Interaction of Acetonitrile with Olefins and Alcohols in Zeolite H-ZSM-5: In Situ Solid-State NMR Characterization of the Reaction Products

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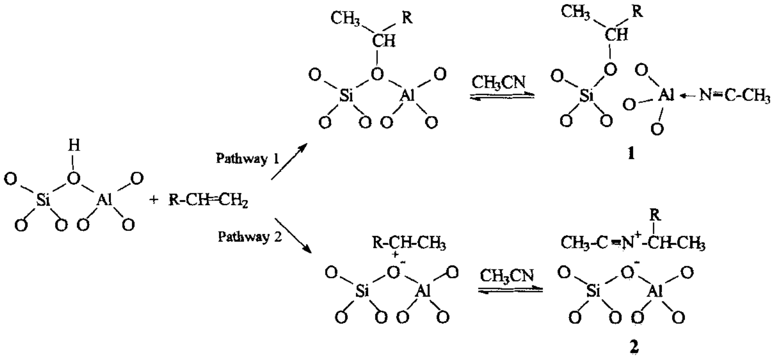
Dedicated to the memory of Professor K. I. Zamaraev

Abstract: The reaction products and intermediates from the interaction of acetonitrile with olefins (oct-1-ene) or alcohols (*tert*-butyl alcohol) in zeolite H-ZSM-5 at 296 K have been characterized with ^{13}C and ^{15}N solid-state NMR. It has been shown that coadsorption of acetonitrile and olefin on H-ZSM-5 gives rise to the intermediate *N*-alkylnitrilium cation, which is formed by trapping by the acetonitrile molecule of an unstable alkylcarbenium ion originating from the adsorbed olefin. The *N*-alkylnitrilium cation represents a persistent species inside a zeolite under anhydrous conditions. Upon admittance of water to the pores of the zeolite, the *N*-alkylnitrilium cation slowly converts into *N*-alkylamide in accordance with the classic Ritter reaction. In the case of acetonitrile and alcohol, just after coadsorption both the intermediate *N*-alkylnitrilium cation and the final *N*-alkylamide are identified simultaneously; the former slowly disappears over a few days. Thus, 1) it has been shown that the Ritter reaction can occur not only in liquid acidic media but also on a solid acid catalyst, zeolite H-ZSM-5; 2) *N*-alkylnitrilium cations have been detected and characterized with solid-state NMR as persistent intermediates in the Ritter reaction for the first time while the reaction proceeds.

Keywords
alcohols · nitriles · NMR spectroscopy · olefins · zeolites

Introduction

Acetonitrile has been reported to be unreactive towards catalytic conversion on acidic zeolites at room temperature.[1] However, when coadsorbed with an olefin on zeolite H-ZSM-5, its IR spectrum exhibits the vibrational band of $\nu(C{\equiv}N)$ at $\tilde{\nu} = 2370\ cm^{-1}$,[2] which is strongly shifted from acetonitrile adsorbed on zeolite-bridged OH groups, the stretch of which is located near $2300\ cm^{-1}$.[2,3] Medin et al.[2] assigned this new band at $\tilde{\nu} = 2370\ cm^{-1}$ to the acetonitrile molecule complexed to a Lewis acid site (structure **1** in Scheme 1), resulting from the cleavage of the Al–O bond in the bridged alkoxy group Si–O(CH_3CHR)–Al ($R = C_nH_{2n+1}$, $n \geq 1$) to give a trigonal environment around the Al atom (Scheme 1). However, later, Bystrov et al. observed a $4\ cm^{-1}$ isotopic shift for the nitrile CN group, if deuterated propene was used for coadsorption, and interpreted the appearance of the band at $\tilde{\nu} = 2370\ cm^{-1}$ as a sequence of coordination of the CH_3CN base to the alkylcarbenium ion CH_3CH^+R generated from an olefin and acting as a very strong Lewis acid (Scheme 1).[4,5] Thus, formation of the *N*-alkylnitrilium cations $CH_3C{\equiv}N^+{-}R^1$ ($R^1 = CH_3CHR$) inside a zeolite was suggested[4–6] (structure **2** in Scheme 1). Unfortunately, infrared studies show the $\nu(C{\equiv}N)$ stretching frequencies of the *N*-alkylnitrilium cations to be raised relative to those of the parent nitriles for $\tilde{\nu} = 70–100\ cm^{-1}$,[7,8] similar to nitrile–Lewis acid complexes.[8–11] Therefore, the IR data alone is not sufficient to distinguish between structures **1** and **2**.



Scheme 1. Possible pathways for the interaction of olefin and acetonitrile with bridged OH groups of acidic zeolite, from refs. [2,4,5].

The aim of the present paper is to characterize more thoroughly with solid-state NMR the species formed upon CH_3CN and olefin (alcohol) coadsorption on acidic zeolite. We hoped

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that we would be able to clarify the nature of the species formed after olefin and CH_3CN coadsorption and thus to verify whether *N*-alkylnitrilium cations **2** do indeed persist inside zeolite H-ZSM-5 or whether coadsorption of an olefin and CH_3CN leads to cleavage of the Al–O bond and simultaneous formation of both stable alkoxy species and CH_3CN coordination to an aluminum atom (structure **1**).

Results

1. NMR spectrum of acetonitrile adsorbed on H-ZSM-5: Adsorption of acetonitrile (CH_3CN, **3**) on H-ZSM-5 has already been studied extensively with NMR.[1] In addition to the data reported in ref. [1] we have found that adsorbed $[1\text{-}^{13}C]CH_3CN$ undergoes cross-polarization, and informative ^{13}C CP/MAS NMR spectra for adsorbed acetonitrile can be obtained (Figure 1). However, no essential differences have been observed between the ^{13}C CP/MAS NMR spectrum and that recorded without CP (not shown), which merely differed in signal-to-noise ratio. Furthermore, we have found that ^{13}C CP/MAS NMR spectra (both with and without CP) are dependent on the acetonitrile (**3**) loading. If the amount of **3** is less than or equal to the amount of Brönsted acid sites (bridged Si–OH–Al groups), then the CN group of **3** exhibits the signal at $\delta = 116$ with numerous spinning sidebands (Figure 1 A). When the acetonitrile loading exceeds the amount of bridged OH groups, the CN group exhibits a more narrow spinning-sideband-free lineshape with the same chemical shift (Figure 1 B).

In the former case the observed ^{13}C CP/MAS NMR spectrum is fixed on the timescale of the sample spinning, that is, isotropic molecular reorientation of adsorbed acetonitrile proceeds with

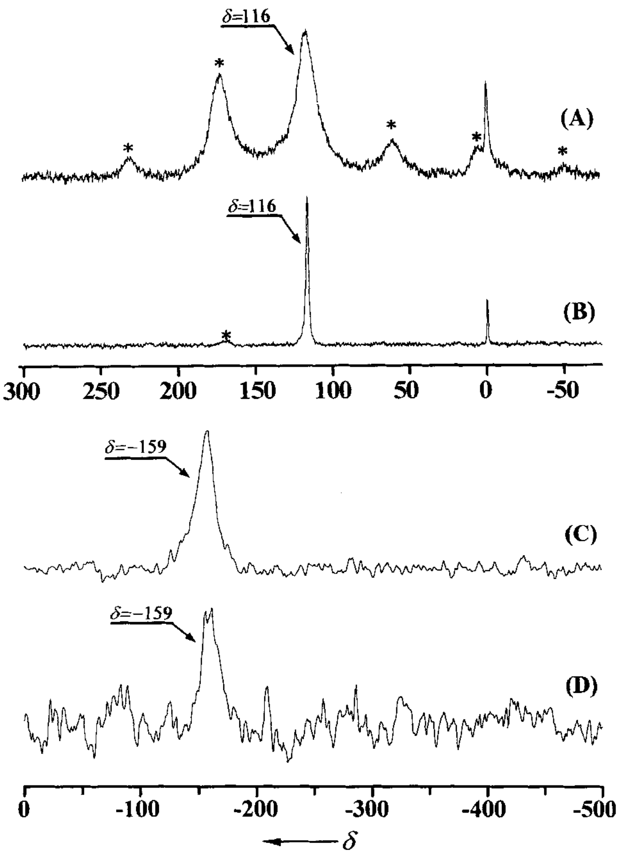


Fig. 1. NMR spectra of acetonitrile adsorbed on H-ZSM-5 zeolite at 296 K. A and B) ^{13}C CP/MAS NMR spectra of $[1\text{-}^{13}C]CH_3CN$ (82% ^{13}C enrichment); C) ^{15}N MAS and D) ^{15}N CP/MAS NMR spectra of $[^{15}N]CH_3CN$ (95% ^{15}N enrichment). Amount of adsorbed acetonitrile: A: 290 $\mu mol\,g^{-1}$, B: 500 $\mu mol\,g^{-1}$, C and D: 310 $\mu mol\,g^{-1}$. Spinning rate was A: 5610 Hz, B: 5050 Hz, C and D: 3300 Hz. Asterisks (*) in the spectra denote spinning sidebands.

