Catalysis Letters 39 (1996) 57–62

Surface complexes in zeolite-catalysed acylation reactions detected by ^{13}C MAS NMR spectroscopy

V. Bosáček

The Heyrovsky Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, 182 23 Prague 8, Czech Republic

E.A. Gunnewegh and H. van Bekkum

Laboratory of Organic Chemistry & Catalysis, Delft University of Technology, Julianalaan 136,
2628 BL Delft, The Netherlands

Received 1 February 1996; accepted 14 February 1996

The state of the acylating agent acetyl chloride, adsorbed on a series of proton and metal ion exchanged zeolites X, Y (faujasite) and ZSM-5, was investigated by ^{13}C MAS NMR spectroscopy. The observed carbonyl signals were assigned to two species: chemisorbed acetyl chloride bound to lattice oxygen (signals near 182 ppm), and acetyl chloride complexed with counter cations in the lattice (signals near 172 ppm). In a few cases signals were observed which have been assigned to "free" acylium cation stabilized on the surface of the solid (signal 160–165 ppm). Experiments in which toluene was adsorbed on to ZnY pretreated with acetyl chloride showed the participation of various adsorbed species in the acylation reaction of toluene.

Keywords: Friedel–Crafts acylation; acetyl chloride; zeolite; surface complex; ^{13}C MAS NMR spectroscopy

1. Introduction

Present day industrial Friedel–Crafts type aromatic acylation methods are environmentally unfriendly. Generally, large amounts of metal chlorides are applied as catalysts, with virtually no options for recycling. Considerable attention has been devoted to the investigation of acylation reactions using zeolitic catalysts, which, as was pointed out in recent reviews [1–3], are very promising for this application. Reactions described in the literature include the acylation of anisole (on HY zeolite) [4], of thiophene and toluene [5,6] by acid chlorides, and of heteroaromatic compounds [7] by acetic anhydride. Interesting results have been obtained in studies with zeolite Beta and the new mesoporous materials, such as MCM-41 [2,8–10].

Many investigations dealing with the mechanisms of Friedel–Crafts catalysis have been published and reviewed (see e.g. refs. [11,12]), but no publications have yet appeared on the mechanism of acylation on heterogeneous catalysts such as zeolites. In this work we have studied the catalytic acylation of toluene under laboratory conditions on HY and ZnY zeolites, with acetyl chloride, acetic acid or acetic anhydride as acylating agents. Important questions arise about the state of the acylating agent on the catalyst: It could take part in the reaction as an acylium counterion, or as chemisorbed fragments forming acetate-like species with lattice oxygen, in a manner analogous to the formation of alkoxy species from chemisorbed carbenium ions [13,14]. For an answer, ^{13}C MAS NMR spectroscopy of adsorbed acylating agents seems to be a particularly promising technique [15], especially since various ^{13}C-labeled species can be employed. The assignment of the observed carbonyl signals, after adsorption of acetyl chloride onto various zeolites, was the first task of this study.

2. Experimental

2.1. Materials and sample preparation

Zn, Ag, Cs and Mg exchanged zeolite samples were prepared from the parent NaY, NaX or Na-ZSM-5 zeolites by ion exchange in aqueous nitrate solutions. H-ZSM-5 and HY samples were prepared from the parent Na-zeolites by ion exchange in aqueous ammonium nitrate solutions. The chemical compositions of the products are summarized in table 1. The ^{13}C1- and ^{13}C2-labeled (99 at%) compounds (acetyl chloride, acetic acid) were purchased from Aldrich. Toluene, ^{13}C labeled (99 at%) in the methyl group, was obtained from MSD isotopes. Prior to use in the in situ acylation experiments, the toluene was diluted to 50% enrichment and purified and dried with lithium hydride. Samples were activated in an all-glass apparatus, under a vacuum of 10^{-3} Pa, at 400°C for at least 10 h, before being sealed off under vacuum and transferred to the adsorption device. The breakable glass seal ("schlagventil") was then opened and a measured amount of adsorbate was loaded onto the adsorbent by means of a gas-burette at the temperature of liquid nitrogen. The cooled sample with adsor-

