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High-resolution solid-state NMR spectroscopy in studies of conversions of hydrocarbons and alcohols on zeolites †

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Abstract. The review surveys advances in high-resolution solid-state ^{1}H and ^{13}C NMR spectroscopy applied to studies of conversions of hydrocarbons and alcohols on zeolite catalysts of an acidic nature. The potential of NMR spectroscopy in studies of mechanisms of chemical reactions and analysis of compounds formed *in situ* is considered. The bibliography includes 134 references.

I. Introduction

NMR spectroscopy has been used for studying solid heterogeneous catalysts and surface chemical reactions over several decades.[1] However, impressive progress in this field has been achieved only with the advent of special techniques for recording NMR spectra and with the development of superconducting magnets producing strong magnetic fields (7 – 18 T). Thus the application of the magic-angle-spinning (MAS) technique in which the sample is rotated rapidly about an axis subtending a magic angle (57 °48′8″)[2–4] with respect to the external magnetic field (2 – 35 kHz) leads to substantial narrowing of NMR signals for nuclei of both solid catalysts (^{1}H, ^{17}O, ^{27}Al, ^{29}Si and ^{51}V) and organic molecules adsorbed on the catalyst surface (^{1}H, ^{13}C, ^{15}N and ^{31}P). The implementation of a technique for recording NMR spectra with the use of cross-polarisation simultaneously with high-power proton decoupling[5–7] enhances the sensitivity of NMR spectroscopy a hundred times and makes possible observations of signals of molecules adsorbed on the catalyst surface.

Presently, high-resolution solid-state NMR spectroscopy is widely used for both characterising structures of heterogeneous catalysts[1,8–13] and studying conversions of organic molecules on their surfaces.[13–17] In many cases, NMR spectroscopy appears to be the unique physical method which provides data on reaction mechanisms and enables one to perform reliable analysis of compounds formed *in situ*, to determine their compositions and structures and to make conclusions about chemical processes that occur on the catalyst surface. Hence, one can go from the hypothetical notion of reaction mechanisms to the understanding of their true mechanisms.

NMR spectroscopy is particularly helpful in studying catalytic conversions at low (as regards traditional organic catalysis) temperatures, for example, in studying low-temperature alkene conversions on zeolites. This field of potentially important low-temperature chemical conversions remains poorly studied due to problems associated with analysis of undesorbable compounds.

Recently, studies of conversions of hydrocarbons and alcohols on zeolites by NMR spectroscopy have attracted growing interest in connection with the solution of the following practical problems:

— a search for ways of enhancing the selectivity of the yields of $C_4 – C_5$ alkenes in the course of catalytic cracking based on zeolite catalysts (HY, USY and HZSM-5);

— synthesis of a motor fuel from methanol on HZSM-5 zeolite.[18]

Discussion about the role of various intermediates, *viz.*, alkoxides and carbenium ions, in catalytic hydrocarbon conversions on solid acids (zeolites and amorphous aluminosilicates), which has lasted for the last decade, gave additional impetus to the application of NMR spectroscopy to the studies of hydrocarbon conversions.

The present review surveys the most interesting results of studies of conversions of various hydrocarbons on solid zeolite catalysts of acidic nature which have been performed in the leading world's laboratories with the use of NMR spectroscopy. The first results of studies of hydrocarbon (alkene) conversions are compared with the results obtained by various research groups within the last five years. The possibilities of other methods (primarily, of IR spectroscopy) in studies of hydrocarbon conversions are considered.

In the present review, the discussion is restricted to the results of chemical studies ‡ obtained by NMR spectroscopy.

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‡ Experimental details and discussion of various possibilities of the use of high-resolution solid-state NMR spectroscopy for characterisation of catalysts and processes that occur on their surfaces have been reported in the literature.[10–13,16,19,20]

II. Alkene oligomerisation

1. Adsorbed products of low-temperature alkene oligomerisation

Until recently, the nature of hydrocarbon products which were formed upon low-temperature oligomerisation of alkenes (ethylene, propene or isobutene) on acidic forms of zeolites (for example, on the HZSM-5 zeolite), remained unclear and was the subject of discussion.[21–38] It was reasonable to suggest that alkene oligomerisation in the presence of an acidic catalyst should afford a long-chain alkene. However, signals at 1660–1670 [ν(C=C)] and 3020–3090 cm^{-1} [ν(=C–H)] expected for the double bonds[39] were not observed in the IR spectra of adsorbed oligomeric products.[21–24,27–29,31,33] Signals with the chemical shifts at δ 110–140 typical of alkene double bonds[40] were absent in the ^{13}C NMR spectra as well.[24–26,30,32,34–38] The only identified signals were those of saturated hydrocarbon fragments of oligomeric products.[21–38]

The absence of signals of alkene fragments in the IR and NMR spectra has been explained within the frameworks of two alternative hypotheses. According to the first hypothesis, adsorbed oligomers are hydrocarbon fragments covalently bonded to oxygen atoms of the zeolite lattice, *i.e.*, the hypothesis postulates that oligomeric alkoxides (alkyl silyl ethers), which do not contain double bonds, are formed.[32–34,38] According to the second hypothesis, adsorbed oligomers are oligomeric aliphatic carbenium ions,[27,28,37] which do not contain double bonds as well. Unfortunately, both hypotheses are self-contradictory. Actually, if oligomers were alkoxides, the ^{13}C NMR spectra should have signals for the carbon atoms of the C–O–Si fragment at δ 70–90.[40,41] However, in a series of studies,[24–26,30,32,34–38] no mention of these signals was presented, while in other studies[15,35,38,42–48] these signals were observed only in the case of small hydrocarbon fragments (Me, Pr^i, Bu^t and Bu^i) bound to the zeolite framework.

The same is true for carbenium ions containing long-chain hydrocarbon fragments for which signals at δ 300–330 (a carbon atom that carries a positive charge)[49–51] in the ^{13}C NMR spectra or bands at 1260–1295 cm^{-1} [$\nu(^+C–C)$ stretching vibration][52,53] in the IR spectra would be expected. However, neither the IR spectra nor the NMR spectra had these signals.

a. Alkoxide nature of the adsorbed oligomers

The ^{13}C CP/MAS NMR spectrum§ of products of ethylene oligomerisation on the HZSM-5 zeolite at 296 K is shown in Fig. 1.[54] On the whole, this spectrum is identical with that obtained previously by van den Berg and co-workers for ethylene oligomers.[30] The signals at δ 14, 22 and 33 were assigned to the terminal CH_3 groups, to the adjacent CH_2 groups and to internal CH_2 groups of linear hydrocarbon fragments of oligomers, respectively.

The spectrum has no signals with noticeable intensities at δ 110–140 (for alkene fragments)[40] or at δ 300–330 (for carbenium ions).[49–51] However, substantial enhancement of the spectrum made it possible to detect a weak broad signal at δ 89, which indicates that adsorbed oligomers contain carbon atoms bound to oxygen atoms of the zeolite framework, *i.e.*, is indicative of the presence of C–O–Si fragments.[41–45] An analogous signal for C–O–Si fragments at δ 86, while substantially more intense, was observed for isobutene oligomers formed upon dehydration of *tert*-butyl alcohol on HZSM-5 zeolite.[35,38] Therefore, evidence for the alkoxide nature of the adsorbed oligomers was obtained.¶

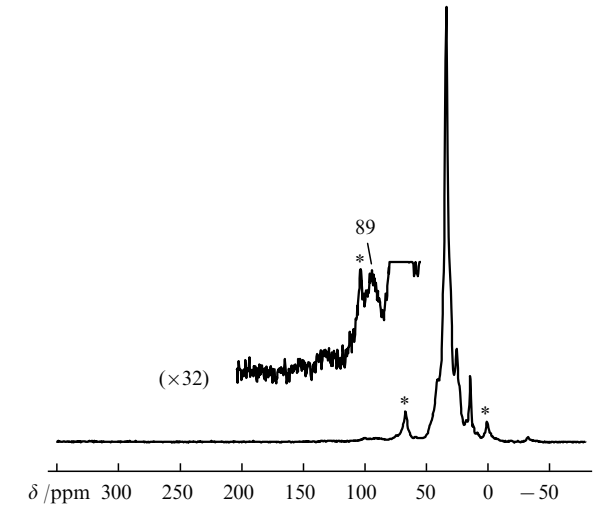


Figure 1. The ^{13}C CP/MAS NMR spectrum of oligomerisation products of ethylene (40%-$^{13}CH_2=CH_2$) on HZSM-5 zeolite at 296 K. Hereinafter, peaks due to the rotation of the sample are marked with asterisks.

b. Carbenium-ion properties of the adsorbed oligomers

An interesting experiment, which gave a deeper insight into the nature of the adsorbed oligomers, was described in Ref. 37. Studies of a possible ethylene oligomerisation product, *viz.*, oct-1-ene containing the selectively ^{13}C-labelled terminal $=CH_2$ group, adsorbed on the HZSM-5 zeolite demonstrated that the terminal $=^{13}CH_2$ group of oct-1-ene was converted into the ^{13}C-labelled terminal methyl group immediately after adsorption (Fig. 2). Then the intensity of the signal for the carbon atom of the terminal $^{13}CH_3$ group at δ 14.3 decreased and the intensities of the signals of internal CH_2 groups of oct-1-ene at δ 30.0 increased with time. This is indicative of the transfer of the selective ^{13}C label from the methyl group of oct-1-ene to its CH_2 groups with the characteristic half-reaction time $\tau_{1/2}$ ~4 h (at 290 K). The redistribution of the carbon label in the adsorbed oct-1-ene was completed in t > 20 h. It is known that the redistribution of

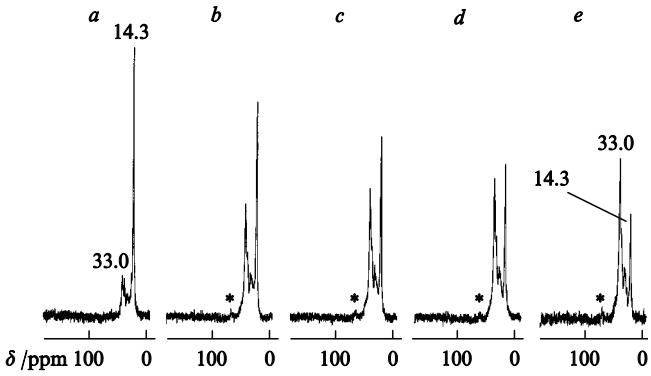


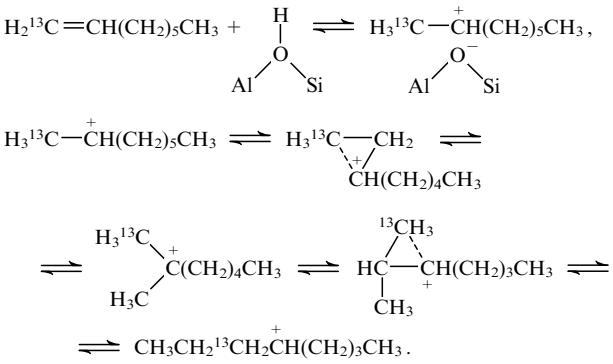
Figure 2. Change in the ^{13}C CP/MAS NMR spectrum of oct-1-ene (containing the ^{13}C-labelled terminal $=CH_2$ group) adsorbed on HZSM-5 zeolite (T = 290 K) with time.[37]
Time /h: 0.17 (*a*), 2.83 (*b*), 6.17 (*c*), 12.83 (*d*), 53 (*e*).

§ The ^{13}C CP/MAS NMR spectrum was recorded with the use of the magic-angle-spinning (MAS) technique at the spinning frequency of 2500–5000 Hz using cross-polarisation (CP).

¶ An explanation of the reasons for the low intensity of the signal for the carbon atom of the COSi fragment in adsorbed ethylene oligomers is offered below, where the interpretation of the spectra is discussed.

carbon labels is typical only of carbenium ions existing as stable species in solutions of superacids.[49–51, 55–57] Based on the aforesaid, it was concluded that carbenium ions were formed upon adsorption of oct-1-ene on the HZSM-5 zeolite. The changes observed in the NMR spectrum are attributable to the following reactions (Scheme 1):

Scheme 1

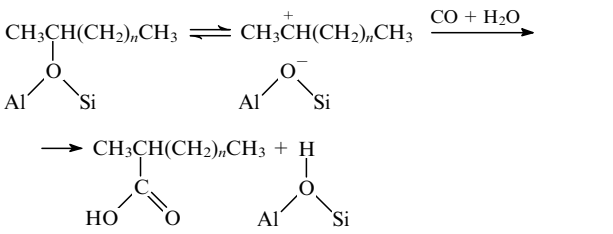


In the adsorption of oct-1-ene on zeolite, the proton of the acidic OH group of the zeolite is transferred to the oct-1-ene molecule. In this case, the terminal $=CH_2$ group is converted into the terminal CH_3 group simultaneously with the formation of a carbenium ion. In the cation formed, the ^{13}C label is redistributed through the formation of protonated cyclopropane intermediates,[49, 50, 55–57] which leads to a decrease in the intensity of the signal for the CH_3 group and to an increase in the intensities of the signals for the internal CH_2 groups with time (Fig. 2).

In spite of the label redistribution typical only of carbenium ions, signals at δ 300–330, which are indicative of the presence of carbenium ions in the system, were not observed in the spectrum. It was thus concluded that either the concentration of the cations formed was too low or these cations were short-lived transient species.