Abstract in Russian:

Аннотация: Методом ЯМР высокого разрешения в твердом теле на ядрах ^{13}C и ^{15}N охарактеризованы интермедиаты и продукты реакции ацетонитрила с олефинами (на примере октена-1) или спиртами (*трет*-бутанол) на цеолите H-ZSM-5 при 296 K. Показано, что при совместной адсорбции ацетонитрила и олефина на цеолит происходит образование N-алкилнитрильного катиона посредством взаимодействия молекулы ацетонитрила с неустойчивым алкильным карбениевым ионом, образующимся в цеолите из молекулы олефина. В отсутствие воды N-алкилнитрильный катион существует внутри каналов цеолита H-ZSM-5 в виде устойчивой частицы. По мере проникновения воды в поры цеолита происходит медленное превращение N-алкилнитрильного катиона в N-алкиламид в полном соответствии с классическим механизмом реакции Риттера. В случае ацетонитрила и спирта в спектрах ЯМР, записанных сразу после адсорбции реагентов, одновременно наблюдаются промежуточный N-алкилнитрильный катион и конечный продукт - N-алкиламид. В последствии, ЯМР сигналы от N-алкилнитрильного катиона медленно (в течение несколько дней) исчезают. Таким образом, показано, что (1) реакция Риттера может быть осуществлена не только с использованием растворов кислот, но и на твердом кислотном катализаторе - цеолите H-ZSM-5; (2) впервые, методом ЯМР высокого разрешения в твердом теле обнаружены и охарактеризованы N-алкилнитрильные катионы в качестве устойчивых интермедиатов реакции Риттера.

characteristic time $t_c > 10^{-3}$ s. The reason for this rigidity of the adsorbed CH_3CN molecules may be a strong interaction with Si–OH–Al groups. Adsorbed on a Brönsted acid site, acetonitrile does not seem to undergo any fast restricted local motions that could average out a large chemical shift anisotropy of the CN group ($\Delta\delta \approx 300$ ppm).

In the second case the observed line shape shows that motional behavior averages out the orientational dependence of the ^{13}C chemical shift. As suggested in ref. [1], this motion may represent an exchange between free acetonitrile and that bound to Si–OH–Al groups. Uncomplexed acetonitrile reorients isotropically inside the zeolite framework, and acetonitrile bound to bridged OH groups may only slowly reorient locally with a characteristic time exceeding 10^{-3} s.

The ^{15}N MAS NMR spectrum of [^{15}N]CH_3CN on H-ZSM-5 (Figure 1C) coincides with that reported in ref. [1]. As is the case with [1-^{13}C]CH_3CN on H-ZSM-5, ^{15}N nuclei in [^{15}N]CH_3CN adsorbed on the zeolite undergo cross-polarization, and thus we have been able to record ^{15}N CP/MAS NMR spectra (Figures 1C,D). Note, however, that the ^{15}N CP/MAS NMR spectrum shows a weak signal with low signal-to-noise ratio that provides evidence for low polarization of ^{15}N nuclei by surrounding protons (zeolite OH groups and CH_3 groups of acetonitrile) in the adsorbed acetonitrile, compared with ^{13}C nuclei in the CN group of this molecule.

2. Preliminary attribution of NMR signals in coadsorbed olefin and acetonitrile: Both ^{13}C and ^{15}N NMR spectra of **3** on H-ZSM-5 exhibit new features when **3** is coadsorbed with olefin (Figures 2A and 3A), which are not detected in the absence of olefin (Figure 1). New features also appear in the ^{13}C MAS NMR spectra of coadsorbed olefin. New signals occur (Figure 2C), different from the signals observed earlier for olefins adsorbed on zeolites (see for example refs. [12–15]). In fact, the new ^{13}C and ^{15}N signals that appeared after olefin coadsorption, originating from the acetonitrile CN group, can be made to stand out further by recording the spectra with cross-polarization. Therefore, in order to emphasize the new features in ^{13}C and ^{15}N NMR spectra of **3** coadsorbed with olefin, we present in this paper only ^{13}C and ^{15}N CP/MAS NMR spectra. Moreover, to stress particularly the specific changes in the spectra of **3** or olefin, reactants with selective ^{13}C or ^{15}N isotope labels were used in our NMR experiments.

Coadsorption of [1-^{13}C]acetonitrile and oct-1-ene: One would expect that the most intense signal in the spectrum recorded after coadsorption of [1-^{13}C]CH_3CN and unlabeled olefin (Figure 2A) would arise from the ^{13}C-labeled CN group of acetonitrile. The observed intense signal at $\delta = 108.8$ is shifted upfield by $\Delta\delta = 7$ ppm with respect to that from [1-^{13}C]CH_3CN on the bridged OH group (Figure 1A). Small signals from unlabeled oct-1-ene (**4**) and the unlabeled CH_3 group of [1-^{13}C]CH_3CN are identified in the spectrum of Figure 2A at $\delta = 14.2$–33.3 and 0.82, respectively.

The appearance of the signal at $\delta = 108.8$ cannot be interpreted unambiguously. On the one hand, the signal at $\delta = 108.8$ is in the vicinity of the ^{13}C chemical shifts for protonated acetonitrile (CH_3CN^+H, **5**) in superacids ($\delta = 108$–108.5 in magic acid, FSO_3H/SbF_5[1, 7]). However, in ref. [1] CH_3CN^+H was reported not to be persistent in H-ZSM-5. On the other hand, there are no reported ^{13}C NMR data either on the ^{13}C chemical shifts for acetonitrile coordinated to Lewis acids or on ^{13}C chemical shifts for the -C≡N$^+$- fragment in the *N*-alkylnitrilium cation **2**. Thus, on the basis of the analysis of a position of the signal at $\delta = 108.8$, which appeared upon coadsorption of **3** with oct-1-ene, we cannot make out whether this signal belongs to **3** on a Lewis acid site or corresponds to a positively charged -C≡N$^+$-fragment of *N*-alkylnitrilium cation **2**.

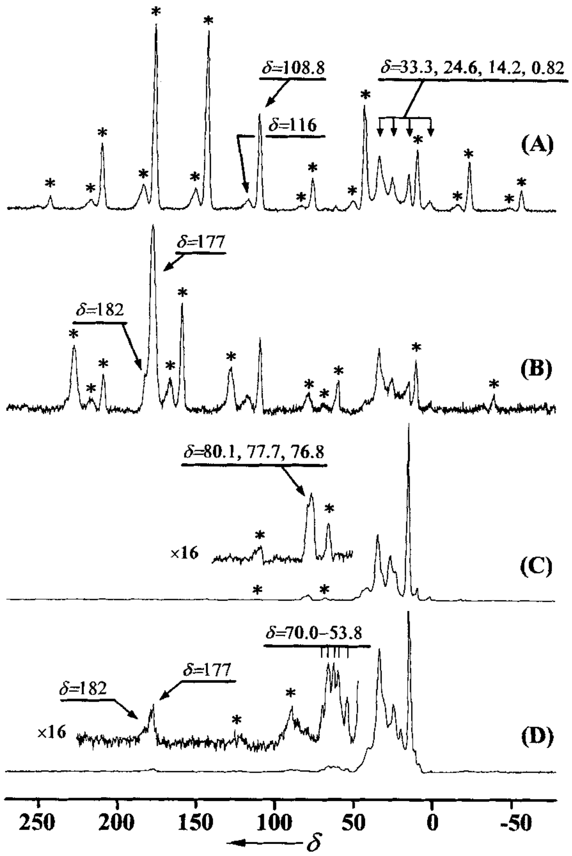


Fig. 2. ^{13}C CP/MAS NMR spectra for the products formed after coadsorption of acetonitrile and oct-1-ene on zeolite H-ZSM-5 at 296 K: A and B) coadsorption of [1-^{13}C]CH_3CN (80% ^{13}C enrichment) and unlabeled oct-1-ene; C and D) coadsorption of unlabeled CH_3CN and [1-^{13}C]oct-1-ene (82% ^{13}C enrichment); before (A and C) and two days after (B and D) exposure of the zeolite sample to atmospheric moisture. Approximately 300 μmol g^{-1} of each of the reactants were coadsorbed. Spinning rate was A: 3355 Hz, B: 5505 Hz, C: 3325 Hz, D: 3336 Hz. Asterisks in the spectra denote spinning sidebands.

