p-Fluoroacetophenone molecule as a probe to study zeolite acidity by ¹⁹F solid-state NMR spectroscopy

A. Simon,*[a] L. Delmotte,[a] J.-M. Chezeau[a] and L. Huve[b]

[a] *Laboratoire de Matériaux Minéraux, URA CNRS 428, Ecole Nationale Superieure de Chimie, 3 rue Alfred Werner, 68093 Mulhouse Cedex, France*
[b] *Shell Recherche, Centre de Recherche de Grand-Couronne, 76530 Grand-Couronne, France*

¹⁹F chemical shift variations of *p*-fluoroacetophenone adsorbed on a MFI zeolite show that this compound is a promising probe for measurements of zeolite acidity strength.

Zeolites are used as acid catalysts in important industrial processes such as the cracking of hydrocarbons in refineries. 'Direct' methods (IR spectroscopy and ¹H NMR of OH groups)[1–3] and methods using probe molecules (titration, calorimetric measurements, NMR of adsorbed bases, *etc.*)[4–6] have been employed to study zeolite acidity properties. However, the evaluation of the acidity strength of these materials still represents a real difficulty. In this work, the use of ¹⁹F MAS NMR using a new probe molecule is presented.

The ¹⁹F nucleus is very interesting for NMR studies with a nuclear spin I of 1/2, a natural abundance of 100%, a high detection sensitivity (83% relative to H), and a large chemical shift range. The principle of the method we propose is to relate the chemical shift of the ¹⁹F nucleus in the adsorbed probe molecule to the strength of the acid sites in the zeolite. This paper presents preliminary results on the adsorption of *p*-fluoroacetophenone on MFI. This organic compound is a good indicator of zeolite acidity strength because it contains a functionality whose pK_{BH^+} value (-6.2)[7] falls in the acidity strength range of zeolites.[9] ¹⁹F chemical shift variation as a function of acidity strength has been determined for *p*-fluoroacetophenone by Taft and Levins[7] and found to vary from δ -107.0 (Hammett acidity function: $H_0 = 0$) to δ -79.4 ($H_0 = -11$) with a shift of 4.9 ppm per H_0 unit near its pK_{BH^+}.

Prior research shows that ¹⁹F NMR of alkaline probe molecules has made pH measurements in biological systems[9] possible. Nicholas *et al.*[10] studied adsorption of *p*-fluoroaniline and *p*-fluoronitrobenzene in zeolites. However, they could only determine the boundaries of the acidity strength for the MFI and FAU zeolites under study.

MFI zeolites were prepared in fluoride media in our laboratory.[11] Acid zeolites with Si/Al ratios of 35.5 and 55 [HZSM-5(35.5), HZSM-5(55)] and a non-acid purely siliceous MFI zeolite [HZSM-5(∞)] were calcined up to 823 K for 6 h under ambient atmosphere. Under these calcination conditions no residual F⁻ (δ *ca.* −64) is observed in the ¹⁹F MAS NMR spectra. After hydration, the zeolite samples were mounted in glass tubes with a bed depth of 5 mm and heated to 673 K at a heating rate of 15 K h⁻¹ *in vacuo*. At this temperature, samples were evacuated for 20 h at a pressure of 10⁻¹ Pa. After cooling, samples were exposed to a saturated vapour of dehydrated *p*-fluoroacetophenone. After adsorption, samples were transferred into the NMR rotor in an argon atmosphere. ¹⁹F MAS NMR spectra (reference CFCl₃) were recorded at 282.4 MHz on a Bruker MSL-300 with a 4 mm Doty probe (pulse length of 4 μs for the π/2 pulse, recycle delay of 6 or 10 s, spinning rate of 7–8 kHz).

Fig. 1 shows the spectra thus obtained for two days adsorption realized at room temperature. The amount of adsorbed *p*-fluoroacetophenone was determined by comparison of ¹⁹F MAS NMR spectra with that of a known amount of an as-synthesized uncalcined MFI zeolite with no aluminium prepared in fluoride medium[11] which contains 4F⁻ ions per unit cell (Table 1). The maximum loading of the probe molecule in the zeolite structure based on geometric constraints alone is eight species per unit cell.