Later, the conclusion that carbenium ions exist in small amounts among adsorbed oligomers was confirmed by the chemical reaction at room temperature involving the adsorbed oligomers, which is characteristic of carbenium ions. It is known that carbenium ions readily react with carbon monoxide in solutions of strong acids[58, 59] to form carboxylic acids. Consequently, carbenium ions formed among oligomeric products would be expected to react with CO and water to form carboxylic acids. Actually, simultaneous adsorption of CO and water on a zeolite specimen containing ethylene oligomers resulted in conversion of oligomers into a mixture of the corresponding oligomeric carboxylic acids (Scheme 2), which is evidenced by the signal of carboxyl groups at δ 189 in the ^{13}C CP/MAS NMR spectrum (Fig. 3).[60, 61]

Scheme 2



The formation of carboxylic acids and the redistribution of the selective ^{13}C label unambiguously suggest that carbenium ions were present among the adsorbed oligomers. In addition, after completion of the reaction of oligomers with CO and H_2O, signals for oligomeric alkoxides at δ 89 were no longer observed in the ^{13}C NMR spectrum (*cf.* Figs 1 and 3), which is indicative of the conversion of alkoxides into acids. These results altogether allowed the conclusion that alkoxides existed in the equilibrium with oligomeric carbenium ions. Though the concentrations of the latter are too low to be detected by ^{13}C CP/MAS NMR spectroscopy, the reactivities of the oligomers are determined by the reactivities of the equilibrium carbenium ions.

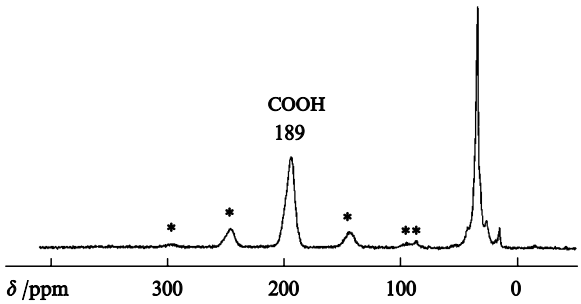
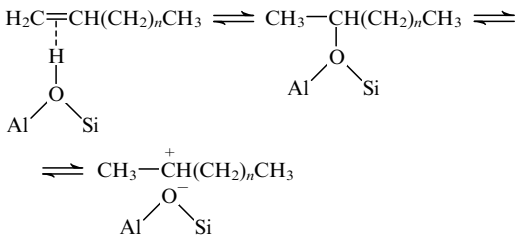


Figure 3. The ^{13}C CP/MAS NMR spectrum of products formed after additional adsorption of $^{13}CO + H_2O$ on zeolite containing ethylene oligomers.

Taking into account that conversion of C_2-C_4 alkenes in a flow reactor at $T < 450$ K afforded C_6-C_{18} alkenes,[62, 63] *i.e.*, oligomeric products can be desorbed as alkenes under particular conditions,† it was concluded that alkenes were present in small amounts among the adsorbed oligomeric products. However, the concentrations of alkenes were so low that these compounds, like carbenium ions, were 'invisible' to NMR spectroscopy.

Hence, the NMR spectral data allow the conclusion that oligomeric products of low-temperature alkene conversions, which are adsorbed on acidic forms of zeolites, exist as three interconvertible forms, *viz.*, as alkoxides, carbenium ions and alkenes (Scheme 3).

Scheme 3



Oligomeric alkoxides present the major adsorbed form.

2. Compositions and structures of products of alkene oligomerisation on HZSM-5 zeolite

In the first studies devoted to oligomerisation of alkenes on HZSM-5 zeolite, qualitative conclusions about the formation of linear oligomers[25, 26, 30, 34] which contain approximately 16 carbon atoms from alkenes (ethylene, propene or isobutene) were made based on the analysis of the positions of the signals for CH_3 and CH_2 groups in the ^{13}C MAS NMR spectra.[30] However, signals for the CH_2 groups of linear fragments and signals for the CH_3 groups of branched fragments of oligomers are observed in the same region of the ^{13}C NMR spectrum (at δ 20–30).[40] Consequently, one cannot infer the structures and lengths of hydrocarbon chains of oligomeric products exclusively from the chemical shifts of signals in the ^{13}C NMR spectra.

It was suggested that 2D *J*-resolved ^{13}C MAS NMR spectroscopy followed by GC-mass spectrometric analysis and traditional high-resolution ^{13}C NMR spectroscopy (in solution) of oligomers which have been extracted from zeolite, be used for establishing the compositions and structures of oligomeric products formed from ethylene on HZSM-5 zeolite.[54]

† Signals of double bonds are also absent in the NMR spectrum of the adsorbed oligomer.

a. 2D *J*-resolved ^{13}C MAS NMR spectroscopic data

Two-dimensional *J*-resolved MAS NMR spectroscopy offers advantages over 1D NMR spectroscopy because not only does it provide data on the chemical shifts of signals for carbon atoms of oligomers but it also allows the determination of the multiplicity of the signals that occurs due to spin-spin coupling between the ^{13}C nuclei and the adjacent protons [the spin-spin coupling constants $J(^{13}C-^{1}H)$].[64, 65] In the 2D NMR spectrum, the assignment of the signal with a particular F2-dimension chemical shift to the CH_n group is made based on the calculation of the number of peaks of this signal on the F1 axis.[36, 38, 64–66] As a result, the ambiguity of the assignment of the signals for carbon atoms is excluded and the true structure of oligomers in the adsorbed form can be determined.

The contour plot of the 2D *J*-resolved ^{13}C MAS NMR spectrum of ethylene oligomers on the HZSM-5 zeolite and the corresponding 1D NMR spectrum are shown in Fig. 4*b*. It can be seen that the signals at δ 30 and δ 34 exist as triplets with the constant $J(^{13}C-^{1}H) = 140 \pm 16$ Hz, which suggests that these signals belong to the CH_2 groups of oligomers. The signal at δ 22 is a singlet characteristic of the quaternary carbon atom. However, it is observed in the region typical of either the terminal CH_3 groups of branched oligomers (in this case, the signal should exists as a quartet on the F1 axis[66]) or the CH_2 group (a triplet on the F1 axis[66]) adjacent to the terminal CH_3 group of the linear fragment of the hydrocarbon chain rather than being located in the region of chemical shifts of the quaternary carbon atom of alkanes (at δ 30–40[40]). The existence of a singlet rather than a doublet at δ 22 suggests that this signal is in fact a triplet for which only the most intense central component is distinct in the spectrum against a background of the noise level.[35, 67] Hence, it was concluded that the signal at δ 22 belongs to the CH_2 groups of oligomers. The existence of four peaks on the F1 axis for the signal at δ 14 indicates that the latter belongs to the terminal CH_3 groups of the oligomer.

To summarise, analysis of the multiplicities of signals of the adsorbed oligomers allowed the conclusion that signals in the region from δ 22 to δ 34 belong to the CH_2 groups, *i.e.*, the oligomers formed are linear hydrocarbon fragments.

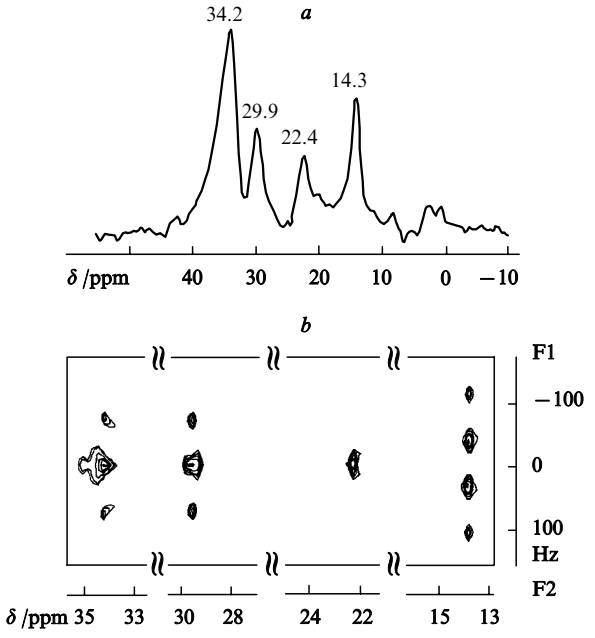


Figure 4. Spin-echo 1D ^{13}C MAS NMR spectrum (*a*) and the contour plot of the 2D *J*-resolved ^{13}C MAS NMR spectrum (*b*) of oligomerisation products of ethylene on HZSM-5 zeolite at 296 K. The observed value of the scalar spin-spin coupling constant $J(^{13}C-^{1}H)$ on the F1 axis is half as large as the real value $J(^{13}C-^{1}H)$ due to the use of a special technique for recording the 2D spectrum.[65]

b. High-resolution solution ^{13}C NMR spectroscopic data

To confirm the conclusions about the structures of oligomers formed from ethylene, a sample of HZSM-5 zeolite with the adsorbed oligomers was dissolved in 10% NaOH[61] and the liberated hydrocarbon products were extracted with diethyl ether, dissolved in benzene-d_6 and analysed by high-resolution ^{13}C NMR spectroscopy. The major characteristics (chemical shifts, the ratio of the intensities of the signals and the multiplicities of the major, most intense signals) of the spectrum of the products desorbed from the zeolite (Fig. 5) are identical with those of the adsorbed oligomers (see Fig. 1). The most intense signals at δ 22 and 33–34 exist as triplets with $J(^{13}C-^{1}H) = 125$ Hz and the signals at δ 10–14 exist as quartets with $J(^{13}C-^{1}H) = 125$ Hz.

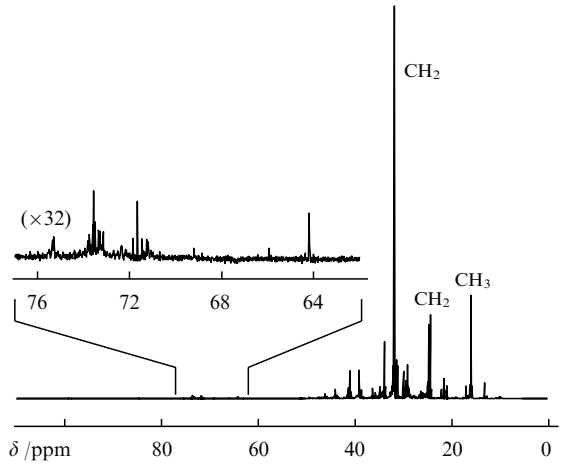


Figure 5. The high-resolution ^{13}C NMR spectrum (in benzene-d_6) of ethylene oligomers extracted from HZSM-5 zeolite after dissolution of the zeolite in NaOH solution.

In the spectra of the extracted products, the intensities of the signals at δ 60–80 are as small as those of the adsorbed oligomers. The fact that the ratio of the signals of the adsorbed products is identical with that of the extracted products as well as the presence of signals for the carbon atoms of the CH_x-OH fragment of alcohols indicate that the oligomers are extracted from the zeolite as alcohols and the structures of the extracted alcohols are analogous to those of the adsorbed alkoxide oligomers. The estimation of the ratio of the signals at δ 14, 22 and 33 (Fig. 5) demonstrated that an average linear oligomeric chain consists of seven carbon atoms $[-(CH_2)_6CH_3]$ bound to an oxygen atom of the zeolite framework.

From the spectrum shown in Fig. 5 it follows that not only linear but also branched oligomers are formed on the HZSM-5 zeolite, which is evidenced by the signals at δ 35–50 belonging to secondary and tertiary carbon atoms.[30, 68] However, linear oligomers predominate apparently due to the specific structure and the size of the channels in the HZSM-5 zeolite.[69] The fact that the ^{13}C NMR spectrum (see Fig. 5) has more than 20 signals from alcohols at δ 60–80 indicates that a mixture of no less than 20 oligomeric alkoxides containing predominantly linear fragments is formed upon adsorption of ethylene on the HZSM-5 zeolite. For a mixture of adsorbed oligomers, only one broad low-intensity signal at δ 89 (see Fig. 1) is observed, which is indicative of the alkoxide nature of the adsorbed oligomers.[54] Previously,[30, 32, 34, 70, 71] attempts to identify this signal have failed for several reasons. First, the adsorbed oligomers exist as a mixture of oligomeric alkoxides (> 50, according to GC-mass spectrometric analysis [53]). Second, the signals for oligomeric alkoxides are broad

but their intensities are low. Third, chemical shifts of the signals vary within the range of > 15 ppm.

In some cases, signals at δ 87–89 observed for various alkenes (Pr^i and Bu^t) [35, 45, 48, 72] were assigned to small hydrocarbon fragments bound to the oxygen atoms of the zeolite framework. However, the fact that the chemical shifts of the signals for alkoxides observed upon propene oligomerisation on HY zeolite [45, 73] or on HZSM-11 zeolite [48] are identical with those observed upon isobutene oligomerisation on HZSM-5 zeolite [35] allows the conclusion that the signals at δ 87–89 (see Refs 35, 45 and 48) should be assigned to oligomeric alkoxides rather than to short hydrocarbon fragments.

c. Data of GC-mass spectrometric analysis

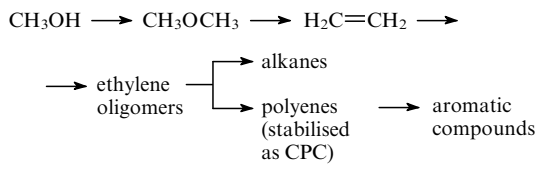
The compositions of ethylene oligomers formed were also determined by GC-mass spectrometric analysis. To do this, the adsorbed oligomers were first converted into a mixture of the corresponding carboxylic acids according to Scheme 2. Then, carboxylic acids were extracted from the zeolite by dissolving the latter in 10% alkali. Subsequent treatment of the mixture of acids with diazomethane [61] made it possible to convert them into the corresponding methyl carboxylates, which were readily separated and analysed by GC-mass spectrometry. It was found that the mixture extracted was comprised of more than 50 different oligomeric products (C_5–C_{14}).