Coadsorption of acetonitrile and [1-^{13}C]oct-1-ene: It has already been shown that in [1-^{13}C]oct-1-ene adsorbed on H-ZSM-5, the selective ^{13}C label scrambles over the hydrocarbon skeleton and the signals from the olefinic >C=C< double bond are not detected.[13–15] Figure 2C shows ^{13}C CP/MAS NMR spectrum for coadsorbed ^{13}C-labeled oct-1-ene and unlabeled CH_3CN. As expected, the most intense signals at $\delta = 14$–34 belong to the paraffinic CH_3 and CH_2 groups of the olefin; the ^{13}C label penetrates to these groups from the terminal olefinic $=CH_2$ group of oct-1-ene.[14] The weak signals of unlabeled **3** are not detected in this spectrum.

A new feature that was not identified in the adsorbed **4** without coadsorbed acetonitrile[14] is detected in Figure 2C. Several lines are clearly visible between $\delta = 76$ and 80. At least three signals are distinguished at $\delta = 80.1$, 77.7, and 76.8; the last signal can be seen as a right-hand shoulder to the signal at $\delta = 77.7$. The position of these lines is in the region of the ^{13}C chemical shifts typical for carbon bound to oxygen in alcohols ($\delta = 50-80$[16]) or alkoxides formed in zeolites ($\delta = 50-90$[15, 17-20]). Therefore, at first glance the presence of these signals in the spectrum speaks in favor of formation of the fragment $Si-O-R^1$ in the structure **1** with three different alkyl fragments R^1 in accordance with the number of lines at $\delta = 76-80$. At the same time, in the case of formation of cation **2**, the carbon atom attached to nitrogen in the fragment $-C-N^+\equiv$ may also exhibit a signal at the same region of the spectrum. For example, ^{13}C chemical shifts of carbon bound to nitrogen in amines may be above $\delta = 50$[21] and in *N*-alkylamides are in the range of $\delta = 50-70$.[22] Thus, on the basis of this spectrum we again can not determine whether the structures **1** or **2** are formed.

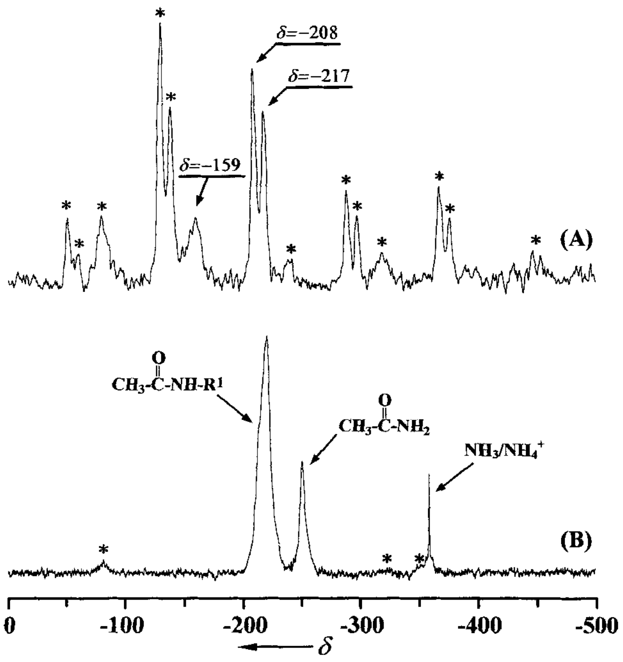


Fig. 3. ^{15}N CP/MAS NMR spectra for the products formed after coadsorption of $[^{15}N]CH_3CN$ (95% ^{15}N enrichment) and oct-1-ene on zeolite H-ZSM-5 at 296 K: A) before exposure of the zeolite sample to atmospheric moisture; B) two days after exposure of the zeolite sample to atmospheric moisture. Approximately 300 $\mu mol\,g^{-1}$ of each of the reactants was adsorbed. Spinning rate was A: 3205 Hz, B: 5595 Hz. Asterisks in the spectra denote spinning sidebands.

Coadsorption of [^{15}N]acetonitrile and oct-1-ene: The ^{15}N CP/MAS NMR spectrum of $[^{15}N]CH_3CN$ on H-ZSM-5 with coadsorbed **4** exhibits three signals (Figure 3A). The chemical shift of one of the signals, namely that at $\delta = -159$, corresponds to **3** on bridged OH groups (see Figure 1C and ref. [1]). The signals at $\delta = -208$ and -217 appear in this spectrum in parallel with the signals at $\delta = 76-80$ in ^{13}C CP/MAS spectrum (see Figure 2C), and therefore their appearance should be related to the formation of the structures **1** or **2**. To assign the signals at $\delta = -208$ and -217 as well as at $\delta = 76-80$ and 108.8 in ^{13}C NMR to the structures **1** or **2** it would be reasonable to compare ^{13}C and ^{15}N (^{14}N) chemical shifts observed for the species formed after coadsorption of **3** and **4** on H-ZSM-5 with the chemical shifts of *N*-alkylnitrilium cations and acetonitrile complexes with Lewis acids. *N*-alkylnitrilium cations were reported to be persistent species in superacidic solutions.[7] Acetonitrile also is well known to form stable complexes with Lewis acids.[8-11] In order to determine whether these new signals, differing from those of both acetonitrile and olefin, belong to the structures **1** or **2**, we further prepared *N*-alkylnitrilium cations and CH_3CN complexes with Lewis acids (see experimental section) and characterized them with NMR.

3. ^{13}C and ^{14}N (^{15}N) NMR characteristics of acetonitrile complexes with Lewis acids: ^{13}C and ^{15}N (^{14}N) NMR spectra of acetonitrile (**3**) adsorbed on solid $AlCl_3$ and **3** in SbF_5/SO_2 solution are shown in Figure 4. As seen from Figure 4A, the CN group of **3** complexed to $AlCl_3$ ($CH_3CN \cdot AlCl_3$, **6**) exhibits the signal at $\delta = 125$ in ^{13}C CP/MAS NMR and at $\delta = -200$ in ^{15}N MAS NMR (Figure 4B).

A 1:5 mixture of **3** and SbF_5 in liquid SO_2 shows three signals in the ^{13}C NMR spectrum (Figure 4C): an intense signal at $\delta = 119.3$ and two smaller ones at $\delta = 121.9$ and 123.1. All three

