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In situ NMR identification of the intermediates and the reaction products in alcohols and hydrocarbons conversion on zeolites

A.G. Stepanov

Boreskov Institute of Catalysis, Pr. Akademika Lavrentieva 5, Novosibirsk 630090, Russia

Abstract

In this paper the possibilities of ^{13}C solid state NMR spectroscopy (^{13}C CP/MAS NMR) are demonstrated for identification of the intermediates and the reaction products in alcohols and hydrocarbons conversion on zeolites. As the particular examples the reactions of ethylene conversion and butyl alcohols dehydration on zeolite H-ZSM-5 are considered.

1. Introduction

among numerous application of NMR spectroscopy in catalysis, ^{13}C solid state NMR (^{13}C CP/MAS NMR) studies of the reactions on acidic form (H-form) zeolites at low temperature (300–500 K) are of particular interest. Low temperature oligomerization of small olefins and alcohols dehydration on zeolites results in oligomeric products that are not desorbed from zeolite pores and therefore can not be analyzed with conventional methods, e.g., with gas chromatography. Under these circumstances ^{13}C CP/MAS NMR can be considered as one of very few instrumental methods that can be applied to in situ analysis of the reaction products as well as to the identification of intermediates on zeolites at low temperature.

In this paper we report on in situ identification with ^{13}C CP/MAS NMR of the intermediates and reaction products that are formed during low temperature conversion of ethylene and butyl alcohols dehydration on zeolite H-ZSM-5. In particular, the following items are considered: (1) identification of possible intermediates (carbenium ions and alkoxy species) during tert-butyl and iso-butyl alcohols dehydration, (2) clarifying the role of various intermediates under butyl alcohols dehydration; (3) in situ analysis of hydrocarbon products formed under ethylene conversion and butyl alcohol dehydration; (4) clarifying the nature of oligomeric species formed at low temperature olefin oligomerization.

2. Experimental

Procedures for the synthesis of H-ZSM-5 zeolite sample (Si/Al = 23–54) and their vacuum treatment before olefin or alcohol adsorption were as described in Refs. [1–6]. To facilitate NMR analysis and selectively monitor the transformation of certain organic fragments during reaction, we used the olefins and alcohols that were selectively labeled with ^{13}C in certain carbon atoms. Registration of ^{13}C NMR spectra at 100.613 MHz with cross-polarization (CP) (or without) and magic angle spinning (MAS) was performed with a Bruker MSL-400 spectrometer in 7 mm zirconia

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rotors under experimental conditions, given in Refs. [1–3,5,6].

3. Results and discussion

3.1. Dehydration of iso-butyl alcohol

Our NMR studies of i-BuOH on H-ZSM-5 showed that after the dehydration was completed at 343–373 K, the signal at 73 ppm was observed (Fig. 1B) [1]. The position of this signal is in vicinity of the signals, typical for carbons adjacent to oxygen atoms [7]. After complete alcohol dehydration the signal 73 ppm can not belong to the initial alcohol. It does not belong also to diisobutyl ether, which can in principle be formed in the reaction, because its chemical shift (86 ppm [1]) differs from the observed one. We have concluded that the signal 73 ppm belongs to intermediate isobutyl silyl ether (IBSE), with the selective ^{13}C label in the CH_2 OH group [1]. At T)343 K the growth of the signals from unlabeled CH_3 group at 19.2 ppm from IBSE and at 30.5 ppm is observed (Fig. 1B,C). According to two dimensional (2D) J-resolved ^{13}C NMR the signal at 30.5 ppm belongs to the CH group of IBSE [2]. Thus we observed rather selective penetration of the ^{13}C label from the CH_2 OH group of IBSE into its CH_3 and CH groups. Scrambling of the ^{13}C carbon atoms is a feature of carbenium ions [8]. Therefore, it is evident that scrambling of the selective ^{13}C label in IBSE can not be fulfilled without existence of isobutyl carbenium ion (IBCI), which should be in equilibrium with IBSE.

