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Differentiation of Diverse Tetrapropylammonium Cations Occluded in MFI-Type Zeolites by ^{15}N CP MAS NMR Spectroscopy

L. DELMOTTE, M. SOULARD, and H. KESSLER
Laboratoire de Matériaux Minéraux, URA CNRS no.428,
Ecole Nationale Supérieure de Chimie, 3 rue Alfred Werner,
68093 Mulhouse Cedex, France

High resolution solid state $^{1}H-^{15}N$ CP MAS NMR spectroscopy was used to study the TPA^+ species present in ZSM-5 samples and in silicalite prepared either in alkaline medium or in a non-alkaline fluoride medium. The resolution of the spectra recorded for the samples prepared in fluoride medium enabled to differentiate two types of TPA^+, compensating or not the framework charge, both present in some of the solids.

Several papers have been devoted to the tetrapropylammonium cations (TPA^+) occluded in ZSM-5 and in silicalite. The carbon atoms have been located by structure determinations on single crystals of ZSM-5 1,2) and TPAF-silicalite,3) and on powder for TPAOH-silicalite.4) The positions of the oxygen atoms of the non framework-charge-compensating TPAOH species could not be established.2,4) However, the F atoms of the TPAF pairs occluded in TPAF-silicalite could be located, they were found in the vicinity of N in the 10-membered ring channels.3) ^{13}C CP MAS NMR spectroscopy gives essentially the same spectra, related to the channel structure, for TPA^+ occluded in ZSM-5 and in TPAOH-silicalite.5) Additional splittings of the C resonances are observed for TPAF-silicalite, they may be due to the presence of the F^- anion.6) The ion pair nature of the TPAF species in this material was established by ^{19}F MAS NMR.7) DSC and DTA have been used too for the characterization of MFI-type materials according to the thermal decomposition of the tetrapropylammonium template.8)

The purpose of the present paper is to show the usefulness of solid state ^{15}N CP MAS NMR to differentiate the TPA^+ species compensating or not the framework charge in ZSM-5 and silicalite samples prepared either in the usual alkaline medium 9) or in a non-alkaline medium in the presence of F^- anions.10)

Whereas ^{15}N NMR (0.35% natural abundance, I = 1/2) is largely used for liquids, only a limited number of solid state ^{15}N CP MAS NMR studies have been reported.[11)] The ^{15}N CP MAS NMR spectra were obtained at 30 MHz on a Bruker MSL 300 pulse spectrometer, the matched radio-frequency amplitudes were 34 kHz. The sensitivity enhancement achieved with the CP MAS technique enabled us to use non enriched TPA^+. Inspite of the small amount of TPA^+ present in the zeolites (≈ 12 wt %), a good signal to noise could be obtained for 8000 to 20000 scans. The Hartmann-Hahn conditions were determined on 5% enriched $^{15}NH_4{}^{15}NO_3$. The maximum signal intensity was observed for 20 ms contact time contrarily to 5 ms as reported.[12)] For the zeolite samples, an optimized contact time of 12 ms, a 3 s recycle time and a 3500 Hz spinning frequency were used. Following Ref.12, the chemical shifts are given with respect to solid NH_4Cl.

Five samples were studied, two were prepared in alkaline medium : a (TPA-ZSM-5 ; Si/Al = 9) and b (TPAOH-silicalite ; Si/Al ≈ 2000), and three were obtained in non-alkaline medium in the presence of fluoride : c (TPAF-silicalite ; Si/Al > 2000), d (TPAF-ZSM-5 ; Si/Al ≈ 90) and e (TPAF-ZSM-5 ; Si/Al ≈ 31). In the latter three the mole fraction $r = TPA^+/(TPA^+ + TPAF)$ of framework charge-compensating TPA^+ corresponding to the Al content is respectively 0, 0.27, and 0.80.

The ^{15}N CP MAS NMR spectra are plotted in Fig.1. All the samples, are characterized by a rather narrow single line around 26 ppm. The resolution enables a differentiation of each of them as shown in Table 1.

Table 1. Characteristics of the ^1H-^{15}N CP MAS NMR spectra

Sample	a	b	c	d	e
Chemical shift (ppm)/NH_4Cl (s)	25.99_6	25.92_7	25.84_2	25.88_0	25.97_3
Line width(ppm)	0.45	0.36	0.12	≈ 0.2	≈ 0.2
Feature	Gaussian	Gaussian	Lorentzian narrow	Asymmetric	+ Shoulder

The samples prepared in alkaline medium show the largest line width. The broadening might be related to crystal defects. The samples synthesized in the presence of fluoride (c,d,e) exhibit a variation of δ and of the line width with Si/Al. The purely siliceous sample c (r=0) is characterized by the narrowest lorentzian-type line with the lowest $\delta = 25.84_2$ ppm. In sample d, where r = 0.27, i.e., the template is essentially associated to F^-, there is a broadening of the line on the low-field side assigned to the contribution of the charge-compensating TPA^+. The signal observed for