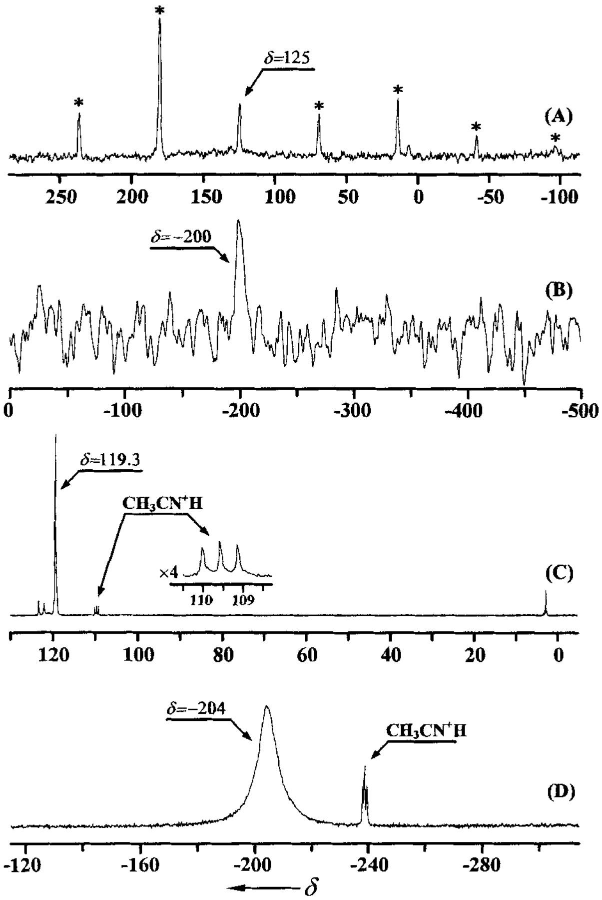


Fig. 4. NMR spectra for the products of the interaction of acetonitrile with Lewis acids. A) ^{13}C CP/MAS NMR of $[1-^{13}C]CH_3CN$ (350 $\mu mol\,g^{-1}$) and B) ^{15}N MAS NMR spectra of $[^{15}N]CH_3CN$ (350 $\mu mol\,g^{-1}$) adsorbed on solid $AlCl_3$ at 296 K; spinning rate was A: 5580 Hz, B: 5395 Hz; asterisks in the spectra denote spinning sidebands. C) ^{13}C and D) ^{14}N high-resolution NMR spectra of acetonitrile with broad-band proton decoupling (CH_3CN:$[1-^{13}C]CH_3CN$ (80% ^{13}C enrichment) $\approx 1:1$) in SbF_5/SO_2 (acetonitrile:SbF_5 = 1:5) solution at $-40\,°C$. The splitting of the signal at 109.5 in spectrum C and at -238 in spectrum D arises from the scalar *J* coupling between ^{13}C and ^{14}N nuclei in protonated acetonitrile.

signals belong to CH_3CN complexes with SbF_5; the intense signal should presumably be assigned to the $CH_3CN \cdot SbF_5$ complex (**7**) and the two smaller signals may be attributed to CH_3CN in *cis*- and *trans*-$[(CH_3CN)_2SbF_4]^+[SbF_6]^-$ complexes, which could be formed by analogy with $[SbF_4(OH_2)_2)]^+[SbF_6]^-$ complexes in the $H_2O/SbF_5/SO_2$ system.[23] The ^{14}N NMR spectrum of $CH_3CN/SbF_5/SO_2$ system exhibits only one broad signal at $\delta = -204$ (Figure 4D), corresponding to the three signals in the ^{13}C NMR spectrum (Figure 4C).

It should be noted that NMR spectra of a mixture of **3** and SbF_5 in SO_2 also gives a small signal from **5**, with the shifts for the CN group at $\delta = 109.6$ (^{13}C NMR) and $\delta = -238$ (^{14}N NMR)[7] (Figures 4C and 4D). Acetonitrile (**3**) in SbF_5/SO_2 solution may be protonated by the traces of HF which are always present in SbF_5[24] or by acidic $[SbF_4(OH_2)_2)]^+[SbF_6]^-$ complex,[23] which may also be present in the initial SbF_5 as admixture. $[SbF_4(OH_2)_2)]^+[SbF_6]^-$ may presumably be formed by the interaction of atmospheric moisture with SbF_5 during the preparation of the complex. NMR characteristics of acetonitrile complexes with the studied Lewis acids are given in Table 1.

4. ^{13}C and ^{14}N NMR characteristics of *N*-alkylnitrilium cations in SbF_5/SO_2 solution: Despite the fact that *N*-alkylnitrilium cations as nitrilium salts with BF_4^- and $SbCl_6^-$ counterions have been known since 1956,[25] they have not previously been characterized with ^{13}C and ^{14}N (^{15}N) NMR; ^{13}C NMR characteristics of these cations would certainly assist in the discrimination between structures **1** and **2** in zeolite.

Figure 5 shows ^{13}C and ^{14}N NMR spectra of SO_2 solution containing a mixture of *t*BuCl, $[1\text{-}^{13}C]CH_3CN$, and SbF_5 in the ratio 1:1:5. The small ^{13}C NMR signals at $\delta = 48$ and 334 represent well-known characteristics of the *tert*-butyl cation **8** (Figure 5A).[26] The intense signals between $\delta = 120$ and 108 arise from the ^{13}C-labeled acetonitrile CN group. The signals at $\delta = 119$ and 109.5 (Figure 5A) are assigned to complexes **7** and **5**,[7] respectively (see also Figure 4C). The appearance of the latter signal in this spectrum seems to be due to the same reason as for SbF_5/SO_2 solution containing only acetonitrile (vide supra) (Figure 4A). The small signals in the spectrum of Figure 5A at $\delta = 27.98$, 65.45, 108.20 should be attributed to the *N*-*tert*-butylacetonitrilium cation (**9**). The *N*-*iso*-propylacetonitrilium cation (**10**) exhibits the same ^{13}C chemical shift for the CN group (complete assignment of the signals for the two cations and reactants is given in Table 1).

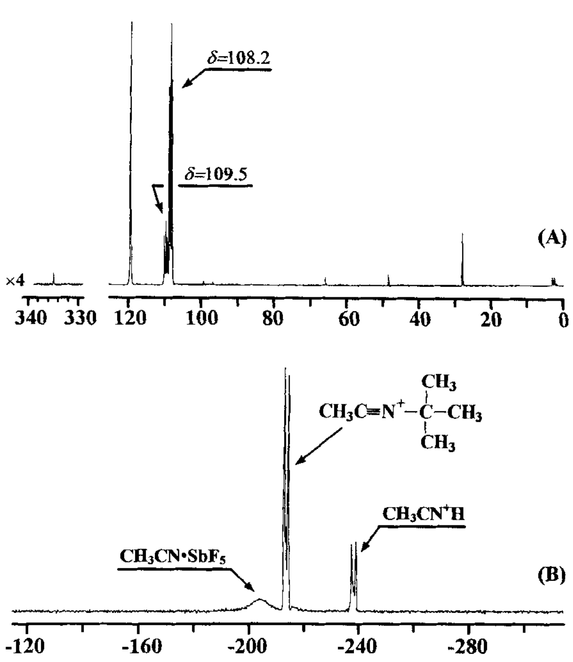


Fig. 5. ^{13}C NMR (A) and ^{14}N NMR (B) high-resolution spectra with broad-band proton decoupling of a mixture of acetonitrile, *tert*-butyl chloride, and SbF_5 ($[1\text{-}^{13}C]CH_3CN$ (80% ^{13}C enrichment):*t*BuCl:SbF_5 = 1:1:5) in SO_2 solution at −40 °C. The splitting of the signals at 108.2 and 109.5 in spectrum A and at −214 and −238 in spectrum B arises from the scalar *J* coupling between ^{13}C and ^{14}N nuclei in *N*-*tert*-butylacetonitrilium cation and protonated acetonitrile, respectively. The small signal at $\delta = 98$ presumably arises from the fluorinated methyl group in the protonated acetonitrile or *N*-*tert*-butylacetonitrilium cation, formed in solution as admixture.

It is significant that ^{13}C NMR signals of the CN group in both protonated acetonitrile and *N*-alkylnitrilium cations are located near $\delta = 108-109$ and shifted upfield with respect to the CN group in free acetonitrile and acetonitrile complexed to Lewis acids (see Figures 4 and 5 and Table 1). The proximity of the ^{13}C chemical shifts of the CN group in both **5** and **2** and large values of scalar *J* couplings, $^1J(^{14}N-^{13}C)$, which are around 40 Hz and are more than three times greater than $^1J(^{14}N-^{13}C)$ in liquid CH_3CN (see Table 1), certainly indicate

Table 1. NMR characteristics (^{13}C, ^{14}N (^{15}N) chemical shifts, δ) of alkyl chlorides, acetonitrile, cationic species, and complexes formed from alkyl chlorides and acetonitrile in SbF_5/SO_2 solution and on solid $AlCl_3$.