Thus we conclude, that i-BuOH dehydration on H-ZSM-5 proceeds via a stage of IBSE formation. IBSE is in equilibrium with IBCI, which in turn can be in equilibrium with olefin. Interaction of olefin with IBCI results to the reaction products – butene oligomers, which further crack to form par-

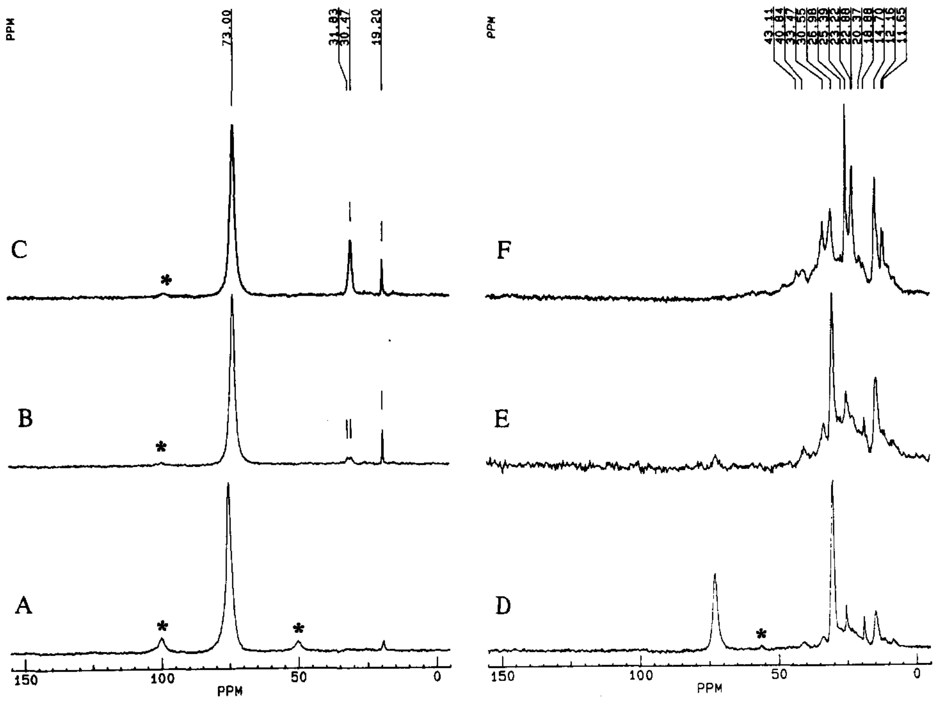


Fig. 1. The change of the ^{13}C CP/MAS NMR spectrum of i-BuOH [1-^{13}C], adsorbed on H-ZSM-5 zeolite (Si/Al = 24) at 296 K in the amount 283 μmol/g, upon successive heating of the sample for a certain period of time at various temperatures: (A) after adsorption on zeolite at 296 K; (B) 70 min at 343 K and 30 min at 373 K; (C) 40 min at 398 K; (D) 60 min at 413 K; (E) 60 min at 423 K; (F) 60 min at 448 K. Asterisks (*) in Figs. 1–6 denote spinning sidebands.