Table 1
Chemical composition of the samples

Zeolite	Elemental unit cell formula	Electronegativity S_{INT}(Sanderson)	Si/Al
NaY	$Na_{56.5}[(AlO_2)_{56.5}(SiO_2)_{135.5}$	2.58	2.40
ZnY	$Zn_{24.3}Na_{4.1}H_{3.9}[(AlO_2)_{56.6}(SiO_2)_{135.4}$	2.92	2.39
AgY	$Ag_{49.6}Na_{1.0}H_{3.6}[(AlO_2)_{54.3}(SiO_2)_{138.7}$	2.89	2.55
CsY	$Cs_{40.9}Na_{14.8}[(AlO_2)_{55.7}(SiO_2)_{136.3}$	2.43	2.45
CsX	$Cs_{43}Na_{42}[(AlO_2)_{85}(SiO_2)_{107}$	2.29	1.26
H-ZSM-5	$H_{4.1}[(AlO_2)_{4.1}(SiO_2)_{91.9}$	3.04	22.4
Na-ZSM-5	$Na_{4.1}[(AlO_2)_{4.1}(SiO_2)_{91.8}$	2.98	22.4
NaX	$Na_{85.8}[(AlO_2)_{85.8}(SiO_2)_{106.2}$	2.39	1.24
MgY	$Mg_{22.2}Na_{10.8}[(AlO_2)_{55.1}(SiO_2)_{136.9}$	2.82	2.48
HY	$H_{53.6}Na_{3.7}[(AlO_2)_{57.3}(SiO_2)_{134.7}$	2.92	2.35

bate was sealed off in a glass ampoule and heated at the prescribed temperature of 85–110°C. An in situ catalytic test was also performed in this ampoule under static conditions where, instead of one adsorbate, a mixture of reactants was frozen on the surface. The sample was then treated at a prescribed temperature and, after cooling, stored at room temperature for the NMR measurement. Immediately before the measurement the sample was opened in a dry-box and loaded into the rotor under an inert atmosphere.

2.2. ^{13}C MAS NMR spectroscopy

^{13}C MAS NMR spectra were measured at 50.32 MHz frequency on a Bruker MSL 200 spectrometer equipped with MAS facilities for high-resolution measurements on solids. The zirconium oxide rotor was employed with a spinning rate of 4.8 kHz. Cross polarization spectra were scanned with a contact time of 1.5 ms using the excitation $\pi/2$ pulse of 5.5 μs in the proton channel. Proton decoupled spectra were also scanned by means of a single pulse excitation in the ^{13}C channel or by means of a Hahn's echo program using a train of $\pi/2$ and π pulses and broad-band proton decoupling during acquisition. Some spectra were also measured at 100.57 MHz on a Varian VXR-400S spectrometer, equipped with a 5 mm Doty scientific MAS probe.

3. Results and discussion

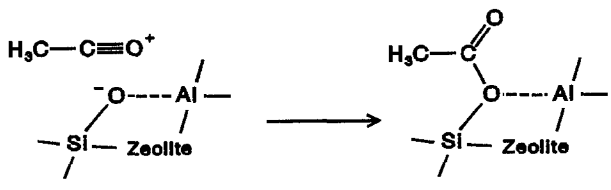
^{13}C NMR signals of acetylium ions in superacidic solutions, such as $FSO_3H–SbF_5–SO_2$, exhibit downfield shifts of 150–152 ppm from TMS for the carbonyl carbons and of 5.5–7.5 ppm for the methyl carbons [17–19]. One of the known methods [16] for the generation of acetylium ions is based on the reaction of silver cations with acetyl chloride (in a solution containing acetic acid, acetic anhydride, acetyl chloride and silver perchlorate) according to the equation:

