1 and 2) and isomerization of the linear skeleton to branched one (pathway 1).



Scheme 2.

3.2. HYDROGEN TRANSFER FROM ZEOLITE FRAMEWORK TO OCTENE-1 MOLECULE

According to scheme 1, the proton of the ≡Al–OH–Si≡ group in the zeolite is transferred into the $^*CH_2=$ group of octene-1 to form carbenium ion species. To prove that hydrogen atom is indeed transferred from the zeolite framework onto octene-1 molecule, we have made the following experiment. First, we converted ≡Al–OH–Si≡ groups into ≡Al–OD–Si≡ via H/D exchange with D_2O at 200°C [15]. Then, we activated the zeolite sample with a conventional procedure (see the experimental section). After that we adsorbed unlabelled octene-1 on the zeolite. In case of hydrogen atom transfer from the zeolite to octene-1, the deuterium label from ≡Al–OD–Si≡ should penetrate into the $CH_2=$ group to give the terminal methyl (CH_2D-) group.

Deuterated methyl groups (CD_3, CHD_2 or CH_2D) in slowly reorienting molecules (the case that should be expected for octene-1 inside the channels of ZSM-5 zeolite), exhibit in ^2H NMR spectra a Pake-powder pattern with quadrupole splitting $q \approx 40$ kHz [8,16,17]. This q value corresponds to fast one-axis rotation of the methyl group around the C–C bond [16,17].

Fig. 5A shows the ^2H NMR spectrum of D-ZSM-5 zeolite. A powder pattern corresponds to a superposition of a more intense signal with quadrupole splitting $q = 176$ kHz from the bridging ≡Al–OD–Si≡ group and a less intense signal from the terminal ≡Si–OD group [18] (vide infra). Fig. 5B shows that 5 min after adsorption of octene-1 the most intense signal in the ^2H NMR spectrum becomes the characteristic signal with solid-like line shape and $q = 38$ kHz from a deuterated methyl group. The appearance of this signal clearly evidences for the fast deuterium transfer from ≡Al–OD–Si≡ to the $CH_2=$ group of octene-1 molecule. This fact well agrees with scheme 1.

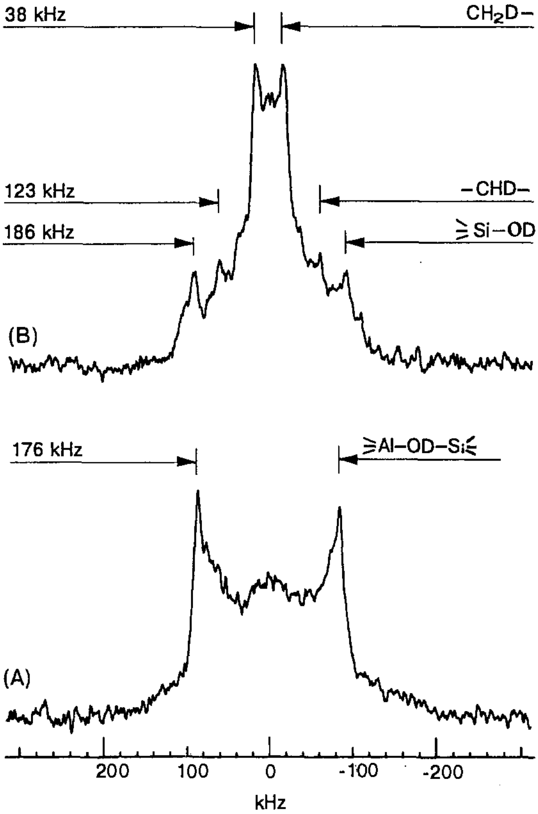


Fig. 5. (A) ^{2}H NMR spectrum of D-ZSM-5 (Si/Al = 54) zeolite, 44000 scans; (B) ^{2}H NMR spectrum of D-ZSM-5 (Si/Al = 54) zeolite 5 min after adsorption of octene-1 (300 μmol/g), 108000 scans. Both spectra were recorded at 173 K in 5 mm i.d. glass sealed tubes, using solid echo pulse sequence as in ref. [8], and 0.4 s repetition time.

A solid-like signal with $q = 186$ kHz that is observed after octene-1 adsorption (fig. 5B) most probably belongs to the terminal ≡Si–OD group that does not participate in H/D isotope exchange between the zeolite and octene-1.

Note, that besides the signal with $q = 38$ kHz, the solid-like signal of small intensity with $q = 123$ kHz is observed in the spectrum of fig. 5B. The value of $q = 123$ kHz is typical for static (in terms of ^{2}H NMR time scale) CD_2 or CHD groups [16–18]. Its appearance suggests the penetration of deuterium atoms into CH_2 groups to form CHD or CD_2 groups. This fact may be related to secondary reactions of carbenium ion rearrangements. Indeed, as seen from fig. 4, the ^{13}C label scrambles from the CH_4 group into the CH_2 groups.