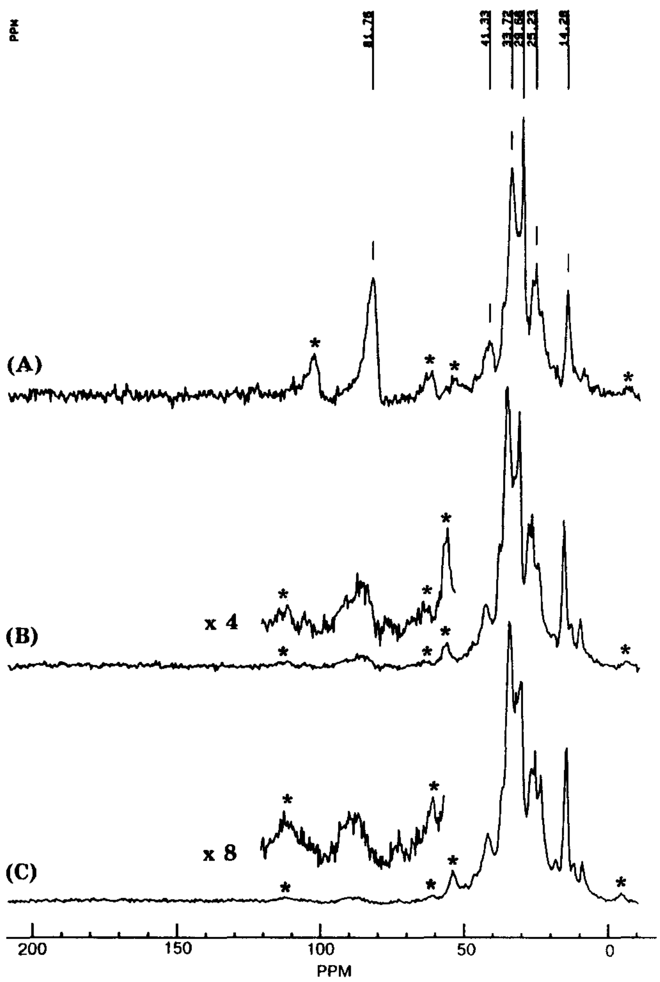


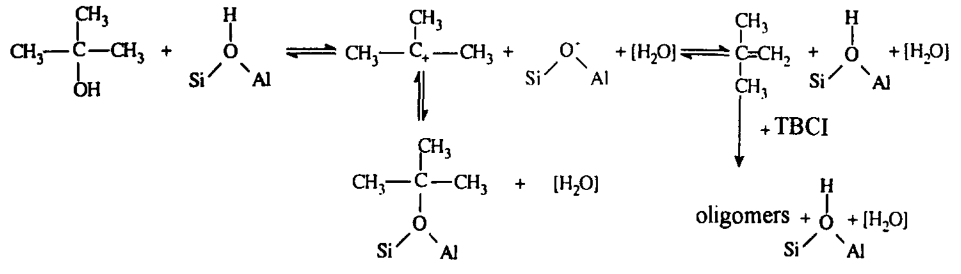
Fig. 2. ^{13}C CP/MAS NMR spectra of the t-BuOH[2-^{13}C] adsorbed on zeolite H-ZSM-5 (Si/Al = 44) at 296 K in the amount 300 μmol/g in dependence of time after alcohol adsorption. (A) 4 hours; (B) 24 hours; (C) 48 hours.

affins, their signals being observed at 10–40 ppm (Fig. 1F).

3.2. Dehydration of tert-butyl alcohol

t-BuOH was reported to undergo a dehydration on H-ZSM-5 slowly at room temperature [3]. As seen from Fig. 2A 4 hours after adsorption, besides the signals from initial alcohol at 81.8 ppm (labeled COH group), the main signals in this spectrum arise from butene oligomers at 10–40 ppm. 48 hours after adsorption the dehydration is completed, mainly the signals from oligomers being observed (Fig. 2C). However, a new signal of small intensity at 86 ppm, different from the signal of t-BuOH is identified among the signals from reaction products (Fig. 2B,C). Parallel studies of this reaction with ^2H and ^{13}C NMR [3,4] allow us to conclude that the signal 86 ppm belongs to tert-butyl silyl ether intermediate (TBSE), i.e. tert-butyl fragment bound to the oxygen of the zeolite framework.

Attention should be paid to appearance of a rather narrow signal at 29.7 ppm from the CH_3 group of the alcohol among the signals from the reaction products – butene oligomers, although the alcohol was formerly labeled with ^{13}C in quaternary carbon atom. This rather selective scram-



Scheme 1.

bling of the ^{13}C carbon atom (alongside with complete scrambling in hydrocarbon products and H/D exchange between D_2O and methyl group of t-BuOH [3]) represents an evidence for the existence of tert-butyl carbenium ion (TBCI) as intermediate in this reaction and that there exists an equilibrium t-BuOH $\rightleftharpoons$ TBCI + H_2O inside zeolite H-ZSM-5.

On the basis of our NMR data the following scheme of t-BuOH dehydration on H-ZSM-5 have been suggested (Scheme 1).

In Scheme 1 TBCI represents key reaction intermediate. At room temperature TBSE can be considered as a stable reaction product, besides butene oligomers. The arguments for this conclusion are as follows. TBSE is formed in small amount just after adsorption, it does not disappear after the dehydration is completed at 296 K [3]. It disappears at T>373 K, when it becomes involved in subsequent chemical transformations.

With the aim of in situ analysis of the products, formed under the dehydration at 448 K, we recorded two dimensional (2D) J-resolved ^{13}C NMR spectrum for these hydrocarbon products (Fig. 3). On the basis of observed multiplicities of carbon signals, their positions in the spectrum [7] and taking into account the of relative signal areas, which were obtained from ^{13}C MAS NMR