The narrow peak ($\Delta\nu_{1/2}$ = 375 Hz) which appears at δ -106.6 for HZSM-5(∞) [Fig. 1(*a*)] has a chemical shift
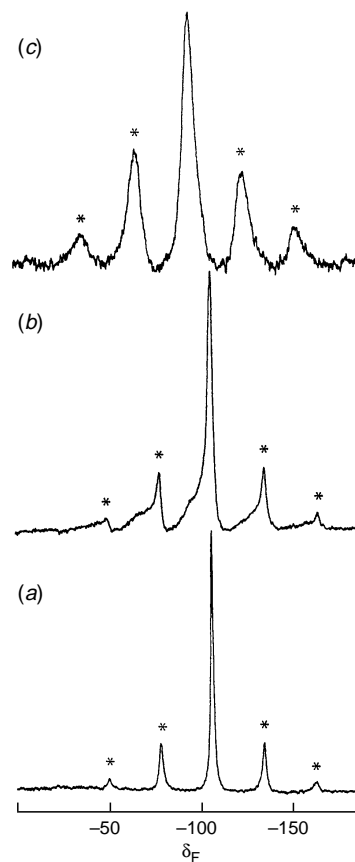
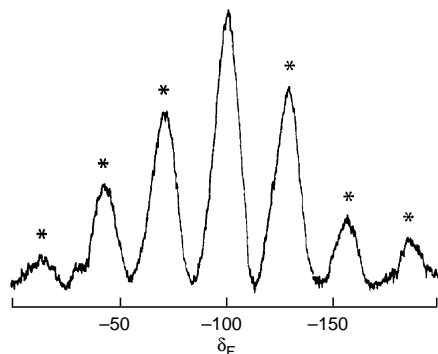**Fig. 1** ¹⁹F MAS NMR spectra of (*a*) HZSM-5(∞), (*b*) HZSM-5(55) and (*c*) dehydrated HZSM-5(35.5) treated with *p*-fluoroacetophenone for 2 days at room temperature; * MAS side-bands

Table 1 Concentration of bridging OH (framework aluminium as determined by ²⁷Al MAS NMR) and *p*-fluoroacetophenone (as determined by ¹⁹F MAS NMR)

|	Concentration in species per unit cell	
Sample	Bridging OH (framework aluminium)	*p*-Fluoroacetophenone
HZSM-5(35.5)	2.3	1.6
HZSM-5(55)	1.7	4.0
HZSM-5(∞)	—	1.5

which is practically identical to that of *p*-fluoroacetophenone molecules in the liquid state (δ -107.0). Furthermore, the symmetrical shape of the signal indicates that fluorinated molecules have no preferential orientation and the small linewidth suggests a high mobility. We assign the peak at δ -106.6 to *p*-fluoroacetophenone molecules involved in weak interactions with this non-acidic zeolite framework.

When the Si/Al ratio decreases to 55, we distinguish different fluorinated molecules populations [Fig. 1(*b*)]. The first corresponds to a relatively narrow ($\Delta\nu_{1/2}$ = 845 Hz) peak situated at δ -106.6. By analogy with the HZSM-5(∞) [Fig. 1(*a*)] this is attributed to molecules which are in weak, interaction with the zeolite framework. The two other populations correspond to broader peaks ($\Delta\nu_{1/2}$ = 1740 and 1630 Hz) situated at lower fields (δ -95.3 and -100.5 respectively). The relative areas of various fluorinated species [δ -95.3 (23.3%), δ -100.5 (16.9%), *ca.* -106.6 (59.3%)] show that for four adsorbed fluorinated molecules per unit cell, the amount of *p*-fluoroacetophenone associated with the peaks situated at δ -95.3 and -100.5 represents 1.6 molecules per unit cell. This value corresponds approximately to the number of zeolite acid sites (Table 1). From the chemical shift values determined by Taft and Levins,[7] it can be deduced that these molecule populations are in interaction with acid sites which have a strength H_0 of -6.4 (δ -95.3) and H_0 -5.4 (δ -100.5). The increase in linewidths could be related to a decrease of the mobility of fluorinated molecules which reveals a stronger interaction with the zeolite framework. However, many interactions, such as

Fig. 2 ^{19}F MAS NMR spectrum of hydrated HZSM-5(35.5) treated with *p*-fluoroacetophenone for 15 days at room temperature; * MAS side-bands
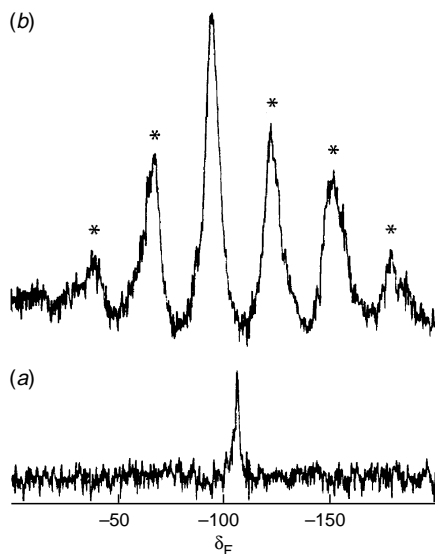
Fig. 3 ^{19}F MAS NMR spectra of (*a*) dehydrated HZSM-5(∞) and (*b*) HZSM-5(35.5) treated with *p*-fluoroacetophenone for 70 h at 423 K; * MAS side-bands

homonuclear dipolar interactions (F–F), heteronuclear dipolar interactions (F–H, F–Al), chemical shift anisotropy, magnetic susceptibility and/or chemical exchange could contribute to the increase in linewidth. A more detailed study will be published elsewhere. Furthermore, measurement of areas corresponding to *p*-fluoroacetophenone molecules in strong interaction with acid sites and *p*-fluoroacetophenone in weak interaction with zeolite framework [Fig. 1(*b*)] shows that this method is quantitative.