4. Discussion

All the data presented above can be explained in terms of two alternative models:

(1) Carbenium ion is the predominant state of octene-1 adsorption in the channels of H-ZSM-5 zeolite.

(2) Species other than carbenium ion, such as alkyl silyl ether or olefin, is the predominant state of octene-1 adsorption. However, a small amount of adsorbed carbenium ion by all means should be present in equilibrium with this species. Carbenium ions will provide scrambling of the ${}^{13}C$ label, as well as fast migration of the ${}^{2}H$ label, over the hydrocarbon skeleton of the adsorbed octene-1.

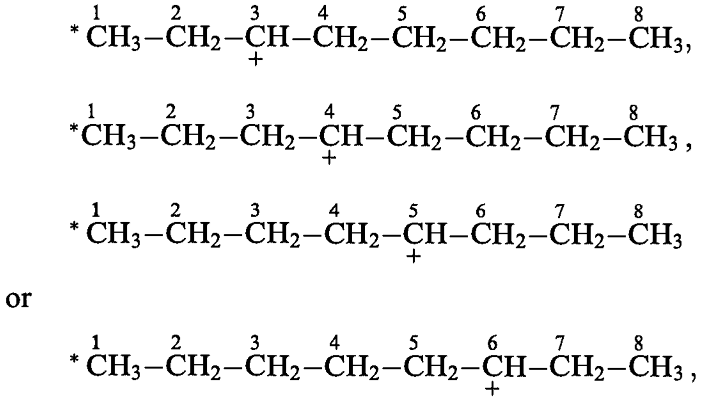
4.1. MODEL 1. FORMATION OF OCTYL CARBENIUM ION FROM OCTENE-1 INSIDE THE ZEOLITE CHANNELS

4.1.1. On the structure of carbenium ion formed from octene-1

According to classical organic chemistry, once formed linear carbenium ions stream to rearrange to give a more stable branched ion [19]. However, according to the ${}^{13}C$ NMR spectrum of fig. 2 only ca. 20% of adsorbed octene-1 transforms into species with the branched hydrocarbon skeleton. This fact suggests that the channels of ZSM-5 zeolite with diameter of ca. 5.5 Å [20] favour the linear structure of the C_8 carbenium ion and hinder its branching at room temperature.

4.1.2. Why are the characteristic signals from carbenium ions not observed?

"Static" carbenium ions exhibit the signals at 320–330 ppm for a carbenium center (C^+), and the signals at 40–60 ppm for the carbon atoms adjacent to the carbenium center [13]. Carbon atoms that are more distant from the C^+ center are usually not perturbed with C^+ and exhibit chemical shifts typical for saturated hydrocarbon chains [13]. Transformation of the $^{*}CH_2=$ group of the adsorbed octene-1-${}^{13}C$ into the $^{*}CH_3$ group with the chemical shift of 14.3 ppm rather than 40–60 ppm indicates that the carbenium center and the $^{*}CH_3$ group are separated by at least one more carbon atom. Thus, carbenium ions of the type, given in scheme 3 should be mainly formed in the zeolite.



$$^{*}\overset{1}{C}H_3-\overset{2}{C}H_2-\underset{+}{\overset{3}{C}}H-\overset{4}{C}H_2-\overset{5}{C}H_2-\overset{6}{C}H_2-\overset{7}{C}H_2-\overset{8}{C}H_3,$$

$$^{*}\overset{1}{C}H_3-\overset{2}{C}H_2-\overset{3}{C}H_2-\underset{+}{\overset{4}{C}}H-\overset{5}{C}H_2-\overset{6}{C}H_2-\overset{7}{C}H_2-\overset{8}{C}H_3,$$

$$^{*}\overset{1}{C}H_3-\overset{2}{C}H_2-\overset{3}{C}H_2-\overset{4}{C}H_2-\underset{+}{\overset{5}{C}}H-\overset{6}{C}H_2-\overset{7}{C}H_2-\overset{8}{C}H_3$$

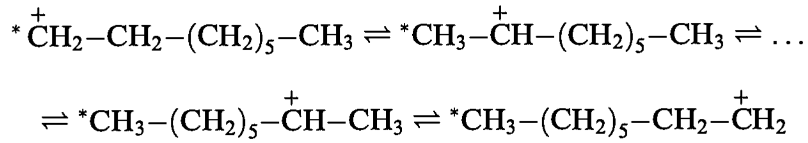
or

$$^{*}\overset{1}{C}H_3-\overset{2}{C}H_2-\overset{3}{C}H_2-\overset{4}{C}H_2-\overset{5}{C}H_2-\underset{+}{\overset{6}{C}}H-\overset{7}{C}H_2-\overset{8}{C}H_3,$$

Scheme 3.