Compound	CH_3	$^{13}C{\equiv}N$	$C{\equiv}^{14}N$	$(CH_3)_3C$		$(CH_3)_2CH$		Ref.
				CH_3	C	CH_3	CH	
CH_3CN (**3**) [a]	0.3	117.7	−136.4 (^{15}N)					[28,29]
CH_3CN^+H (**5**) [c]		107.8	−237.4					[7]
	2.45	109.5	−238					this work
$CH_3CN \cdot AlCl_3$ (**6**)	6.8	125	−200 (^{15}N)					this work
$CH_3CN \cdot SbF_5$ (**7**) [b]	2.64	119.3	−204					this work
$(CH_3)_3C^+$ (**8**)				46.5	332.8			[26,39]
				48.5	334.8			this work
$CH_3CN^+C(CH_3)_3$ (**9**) [d]	3.03	108.2	−214	27.98	65.45			this work
$CH_3CN^+CH(CH_3)_2$ (**10**) [e]	2.92	108.2	−222			20.5	53.7	this work
$(CH_3)_3CCl$ (**19**)				33.45	65.15			[27]
$(CH_3)_2CHCl$ (**20**)						26.85	53.75	[27]

[a] $^1J(^{13}C-^{13}C(CH_3)) = 56.5$ Hz, $^1J(^{13}C-^{14}N) = 12.5$ Hz (ref. [30]). [b] $^1J(^{13}C-^{13}C(CH_3)) = 55.2$ Hz. [c] $^1J(^{13}C-^{14}N) = 43.5$ Hz, $^1J(^{13}C-^{13}C(CH_3)) = 76.3$ Hz, $^1J(^{14}N-^1H(NH)) = 97.3$ Hz, $^2J(^{13}C-^1H(CH_3)) = 9.8$ Hz, $^2J(^{13}C-^1H(NH)) = 43.5$ Hz. [d] $^1J(^{13}C-^{14}N) = 40.8$ Hz, $^1J(^{13}C-^{13}C(CH_3)) = 60.0$ Hz, $^2J(^{13}C-^1H(CH_3)) = 10.6$ Hz. [e] $^1J(^{13}C-^{14}N) = 42.7$ Hz.

that both the shifts and J couplings are affected by positive charge on the nitrogen atom.

It is of interest also to note that carbon atoms in the alkyl fragment attached to the nitrogen in the two *N*-alkylnitrilium cations studied exhibit ^{13}C chemical shifts very close to those for carbons in the corresponding parent alkyl chlorides,[27] whereas methyl groups in alkyl fragments are shifted downfield relative to the same methyl groups in alkyl chlorides (see Table 1).

^{14}N NMR spectra of SbF_5/SO_2 solutions of the two prepared *N*-alkylnitrilium cations show three signals. Two of them are absolutely identical: at $\delta = -238$ from **5** and at $\delta = -204$ from complex **7**. The third signal in each of the solutions belongs to cations **9** ($\delta = -214$) or **10** ($\delta = -222$) (see Figure 5B and Table 1).

Thus we have obtained ^{13}C and ^{14}N NMR characteristics of CH_3CN complexes with Lewis acids and *N*-alkylnitrilium cations; now we shall use them for final identification of the products formed from the interaction of CH_3CN and olefins on zeolite H-ZSM-5.

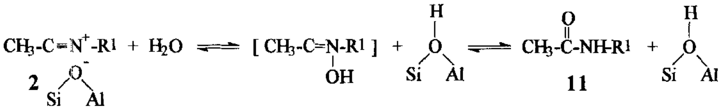
5. Attribution of the NMR signals observed for acetonitrile and oct-1-ene coadsorbed on H-ZSM-5: As has been shown above, ^{13}C chemical shifts for CH_3CN complexed to the Lewis acid ranged from $\delta = 119$ to 125, that is, they are in the region of the chemical shifts for liquid (free and uncomplexed) acetonitrile ($\delta = 118$[28,29]) and for **3** adsorbed on bridged OH groups ($\delta = 116-119$[11]). At the same time, the ^{13}C chemical shift for the CN group in *N*-alkylnitrilium cations (**2**) is $\delta = 108.2$ (see Table 1), that is, explicitly different from both **3** on bridged OH groups and **3** complexed to the Lewis acid, and very close to the shift of the signal observed for CN group in **3** coadsorbed with olefin on zeolite (Figure 2A). This means that if the structure **1** were formed, that is, if coordination of **3** to a strong Lewis acid site in the zeolite took place (Scheme 1, pathway 1), then we would observe an additional signal in the vicinity of $\delta = 119$ besides the signal from **3** on the bridged OH group, and we would not observe any signal at $\delta = 108$, which is identified for **3** coadsorbed with olefin. Thus we conclude that the ^{13}C chemical shift at $\delta = 108$ is indicative of the formation of *N*-alkylnitrilium cation (structure **2**) in accordance with pathway 2 in Scheme 1.

The ^{14}N (^{15}N) chemical shifts turned out to be less informative for distinguishing between structures **1** and **2**. Indeed, besides the signal of **3** on bridged OH groups at $\delta = -159$, the observed signals at $\delta = -208$ and -217 for coadsorbed **3** and oct-1-ene are located in the vicinity of the signals for **3** on Lewis acids at -200 and -204. Simultaneously, *N*-alkylnitrilium cations exhibit signals with the same chemical shift range, namely, at $\delta = -214$ and -222. These experimental facts do not allow us to use ^{14}N (^{15}N) chemical shifts for discriminating reliably between structures **1** and **2**.

We conclude that the species formed after acetonitrile and olefin coadsorption on H-ZSM-5 are *N*-alkylnitrilium cations (structure **2**). In the case of coadsorbed **4**, several cations are formed. They are characterized by a common signal at $\delta = 108.8$ (CN groups; Figure 2A) and by three signals from the $-C{\equiv}N^+-R^1$ fragment at $\delta = 76-80$, corresponding to the three different alkyl fragments R^1 (Figure 2C). Three signals at $\delta = 76-80$ in ^{13}C NMR correspond to the two signals at $\delta = -208$ and -217 in ^{15}N NMR (Figure 3A). (Complete assignment of NMR chemical shifts for the species formed in H-ZSM-5 are given in Table 2.)

6. Interaction of *N*-alkylnitrilium cations with water: A transformation of the formed adsorbed species when they come into contact with water is in good agreement with the expected reaction of the cations **2** with water to produce *N*-alkylacetamides (**11**, vide infra).[31] Simultaneously, **3** that has not reacted with olefin to form cation **2** and has remained adsorbed on H-ZSM-5 may undergo hydrolysis to give acetamide (**12**), acetic acid (**13**), and ammonia (**14**).[1,8,31] Indeed, if atmospheric moisture is admitted to the zeolite sample with coadsorbed acetonitrile and oct-1-ene, new lines with NMR characteristics different from those for *N*-alkylnitrilium ions **2** and unreacted acetonitrile appear both in ^{13}C and ^{15}N spectra (Figures 2A,B, 3A,B; see also Table 2). The observed changes in NMR spectra can be rationalized in terms of the transformations of the cation **2** and acetonitrile as depicted in Schemes 2 and 3.

When ^{13}C-labeled acetonitrile, $[1-^{13}C]CH_3CN$, was used for coadsorption (Figure 2B), the signal at $\delta = 177$ from the carbon

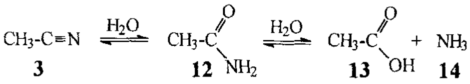


Scheme 2. Transformation of *N*-alkylnitrilium cation through interaction with water in H-ZSM-5.

Table 2. NMR chemical shifts (^{13}C, ^{15}N chemical shifts, δ) for the species formed on adsorption of acetonitrile, oct-1-ene, or *tert*-BuOH, or coadsorption of acetonitrile with oct-1-ene or *tert*-BuOH on H-ZSM-5 at 296 K.

Compound	CH_3	$^{13}C{\equiv}N$ $^{13}C{=}O$	^{15}N	$(CH_3)_3C$ CH_3	 C	CHR–CH_3 CH
$CH_3CN^+-CHR-CH_3$ (**2**)		108.8	–208 –217			76.8;77.7;80.1
CH_3CN (**3**)	0.82	116	–159			
Oct-1-ene (**4**) [a]						14.3(CH_3); 24.9,30–33(CH_2)
$CH_3CN^+C(CH_3)_3$ (**9**)		108.0	–212		69.6	
$CH_3-CO-NH-CHR-CH_3$ (**11**)		177	–220			53.8–70.0
$CH_3-CO-NH_2$ (**12**)		177	–250			
$CH_3-CO-OH$ (**13**)		182				
NH_3/NH_4^+ (**14**)			–358			
tert-BuOH (**15**) [b]				29.7	81.8	
$CH_3-CO-NH-C(CH_3)_3$ (**16**)	24.8	177.1	–217	27.5	59.5	

[a] Ref. [14]. [b] Refs. [15, 18].



$$\underset{\mathbf{3}}{CH_3\text{-}C{\equiv}N} \xrightleftharpoons{H_2O} \underset{\mathbf{12}}{CH_3\text{-}C(=O)NH_2} \xrightleftharpoons{H_2O} \underset{\mathbf{13}}{CH_3\text{-}C(=O)OH} + \underset{\mathbf{14}}{NH_3}$$

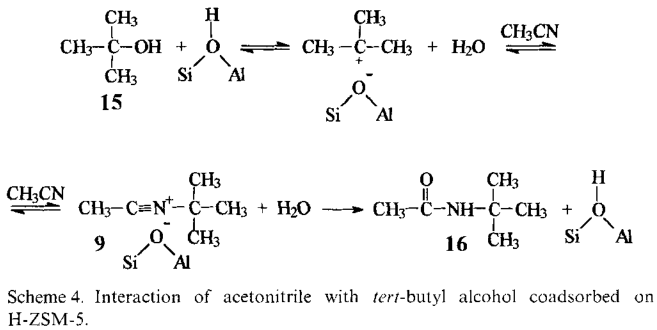
Scheme 3. Transformation of acetonitrile through interaction with water in H-ZSM-5.

atom of the -(C=O)–N- fragment of compounds **11** and **12**[22] becomes clearly distinguishable from the signals of both **2** and **3** at $\delta = 108.8$ and 116, respectively. The signal from acetic acid **13** is seen at $\delta = 182$ as a left-hand shoulder to the signal at $\delta = 177$.