III. Dehydration of alcohols

1. Methyl alcohol

NMR studies of alcohol conversions on zeolites attracted interest immediately after 'Mobil' had discovered conversions of methanol into a motor fuel on HZSM-5 zeolite.[74, 75] The first NMR spectral study devoted to conversions of methanol [76] had already demonstrated the possibility of the application of ^{13}C MAS NMR spectroscopy in the analysis of intermediates and reaction products. Evidence was obtained for the conversion of methanol first into dimethyl ether and then into a mixture of hydrocarbons *via* intermediate carbenium ions rather than carbenes, as had been suggested previously by Chang and Silvestri.[18] Anderson and Klinowski [78, 79] noted the difference in the composition of the products which were present in the gas phase and in zeolite pores. Thus in no case were C_{10} aromatic products observed among the desorbed products, but these compounds were found *in situ* in zeolite pores. It was thus concluded that products were formed within zeolite pores under conditions of the equilibrium reaction, the composition of the desorbed products being determined by the pore size of the zeolite. Hence, the effect of the internal specific size and the pore structure on the composition of the products desorbed was experimentally demonstrated.

In the study devoted to methanol conversions,[79] it was noted that ethylene was formed as an important intermediate. It was also reported that the reaction performed under conditions similar to those used in a flow reactor (small contact time) yielded intermediate C_4 alkenes and cyclopentenyl cations (CPC).[80] Below is given the scheme of conversions of methanol into a mixture of hydrocarbons on the HZSM-5 zeolite.



2. *tert*-Butyl alcohol

Conversions of aliphatic C_3–C_4 alcohols on acidic zeolites were studied with the aim of obtaining more detailed information on the mechanism of dehydration. The molecular sizes of these alcohols are comparable with the pore sizes of zeolites.

Dehydration of C_3–C_4 alcohols starts at substantially lower temperature (300–400 K) than that of methanol (550–700 K). This enables one to obtain more detailed information on the nature of intermediates based on the data of NMR spectroscopy and, consequently, to draw conclusions about the mechanism of these reactions. In addition, it becomes possible to reveal the effect of the pore size of a zeolite on the course of dehydration of isomeric alcohols and to analyse subsequent conversions of the products formed upon primary dehydration. In the present review, the results of studies of dehydration of isomeric butyl alcohols are considered in detail.

Dehydration of *tert*-butyl alcohol on HZSM-5 zeolite occurs at room temperature.[81] NMR spectral studies of this reaction, which is not complicated by secondary processes of cracking of the products formed, are of considerable interest for the understanding of the mechanisms of dehydration and subsequent oligomerisation of isobutene formed upon dehydration.[35, 38, 46, 70] It was found [46] that the dehydration of Bu^{t}OH containing the ^{13}C-labelled tertiary carbon atom on HZSM-5 zeolite (Si : Al = 36) was accompanied by complete redistribution of the labels in the oligomeric products. It was thus concluded that carbenium-ion intermediates were involved in dehydration of the alcohol and that *tert*-butyl silyl ether (TBSE) was formed as a stable intermediate, *i.e.*, the *tert*-butyl fragment was covalently bound to the oxygen atom of the zeolite framework. The authors [46] believed that the formation of TBSE is evidenced by the signal at δ 77 corresponding to the carbon atom bound to the oxygen atom of the zeolite ‡ as well as by the unusually large chemical shift of the carbon atom bound to the oxygen atom of the zeolite framework compared to that of the carbon atom in the initial Bu^{t}OH, which is generally observed in neat alcohol or in neutral solutions.

More recent studies [33, 35] demonstrated that the conclusion about the formation of TBSE as a stable intermediate [46, 70] was erroneous. A special NMR spectral study [35] showed that dehydration of Bu^{t}OH on an HZSM-5 zeolite with Si : Al = 24 at room temperature proceeded slowly and was completed in > 15 h (Figs 6 and 7). With an HZSM-5 zeolite in which Si : Al = 36, *i.e.*, the zeolite in which the concentration of reactive acidic OH groups is 1.5 times lower, the dehydration time could only increase. Hence, it was concluded that dehydration of alcohols cannot be completed in 1.5 h (the reaction time in the study [46]) and, consequently, the signal at δ 77 can be assigned only to the initial unconsumed alcohol.[35] The difference between the chemical shift of the carbon atom of the C–O fragment in the adsorbed alcohol (at δ 82 [35, 70] or at δ 77 [46]) and that of this carbon atom in the initial solution (at δ 68.97 [40]) should be attributed to specific interactions between the alcohol and the centres of its adsorption (Brønsted acidic OH groups) as well as to a possible change in the geometry of the alcohol upon its adsorption in zeolite channels.[82]

IR spectral studies [33] demonstrated that the rates of oligomerisation and isomerisation of isobutene liberated upon dehydration are substantially higher than that of its dehydration. Hence, the products observed in the NMR spectrum are isobutene oligomers.

The identity of the spectra of isobutene oligomers prepared from Bu^{t}OH containing selectively ^{13}C-labelled CH_3 or C–OH groups suggests the complete redistribution of the selective ^{13}C labels (*cf.* Figs 6 and 7) and confirms the conclusions made by Aronson *et al.*[46] that carbenium-ion intermediates are involved in dehydration and oligomerisation of Bu^{t}OH.

The formation of the *tert*-butyl carbenium ion (TBCI) and isobutene as intermediates, which exist in equilibrium with the initial alcohol,[35] is evidenced by the experimental data on the incorporation of the deuterium label from D_2O into the methyl group of *tert*-butyl alcohol which had previously been adsorbed on zeolite (Fig. 8, Scheme 4).

‡ It was suggested that dehydration of the alcohol on HZSM-5 zeolite with the Si : Al ratio of 36 was completed in 1.5 h.

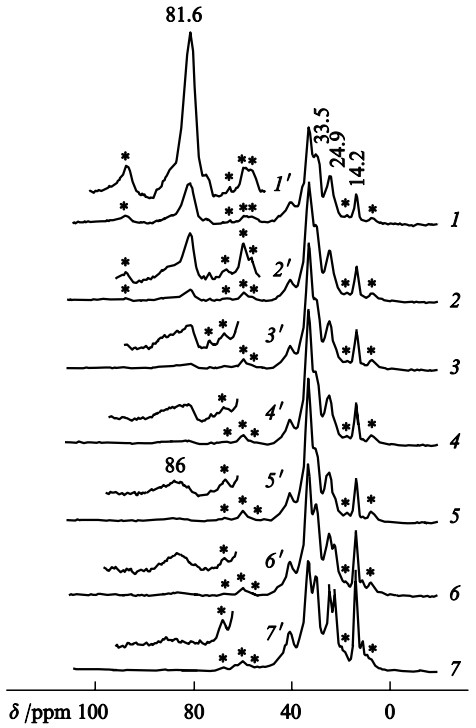


Figure 6. Changes in the ^{13}C CP/MAS NMR spectra of *tert*-butyl alcohol (containing the selectively ^{13}C-labelled C–OH group) with time at 296 K (*1*–*5*), 373 K (*6*) and 448 K (*7*) after adsorption on HZSM-5 zeolite (Si : Al = 24). Spectra *1′*–*7′* at δ 60–110 are given with a fourfold amplification.
Time /h: (*1*) 0.33; (*2*) 2.83; (*3*) 5.5; (*4*) 8.0; (*5*) 15.5; (*6*) 1; (*7*) 1. The signal at δ 82 belongs to the ^{13}C–OH group of the unconsumed initial alcohol.

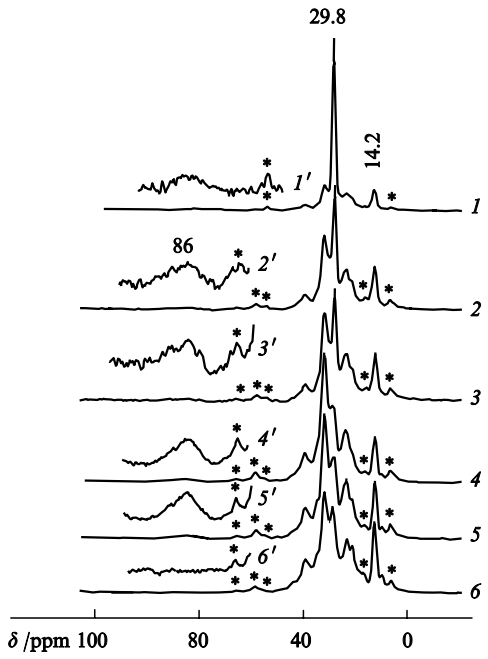


Figure 7. Changes in the ^{13}C CP/MAS NMR spectra of *tert*-butyl alcohol (containing the selectively ^{13}C-labelled CH_3 group) with time at 296 K (*1*–*4*), 373 K (*5*) and 448 K (*6*) after adsorption on HZSM-5 zeolite (Si : Al = 24). Spectra *1′*–*6′* at δ 60–110 are given with an eightfold amplification.
Time /h: (*1*) 0.33; (*2*) 2.83; (*3*) 5.5; (*4*) 15; (*5*) 1; (*6*) 1. The signal at δ 29.8 belongs to the $^{13}CH_3$ group of the initial alcohol.

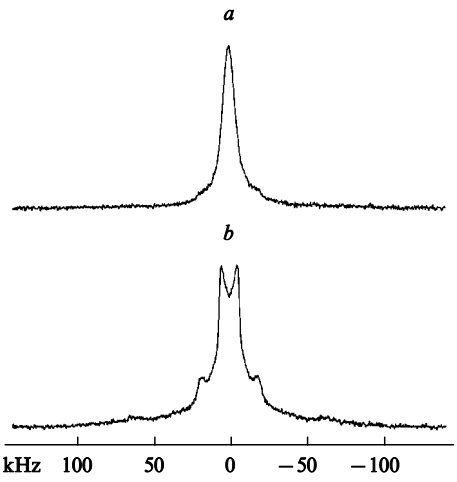
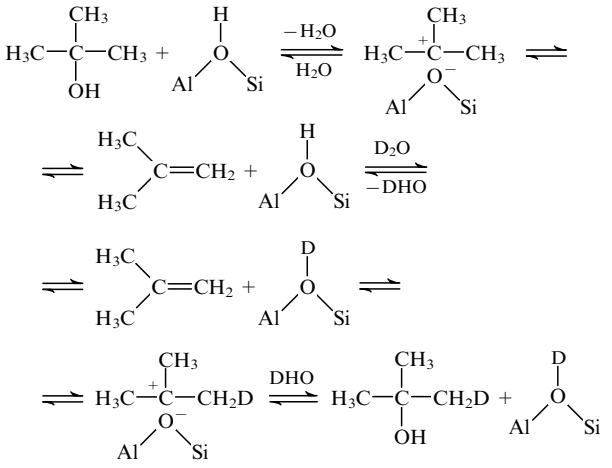


Figure 8. The static ^2H NMR spectra observed after adsorption of D_2O on a HZSM-5 zeolite specimen with the previously adsorbed Bu^tOH recorded within 5 min (*a*) and 1 h (*b*) after adsorption of D_2O (T = 296 K). (*a*) the shape of the spectral line corresponds to deuterated water; (*b*) the shape of the spectral line corresponds to superposition of three signals, *viz*., a signal for the $(CD_3)_3C$ fragment of alcohol with the observed quadrupole splitting $Q_3 \approx 10$ kHz and signals for the CD_3 and CD_2 groups (weak signals) of oligomers with $Q_2 \approx 38$ kHz and $Q_1 \approx 123$ kHz, respectively.

Scheme 4

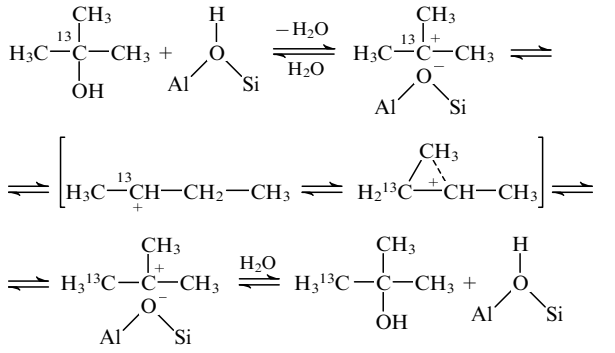


It was also demonstrated that if zeolite containing a smaller number of acidic OH groups was used, *i.e*., in the case of slower dehydration of the alcohol, the selective ^{13}C label from the C–O group of the alcohol was transferred to its CH_3 group (Fig. 9).[38] This redistribution of the ^{13}C label confirms that TBCI is formed as an intermediate, which exists in equilibrium with the initial alcohol, in the course of dehydration. An analogous redistribution of the carbon labels was also observed in the case of carbenium ions in superacid solutions (Scheme 5).[49, 50]

In spite of the above-considered experimental evidence for the formation of TBCI, the signal at δ 330 characteristic of the carbenium ion was not observed.[51] It was thus concluded that the cation formed in zeolite is either transient or present in an amount insufficient for detection by ^{13}C NMR spectroscopy.