We did not observe the signal at 320–330 ppm from "static" carbenium ions in our spectra at both ambient temperature and at temperature as low as $-100°C$. For fast hydride shift between two internal carbon atoms (e.g. atoms 3 and 4 or 4 and 5) in the dynamic diatomic carbenium center the signal between ca. 300 ppm and ca. $(1/2)300 + (1/2)50 = 175$ ppm should be observed. An average signal between ca. 50 ppm and ca. $40 = (1/2)50 + (1/2)30$ ppm from carbon atoms adjacent to carbenium center should also be observed.

Thus, the signal at 40 ppm in the spectra of figs. 1 and 2 may have a contribution from the carbon atom adjacent to the carbenium center. However, we certainly do not observe the expected signal between 300 and 175 ppm from the supposed dynamic carbenium ions. Probably, this signal is too broad to be observed. Such broadening can arise due to slow or intermediate (in the ^{13}C NMR time scale) exchange of the C^+ site between two or more carbon atoms via hydride shift reactions (see scheme 4).



$$ {}^{*}\overset{+}{C}H_2-CH_2-(CH_2)_5-CH_3 \rightleftharpoons {}^{*}CH_3-\overset{+}{C}H-(CH_2)_5-CH_3 \rightleftharpoons \dots $$

$$ \rightleftharpoons {}^{*}CH_3-(CH_2)_5-\overset{+}{C}H-CH_3 \rightleftharpoons {}^{*}CH_3-(CH_2)_5-CH_2-\overset{+}{C}H_2 $$

Scheme 4.

In practice this means that the exchange frequency ν_{ex} should be

$$ 3 \times 10^2 \leqslant \nu_{ex} \leqslant 3 \times 10^4 \text{ Hz}. \qquad (1) $$

For conditions of slow or intermediate exchange to be fulfilled both at room temperature and at $-100°C$, the activation energy of exchange must be smaller than 3.5 kcal/mol. Note, that for $\nu_{ex} \approx 3 \times 10^4$ Hz and $E^{\neq} \leqslant 3.5$ kcal/mol the activation entropy for the exchange process should be $\Delta S^{\neq} \leqslant -20$ kcal/mol. Such a low value of $\Delta S^{\neq}$ suggests that hydride shift in the adsorbed carbenium ion (see scheme 4) is a complicated process that may involve simultaneous rearrangement of several chemical bonds.

As we have mentioned above, two of eight carbon atoms of adsorbed octene-1 are not visible in ^{13}C NMR. These unobservable signals may be attributed to the C^+ center and next to it carbon atom, which are in a condition of slow or intermediate exchange (see eq. (1)). If we compare the observed ratio between ^{13}C signal intensities of adsorbed octene-1 with the natural isotope abundance (see table 1), and the expected ratio CH_3 : CH_2(outer): (CH_2)(inner) = 1 : 1 : 1 for the carbenium ions of scheme 3, then we must conclude that none of these four carbenium ions can be the main form of octene-1 adsorption on H-ZSM-5. According to experimental ratio CH_3 : CH_2(outer) : (CH_2)(inner) = 1 : 1 : 4, the carbenium ion of the type $^{+}CH_2-CH_2-(CH_2)_4-CH_2-CH_3$ is mainly formed inside H-ZSM-5 from *octene-1 with the natural isotope abundance*. In this case observation of the labelled terminal $^{*}CH_3$ group just after adsorption of *octene-1-^{13}C with the ^{13}C label in the terminal $^{*}CH_2{=}$ group*, is explained by fast migration of the ^{+}C

center from the one side of octene-1 hydrocarbon skeleton to the opposite side (see scheme 4).

Thus, all NMR data presented here can be explained by assuming that the carbenium ion is the main state of octene-1 adsorption in the channels of H-ZSM-5 zeolite.

4.1.3. *Kinetic and thermodynamic parameters for carbon scrambling*

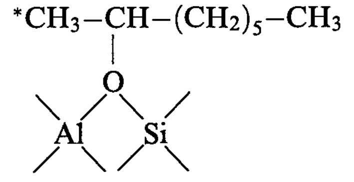
We have not observed the preferential growth of the signal at 25 ppm from the CH_2(outer) group, upon the decrease of the intensity of the signal at 14.3 ppm from the CH_3 group. The ^{13}C label could penetrate into this CH_2 group according to pathway 2 of scheme 2. As seen from fig. 4, the intensity of the signals at 30–33 ppm from the CH_2(inner) groups preferentially increases with time. These facts suggest that rearrangements via pathway 1 of scheme 2 proceed faster than rearrangements via pathway 2. From the kinetics of the decrease with time of the intensity of the signal at 14.3 ppm, for the process

$$^{*}\mathrm{CH_3} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} {}^{*}\mathrm{CH_2(inner)}$$