In the case of moisture admittance to the sample with coadsorbed $[1\text{-}^{13}C]$oct-1-ene and unlabeled **3**, five new lines between $\delta = 53.8\text{-}70.0$, different from the signals of **2** in this region of the ^{13}C NMR spectrum (a weak signal from **2** is seen at $\delta = 79$), are identified in Figure 2D. Five signals at $\delta = 53.8\text{-}70.0$ belong to the carbon adjacent to nitrogen in the fragment -NH–R^1 of **11**; five signals indicate the formation of the five different *N*-alkylacetamides **11** with various R^1. The small signals at $\delta = 177$ and 182 from the unlabeled CH_3–(C=O)- fragment of **11**, **12**, and **13** are also seen in the spectrum in Figure 2D.

^{15}N NMR provides further evidence for the transformations of **2** and **3** under their interaction with atmospheric moisture according to Schemes 3 and 4. Figure 3B shows the ^{15}N CP/MAS NMR spectrum of coadsorbed $[^{15}N]CH_3CN$ and unlabeled oct-1-ene. There are three new signals: the signals at $\delta = -250$ and -358 belong to acetamide (**12**)[32] and NH_3/NH_4^+[33] (**14**), respectively. The position of the third signal at $\delta = -220$ is close to that from nitrogen in the cations **2** (see Figure 3A). However, taking into account that under the conditions used this system contains a mixture of compounds **2**, **3**, **11**–**14** (see Figures 2B,D, 3B) the signal at $\delta = -220$ should be attributed to a superposition of the signals from both **2** and **11**.

7. Interaction of acetonitrile with *tert*-butyl alcohol coadsorbed on H-ZSM-5: If alcohol and acetonitrile were coadsorbed on zeolite, then similar transformations (like those in the case of **3** and olefin **4**) can be followed with NMR. Figures 6 and 7 depict the ^{13}C and ^{15}N CP/MAS NMR spectra of *tert*-butyl alcohol **15** and **3** coadsorbed on H-ZSM-5. Analysis of the signals observed in these spectra leads us to a conclusion about the formation of the *N*-*tert*-butylacetonitrilium cation (**9**) and *N*-*tert*-butylacetamide (**16**) according to Scheme 4.



Scheme 4. Interaction of acetonitrile with *tert*-butyl alcohol coadsorbed on H-ZSM-5.

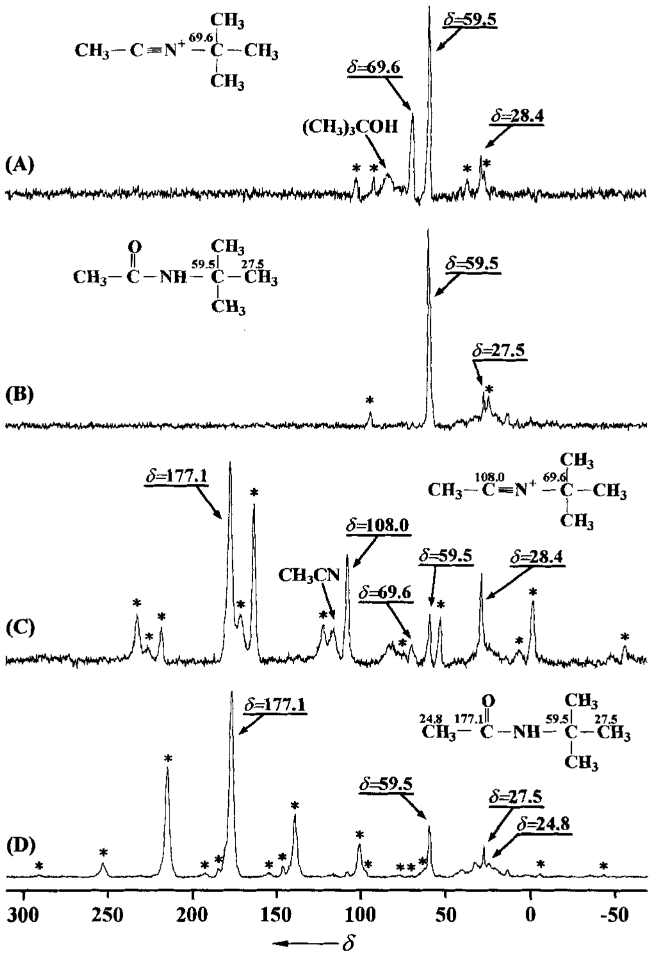


Fig. 6. ^{13}C CP/MAS NMR spectra for the products formed after coadsorption of *tert*-butyl alcohol and acetonitrile on H-ZSM-5 zeolite at 296 K: A and B) coadsorption of the $[2\text{-}^{13}C]t$BuOH (82% ^{13}C enrichment) and unlabeled CH_3CN; C and D) coadsorption of $[2\text{-}^{13}C]t$BuOH (10% ^{13}C enrichment) and $[1\text{-}^{13}C]CH_3CN$ (82% ^{13}C enrichment). A and C: 4 h after coadsorption. B and D: 4 d after coadsorption. 320 μmol g^{-1} of the alcohol and 320 μmol g^{-1} of acetonitrile were adsorbed. Spinning rate was A: 3300 Hz, B: 3500 Hz, C: 5500 Hz, D: 3800 Hz. Asterisks in the spectra denote spinning sidebands.

If $[2\text{-}^{13}C]t$BuOH and unlabeled CH_3CN are coadsorbed on zeolite, then two intense signals from the ^{13}C-labeled carbons at $\delta = 69.6$ and 59.5 are identified, besides the signal from the ^{13}C-labeled C–OH group of the unreacted alcohol at $\delta = 82$[15, 18] and a weak signal from unlabeled methyl groups at $\delta = 28.4$ from the $[2\text{-}^{13}C]t$BuOH and/or a reaction product (Figure 6A). Storage of the zeolite sample with these coadsorbed reactants at 296 K for a few days or heating the sample at 373 K for 30 min resulted in the complete disappearance of the signal at $\delta = 69.6$ (Figure 6B); only the signal at $\delta = 59.5$ remained in the spectrum, along with a weak signal at $\delta = 27.5$. In the spectrum with coadsorbed $[1\text{-}^{13}C]CH_3CN$ (82% ^{13}C enrichment) and $[2\text{-}^{13}C]t$BuOH (10% ^{13}C enrichment), intense signals at $\delta = 108.0$ and 177.1 are clearly observed from the ^{13}C-labeled carbon atoms originating from the acetonitrile reactant (Figure 6C). The signals at $\delta = 69.6$ and 59.5, which are now of smaller intensity compared with these signals in Figure 6A, are also visible. In this spectrum the signals from unreacted alcohol and acetonitrile are seen at $\delta = 84$[15, 18] and 116, respectively. Long standing of the zeolite sample containing these specifically ^{13}C-labeled coadsorbates at 296 K results in the disappearance of the signal at $\delta = 108.0$. Finally, an intense signal at $\delta = 177.1$ remains in the spectrum besides the signals of smaller intensity at $\delta = 59.5$ and 27.5.