$$CH_3C(O)Cl + Ag^+ \rightarrow CH_3C^+(O) + AgCl$$

If we carry out a similar reaction in zeolite AgY, where silver cations are available for contact with acetyl chloride in SII positions, the same reaction is assumed to take place with the production of acetylium cations. Although the acylium ion is a relatively weak electrophile due to the stabilisation by resonance structures involving carbenium (positively charged carbon) and oxonium (positively charged oxygen) ions, the latter being the most important, it is able to react with any nucleophilic species in the vicinity [20].

3.1. Chemisorbed acetyl on lattice oxygen

Experiments were performed intentionally with low coverage of zeolitic cavities to reduce the probability of a collision of acetyl chloride with another molecule. The created acylium ion may then react with an available nucleophile, e.g. a lattice oxygen, to form acetate-like structures as depicted below:



Of course, these structures will exhibit ^{13}C NMR signals significantly different from those of acylium ions due to the change in orbital hybridization from sp to sp^2, as well as the different chemical environment of the carboxyl carbon. Consequently, in addition to the effects mentioned, the influence of the lattice oxygen electronegativity in the charge distribution should also be manifested. All these factors, together with the local electrostatic field, will influence the carbon shielding and hence the position of the ^{13}C NMR signal.

It is well known that the chemical shift of the carbonyl carbon in liquid acetic acid is observed at 177 ppm [17],

Table 2
^{13}C chemical shifts (ppm TMS) of adsorbed acetyl chlorides and acetic acids (mixture of ^{13}C1 and ^{13}C2 labeled) on zeolites

Sample	mmol/g	Signals[a] (ppm TMS)			
acetyl chloride					
NaY	0.22	184.4	174.0	162 w	20.4
AgY	0.11	185.1	vw	168	21.1
ZnY	0.22	183.9	171.5		19.6
HY	0.28	184.7	173.5		20.5
CsY	0.32	184.0	171.9		21.9
MgY	0.22	184.3	175.0	168 sh 155	32 20.1
NaX	0.11	183.5	174.2		21.5
CsX	0.32	183.0	173 br		21.8
Na-ZSM-5	0.22	180.2	174.0		21.3
H-ZSM-5	0.22	182.6	175.5		18.7
acetic acid					
NaY	0.12		177.1		19.6
ZnY	0.16	183.1			19.3
HY	0.16	182.3			20.7
CsY	0.16		177.1		21.2
H-ZSM-5	0.11	182.4			18.6
Na-ZSM-5	0.12	182 sh	177.4		19.9

[a] br = broad, sh = shoulder, vw = very weak, w = weak.

but the isotropic values of the same carbon in solid salts of acetic acid are situated in the interval from 177 to 185 ppm as given in ref. [21]. The protonation of acetic acid causes still larger deshielding of the carboxyl carbon up to a value of 193 ppm (Maciel and Traficante [22] and Olah et al. in a superacid [18]). Acetic acid (^{13}C1-labeled) adsorbed on the investigated zeolites exhibits only one signal at 177 for e.g. NaY or CsY, and at 183 ppm for samples with divalent cations in the lattice, as presented in table 2. These data suggest an interaction of the counterions in the zeolite with acetate-like species. The Brønsted acid zeolites HY and H-ZSM-5 exhibit signals at 182 ppm after adsorption of acetic acid, revealing the interaction of the acid with the proton sites.