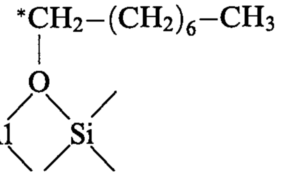
the following values were obtained for the rate constants and activation energies of carbon atom scrambling: $k_1 = 0.14\ \mathrm{h}^{-1}$ at 290 K, $E_1 = 11.5 \pm 2.0$ kcal/mol, $k_{-1} = 0.023\ \mathrm{h}^{-1}$ at 290 K, $E_{-1} = 9.5 \pm 1.2$ kcal/mol, and for thermodynamic parameters of this scrambling at 290–343 K: $K = k_1/k_{-1} = 6$ at 290 K, $\Delta H = 2.0 \pm 0.1$ kcal/mol, $\Delta S = 10.6 \pm 1.0$ cal/(mol K). The obtained values are in a reasonable agreement with activation energies for carbon atom scrambling in carbenium ions in solution [11–13] and in solid state [14]. Note, that the characteristic frequency of ^{13}C label migration between the CH_3 group and the CH_2(inner) groups is $\nu_{ex} = k_1 = 0.14\ \mathrm{h}^{-1} = 3.9 \times 10^{-5}$ Hz. It is too small to fit condition (1). This means that scrambling of the ^{13}C label (scheme 2) and migration of the C^+ center via hydride shift (scheme 4) are different processes, the former being much slower than the latter.

4.2. MODEL 2. FORMATION OF OCTYL SILYL ETHER OR ADSORBED OCTENE AS ALTERNATIVES TO CARBENIUM ION

In principle, after proton transfer from the acidic ≡Al–OH–Si≡ group on adsorbed octene-1-^{13}C molecule, which can proceed both according to Markovnikoff rule and against it, stable octyl silyl ethers of the type

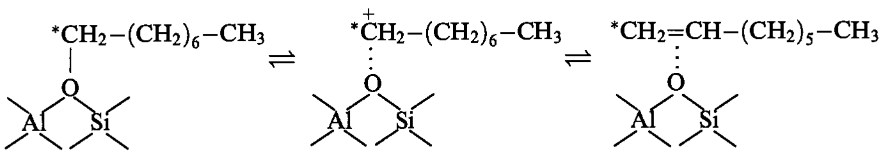


or



may be formed as predominant species [21]. Another possibility is the formation (upon the transfer of the proton from the carbenium ion back to the ≡Al–O$^-$–Si≡ site) of the adsorbed octene-1 molecule in which the olefin moiety is shifted from its initial position in octene-1-^{13}C. Such migration of this moiety can be provided, e.g., by the hydride shift process in scheme 4. The formation of such olefinic or alkyl silyl ether species could be an alternative to carbenium ion formation. The scrambling of ^{13}C and ^{2}H labels in adsorbed octene-1 can be explained by the existence of a small concentration of octyl carbenium ion as an excited state, which is in equilibrium with octyl silyl ether or octene as the ground state [21].

Static alkyl silyl ethers are known to exhibit the ^{13}C NMR signals at 70–80 ppm [22–25], which are typical for C–O groups [26]. Olefins are known to exhibit the ^{13}C NMR signals near 110–140 ppm from the olefinic moiety [9,10]. However, no signals around 70–80 ppm or 110–140 ppm are observed in the spectra of figs. 1 and 2. The absence of such signals can be explained by interconversions of the type depicted in scheme 5, provided that conditions of intermediate exchange (see eq. (1)) are fulfilled for them.



Scheme 5.

Thus, both models 1 and 2 can explain all our NMR data.

5. Conclusions

Octene-1 adsorbed on H-ZSM-5 zeolite exhibits carbenium ion properties at ambient temperature. The following conclusions can be made about the origin and properties of the adsorbed carbenium ions: (i) According to ^{2}H NMR, hydrogen transfer from the acidic ≡Al–OH–Si≡ group into the $CH_2=$ group of octene-1 occurs. (ii) According to ^{13}C NMR, scrambling of the ^{13}C isotope label over various positions in the hydrocarbon skeleton is observed. (iii) All the NMR data can be equally well explained in terms of two alternative models: (1) carbenium ion is the main state of octene-1 adsorbed in the zeolite channels; (2) carbenium ion is not the main adsorption state, but is in equilibrium with an octyl silyl ether or octene, which are the main adsorption states. (iv) Activation barriers for carbon scrambling and thermodynamic parameters of the scrambling are in a good accordance with those for carbenium ions in liquid and solid states. (v) The structure of the carbenium ion is presumably controlled by the zeolite framework, making it to be linear rather than a branched one.

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