Based on the analysis of the behavior of different signals in the NMR spectra with time for coadsorbed **15** and **3**, we conclude that the group of signals at $\delta = 27.5$, 59.5, and 177.1 should be assigned to the final reaction product and the signals at $\delta = 69.6$ and 108.0 that disappear with time to the intermediate in this reaction. According to their chemical shifts the signals from the former group belong to *N-tert*-butylacetamide **16** (see Table 2). Indeed, ^{13}C chemical shifts observed for **16** are in good agreement with those reported in solution (**16** exhibits the following ^{13}C chemical shifts in solution: $\delta = 23.6$ (CH_3), 28.55 (CH_3, *tert*-butyl group), 49.9 (quaternary carbon), 169.0 (C=O)[22]). ^{13}C chemical shifts for the signals disappearing with time agree well with ^{13}C NMR characteristics for the cation **9** in solution (see Table 1). Therefore, these signals should be attributed to *N-tert*-butylacetonitrilium cation **9** (Table 2). It should be noted here that some of the carbons in organic molecules adsorbed in zeolite, especially those strongly interacting with bridged OH groups, often exhibit additional chemical shifts[34] (e.g., a C–OH group in adsorbed *t*BuOH shifts downfield by a further $\Delta\delta = 13$ ppm[15, 18]). Therefore, it is no wonder that the ^{13}C chemical shifts in some of the carbons in adsorbed **9** and **16** are shifted with respect to these shifts in solutions of $\Delta\delta = 5-10$ ppm.

Comparison of the ^{15}N CP/MAS NMR spectrum of the final *N-tert*-butylacetamide **16** (Figure 7A) with the spectrum recorded after keeping of coadsorbed [^{15}N]CH_3CN and **15** for 4 hours (Figure 7B) leads us to conclude that the signal from *N-tert*-butylacetonitrilium cation (**9**) is located at $\delta \approx -212$. It is seen as a left shoulder to the signal at $\delta = -217$ from *N-tert*-butylacetamide (**16**). The signal at $\delta = -159$ belongs to unreacted [^{15}N]CH_3CN. The ^{13}C and ^{15}N chemical shifts observed for the adsorbed intermediate **9** and the product **16** are given above the corresponding atoms of the molecules **9** and **16** depicted in Figures 6 and 7 (see also Table 2).

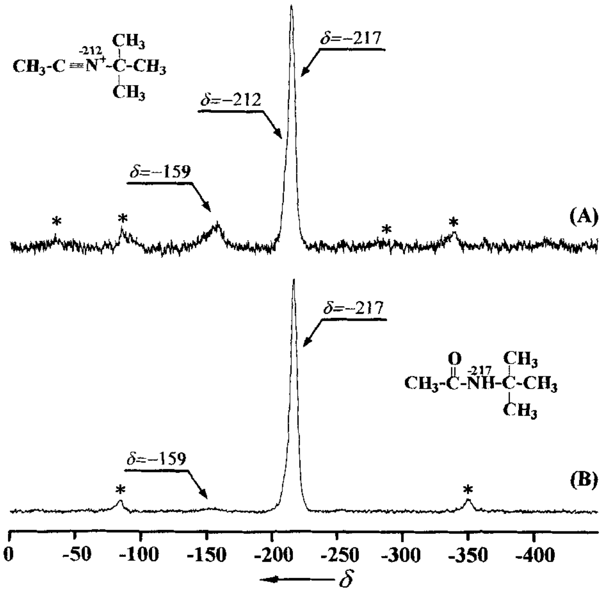


Fig. 7. ^{15}N CP/MAS NMR spectra for the products formed after coadsorption of *tert*-butyl alcohol and [^{15}N]acetonitrile (95% ^{15}N enrichment) on zeolite H-ZSM-5 at 296 K: A) 4 h after coadsorption; B) 4 d after coadsorption. 300 μmol g^{-1} of both alcohol and acetonitrile were adsorbed. Spinning rate was A: 5000 Hz, B: 5400 Hz. Asterisks in the spectra denote spinning sidebands.

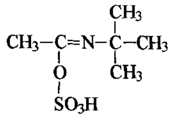
In this series of experiments the reaction was carried out in a sealed NMR tube and atmospheric moisture was excluded from the zeolite sample. Under these conditions the amount of water evolved from the reaction (Scheme 4) seems not to be sufficient to hydrolyse acetonitrile according to Scheme 3. This appears to be the reason that the signals from acetamide (**12**), acetic acid (**13**), and ammonia (**14**) are not identified in Figures 6 and 7.

Discussion

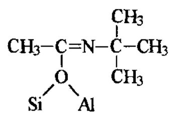
It follows from our experimental data that, upon coadsorption of acetonitrile and olefin on zeolite H-ZSM-5, the cleavage of the Al–O bond in the bridged Si–OH–Al group, proposed in Scheme 1, to form simultaneously a strong Lewis acid center with an acetonitrile molecule coordinated to it and an alkoxy group[2] (structure **1**) does not occur. Interaction of acetonitrile with olefin results in the formation of *N*-alkylnitrilium cations **2** (Scheme 1). In the presence of water cation **2** transforms further to *N*-alkylamides.

It has been known since 1948 that interaction of olefins (alcohols) with alkylnitriles in acidic media produces *N*-alkylamides (the Ritter reaction).[31] Therefore, the observed transformation of acetonitrile and olefin (alcohol) on H-ZSM-5 is in good accordance with the classic Ritter reaction.[8, 31]

It is generally accepted that the Ritter reaction proceeds via intermediate *N*-alkylnitrilium cations.[8, 31] However, up till now nobody has reliably identified the suggested intermediate cation spectroscopically in acidic solution during the reaction. In this respect, the key intermediate in the Ritter reaction has often been depicted as the species **17**, that is, one covalently bonded to sulfuric acid by an oxygen atom, rather than the free ion **2**.[8] In the zeolite the species **18**, analogous to **17** in acidic solution, should be expected as intermediate. However, if the species **18** were formed, the ^{13}C chemical shift for the carbon atom attached to the oxygen in the fragment -C(O)=N- would be at $\delta = 150-160$,[35] rather than at $\delta = 108-109$, which is actually observed in the spectra. Thus, our data are in favor of the earlier suggestions[4, 5] on the cationic nature of the intermediate formed upon acetonitrile and olefin coadsorption on acidic zeolites.


$CH_3-C(OSO_3H)=N-C(CH_3)_3$

17


$CH_3-C(O[Si,Al])=N-C(CH_3)_3$

18

The reaction on the zeolite possesses some peculiarities. In the absence of water inside zeolite pores it is stopped at the stage of the formation of *N*-alkylnitrilium cations (**2**). Only if water is present in the zeolite or water is formed in situ, for example, if the alcohol is involved in the reaction, the cation **2** further transforms into the typical product of the Ritter reaction, *N*-alkylamides.

N-alkylnitrilium cation **2** is not a mobile species inside zeolite H-ZSM-5: numerous spinning sidebands from the CN group in adsorbed cation **2** (see, e.g., Figure 2A) provide evidence that it is strongly bound to the adsorption site, a negatively charged oxygen atom in the zeolite framework, similar to other stable cations in zeolites—cyclopentenyl,[13, 15, 36] indanyl,[37] and cyclic carboxonium ions.[38] In superacidic solutions or in the solid state, cations **2** exist as stable species with SbF_6^-, $SbCl_6^-$, and BF_4^- negatively charged counterions.[7, 25] Moreover, they can be further stabilized by additional solvation with Lewis acids SbF_5, $SbCl_5$, or BF_3 by coordination of a halogen atom to the cationic center.[25, 39]

The effect of stabilization of positively charged carbocationic species by solvation that occurs in superacidic solution[39] is absent inside a zeolite. Therefore, one might expect that without this stabilizing effect formation of alkoxy-type species **18** as intermediates with covalent C–O bonds would be more probable, these being more stable than carbenium ions.[40, 41] Nevertheless, as we have mentioned above, the cation **2**, rather than alkoxy species **18**, actually occurs as intermediate in the Ritter reaction. This fact requires further studies and, in particular, quantum-chemical estimation of the energy of stabilization of both cation **2** and species **18** with covalent C–O bonds.