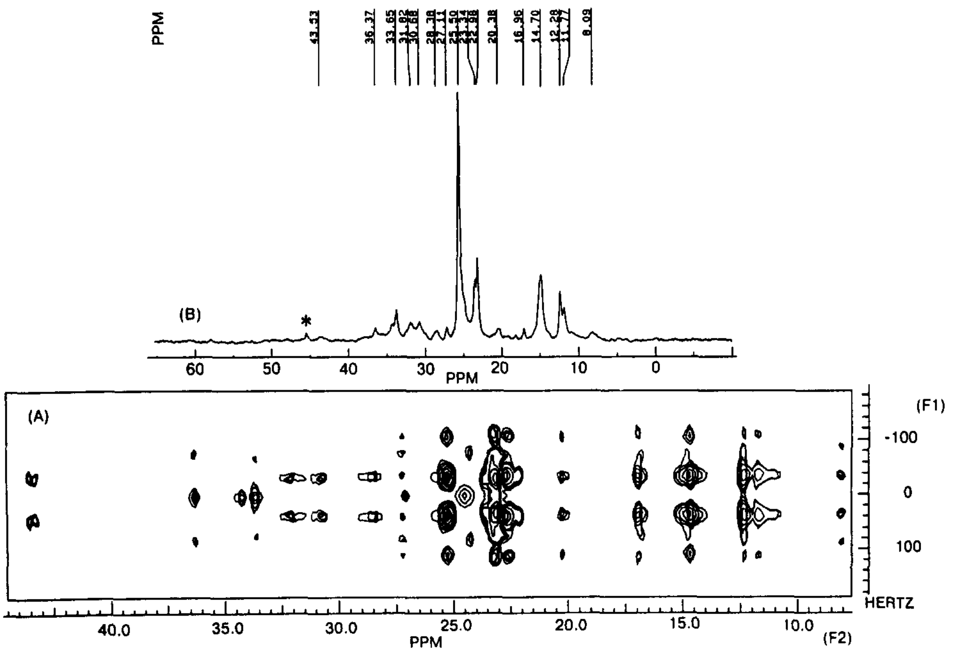


Fig. 3. (A) Contour plot of 2D J-resolved ^{13}C solid state MAS NMR spectrum for the products of t-BuOH[2-^{13}C] dehydration on zeolite H-ZSM-5 at 448 K. Corresponding one dimensional ^{13}C MAS spin echo NMR spectrum (B) is given above the contour plot.

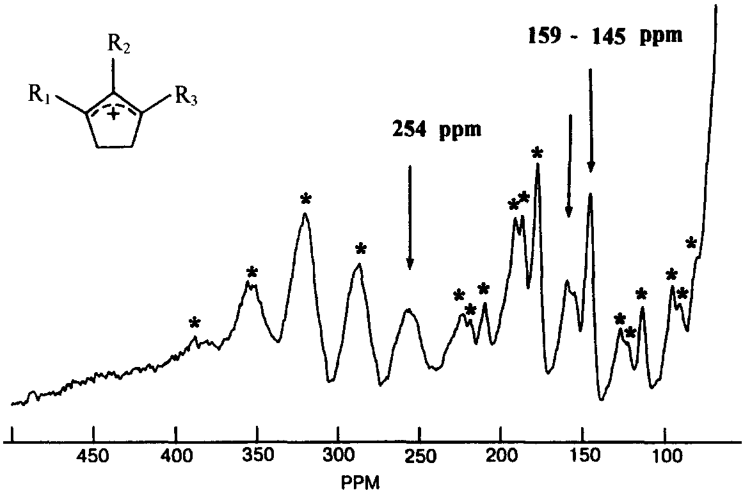


Fig. 4. Sixteenfold extension of the region 100–500 ppm of ^{13}C CP/MAS NMR spectrum for the products of t-BuOH[2-^{13}C] dehydration on zeolite H-ZSM-5 at 448 K. Spinning rate was 3.2 kHz.

spectrum, recorded without cross-polarization, the following distribution of paraffins was found: propane 1%, butane 2%, isobutane 17%, isopentane 18%. pentane 17%, C6 and higher paraffins 45%.

Under alcohols dehydration a formation of olefins rather than paraffins should be expected. If paraffins are formed, then hydrogen deficient hydrocarbons such as a coke or aromatics should also be formed. However, instead of the signals from a coke the signals from the cyclopentenyl carbenium ions (CPCI) at 145–159 and 254 ppm [9,10] were observed in our spectra (Fig. 4). We believe that these stable carbenium ions are those hydrogen deficient species that are formed simultaneously with paraffins, when long chain olefins, formerly formed from the alcohols, further undergo disproportionation inside zeolites. Simultaneous formation of paraffins and CPCI is indicative of the similarity of the chemical processes of olefin conversion on zeolite H-ZSM-5 and in solution of strong sulfuric acid [11,12].