The signal at δ 86, which was observed in the ^{13}C NMR spectrum in the course of dehydration of Bu^tOH, was originally assigned to stable *tert*-butyl silyl ether formed in the reaction (see Figs 6 and 7).[35] However, it was found that this signal appeared simultaneously with signals of oligomers and persisted after completion of dehydration. This signal disappeared only at a temperature higher than 373 K at which cracking of oligomers

Scheme 5



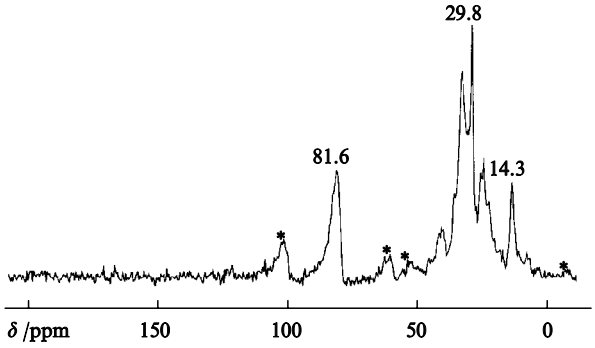
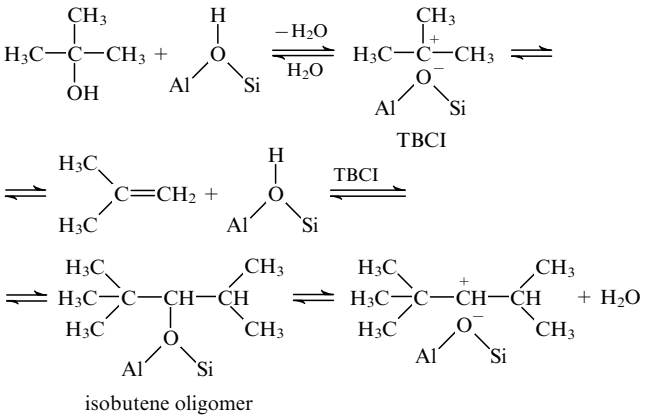


Figure 9. The ^{13}C NMR spectrum of *tert*-butyl alcohol (containing the selectively ^{13}C-labelled C–OH group) recorded within 4 h after its adsorption on HZSM-5 zeolite (Si : Al = 44). The signal at δ 82 belongs to the C–OH group of the unconsumed alcohol. The narrow signal at δ 29.7 against the background of the signals of oligomers at δ 14–40 occurs due to the incorporation of the ^{13}C label from the C–OH group into the CH_3 group of the alcohol.

accompanied by their conversions into a mixture of alkanes and cyclopentenyl cations occurred[38] (see below). Hence, it was concluded that the signal at δ 86 should be assigned to C–O groups of oligomers covalently bound to the oxygen atoms of the zeolite framework. It was thus suggested that dehydration of Bu^{t}OH on the HZSM-5 zeolite proceeds according to Scheme 6 to form intermediate TBCI, which reacts with isobutene formed from TBCI to give oligomeric products. These products in the adsorbed state are oligomeric alkoxides which exist in equilibrium with oligomeric carbenium ions. It is to these alkoxides that the signal at δ 86 belongs.

Scheme 6

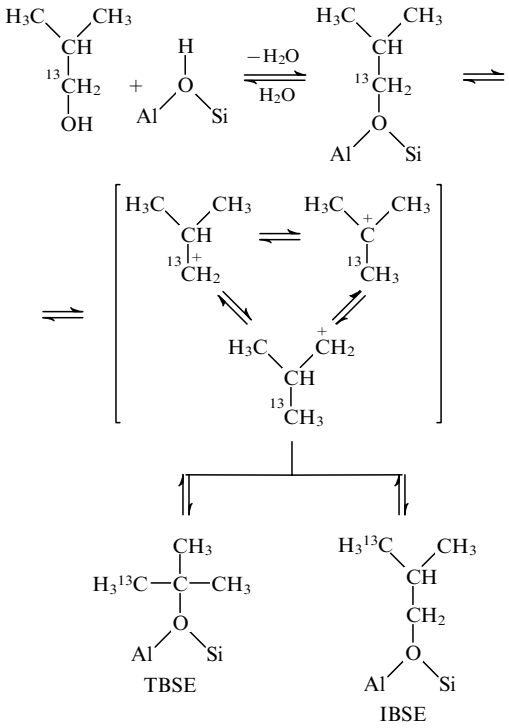


3. Isobutyl alcohol

IR spectral studies of the kinetics of dehydration of isobutyl alcohol on an HZSM-5 zeolite (Si : Al = 20)[83] demonstrated that dehydration of the alcohol at 373 K was completed in 30 min. An adsorbed intermediate retained the structure of the hydrocarbon skeleton of the initial alcohol. It was thus concluded that diisobutyl ether was formed as an intermediate. However, analysis of the ^{13}C NMR spectra demonstrated that the intermediate was in fact isobutyl silyl ether (IBSE).[47] The chemical shifts of the carbon atoms of the CH_3 and CH groups of the alkoxide intermediate (δ 19.2 and δ 30.5, respectively) coincide with those of the carbon atoms of the analogous groups in the initial alcohol, while the chemical shift of the carbon atom of the CH_2 group (δ 73.0, Fig. 10 *c*) is close to that of the CH_2 group in the initial alcohol (δ 74.9, Fig. 10 *a*) but differs substantially ($\Delta\delta$ ~10 ppm)[47] from that of the carbon atom of the CH_2 group in diisobutyl ether (δ 84.6).[47]

Prolonged storage of Bu^{i}OH adsorbed on the zeolite at 373 K or 398 K resulted in an increase in the intensities of the signals at δ 19.2 and δ 30.5 (Fig. 10 *c*,*d*) due to redistribution of the selective ^{13}C label in IBSE, which suggests the formation of the carbenium ion as an intermediate. In this case, the intensity of the signal at δ 19.2 increased due to the incorporation of the selective carbon label from the CH_2 group to the CH_3 group of IBSE[47] and the intensity of the signal at δ 30.5 increased due to the predominant formation of TBCI and its stabilisation as TBSE whose methyl group resonates at δ 30.5. This signal is close to that of the methyl group of *tert*-butyl alcohol (δ 31[35]). An increase in the intensity of the signal at δ 30.5 was originally attributed to the incorporation of the selective ^{13}C label into the CH_3 group of TBSE[47] or into the CH group of IBSE[84] *via* the linear *sec*-butyl cation, which is thermodynamically more stable in the zeolite.[85] However, more recent studies of the reaction of isobutyl alcohol with carbon monoxide on the zeolite demonstrated that trimethylacetic acid was selectively formed in this reaction[61] (see below), which is unambiguously indicative of the predominant formation of TBCI in the reaction of IBSE with carbon monoxide. Hence, it is reasonable to relate an increase in the intensities of the signals at δ 19.2 and δ 30.5 (Fig. 10 *c*,*d*) to the equilibria on the zeolite shown in Scheme 7.

Scheme 7



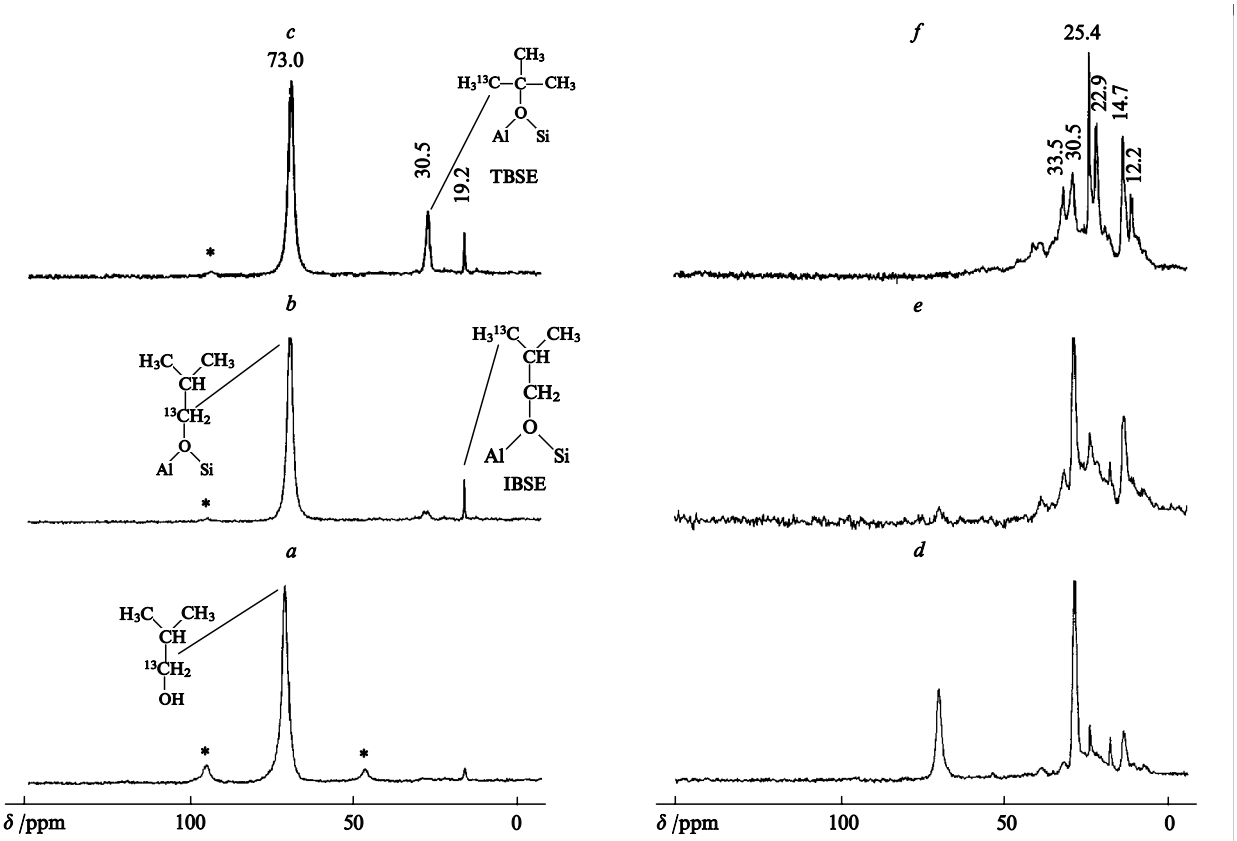


Figure 10. Changes in the ^{13}C NMR spectrum of isobutyl alcohol (containing the selectively ^{13}C-labelled CH_2 group) adsorbed on HZSM-5 zeolite (Si : Al = 24) upon successive heating of the specimen at different temperatures.
Temperature /K (duration of heating, min): (*a*) 296 (without heating); (*b*) 343 (70) + 373 (30); (*c*) 398 (40); (*d*) 413 (60); (*e*) 428 (60); (*f*) 448 (60).

Further increase in the temperature (Fig. 10 *d*–*f*) caused subsequent conversions of IBSE and TBSE into a mixture of alkanes (Fig. 10 *f*) and CPC (see Scheme 12 below) *via* butene oligomers.[38]

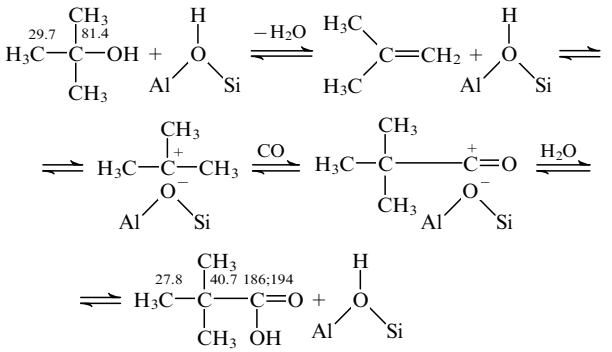
IV. Reactions of alkenes and alcohols with carbon monoxide and acetonitrile

The experimental evidence for the involvement of carbenium ions in conversions of alkenes and alcohols on zeolites obtained in NMR studies was further confirmed by a series of chemical reactions which occurred on zeolites under mild conditions.[49, 50, 86]

1. The Koch reaction

Selective conversions of isomeric butyl alcohols in the presence of carbon monoxide and of alkenes (ethylene, isobutene and oct-1-ene) in the presence of CO and water on the HZSM-5 zeolite to form carboxylic acids (the Koch reaction[59, 87]), which were studied with the use of ^{13}C NMR spectroscopy,[60, 61] were found to occur at lower temperatures (20–100 °C) compared to those (300–500 °C) normally used in catalytic reactions on zeolites. Actually, the use of labelled reagents (alcohols, alkenes and CO) for the analysis of products of their reactions on the HZSM-5 zeolite provided conclusive evidence of selective conversions of alcohols and alkenes into carboxylic acids. Thus the following changes in the ^{13}C NMR spectra (Fig. 11) were observed in the reaction of Bu^{t}OH with CO at room temperature: when Bu^{t}OH containing the ^{13}C-labelled tertiary carbon atom was used, a signal at δ 40.7 belonging to the tertiary carbon atom of trimethylacetic acid (TMAA) was observed (Fig. 11 *a*); when Bu^{t}OH containing the ^{13}C-labelled CH_3 group was used, a signal at δ 27.8 belonging to the methyl group of the acid was observed (Fig. 11 *b*); and when labelled carbon monoxide was used, a signal at δ 186–194 belonging to the carboxyl group was observed (Fig. 11 *c*). The formation of TMAA from Bu^{t}OH and CO on a zeolite catalyst at room temperature agrees well with the general concepts of the mechanism of this reaction in solutions of acids and superacids.[58, 59] In both cases, the carbenium ion is the key intermediate (Scheme 8).

Scheme 8



Hereinafter, the chemical shifts for the carbon atoms are given above the corresponding atoms.

The special role of carbon monoxide in this reaction is to capture TBCI formed upon elimination of the water molecule from the alcohol and to hinder its rapid oligomerisation[35, 38, 46] by converting it into the acylium cation, which reacts with water to form acid.

Trimethylacetic acid is also selectively formed from Bu^{i}OH and isobutene, which suggests the presence of TBCI. Ethylene is selectively converted into 2-ethyl-2-methylbutyric acid, which is indicative of rapid oligomerisation of ethylene to form the C_6

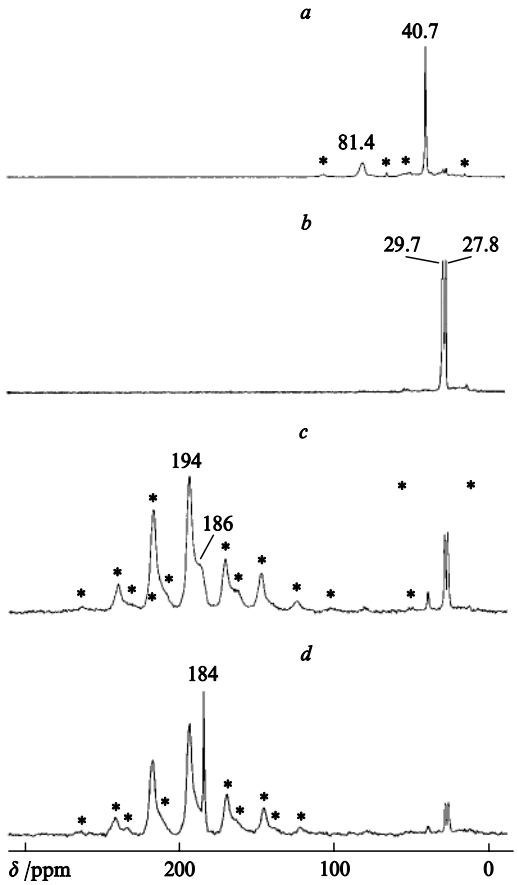


Figure 11. The ^{13}C CP/MAS NMR spectra of the product formed upon adsorption of Bu^{t}OH and CO on HZSM-5 zeolite at 296 K. Bu^{t}OH containing the ^{13}C-labelled tertiary carbon atom (*a*); Bu^{t}OH containing the ^{13}C-labelled methyl group (*b*) and labelled CO (*c*). The spectrum (*d*) is the spectrum (*c*) recorded without CP.