From our results on adsorbed acetyl chloride presented in table 2 it is seen that for most of the samples two carbonyl signals are detected: one above 170 ppm and another in the region above 180 ppm. We propose, from the analogies mentioned above, that the signals of adsorbed acetyl chloride above 180 ppm are to be assigned to acetate-like chemisorbed species created by a reaction of acylium ion with a lattice oxygen. In such a chemisorbed complex the influence of the electronegativity of the lattice oxygen is expected, as found in the case of surface methoxyls created from evolved methyl cations [13,14]. However, the shielding in the case of carboxyl carbons is more complicated due to the presence of a double bond and the free electron pairs on oxygen, so that it is not reasonable to expect a simple linear relationship between the chemical shift and the electronegativity of the lattice as was observed [13,14] for the case of the single bond system in $\rangle C{=}O{-}H$ or in surface methoxyls $\rangle C{=}O{-}CH_3$. Indeed, the ^{13}C1 chemical shifts of the relevant signal, plotted against the intermediate electronegativity of various zeolites in fig. 1, do not give a linear correlation. While the signals of Na, Cs, Ag forms of X and Y zeolites follow the expected increase in deshielding with increasing electronegativity of lattice oxygen, the points for ZnY, H-ZSM-5 and Na-ZSM-5 deviate strongly from this relationship. The reason for this effect is not yet clear.

3.2. *Adsorption complexes of acetyl chloride*

Generally ^{13}C spectra of adsorbed acetyl chloride show two signals in the carbonyl/carboxyl region (figs. 2 and 3). Since the ^{13}C NMR spectra of physically adsorbed molecules are, in general, not very different from those in the liquid state (see e.g. ref. [23]), we can expect the spectrum of the physically adsorbed part of the acetyl chloride, not consumed by reaction, to exhibit signals only slightly shifted from those of unperturbed acetyl chloride: e.g. 170.4 ppm (carbonyl carbon) and

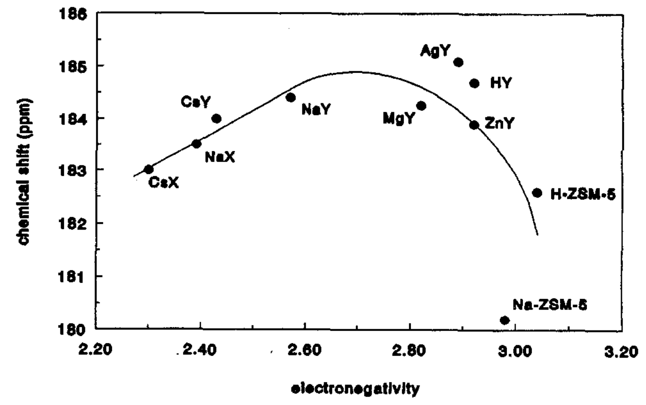


Fig. 1. Correlation graph of the ^{13}C1 signal of the adsorption complex of acetyl chloride against the equalised electronegativity (S_{INT}) of the studied zeolites (see table 2).

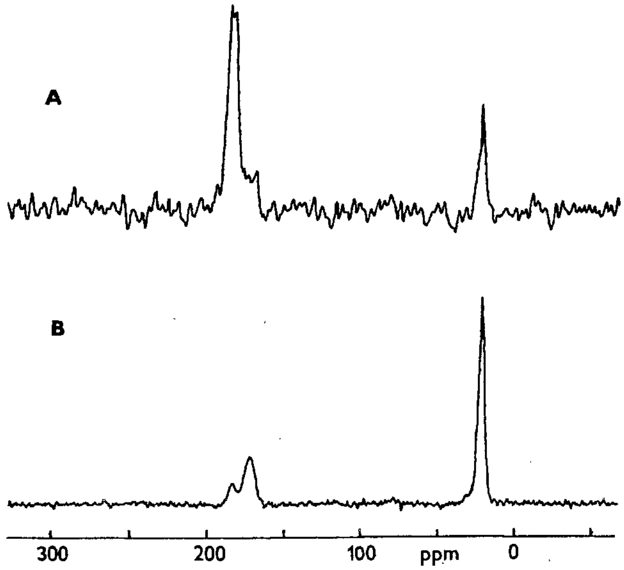


Fig. 2. ^{13}C CP MAS NMR spectra of (A) AgY zeolite with adsorbed acetyl chloride (0.11 mmol/g) after treatment at 100°C for 30 min; (B) CsY zeolite with adsorbed acetyl chloride (0.32 mmol/g) after treatment at 100°C for 30 min.