Note that according to our NMR experiments butene oligomers undergo disproportionation to a small extent even at room temperature. Indeed, we observed the signals from paraffins in ^{13}C spin-echo MAS NMR spectrum not only at 448 K, but at 373 K and even at 296 K (e.g., the signal from isobutane at 25.5 ppm).

3.3. Ethylene conversion

It was reported that ethylene conversion at 373 K resulted to the linear oligomers [13]. This conclusion was made by analyzing the chemical shifts of the signals for the reaction products. However, one can not unambiguously attribute the signals to certain $CH_n (n = 0–3)$ groups solely from the position of the peaks in the spectrum, because of the overlapping of CH_n signals with different values of n [7]. With the aim of more reliable assignment of observed singlet peaks to certain CH_n groups on the basis of their multiplicities, we recorded 2D J-resolved ^{13}C NMR spectrum for the products of ethylene conversion at 373 K (Fig. 4) [5].

As it turned out 2D J-resolved ^{13}C NMR spectrum for ethylene at 373 K and that for t-BuOH at 448 K on H-ZSM-5 are identical (see Figs. 3, 5). This fact indicates that at 373 K ethylene oligomers undergo cracking to form paraffins. Thus, the ^{13}C NMR signals observed earlier at 10–40 ppm for the products of ethylene conversion at 373 K [13] should be attributed to a mixture of C3–C7 and higher paraffins and, in part, to uncracked ethylene oligomers, rather than exclusively to linear ethylene oligomers.

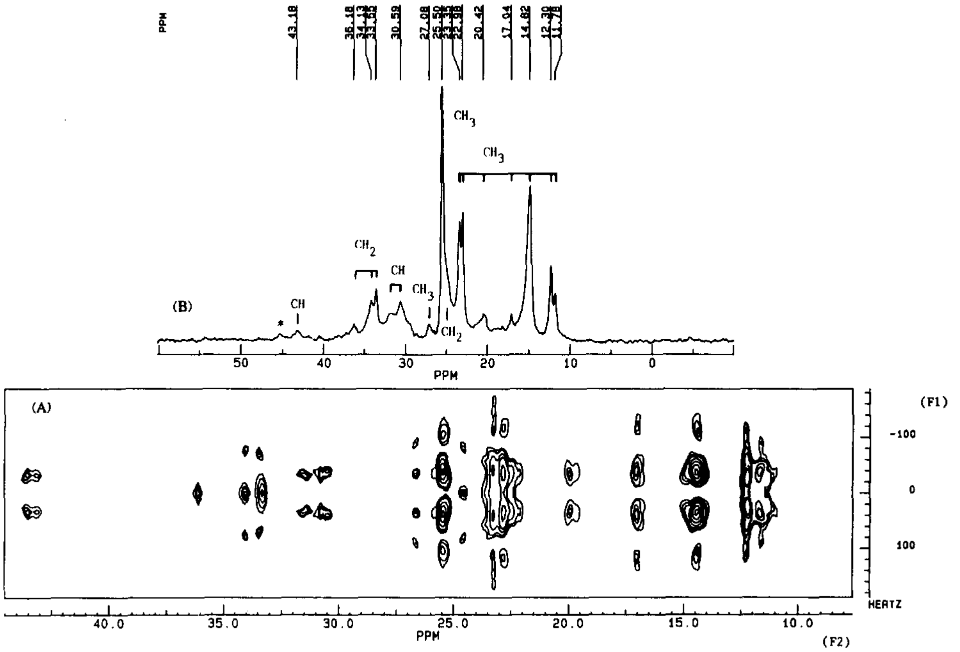


Fig. 5. (A) Contour plot of 2D J-resolved ^{13}C MAS solid state NMR spectrum for the products of ethylene conversion in zeolite H-ZSM-5 at 373 K. Corresponding one dimensional ^{13}C MAS spin echo NMR spectrum (B) is given above the contour plot.

3.4. On the nature of oligomers formed from olefins on H-form zeolites at low temperature

It is expected that low temperature conversion of small olefins on H-form zeolites should result to the long chain olefins [14]. However, the ^{13}C NMR signals from the olefinic moiety at 110–140 ppm [7] are not observed in the spectra of oligomeric products [14].

To clarify the nature of oligomeric species formed after olefin oligomerization, we adsorbed octene-1 on zeolite H-ZSM-5 at 296 K. Octene-1 can be considered as one of the products of ethylene oligomerization at room temperature.