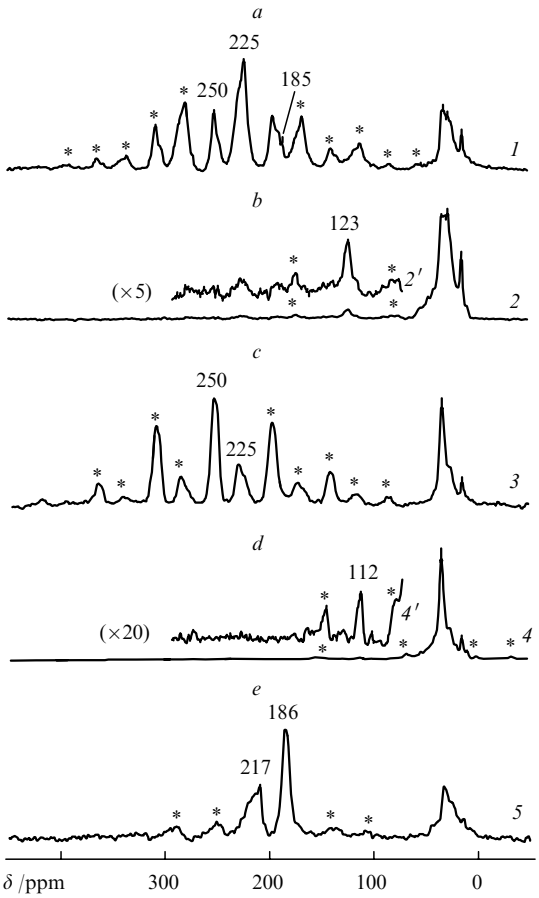


Figure 12. The ^{13}C CP/MAS NMR spectra of the products formed after adsorption of alkenes and CO on HZSM-5 zeolite in the absence of water at 296 K.
(*a*) $(CH_3)_2C{=}CH_2$ + ^{13}CO; (*b*) $(CH_3)_2C{=}CH_2$ + CO; (*c*) $CH_2{=}CH_2$ + ^{13}CO; (*d*) $^{13}CH_2{=}CH_2$ + CO; (*e*) $(CH_3)_2C{=}CH_2$ + ^{13}CO + H_2O. Curves (*1*–*5*) without amplification; (*2′*) with a fivefold amplification; (*4′*) with a twenty fold amplification.

carbenium ion followed by termination of the growing oligomeric chain by carbon monoxide.

Subsequent NMR spectral studies demonstrated also that benzene can undergo carbonylation to form benzoic acid on HY zeolite [88] and sulfatised zirconia.[89]

2. Friedel–Crafts-like acylation of alkenes

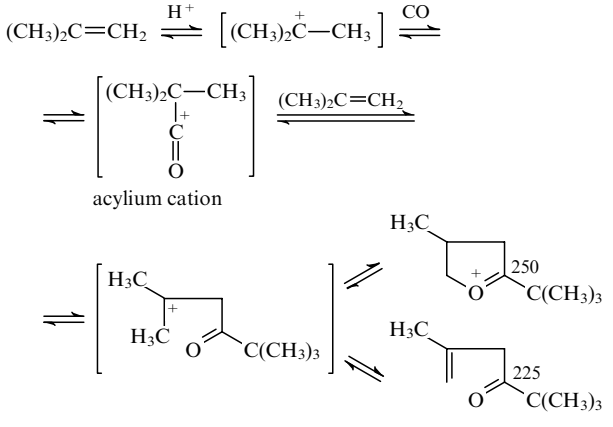
In the absence of water adsorbed on zeolite, the alkyl cation which is formed upon adsorption of alkenes on zeolite reacts with CO to give the acylium cation. The latter reacts with another alkene molecule to form unsaturated ketone. This represents the Friedel-Crafts-like acylation of alkenes,[90–92] the acylating agent being formed *in situ* from the alkene and CO on the zeolite.

Actually, the ^{13}C NMR spectrum of the product formed in the case of simultaneous adsorption of isobutene and ^{13}CO on the HZSM-5 zeolite has two intense signals for the ^{13}C-labelled carbonyl group [93] at δ 225 and δ 250 (Fig. 12 *a*,*b*). The signal at δ 225 belongs to unsaturated ketones formed in the reaction and the signal at δ 250 belongs to stable cyclic five-membered carboxonium ions (Scheme 9).[94]

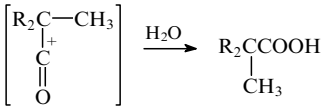
The ^{13}C CP/MAS NMR spectra of the products formed after the adsorption of ^{13}C-labelled ethylene and CO on the HZSM-5 zeolite are shown in Fig. 12 *c*,*d*.

If a zeolite specimen was kept in air, *i.e.*, was exposed to atmospheric moisture, the signal for the carboxonium ion at δ 250 disappeared, the signal for unsaturated ketones was shifted downfield (to δ 217) and a signal belonging to carboxylic acids appeared at δ 186 (Fig. 12 *e*). It was thus concluded that carboxonium ions were decomposed in the presence of moisture and the

Scheme 9



equilibrium shown in Scheme 9 was shifted towards acylium cations, which reacted with water to form carboxylic acids.



Hydroxy ketones, which are the products of the reaction of unsaturated ketones or carboxonium ions with water, were not detected in the reaction under consideration.

3. The Ritter reaction

Since the discovery of the reactions of alcohols and alkenes with nitriles (the Ritter reaction) in 1948,[95–98] it was believed that the formation of *N*-alkylamides occurs *via* an intermediate *N*-alkylnitrilium cation $CH_3C\equiv N^+R$.

$$ROH + CH_3CN \xrightarrow[-H_2O]{H^+} H_3CC\equiv\overset{+}{N}R \xrightarrow[-H^+]{H_2O} H_3C\overset{O}{\overset{\|}{C}}NHR$$

However, the experimental spectral supporting evidence for the formation of *N*-alkylnitrilium cations was long absent, which has cast doubt on the existence of a cationic intermediate.[98] It was suggested that this reaction afforded a sulfate $CH_3C(OSO_3H)=NR$ (the reaction was carried out in sulfuric acid) as an intermediate.[95,98]

It was demonstrated[99,100] by ^{13}C and ^{15}N MAS NMR spectroscopy that the Ritter reaction can be performed on zeolite catalysts. These studies provided the first experimental proof for the formation of *N*-alkylnitrilium cations as stable intermediates in the reactions of alkenes (or alcohols) with carbonitriles.

The ^{13}C NMR spectra of the intermediate *N-tert*-butylacetonitrilium cation and of the final *N-tert*-butylacetamide, which were formed in the reaction of Bu^tOH with CH_3CN on the HZSM-5 zeolite, are shown in Fig. 13. It was found that *N*-alkylnitrilium cations are long-lived stable species in the absence of moisture.

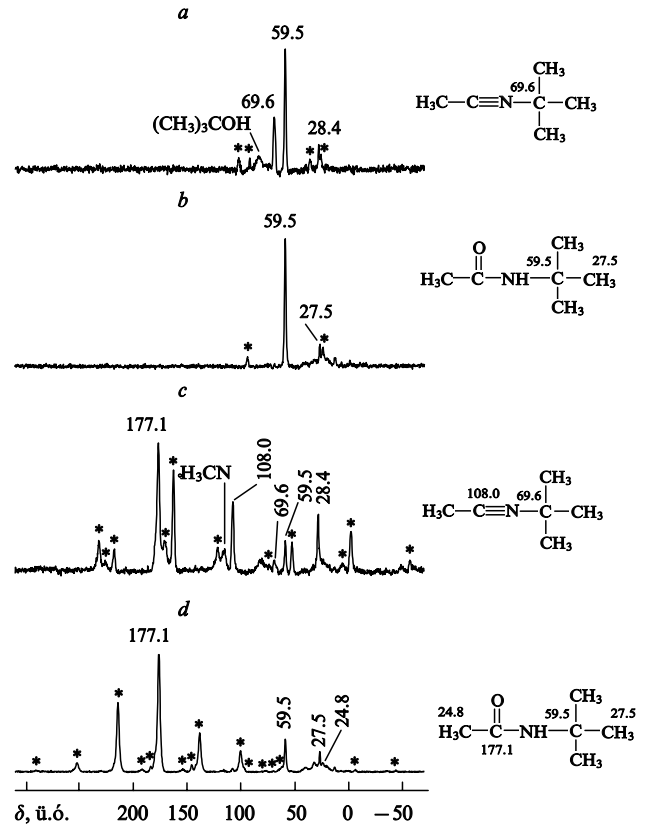
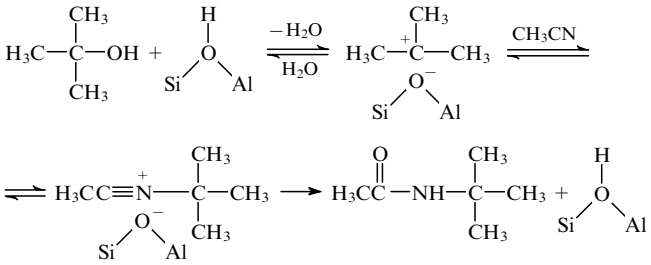


Figure 13. The ^{13}C NMR spectra of the products formed upon simultaneous adsorption of *tert*-butyl alcohol and acetonitrile on HZSM-5 zeolite at 296 K; (*a*) and (*b*) simultaneous adsorption of Bu^tOH containing the labelled tertiary carbon atom and CH_3CN; (*c*) and (*d*) adsorption of labelled Bu^tOH (10% enrichment with the ^{13}C isotope) and CH_3CN (80% enrichment with the ^{13}C isotope); (*a*) and (*c*) the spectra were recorded within 4 h after the adsorption; (*b*) and (*d*) the spectra were recorded within 4 days after the adsorption.

Hence, the reaction mechanism proposed for the Ritter reaction[95] was additionally confirmed by the detection of stable *N*-alkylnitrilium cations on zeolites using NMR spectroscopy. The behaviour of the acetonitrile molecule in the Ritter reaction is analogous to that of the CO molecule in the Koch reaction, *i.e.*, acetonitrile acts as a trap for the alkylcarbenium ion thus stabilising the unstable alkyl cation (Scheme 10) and preventing secondary reactions involving highly reactive alkyl cations (oligomerisation and cracking).

Scheme 10

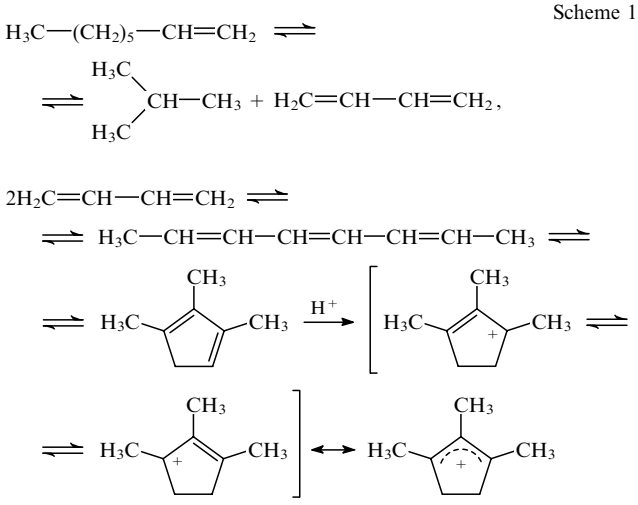


The identification of stable *N*-alkylnitrilium cations confirmed the suggestions made previously that alkylcarbenium cations can be stabilised on zeolite through their interactions with acetonitrile molecules[101–103] and disproved the suggestion[104] that strong Lewis centres to which acetonitrile molecules are coordinated are formed on the zeolite.

V. Analysis of hydrocarbon products and intermediates formed from alkene oligomers

Adsorbed hydrocarbon products were analysed *in situ* by studying dehydration of Bu^tOH on HZSM-5 zeolite in a wide temperature range (296–637 K) as an example using ^{13}C CP/MAS NMR spectroscopy.[38] It was found that heating (448 K) of a zeolite specimen containing adsorbed alcohol resulted in the appearance of two groups of signals at *ca.* δ 10–40 and δ 150–250 in the ^{13}C NMR spectrum (Fig. 14). The signals at δ 10–40 correspond to a mixture of acyclic alkanes (Fig. 14*a*) and those at δ 100–450 correspond to stable cyclopentenyl cations (Fig. 14*d*). The simultaneous formation of alkanes and CPC from oligomers of isobutene, which is formed in the first stage of dehydration of *tert*-butyl alcohol, occurs as a result of cracking of oligomers (for example, of oct-1-ene; Scheme 11). The diene formed upon cracking of the alkene undergoes further dimerisation and cyclisation to form alkyl-substituted cyclopentadienes, which are stabilised within channels of the HZSM-5 zeolite as CPC.