33.6 ppm (methyl carbon) in liquid acetyl chloride [17]. The observed carbonyl signals, besides those discussed above, were found in the interval from 170 to 175 ppm, only slightly shifted to lower field, i.e. in the direction of decreased shielding. Signals of the methyl carbons were detected only in experiments with a mixture of labeled $^{13}CH_3C(O)Cl$ and $CH_3{}^{13}C(O)Cl$, at values of 29–32 ppm. We therefore assign the observed signals in the region of 170–175 ppm to adsorption complexes of acetyl chloride with the zeolite. Interaction with the counter cations should be considered here. Complexes with cationic sites are preferred for polar molecules. Their influence on acetyl chloride molecules will depend on the type of intermolecular interactions in the complex. In turn, the effects on the NMR spectrum will depend on the type of donor–acceptor bonds and/or on pure electrostatic effects. The chemical shift of carbonyl carbon for weak interactions of electrostatic origin will depend on the cationic radii; the deshielding should be less for large Cs^+ cation than for Na^+ cation. Indeed, the mean value of the carbonyl chemical shift from all measured samples of CsX or Y zeolites is found to be 172.2 ppm, in comparison with 173.8 for NaY. For ZnY zeolite the situation is not so clear because of insufficient information about the coordination complex with Zn. Taking into account the semipolar covalent Zn–O bonds and the confirmed existence of $Zn(OH)^+$ cations [24], it seems reasonable to expect that the polarization of acetyl chloride would be relatively low and, therefore, the small chemical shift of the $>$C=O carbon signal seems to be well in line with these facts.

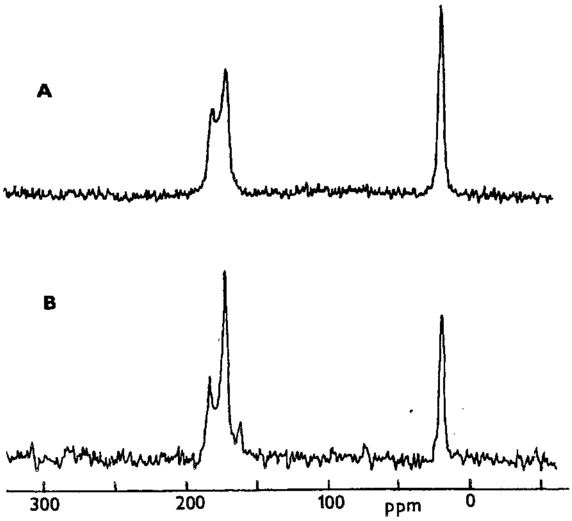


Fig. 3. ^{13}C CP MAS NMR spectra of (A) NaX zeolite with adsorbed acetyl chloride (0.11 mmol/g) after treatment at 100°C for 30 min; (B) NaY zeolite with adsorbed acetyl chloride (0.22 mmol/g) after treatment at 100°C for 30 min.

Another important aspect is the polarization effect of the cations, which initiates the cleavage of the C–Cl bond, leading to the formation of the acylium cation. From the results in table 2 it is seen that AgY zeolite, where the acylium ion is so easily created, does not exhibit any strong signal for physically adsorbed acetyl chloride owing to its complete transformation into acylium ions and, via a reaction with surface oxygen, to an acetate-like structure, characterized by a strong signal at 183 ppm (see fig. 2a and, in contrast, fig. 2b for CsY). On Na forms of the zeolites both signals have been found (i.e. 183 and 172 ppm), while on CsX and CsY the signal at 183 ppm was weak or nondetectable (see figs. 3 and 2b). In another experiment it was shown that, at lower loading (0.12 mmol/g) of CsY with acetyl chloride, the ratio of physically adsorbed acetyl chloride to acetate-like chemisorbed species remains the same. The signal at 183 ppm was also then found to be very weak compared to the signal at 172 ppm. It follows from these experiments that the acylating effectivity or catalytic activity should follow the sequence $Ag^+ > Na^+ > Cs^+$, provided that the created acylium ion immediately reacts with the reactant, in the product forming step.