When we adsorbed octene-1, labeled with ^{13}C in the terminal $=CH_2$ group, we found [6] that just after adsorption the labeled $=CH_2$ group was transformed into the labeled terminal CH_3 group of octene-1 and further, a scrambling of the labeled carbon atom from the CH_3 group into the next CH_2 and long distant inner CH_2 groups was observed (Fig. 6). From the kinetics of the decrease with time of the intensity of the signal 14.3 ppm, for the process

$$CH_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_2(\text{inner})$$

the following values were obtained for the rate constants and activation energies of carbon atom scrambling: $K_1 = 0.14\ h^{-1}$ at 290 K, $E_1 = 11.5 \pm 2.0$ kcal/mol, $k_1 = 0.023\ h^{-1}$ 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 kinetic and thermodynamic parameters for carbon scrambling in carbenium ions in solution [8,15] and solid state [16].

We have also found with ^2H NMR [6] that after adsorption of octene-1 on deuterated ZSM-5, the deuterium atom from the acidic site of zeolite framework is transferred on octene-1 molecule, and olefinic $=CH_2$ group is transformed into the methyl CH_2D group.

Thus, adsorbed on H-ZSM-5 octene-1 exhibits carbenium ion properties: (1) the proton from the acidic site of the zeolite framework is transferred

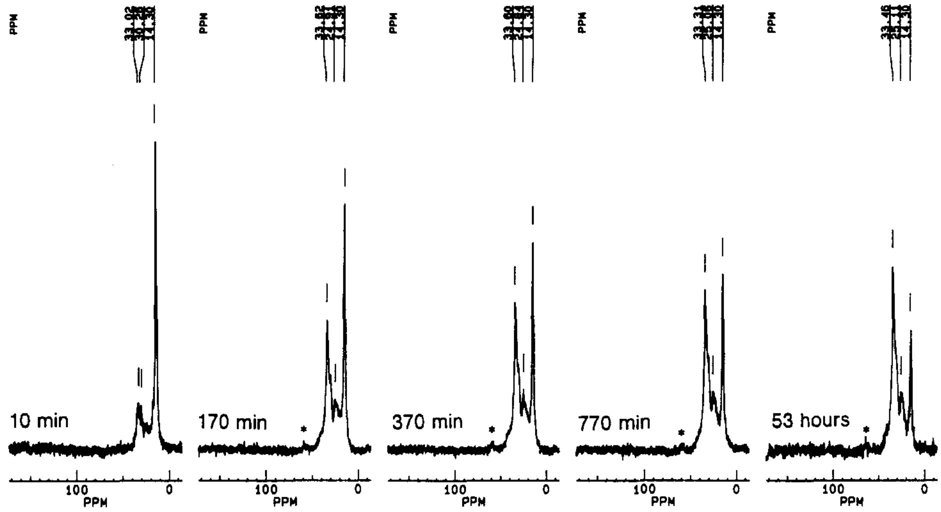


Fig. 6. The change with time of the ^{13}C CP/MAS NMR spectrum of octene-1 (labeled with ^{13}C in the $=CH_2$ group) adsorbed (290 μmol/g) on zeolite H-ZSM-5 (Si/Al = 44). All the spectra were recorded at 290 K after preliminary retaining of the zeolite sample with adsorbed octene-[1-^{13}C] at 290 K for the period of time, which is indicated above each spectrum.

on octene-1 molecule, (2) scrambling of the ^{13}C selectively labeled carbon atom occurs at room temperature. On the basis of these facts as well as taking into account the absence in our spectra the signals from olefinic double bond at 110–140 ppm [7] or from the stable carbenium ions at 330 ppm [15] or the signals from alkyl-silyl ethers at 70–80 ppm [1–3,9] we have come to the conclusion: all our NMR data can be well explained in terms alternative models. (1) Carbenium ion is the main state of octene-1 adsorbed in the zeolite channels. The signals from carbenium ion center (C^+) at 330 ppm is not observed because of the migration of the C^+ center over hydrocarbon skeleton by means of a hydride shift reaction, hydrogen migration in this reaction proceeds with rate, which corresponds to an intermediate (in ^{13}C NMR time scale) regime of exchange. (2) Carbenium ion is not the main adsorption state, but is in equilibrium with the octyl silyl ether or octene-1, which are the main adsorption states. Neither the signals from olefinic double bonds or octyl silyl ether or carbenium ion are observed because of the intermediate regime of exchange among these three states.

4. Acknowledgement

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5. References

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