Scheme 11



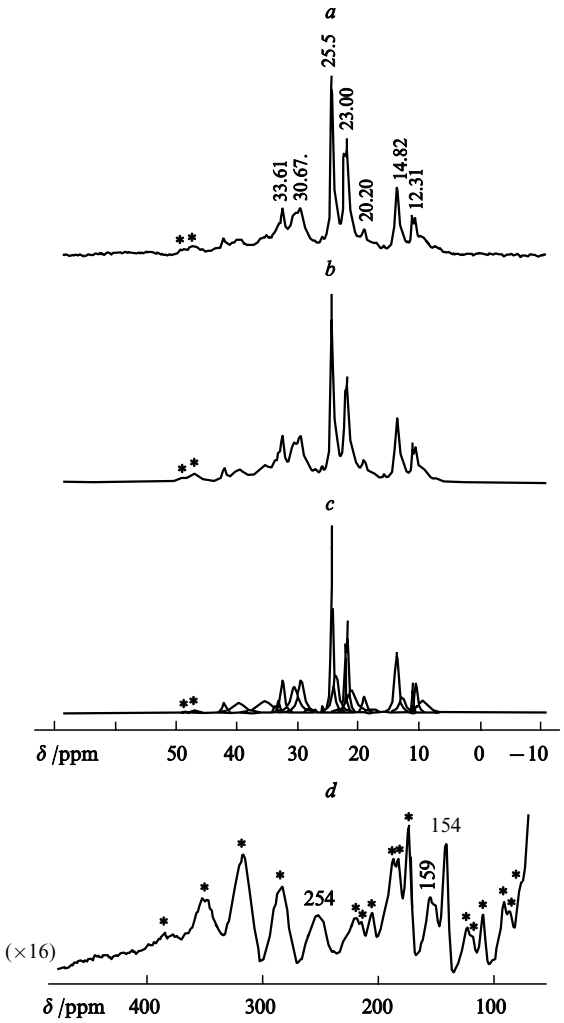


Figure 14. The ^{13}C MAS NMR spectra of the conversion products of Bu^{t}OH on HZSM-5 zeolite at 448 K at δ 10–60 (*a*–*c*) and at δ 100–450 (*d*).
(*a*) experimental data; (*b*) a model spectrum obtained by superposition of 25 signals of the mixture of 11 hydrocarbons; (*c*) the spectrum of the cyclopentenyl cation (a 16-fold amplification of the intensities of the signals).

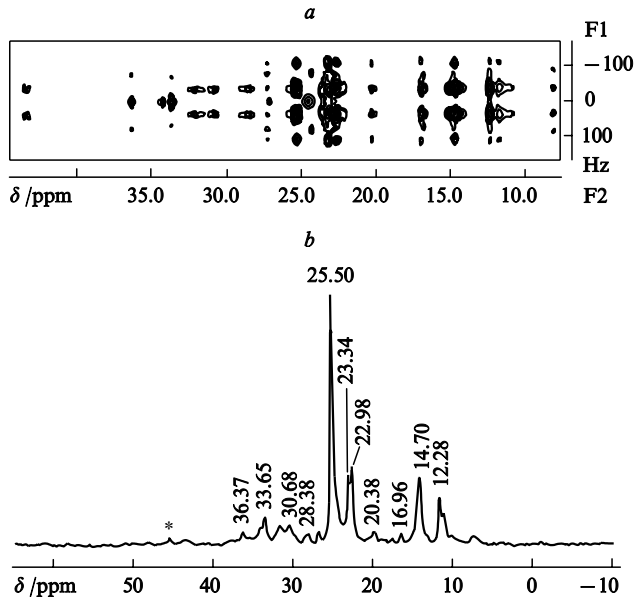


Figure 15. Contour plot of the 2D *J*-resolved ^{13}C MAS NMR spectrum of the products of Bu^{t}OH conversion on HZSM-5 zeolite at 448 K (*a*). The 1D spin-echo ^{13}C NMR spectrum (*b*) corresponding to the spectrum of the standard one-pulse excitation (see Fig. 14 *a*). The observed value of the spin-spin coupling constant $J(^{13}C-{}^{1}H)$ on the F1 axis is half as large as the true value of $J(^{13}C-{}^{1}H)$ due to the use of a special technique for recording the 2D NMR spectrum.[35, 61, 63]

The simultaneous formation of acyclic alkanes and CPC on the HZSM-5 zeolite indicates that the mechanisms of conversions of alkenes on zeolites and in sulfuric acid are similar.

Actually, as early as 1936, Ipatieff and Pines [105, 106] demonstrated that a mixture of alkanes and cycloalkenes was formed when isobutene was passed through concentrated sulfuric acid at 0 °C. Cycloalkenes, as was demonstrated by Deno and co-workers in the early 1960s using NMR spectroscopy,[107] exist in 96% H_2SO_4 as stable alkyl-substituted CPC.

The use of 2D *J*-resolved ^{13}C MAS NMR spectroscopy for the analysis of the multiplicities of signals at δ 10–40 corresponding to hydrocarbon products (Fig. 15) allowed the determination of the number of hydrogen atoms attached to the carbon atoms in the CH_n groups ($n = 0-3$).

Based on the analysis of the ^{13}C chemical shifts, the relative intensities of the signals (see Fig. 14) and the multiplicities (see Fig. 15), it was found that a mixture of hydrocarbons was formed at 448 K and the relative amount of hydrocarbons that occurred in the adsorbed state (Table 1) was determined.

An increase in the reaction temperature to 573 K led to the redistribution of the intensities of signals for alkanes at δ 10–40 (Fig. 16). In this case, propane and butanes were prevailing

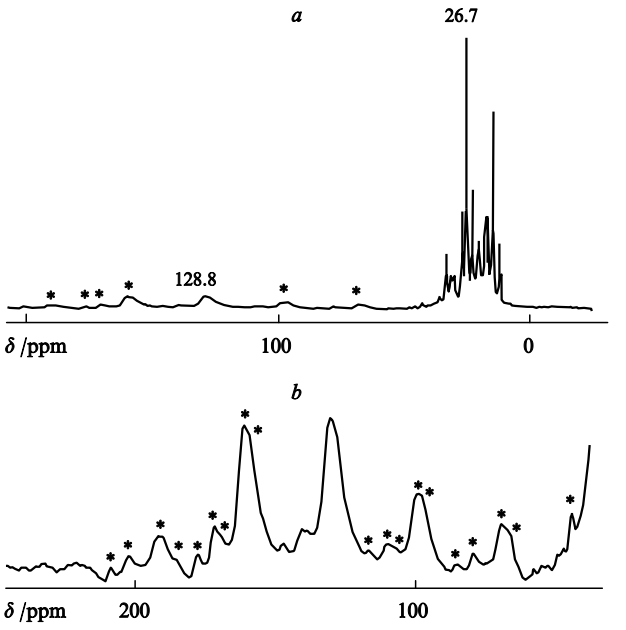


Figure 16. The ^{13}C CP/MAS NMR spectra of the conversion products of Bu^{t}OH on HZSM-5 zeolite at 573 K [spectrum (*b*) is given with an eightfold amplification of the intensities of the signals at δ 40–240].

Table 1. Assignment of the signals in the ^{13}C NMR spectrum and the relative amounts of alkanes, isobutene oligomers and aromatic hydrocarbons formed upon conversion of Bu^{t}OH on HZSM-5 zeolite at 373–673 K.

Hydrocarbon	δ /ppm [a]					Relative amount (mol %) at different temperatures (K)			
	$^{13}CH_3-$	$-^{13}CH_2-$	$^{13}CH_3CHCH_3$	$-^{13}CH<$	$-^{13}C-$	373	448	573	673
Ethane	7.5 (5.7)					–	–	–	8.7
Propane	17.0 (15.4)	18.0 (15.9)				< 1	1.0	29.8	59.2
n-Butane	14.7 (13.1)	27.1 (24.9)				–	< 1.7	18.5	5.3
Isobutane			25.5 (24.3)	25.5 (25.0)		6	17.2	19.6	5.3
n-Pentane	14.7 (13.7)	24.5; 36.6 (22.6; 34.6)				–	17.2	3.7	–
Isopentane	11.8 (11.4)	33.6 (31.7)	23.0 (21.9)	30.7 (29.7)		5	17.9	11.7	–
Neopentane					31.8 (31.4)	–	0.7	–	–
n-Hexane	14.7 (13.7)	24.5; 33.7 (22.8; 31.9)				–	6.9	–	–
2-Methylpentane	14.7 (14.0)	20.2; 40.9 (20.5; 41.6)	23.5 (22.4)	28.4 (27.6)		7	4.1	–	–
2,3-Dimethylbutane			20.2 (19.1)	34.9 (33.9)		–	3.4	–	–
2,2-Dimethylbutane	8.5 (8.5)	36.6 (36.5)			30.7 (30.2)	–	2.1	–	–
Alkanes (C_7 and above) + isobutene oligomers	10.6 11.8 13.9	22.3; 23.4; 30.7; 34.2; 36.6; 40.9		43.4 30.7		82	27.8	–	–
o- and *p*-Xylenes	20.7 (19.6; 20.9)					–	–	16.7 [b]	13.4 [b]
Toluene + *m*-xylene	22.5 (32.3)					–	–	–	8.1 [b]

Note. The assignment was made relative to the total amount of hydrocarbons whose CH_n signals are observed at δ 10–40. [a] The chemical shifts of CH_n groups of the adsorbed hydrocarbons were taken from the spectra shown in Figs 14–17 (the accuracy of the determination was ±0.5 ppm). The chemical shifts of the same hydrocarbons in a solution were taken from the literature [40] and are given in parentheses. [b] The values were determined only from the intensities of the CH_3 groups without considering the intensities of the carbon atoms of the benzene ring of toluene or xylenes.

alkanes (Table 1), signals for CPC at δ 150 and δ 250 disappeared and a signal at δ 128, which belongs to a mixture of monocyclic and fused aromatic hydrocarbons with the latter predominating, appeared. The changes in the ^{13}C NMR spectrum are indicative of cracking of alkanes formed at 448 K. When the temperature was further increased to 673 K, C_2-C_4 alkanes (with propane predominant) and aromatic hydrocarbons, *viz*., toluene and xylene, were obtained as the major reaction products (Fig. 17).

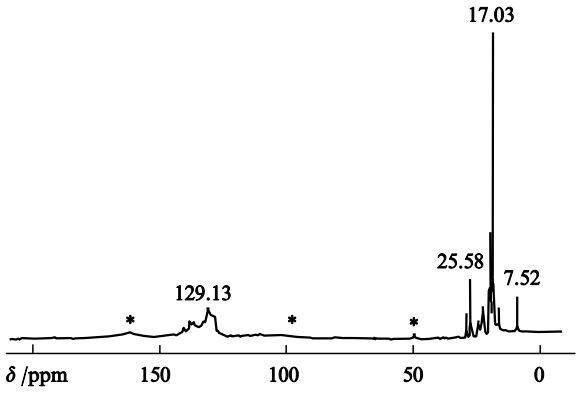


Figure 17. The ^{13}C MAS NMR spectrum of the conversion products of Bu^{t}OH on HZSM-5 zeolite at 673 K.

At 373 and 296 K, alkanes were also formed from isobutene oligomers.[38] However, at these temperatures, isobutene oligomers covalently bound to the oxygen atoms of the zeolite framework, *viz*., alkoxides, were obtained as the major conversion products of Bu^{t}OH on HZSM-5 zeolite, which is evidenced by the presence of a broad signal for the C–O groups at δ 89 in the spectrum of oligomeric products (Fig. 18).

The sequence of conversions (according to the ^{13}C MAS NMR spectral data) of alkene oligomers adsorbed on acidic zeolite in the temperature range of 296–637 K is shown in Scheme 12.[38]

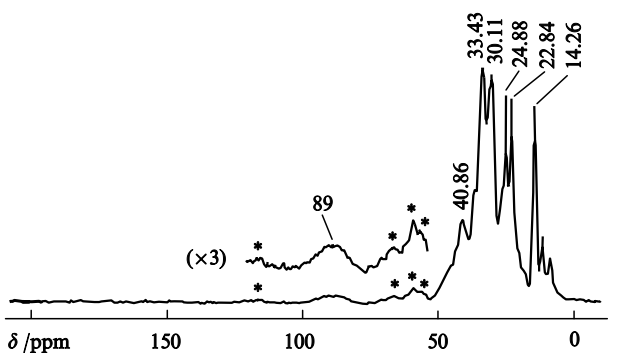
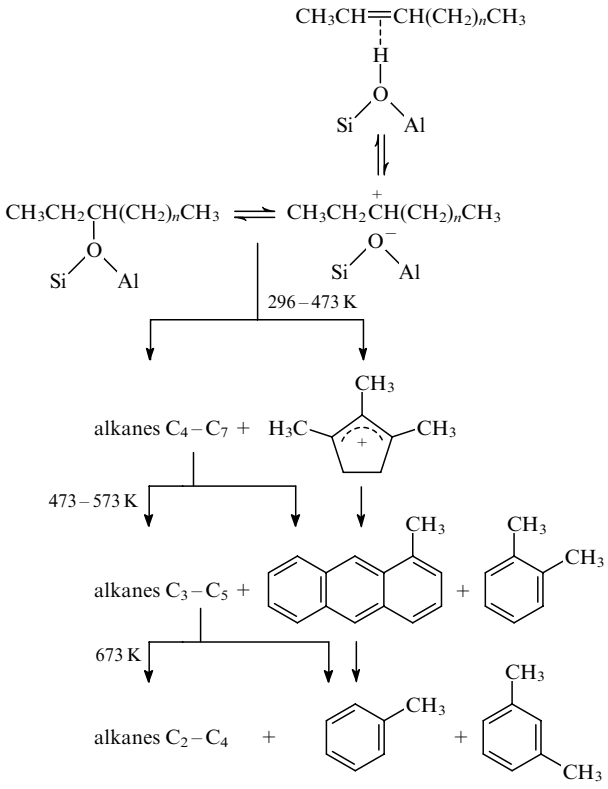


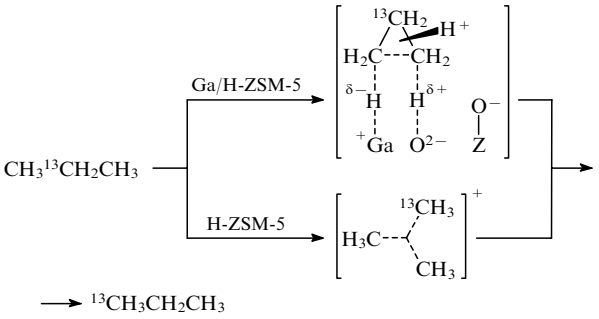
Figure 18. The ^{13}C CP/MAS NMR spectrum of the conversion products of Bu^{t}OH on HZSM-5 zeolite at 373 K.