The assignments of the signals above 180 ppm to the chemisorbed acetyl on the lattice oxygen and those above 170 ppm to the cation coordination complex of acetyl chloride, are supported by preliminary results of the adsorption of acetic anhydride on zeolites. The adsorption and cleavage of acetic anhydride are expected to lead to the formation of acetates and surface-bonded acetyl. Further investigations of these aspects are in progress.

3.3. Free acylium ion stabilized on the surface

Concerning the existence and detection of free acylium ions on the surface of zeolites by ^{13}C NMR spectroscopy, it should be pointed out that in some of the experiments given in table 2 a weak signal at 160–165 ppm was detected, which may be assigned to perturbed acylium ions. As described by Olah et al. [18,19], the signals of acylium ion in a superacid are located at 150–152 ppm for the carbonyl carbon and at 5.5–7.5 ppm for methyl carbon. It is interesting that in our study such signals around 160 ppm were observed on samples with relatively high amounts of adsorbed acetyl chloride. From this finding it could be deduced that the concentration of such species is small. The detection of reactive free acylium ions is not as unlikely as might seem at first sight, because the existence of stabilized acylium ions in some salts, and in solutions under special conditions, is well known [25]. Nevertheless, further investigations are necessary for a more detailed discussion of this.

3.4. *Oligomerisation of adsorbed species*

In some experiments carried out with a mixture of ^{13}C labeled acetyl chloride in the C1 and C2 positions, new signals appeared at 104–108 ppm (ZnY and CsY). We have reasons to suppose these to be associated with the oligomerisation (possibly via ketene formation) of acetyl chloride or acylium ions, in the products of which the participation of keto/enol tautomeric forms is expected, exhibiting the signals of C=C– carbon in this region.

3.5. *Acylation of toluene in the adsorbed phase*

The last question to be dealt with, is the possible role of the two forms, chemisorbed and physically adsorbed donor–acceptor complexes of acetyl chloride, in the acylation reaction. For this purpose an experiment was carried out, in which, on an activated sample of a ZnY zeolite, acetyl chloride (a mixture with ^{13}C1 and ^{13}C2 labeling) was preadsorbed at the temperature of liquid nitrogen. Toluene, ^{13}C labeled in the CH_3 group, was then added in different molar ratios with respect to acetyl chloride. The sample ampoule containing the adsorbent/adsorbate system was shaken at room temperature and then heated to the reaction temperature (usually 80–110°C) for 60 min. Spectra obtained from these samples exhibit, as shown in figs. 4B and 4C, interesting signals which were assigned in the following way: the signal observed at 213.5 ppm undoubtedly gives evidence that acylation of the aromatic ring has taken place, because it belongs to the perturbed (by cation or proton) form of a keto group on an aromatic ring. The direction of its signal shift indicates deshielding process. It may be noted that 4-methylacetophenone in solution exhibits ^{13}C chemical shifts of 197.6 ppm for the carbonyl carbon, 26.4 ppm for the methyl carbon in the acetyl group and 21.6 ppm for the methyl at the aromatic ring. As a result of the fact that toluene was only labeled with ^{13}C carbon in the methyl group, the aromatic carbons exhibit very weak signals at 130–135 ppm. A strong signal is detected at 184 ppm, which is obviously associated with the chemisorbed form of acylium ion forming the acetate-like structure with the lattice oxygen. On the other hand, a signal at 172 ppm, usually observed on ZnY zeolite and assigned to the donor–acceptor complex, was very weak. In the region of the methyl carbon, a strong signal for the methyl group in toluene is detected at 20 ppm. The shoulder at 24.6 ppm, clearly to be seen in spectrum 4C, can be assigned to the methyl of the acetyl group bonded to the aromatic ring. Spectrum 4C represents the ZnY sample on which toluene was adsorbed in excess with respect to actetyl chloride. From this spectrum the disappearance of the signal at 172 ppm can be seen. For comparison, in fig. 4A the carbonyl signals are shown from the ZnY sample on which acetyl chloride was adsorbed in the absence of toluene. We propose that the disappearance of the signal at 172 ppm is the result of the preferential participation of the cation coordination complex of acetyl chloride in the acylation reaction. When acetyl chloride was loaded in excess with respect to toluene, a weak signal at 172 is still to be detected in the ^{13}C NMR spectrum (fig. 4B). These observations are in agreement with the known role of donor–acceptor complexes, formed between acylium ion precursors and Lewis acids, as acylation agents in the Friedel–Crafts acylation on aromatic compounds [11]. Acylium ion bonded to lattice oxygen is also able to react with toluene under the present static conditions, but apparently with more difficulty, so that it still remains detectable in the NMR spectrum after contact with toluene at 85°C. It is emphasized that the results presented above were obtained under static conditions, so that one must be