In the HZSM-5(35.5) sample, the ^{19}F MAS NMR spectrum reveals only one broad peak ($\Delta\nu_{1/2}$ = 1830 Hz) situated at δ -95.6 [Fig. 1(*c*)]. Analysises (Table 1) show that there are fewer adsorbed fluorinated molecules than zeolite acid sites. At such an Si/Al ratio, most acid sites in the MFI zeolite structure should be accessible. The main reason for this low adsorption rate may be the blocking up of the channels by molecules in interaction with acid sites because channels are not blocked prior to adsorption of *p*-fluoroacetophenone (*n*-hexane adsorption rate at 298 K is 11.6%).

On partially hydrated HZSM-5(35.5) (3–8%) loaded with *p*-fluoroacetophenone, we observed only one broad peak ($\Delta\nu_{1/2}$ = 3340 Hz) situated at δ -100.2 (H_0 -5.4) (Fig. 2). This is indicative of a decrease of acidity induced by water molecules which react with zeolite acid sites[12] and level their acidity. Chemical shift exchange between water and *p*-fluoroacetophenone molecules, and important dipolar interactions between F and H of H_2O and H_3O^+ chemical species may induce the increase in linewidth.

When adsorption on dehydrated zeolites is realized at 423 K (Fig. 3) only a few *p*-fluoroacetophenone molecules are trapped inside HZSM-5(∞) unlike HZSM-5(35.5). In the latter, strong zeolite acid sites related to aluminium interact with *p*-fluoroacetophenone and the thermal energy is not high enough at 423 K to break these interactions.

In conclusion, this work shows that *p*-fluoroacetophenone acts as a quantitative acidity strength indicator *via* ^{19}F MAS NMR. The ^{19}F chemical shift value allows the acidity strength to be determined, whereas the area of the signal can be related to the number of acid sites. However, we can foresee several limitations to this method. In aluminium-rich zeolites, the adsorption of a probe molecule might prevent another molecule to reach an acid site close to the first one. In some structures, small cavities could be inaccessible to the *p*-fluoroacetophenone molecules, whereas in structures with only one-dimensional channels, the adsorption of such a molecule could prevent others to progress inside the channels. All these limits are also encountered by reacting molecules when zeolites are used as catalysts.

References

1 W. E. Farneth and R. J. Gorte, *Chem. Rev.*, 1995, **95**, 615.
2 H. Pfeifer, D. Freude and J. Kärger, *Catalysis and Adsorption by Zeolites*, ed. G. Ohlmann *et al.*, Elsevier, Amsterdam, 1991.
3 P. Batamack, C. Dorémieux-Morin and J. Fraissard, *J. Chim. Phys.*, 1992, **89**, 423.
4 L. Moscou and R. Moné, *J. Catal.*, 1973, **30**, 417.
5 H. Van Bekkum, E. M. Flanigen and J. C. Jansen, *Introduction to Zeolite Science and Practice*, Elsevier, Amsterdam, 1991, **58**, 270.
6 E. Brunner, *J. Mol. Struct.*, 1995, **355**, 61.
7 R. W. Taft and P. L. Levins, *Anal. Chem.*, 1962, **34**, 436.
8 L. W. Beck and J. F. Haw, *J. Phys. Chem.*, 1995, **99**, 1076.
9 C. J. Deutsch and J. S. Taylor, *Annu. NY Acad. Sci.*, 1987, **508**, 33.
10 J. B. Nicholas, J. F. Haw, L. W. Beck, T. R. Krawietz and D. B. Ferguson, *J. Am. Chem. Soc.*, 1995, **117**, 12 350.
11 J. L. Guth, H. Kessler, J. M. Higel, J. M. Lamblin, J. Patarin, A. Seive, J. M. Chézeau and R. Wey, *Zeolite Synthesis*, ed. M. L. Ocelli and H. E. Robson, ACS Symp. Ser., 1989, **398**, 176.
12 F. Deng, Y. Du, C. Ye, J. Wang, T. Ding and H. Li, *J. Phys. Chem.*, 1995, **99**, 15 208.