Scheme 12



VI. Activation of alkanes at low temperatures. Isotope (H/D) exchange between alkanes and acidic OH groups of zeolite

The results of the studies [108–112] demonstrate that NMR spectroscopy is a particularly informative and unique method for investigating conversions of lower alkanes (propane and isobutane) on acidic zeolites at low (as regards traditional conversions of alkanes on zeolites) temperature (350–550 K). It was found [108] that the selective ^{13}C label of the CH_2 group was incorporated into the CH_3 group of propane adsorbed on Ga/HZSM-5 zeolite at 573 K. According to the results of the studies,[50, 55–57] the redistribution of the selective carbon label indicates that the isopropylium ion which is responsible for this redistribution is formed as an intermediate on the zeolite, although Derouane and co-workers [108] believed that the label redistribution observed in the case of Ga/HZSM-5 zeolite proceeds with the participation of a transition complex of propane with the Ga atom,[108] while in the case of pure HZSM-5 zeolite,[109] the redistribution involves the *C*-ethylmethanium (carbonium) ion.[113]



The observed redistribution of the ^{13}C label in propane indicates that propane is activated and can undergo subsequent chemical conversions (cracking and alkylation [114]).

Yet another example of the use of NMR spectroscopy for studying activation of alkanes at low temperature is investigation of hydrogen isotope exchange [110, 111] and activation of alkanes in the presence of CO and H_2O.[112] The H/D isotope exchange between alkanes and acidic OH groups of zeolites proceeds at rather low temperatures (20–200 °C) at which the alkane does not undergo isomerisation and cracking.[115–121] The isotope exchange involving stages of cleavage and formation of C–H bonds in alkane and O–H bonds in zeolite is indicative of activation of alkane. Hence, it is not surprising that a large number of experimental [115–124] and theoretical [121–124] studies were devoted to the elucidation of the mechanism of the hydrogen exchange. Recently, ^1H MAS NMR spectroscopy was used for investigating the kinetics and mechanism of the H/D exchange of alkanes.[110, 111]

1. Propane

In studies of the kinetics of the H/D isotope exchange between deuterated propane and acidic groups of HZSM-5 zeolite (150–250 °C), the simultaneous incorporation of protium from the acidic HO groups into the deuterated methyl and methylene groups of propane was observed. It was found that the intensities of the signals for the CH_3 and CH_2 groups of propane at δ 1.0 and δ 1.45, respectively, in the ^1H MAS NMR spectrum increased with time (Fig. 19). Analysis of the kinetics of the incorporation of protium into the methyl and methylene groups of propane revealed a noticeable difference in the rates of hydrogen exchange for these groups (Fig. 20). The corresponding rates, which were

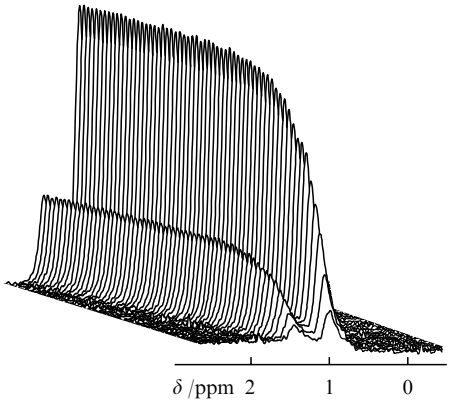


Figure 19. Changes in the intensities of the signals for the methyl (δ 1.0) and methylene (δ 1.45) groups with time at 519 K in the ^1H MAS NMR spectrum of propane C_3D_8 adsorbed on HZSM-5 zeolite. The first spectrum (at the bottom) and the last spectrum were recorded within 3 min and 5 h after the adsorption. The intervals at which the spectra were recorded were 5 min.

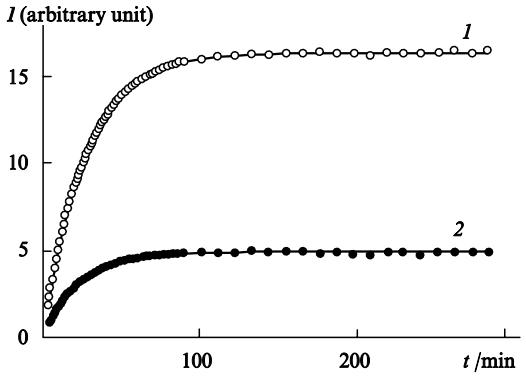


Figure 20. Kinetic curve of the transfer of the proton from acidic OH groups of zeolite to the methyl (curve *1*) and methylene (curve *2*) groups of propane C_3D_8 at 519 K.

calculated by the kinetic equation $I_t = I_\infty[1-\exp(-Rt)]$ [I_t and I_∞ are the integral intensities of the signals for the CH_n groups (n = 2 or 3) in the ^1H MAS NMR spectrum at times t and $t = \infty$ (equilibrium)] are $R(CH_3) = 0.03816$ min^{-1} and $R(CH_2) = 0.0436$ min^{-1}. The time $t = 0$ corresponds to the beginning of the experiment when the temperature was increased from room temperature to 519 K. The activation energies of hydrogen exchange for the methyl and methylene groups were determined ($E_{CH_3} = 118 \pm 2$ kJ mol^{-1} and $E_{CH_2} = 117 \pm 4$ kJ mol^{-1}) from the temperature dependence of the reaction rate of hydrogen exchange (from the Arrhenius parameters; Fig. 21).[110]

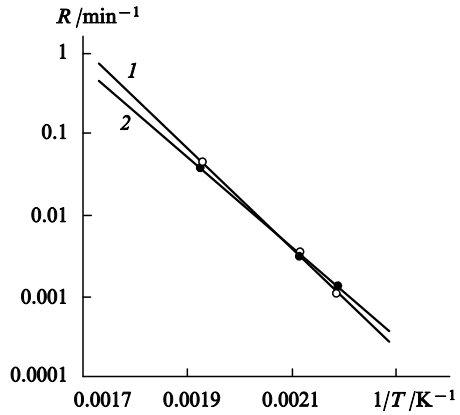
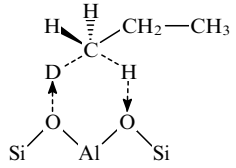


Figure 21. Dependence of the rate of the H/D exchange for the methyl (*1*) and methylene (*2*) groups of propane on HZSM-5 zeolite in terms of the Arrhenius parameters.

Taking into account the absence of selective or predominant enrichment of the methyl groups with protium, the fact that the H/D exchange is not inhibited by carbon monoxide and the fact that the experimental activation energies are close to those theoretically calculated for methane and ethane,[122–124] it was concluded that H/D exchange with the acidic OH protons occurs independently for each group (without the formation of a single carbenium-ion intermediate or a transition state) *via* an intermediate pentavalent transition state in which the hydrogen atoms that are exchanged lie halfway between the carbon atom of the methyl (methylene) group and the oxygen atoms of the zeolite.



The data obtained do not also contradict the formation of the carbonium ion as a two-electron three-centre intermediate state involved in the hydrogen exchange in the propane–superacid DF–SbF_5 system.[125] The difference in the rate of exchange for the methyl and methylene groups was attributed to the difference in the σ-basicity of the C–H bonds of the primary (CH_3) and secondary (CH_2) groups of the alkane.[126]

2. Isobutane

In the case of the hydrogen exchange in isobutane, the situation is different (Fig. 22). In this case, only methyl groups are subjected to H/D exchange,[118–120, 127] which is manifested in an increase in the intensity of the signal at δ 1.0 (Fig. 22*b*).[111] The expected increase in the intensity of the signal for the CH group at δ 1.85 (Fig. 22*c*) was not observed. Measurements of the rates of hydrogen exchange in the temperature range of 80–150 °C allowed the determination of the activation energy of the exchange (50 ± 2 kJ mol^{-1}) which is half as large as that of

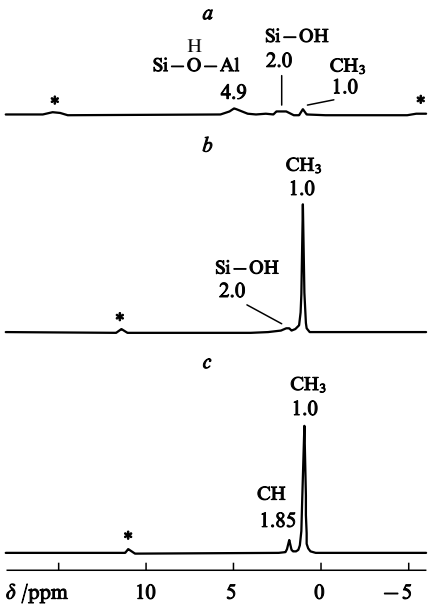
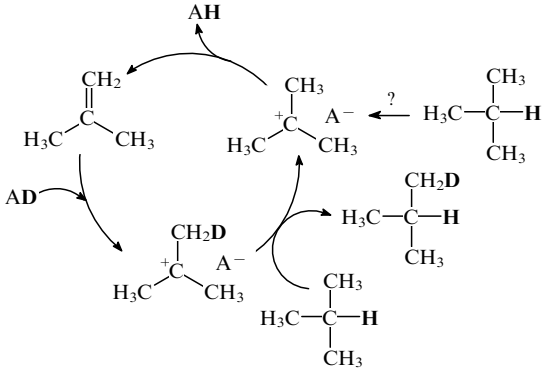


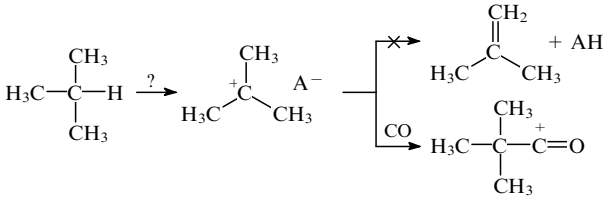
Figure 22. The ^{13}C MAS NMR spectra of isobutane adsorbed on HZSM-5 zeolite at 295 K.
(*a*) the spectrum of isobutane-d_{10} before the temperature was increased to 425 K or of isobutane-d_{10} in the presence of CO after storage of the sample at 475 K for 10 h; (*b*) the spectrum of isobutane-d_{10} after storage of the sample at 425 K for 70 min; (*c*) the spectrum of nondeuterated isobutane.

propane. It was also found that carbon monoxide completely inhibits the regiospecific hydrogen exchange (Fig. 22*a*). The mechanism of the regiospecific hydrogen exchange for isobutane was explained within the framework of the catalytic cycle[118, 120] shown in Scheme 13.

Scheme 13



The regiospecificity of the H/D exchange is achieved due to formation of TBCI and isobutene as intermediates, which exist in equilibrium with each other. Carbon monoxide, which is present in the system, reacts with TBCI to give the oxocarbenium ion. The latter cannot undergo reversible deprotonation to form the alkene, which results in complete inhibition of the hydrogen exchange.



VII. Activation of alkanes at low temperatures. Carbonylation

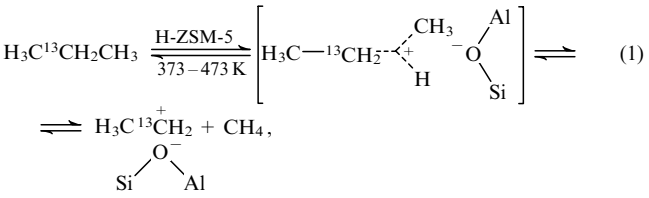
In addition to the hydrogen exchange in alkanes at 20–200 °C, NMR spectral studies allowed observation of carbonylation at 100–200 °C,[112] which is also indicative of the possibility of activation of alkanes on acidic zeolites at low temperatures.

Based on the assumption that alkanes are formed from carbenium ions and alkenes[118,119,127] as intermediates upon hydrogen exchange at low temperature and taking into account that alkenes (carbenium ions) can react with carbon monoxide and water on zeolites[61] to form carboxylic acids, it was suggested that carboxylic acids can be formed from alkanes at low temperature[112] at which hydrogen exchange is observed but alkanes do not undergo cracking.

1. Propane

It was found that heating of a zeolite specimen containing adsorbed propane, CO and water at 373–473 K led to changes in the NMR spectra compared to those of the initial reagents. In the case of simultaneous adsorption of ^{13}C-labelled propane, carbon monoxide and water, the ^{13}C CP/MAS NMR spectrum has a signal at δ 191 for the carboxy group of isobutyric acid formed along with signals at δ 17.0 and δ 18.2 belonging to the initial propane (Fig. 23 *a*). The ^{1}H MAS NMR spectrum of the same specimen has a signal for methane at δ 0.25, signals for the initial propane at δ 1.0 and δ 1.45 and a signal for water adsorbed on acidic OH groups of zeolite at δ 6.2 (Fig. 23 *c*). In the case of adsorption of labelled propane-2-^{13}C, the ^{13}C MAS NMR spectrum has a signal for ethane-1-^{13}C at δ 7.3, a signal for the carbon atom of the ^{13}CH group of isobutyric acid at δ 36.4 and signals for unconsumed propane-2-^{13}C and CO at δ 18.2 and δ 185, respectively (Fig. 23 *b*). These changes agree well with activation of propane-2-^{13}C on zeolite and protolytic cleavage of the C–C bond of propane to form $^{13}CH_4$, $^{13}CH_3CH_3$ and $(CH_3)_2{}^{13}CHCOOH$ according to Scheme 14. Actually, in the course of the reaction of ^{13}C-labelled propane with CO and H_2O, the selectively ^{13}C-labelled CH_2 group of propane was converted into the ^{13}CH group of isobutyric acid (δ 36.4). Methane, which is observed only in the ^{1}H MAS NMR spectrum, is formed in the stage (1) due to the protolytic attack of the acidic group of zeolite on the C–C bond of propane. The ethyl cation formed in the same stage reacts with another molecule of labelled propane to give ethane and the isopropyl cation [stage (2)]. The latter reacts with CO and water to form isobutyric acid [stage (3)].