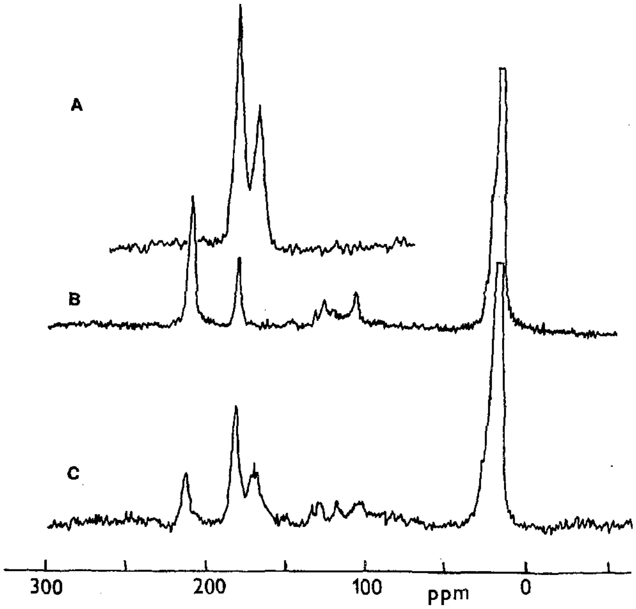


Fig. 4. ^{13}C CP MAS NMR spectra of ZnY samples loaded with toluene and/or acetyl chloride after treatment at 100°C for 30 min. (A) Loaded with acetyl chloride (0.22 mmol/g); (B) loaded with acetyl chloride (0.35 mmol/g) and toluene (0.60 mmol/g); (C) loaded with acetyl chloride (0.35 mmol/g) and toluene (0.25 mmol/g).

cautious in extrapolating to reactions under dynamic conditions. It is interesting that in an in situ acylation experiment with zeolite HY, loaded with toluene and acetyl chloride, the formation of 4-methylacetophenone was also detected.

4. Conclusions

Acetyl chloride, as an acylating agent adsorbed on the surface of Y zeolites, gives rise to different kinds of adsorbed species: adsorbed acetyl chloride in the form of complexes with cations, acetate-like structures created by chemisorbed acylium ion species at lattice oxygen and "free" acylium ions stabilized by adsorption on nonspecific surface sites. On the admission of toluene to preadsorbed acylating agent, an acylation reaction takes place in which the coordination complex of acetyl chloride with Zn seems to be more reactive than the chemisorbed acetate-like species.