It follows from the observation of the cation **2** rather than species **11** that for cation **2** as well as for cyclic cations[13, 15, 36–38] the negatively charged oxygen of the zeolite framework in particular, and the zeolite framework as a whole, can play both the role of counterion and that of additionally solvating and stabilizing molecules, like SbF_6^- in superacidic solutions.[8]

Unlike *N*-alkylnitrilium cation **2**, alkylcarbenium ions CH_3CH^+R are not stabilized inside H-ZSM-5 zeolite and they have never been observed spectroscopically as persistent intermediates in hydrocarbon conversion on zeolites. However, spectroscopic data provide evidence for formation of alkylcarbenium ions as active transient intermediates,[13–15, 17, 34, 38, 42–44] rather than alkoxy species[15, 17–20, 43] in low-temperature hydrocarbon and alcohol conversion on zeolites. Alkoxy species are also often considered to be active intermediates on zeolites,[17, 40, 41, 43, 45] despite the fact that they represent rather stable species[17–20, 40, 41] and can be thought of as the reaction products.[15, 18, 44] One can assume that alkylcarbenium ions are not registered spectroscopically inside zeolites because zeolites do not possess sufficient solvating ability to stabilize these alkyl cations as occurs in the presence of strong Lewis acids in superacidic solutions, where the alkylcarbenium ions are solvated completely, for example with SbF_5.[39]

In the case of formation of alkylcarbenium ions in zeolite in the presence of coadsorbed acetonitrile, the transient alkylcarbenium ion formed is stabilized by coordination of acetonitrile. In this respect, a molecule of acetonitrile serves as a trap for alkylcarbenium ions. Thus we conclude that formation of *N*-alkylnitrilium cations **2** persistent in the zeolite is further evidence in favor of the formation of transient alkylcarbenium ions as key reaction intermediates, rather than stable alkoxy species under low-temperature hydrocarbon and alcohol conversion on acidic zeolites.

Conclusion

The following conclusions have been drawn from the NMR data for acetonitrile and oct-1-ene or *tert*-butyl alcohol coadsorbed on H-ZSM-5:

1) The Ritter reaction is observed between coadsorbed acetonitrile and alcohol on H-ZSM-5 to form *N*-alkylamides at 296 K. Thus this reaction can occur not only in liquid acidic media but also on a solid acid catalyst, zeolite H-ZSM-5.
2) Interaction of acetonitrile and olefin on H-ZSM-5 under anhydrous conditions gives rise to *N*-alkylnitrilium cations. Their interaction with water results in the formation of the final *N*-alkylamides.
3) *N*-alkylnitrilium cations represent persistent intermediates in the Ritter reaction on H-ZSM-5; they have been detected with ^{13}C CP/MAS NMR for the first time during the reaction.
4) The data obtained are evidence for the formation of intermediate alkylcarbenium ions from olefins and alcohols upon their adsorption on acidic zeolite. Acetonitrile serves as a trap for alkylcarbenium ions, converting transient alkylcarbenium ions into persistent *N*-alkylnitrilium cations. The stabilization of alkylcarbenium ions inside H-ZSM-5 zeolite occurs by coordination of acetonitrile to form *N*-alkylnitrilium ions, which have been detected with solid-state NMR.

Experimental Section

Sample preparation for solid-state NMR experiments: Approximately 0.1 g of zeolite H-ZSM-5 (Si/Al = 49, concentration of acidic Si–OH–Al groups ≈300 $\mu mol\,g^{-1}$) was loaded into a glass tube and activated by heating at 450 °C for 2 h in air and for 4 h under vacuum (10^{-3} Pa). Then we froze out equal amounts (≈300 $\mu mol\,g^{-1}$) of olefin (alcohol) and acetonitrile onto H-ZSM-5 under vacuum at the temperature of liquid nitrogen. After sealing off the tube containing the zeolite sample from the vacuum system, the sample was slowly warmed to room temperature and kept at 296 K for a few hours before the reaction products were analyzed. Analysis of the products was made directly inside the zeolite sample with ^{13}C and ^{15}N CP/MAS NMR in a sealed glass tube inserted into a 7 mm zirconia rotor.

Preparation of acetonitrile complexes with Lewis acids:
$CH_3CN \cdot AlCl_3$ complex (6): Anhydrous, highly dispersed $AlCl_3$ powder (0.1 g) was loaded into a glass tube in a drybox. The tube was then sealed onto a high vacuum system and evacuated for 4 h at 100 °C under vacuum (10^{-3} Pa). After the sample had been cooled to room temperature it was exposed to acetonitrile vapor (2.0×10^3 Pa, calibrated volume of 84 mL, i.e. ≈70 µmol) containing a mixture of [1-^{13}C]CH_3CN (80% ^{13}C isotope enrichment) and [^{15}N]CH_3CN (95% ^{15}N isotope enrichment) (1:1). The vapor was completely consumed by the $AlCl_3$ powder within 10 minutes at 296 K. The tube with acetonitrile adsorbed on $AlCl_3$ was sealed off from the vacuum system and then placed into the zirconia rotor for recording of ^{13}C and ^{15}N solid state NMR spectra of acetonitrile complexed to $AlCl_3$.

$CH_3CN \cdot SbF_5$ complex (7): 2.8 mmol of CH_3CN (or [1-^{13}C]CH_3CN) in 1 mL of liquid SO_2 was added to the solution of SbF_5 (14 mmol) in SO_2 (2 mL) at −40 °C while being stirred. The resulting solution, containing a mixture of CH_3CN and SbF_5 (1:5), was stored at temperature of −20 °C for 2 d before ^{13}C and ^{14}N high-resolution NMR spectra were recorded.

Preparation of *N*-alkylnitrilium cations: Two *N*-alkylnitrilium cations (*N-tert*-butylacetonitrilium cation **9** and *N-iso*-propylacetonitrilium cation **10**) were synthesized according to the procedure of Olah and Kiovsky [7] by consecutive addition under vacuum of alkyl chloride (*t*BuCl **19** or *i*PrCl **20**) and CH_3CN (**3**) (or [1-^{13}C]CH_3CN) to the solution of SbF_5 (14 mmol) in SO_2 (3 mL) while this was stirred at −60 °C. In the resulting solution, the ratio

3:**19**(**20**):SbF_5 was 1:1:5. The solutions with the formed cations were stored at −20 °C for 2 d before the cations were characterized with ^{13}C and ^{14}N NMR.

Solid-state NMR measurements: ^{13}C and ^{15}N NMR spectra with cross-polarization (CP) and magic angle spinning (MAS) [46,47] were acquired on a Bruker MSL-400 NMR spectrometer operating at 100.613 (^{13}C) and 40.547 (^{15}N) MHz at 296 K. The following conditions were used for CP experiments: the proton high-power decoupling field was 12 G (4.9 µs 90° ^{1}H pulse) for both ^{13}C and ^{15}N CP NMR, contact time was 3 ms for ^{13}C and 5 ms for ^{15}N CP experiments at Hartmann–Hahn matching conditions 51 kHz, delay between scans was 3 s. One-pulse excitation ^{15}N solid-state MAS NMR spectra were acquired with 45° flip angle pulse of 2.5 µs duration and repetition time 10 s. Number of scans for both ^{13}C and ^{15}N solid-state NMR ranged from 800 to 16000, spinning rate was 3.3–5.5 kHz. Chemical shifts were measured with respect to TMS for ^{13}C nuclei and relatively to NO_3^- ion for ^{15}N nuclei as external references.

High-resolution NMR measurements: ^{13}C and ^{14}N high-resolution NMR measurements were performed on a Bruker MSL-400 NMR spectrometer at 100.613 (^{13}C) and 28.914 (^{14}N) MHz in sulfur dioxide solution at −20 to −40 °C. The 45° flip angle pulse of 6–7 µs duration (^{13}C, ^{14}N) and repetition time between pulses of 8 s (^{13}C) and 1 s (^{14}N) were used for spectra acquisition. Chemical shifts were measured with respect to external references: TMS for ^{13}C nuclei and CH_3CN for ^{14}N nuclei; the shift of CH_3CN was taken as $\delta = -136.4$ [29] relative to the NO_3^- ion. NMR measurements were carried out with and without broadband proton decoupling. The latter procedure was used to identify and measure $^{1}J(^{13}C\text{-}^{1}H)$ and $^{1}J(^{14}N\text{-}^{1}H)$ couplings to help us in assignment of NMR signals.

Acknowledgments: The authors are grateful to Dr. V. N. Romannikov for the synthesis of the sample of zeolite H-ZSM-5. This research was supported in part by grant no. 95-03-08780 from the Russian Foundation for Basic Research.

Received: July 1, 1996 [F406]

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