Scheme 14



$$CH_3{}^{13}\overset{+}{C}H_2 + CH_3{}^{13}CH_2CH_3 \rightleftharpoons CH_3{}^{13}CH_3 + CH_3{}^{13}\overset{+}{C}HCH_3, \quad (2)$$

$$CH_3{}^{13}\overset{+}{C}HCH_3 + CO + H_2O \longrightarrow (CH_3)_2{}^{13}CHCOOH + H^+. \quad (3)$$

2. Isobutane

The reaction of isobutane with carbon monoxide and water on zeolite proceeds analogously.[112] After heating of a zeolite specimen containing adsorbed isobutane, ^{13}CO and water at 423 K for 3 h, the ^{13}C CP/MAS NMR spectrum has four signals, *viz*., signals for TMAA at δ 193 and δ 27.7, a signal for the initial isobutane at δ 25.5 and a signal for the intermediate Si–C(OOH)–Al at δ 172 (Fig. 24). The ^{1}H MAS NMR spectrum of the same specimen has signals for the initial isobutane at δ 1.0 and δ 1.8, a signal for H_2O/Si–OH–Al at δ 6.6 and signals for the reaction products, *viz*., H_2 and TMAA, at δ 4.1 and δ 1.45, respectively (Scheme 15).

No conversion products were detected in a special NMR spectral study of conversions of propane and isobutane on HZSM-5 zeolite in the absence of CO and water in the same temperature range. However, cracking products of these alkanes,

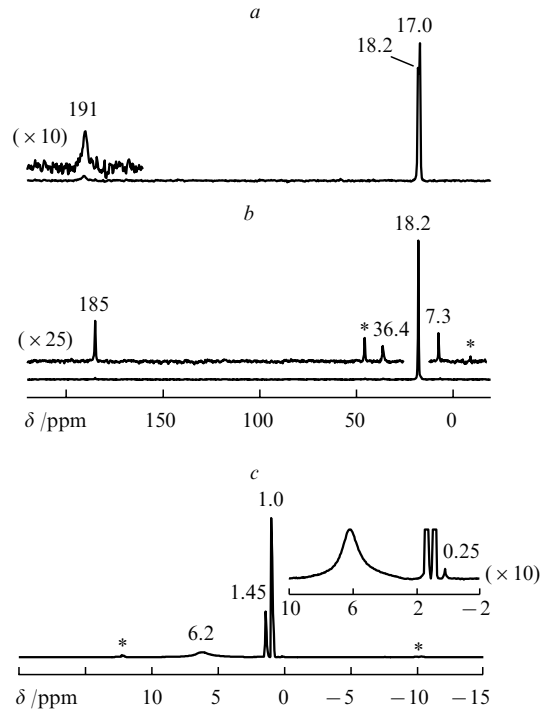


Figure 23. NMR spectra of propane, carbon monoxide and water adsorbed on HZSM-5 zeolite at 473 K. The samples were heated at 473 K for 3 h.
(*a*) the ^{13}C CP/MAS NMR spectrum, simultaneous adsorption of propane, ^{13}CO and water; (*b*) the ^{13}C MAS NMR spectrum, simultaneous adsorption of propane-2-^{13}C, CO and water; (*c*) the ^{13}C MAS NMR spectrum, simultaneous adsorption of propane, ^{13}CO and water.

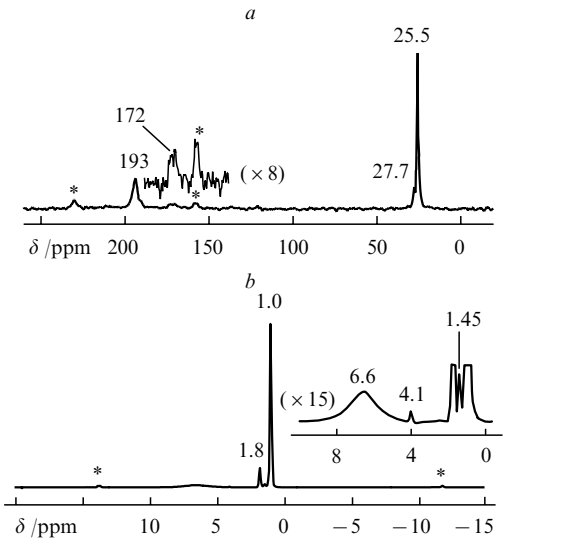
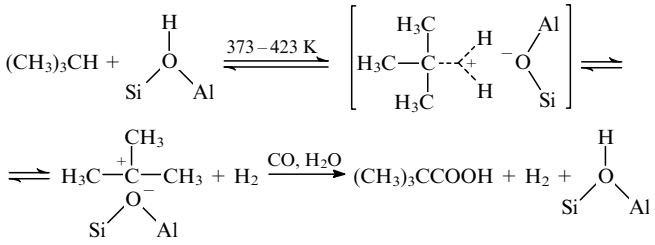


Figure 24. NMR spectra of conversion products of isobutane, ^{13}CO and water adsorbed on HZSM-5 zeolite.
(*a*) the ^{13}C CP/MAS NMR spectrum; (*b*) the ^{13}C MAS NMR spectrum.

Scheme 15



such as hydrogen (in the case of isobutane), ethane and methane (in the case of propane), were detected by gas-chromatographic analysis. The amounts of these compounds were so small that they could not be detected by NMR spectroscopy. It was concluded that in the presence of H_2O and CO (a trap of carbenium ions), the cracking equilibrium of alkanes was shifted to the corresponding acids formed from CO and carbenium ions. In this case, the reaction product, *viz*., a carboxylic acid, was accumulated in amounts detectable by NMR spectroscopy. The low degrees of conversion of propane and isobutane into the corresponding acids at 373–423 K (1%–2%) are attributable to the presence of insignificant amounts of superacidic centres in the zeolite (no more than 1%–2% of the total amount of acidic protonic centres) on which cracking occurs at these low temperatures.

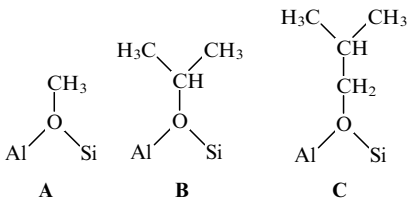
VIII. The nature of intermediates in conversions of alkanes, alkenes and alcohols

The nature of intermediates in the reactions of hydrocarbons and alcohols on heterogeneous catalysts of the acidic nature has long been the subject of discussion. According to the classical concepts of conversions of organic molecules in the presence of acids, alkyl-type carbenium ions represent reactive intermediates in these reactions. However, the absence of direct experimental evidence for the formation of alkyl-type carbenium ions on acidic centres of zeolites has cast doubt on the possibility of their formation as stable species.

The first results of quantum-chemical calculations [128, 129] demonstrated that carbenium ions are not located in a local minimum on the potential energy surface and these ions can be formed on zeolites only as an unstable transition state. More recent studies [130–132] demonstrated that alkoxides are key intermediates, while carbenium ions are formed upon thermal excitation of alkoxides where the C–O bond is elongated. Theoretical calculations [133] also indicated that acid catalysis on zeolites occurs with the involvement of alkoxide intermediates and without the participation of carbenium ions. Some NMR spectral data (for example, those obtained in studies of oligomerisation products of propene [134]) were interpreted without regard for the participation of carbenium ions in the reaction.

Recently, considerable progress has been achieved in the identification of various intermediates (carbenium ions and alkoxides) by NMR spectroscopy and in the understanding of the role of these intermediates in conversions on solid acids. The reliable evidence was obtained for the formation of alkoxide intermediates in the case of lower hydrocarbons (MeO,[42–44] Pr^iO [134] and Bu^iO [47]) and oligomeric alkoxides [54] and their role as intermediates was revealed. The methoxide (**A**) and isobutoxide intermediates (**C**) are stable species at 293–373 K, while the isopropoxide intermediate (**B**) oligomerises even at 200 K.[134]

Apparently, this fact indicates that isopropoxide rather than the isopropylium ion is a reactive intermediate in the oligomerisation of propene.[134] However, these conclusions were drawn without considering the characteristic time of the ^{13}C-carbon redistribution in carbenium ions, which should be approximately



39 days at 230 K.[134] Taking into account that oligomerisation proceeds substantially faster (is completed in several hours), the formation of the carbenium ion, which rapidly undergoes oligomerisation, from isopropoxide must not be ruled out.

The redistribution of the selective ^{13}C label in oct-1-ene at room temperature, which is indicative of the formation of carbenium ions, as well as the alkoxide nature of adsorbed alkene oligomers [54] allow conclusions to be drawn about the existence of the equilibrium between the alkoxide and carbenium-ion intermediates, the latter being formed in small amounts undetectable by NMR spectroscopy.

The formation of carbenium ions on zeolites is additionally confirmed by the fact that chemical reactions typical of carbenium ions proceed under mild conditions (room temperature). It appeared that unstable carbenium ions undetectable by NMR spectroscopy can be stabilised by introducing these ions into the reaction with CO and CH_3CN to obtain cyclic carboxonium [93] and alkylnitrilium [99, 100] cations, respectively, which can be detected by NMR spectroscopy. The hydrogen H/D exchange between D_2O and the methyl groups of Bu^tOH [35, 81] and the transfer of the ^{13}C label from the tertiary carbon atom to the methyl group of Bu^tOH [38] are also indicative of the formation of the carbenium ion upon dehydration of Bu^tOH on zeolite. Recent quantum-chemical calculations [85] of the stability of alkylcarbenium ions adsorbed on zeolite taking into account the stabilising effect of the zeolite lattice (it was believed that 16 oxygen atoms rather than two atoms, as was assumed in all the previous studies,[128–133] are involved in stabilisation of the intermediate formed) revealed a local minimum for carbenium ions. It was found that the stability of alkyl carbenium ions is 10–20 kJ mol^{-1} lower than that of the corresponding π-complexes of alkenes. Taking into account the experimental data obtained by NMR spectroscopy, it may be concluded that alkylcarbenium ions exist in zeolites as real structures (although they are very unstable and highly reactive) along with more stable alkoxide intermediates.

Alkyl-substituted cyclopentenyl cations belong to another type of carbocationic intermediates that exist in zeolites.[45] Their formation from alkene oligomers on zeolites simultaneously with alkanes indicates that conversions of alkenes on zeolites and in a solution of concentrated sulfuric acid occur analogously.[38] These cations are intermediates, which form aromatic hydrocarbons at higher temperature.

IX. Conclusion

Recently, considerable progress has been made in the understanding of the mechanisms of hydrocarbon conversions on the surface of zeolites of acidic nature. This progress was achieved primarily due to the successful use of high-resolution solid-state NMR spectroscopy for the *in situ* analysis of intermediates and the final products of hydrocarbon conversions. In some cases where the expected intermediate was not observed due to its instability or low concentration (alkyl-type carbenium ions), this was identified from the characteristic reactions, *viz*., from the redistribution of selective carbon labels or from the reactions with cation traps (CO or CH_3CN). Based on the NMR spectral data, possible pathways of conversions of alkenes and alcohols on zeolites at low temperature were suggested. Carbonylation of alkenes and alcohols (the Koch reaction), Friedel–Crafts-like acylation of alkenes where an acylating agent is formed directly from the alkene and CO on

zeolite and the reactions of alkenes with acetonitrile to form *N*-alkylamides (the Ritter reaction) were studied. Interestingly, the *N*-alkylnitrilium cation as a stable intermediate in the Ritter reaction was first detected and characterised by NMR spectroscopy on zeolite rather than in solution. Hence, presently not only does solid-state NMR spectroscopy confirm or refute the parallels between the mechanisms of conversions of hydrocarbons in solutions and on the surface of solid acidic catalysts, but it also enables one to obtain original data on the mechanisms of chemical conversions. The Friedel – Crafts-like reaction of alkenes with CO adsorbed on zeolite to form unsaturated ketones and carbonylation of alkanes (propane and isobutane) to form carboxylic acids are examples.

The use of NMR spectroscopy for the analysis of products formed *in situ* on zeolites provides a deeper insight into the effect of the internal structure of zeolite pores on the composition of the products, which was clearly exemplified by conversions of methanol on HZSM-5 zeolite. NMR spectroscopy is more informative than IR and UV spectroscopy in the analysis of the structures of adsorbed hydrocarbons. As a result, NMR spectral studies made it possible to identify stable alkyl-substituted cyclopentenyl cations, which were formed in zeolites as intermediates in the conversions of alkenes into aromatic compounds, and to establish their structures. *In situ* studies of the kinetics of the hydrogen exchange of alkanes by NMR spectroscopy allowed conclusions about the nature of intermediates of this exchange to be drawn.

It would be expected that the experimental data on hydrocarbon conversions obtained by NMR spectroscopy and conclusions about the mechanisms of these conversions will be rationally used in the development of new industrially important processes of hydrocarbon conversions, such as alkylation or isomerisation of alkenes and alkanes, and the data on the nature of intermediates will provide the basis for quantum-chemical calculations.

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