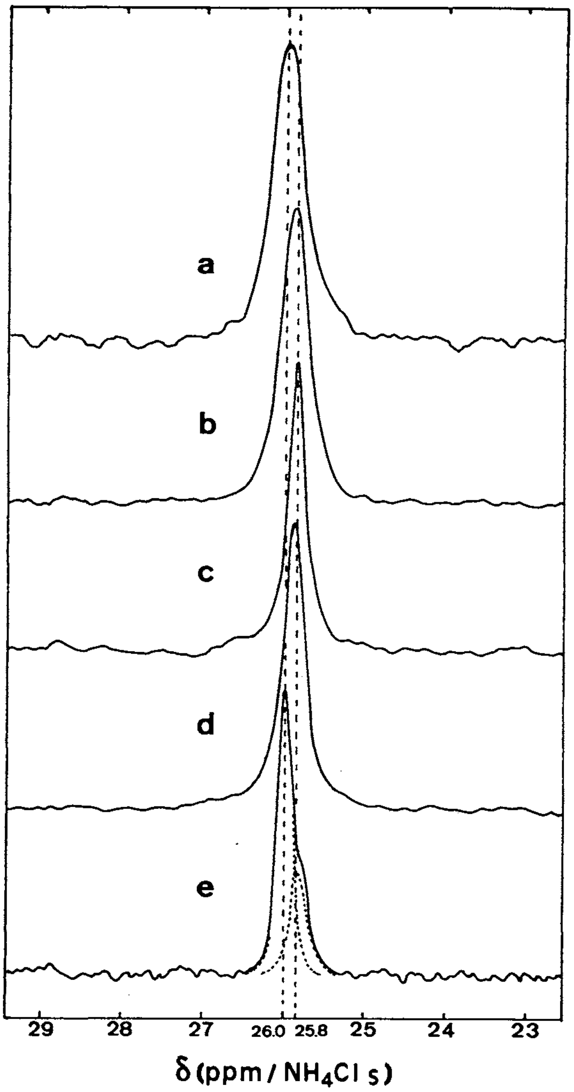

Fig.1. ^{15}N CP MAS NMR spectra.

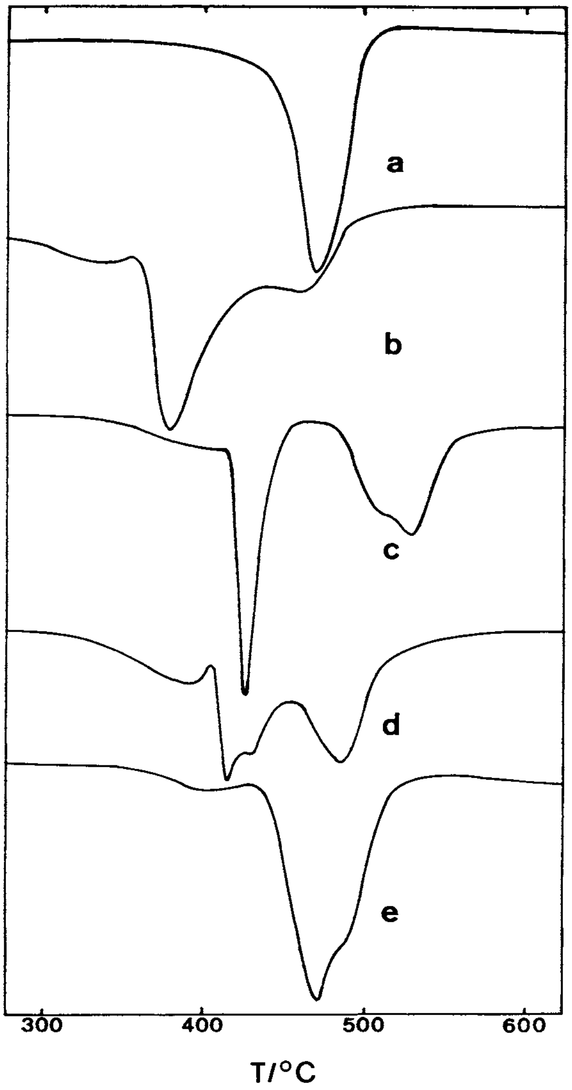

Fig.2. DTA curves (10°C min^{-1}; argon flow).

a : TPA-ZSM-5; Si/Al = 9 , b : TPAOH-silicalite; Si/Al ≈ 2000
c : TPAF-silicalite, Si/Al > 2000 , d : TPAF-ZSM-5; Si/Al ≈ 90
e : TPAF-ZSM-5; Si/Al ≈ 31

sample d (r = 0.8) shows a rather narrow line centred at 25.97_3 with a shoulder on the high-field side (the decomposition of the signal is shown in Fig.1). The strong line is assigned to TPA^+ balancing the framework charge and the shoulder to TPA^+ ion-paired with F^-.

Fig.2 gives the DTA curves recorded for the five samples. Each sample shows a characteristic TPA decomposition pattern related to the Si/Al ratio. Such curves are discussed extensively in Ref.8.

The ^{15}N chemical shift range is known to be very large,[11)] it is therefore surprising that the values observed in our study are so close.

The resolution of the spectra enables however to distinguish both TPA^+ species present simultaneously in samples d and e. The δ values are notably different from the value that we observed for solid TPABr (δ = 29.59 ppm) whose structure is symmetrical.[13)] It should be mentioned too that no signal could be detected for TPA^+ occluded in TPAF-$AlPO_4$-5 [14)] and TPAOH-$AlPO_4$-5 [15)] molecular sieves.

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