Acknowledgement

Financial support by the Dutch Innovation Oriented Research Program on Catalysis is acknowledged. The work was partially carried out in the J. Heyrovsky Institute in the frame of the project of COST Chemistry Action D5 and supported by the Ministry of Education of the Czech Republic (OCD5.10) and the Commision of the European Communities (PECO, ERBCIPECT 926042). The authors wish to thank Ir. A. Sinnema, Dr. R.S. Downing and Dr. L. Kubelková for helpful discussions.

References

[1] W.F. Hölderich and H. van Bekkum, Stud. Surf. Sci. Catal. 58 (1991) 631.
[2] H. van Bekkum, A.J. Hoefnagel, M.A. van Koten, E.A. Gunnewegh, A.H.G. Vogt and H.W. Kouwenhoven, Stud. Surf. Sci. Catal. 83 (1994) 379.
[3] P.B. Venuto, Microporous Mater. 2 (1994) 297.
[4] A. Corma, M.J. Climent, H. Garcia and J. Primo, Appl. Catal. 49 (1989) 109.
[5] D.E. Akporiage, K. Daasvatn, J. Solberg and M. Stöcker, Stud. Surf. Sci. Catal. 78 (1993) 521.
[6] A. Finiels, A. Calmettes, P. Geneste and P. Moreau, Stud. Surf. Sci. Catal. 78 (1993) 595.
[7] W.F. Hölderich, H. Lermer and M. Schwarzmann, DE 3.618.964, to BASF A.G.
[8] J.P. Bourgogne, C. Aspisi, K. Ou, P. Geneste, R. Durand and S. Mseddi, French Patent Appl. 90.11856 (1992) to PLASTO S.A.
[9] E.A. Gunnewegh, S.S. Gopie and H. van Bekkum, J. Mol. Catal., accepted.
[10] E.A. Gunnewegh, R.S. Downing and H. van Bekkum, Stud. Surf. Sci. Catal. 97 (1995) 447.
[11] B. Chevrier and R. Weiss, Angew. Chem. 86 (1974) 12.
[12] J.J. Scheele, *Electrophilic Aromatic Acylation*, PhD Thesis, Delft University of Technology, The Netherlands (1991).
[13] V. Bosáček, J. Phys. Chem. 97 (1993) 10732.
[14] V. Bosáček, Z. Phys. Chem. 189 (1995) 241.
[15] I.I. Ivanova and E.G. Derouane, Stud. Surf. Sci. Catal. 85 (1994) 358.
[16] C.K. Ingold, *Structure and Mechanism in Organic Chemistry* (Cornell University Press, New York, 1953) ch. VI.
[17] H.O. Kalinowski, S. Berger and S. Braun, *^{13}C NMR Spectroskopie* (Thieme, Stuttgart, 1984).
[18] G.A. Olah , A. Germain and A.M. White, in: *Carbonium Ions*, Vol. V, eds. G.A. Olah and P. von R. Schleyer (Wiley Interscience, New York, 1976) ch. 15.
[19] G.A. Olah and A.M. White, J. Am. Chem. Soc. 91 (1969) 5801.
[20] Y. Sato, M. Yato, T. Ohwada, S. Saito and K. Shudo, J. Am. Chem. Soc. 117 (1995) 3037.
[21] S. Ganapathy , V.P. Chacko and R.G. Bryant, J. Magn. Res. 57 (1984) 239; J. Chem. Phys. 81 (1984) 661.
[22] G.E. Maciel and D.D. Traficante, J. Phys. Chem. 69 (1965) 1030.
[23] H. Pfeifer, W. Meiler and D. Deininger, *Annual Reports on NMR Spectroscopy*, Vol. 15 (Academic Press, New York, 1983) p. 291.
[24] D.K. Murray, T. Howard, P.W. Goguen, T.R. Krawitz and J.F. Haw, J. Am. Chem. Soc. 116 (1994) 6354.
[25] F.P. Boer, J. Am. Chem. Soc. 90 (1968) 6706.