Characterization of acid sites on γ-alumina and chlorinated γ-alumina by ^{31}P NMR of adsorbed trimethylphosphine

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^{31}P MAS NMR of adsorbed trimethylphosphine (TMP) has been used to characterize the surface acid properties of γ-alumina and chlorinated γ-alumina. Combined with thermodesorption of TMP, NMR has allowed the determination of the strength distribution of Brønsted and Lewis acid sites on these samples. γ-alumina chlorination with 1,2-dichloropropane at 500°C first increases the numbers of "strong" Lewis and "strong" Brønsted acid sites, second decreases the number of "weak" Lewis acid sites. The "strong" sites are the ones TMP is desorbed from above 200°C and the "weak" sites up to 200°C.

Keywords: NMR, TMP, thermodesorption, acid sites, strength distribution, gamma alumina, chlorine

1. Introduction

γ-alumina is widely used as acid support of catalysts in refining processes such as hydroprocessing and reforming [1]. However, the surface acidity of the γ-alumina is still not well characterized. Determination of surface acid properties is required to understand the catalytic behavior of catalysts.

The solid surface acidity is characterized by the nature (Brønsted or Lewis type), the amount, the strength and the distribution in strength of the acid sites [2].

A large number of characterization methods is used to determine the acidity of solid state materials [2]. Among these methods, we can distinguish global methods from selective methods. The global methods do not make the difference between Brønsted and Lewis acid sites. However, it is a good way to determine the amount, the strength and the strength distribution of sites. Temperature-programmed desorption, calorimetric measurements of adsorbed bases and titration methods using a series of Hammett indicators are some of them. Selective methods are able to measure Lewis and Brønsted acidity, e.g. the infrared spectra of probe molecules such as pyridine or other bases have been used to provide evidence for both Brønsted and Lewis acid sites. The limitation of this technique lies in the difficulty to determine the molar extinction coefficients of each adsorbed species in order to lead to a quantitative study. Recently, solid state NMR spectroscopy of basic probe molecules has emerged as a promising approach for evaluating not only the type of acid sites on zeolites and other aluminosilicates, but also the number of acid sites. Nitrogen-15 bases, including ammonia, pyridine, trimethylamine and *n*-butylamine, have been effectively used [3–6]. However, the small magnetogyric ratio of ^{15}N results in sensitivity problems. These difficulties have been overcome by adopting ^{31}P-containing probe molecules. The ^{31}P nucleus is an attractive candidate for surface acidity characterization studies as it possesses a large chemical shift range and it is, from an NMR point of view, a sensitive nucleus. Among the possible phosphored bases, trimethylphosphine has been employed to probe Brønsted and Lewis acidity in zeolites [7–10] and other materials [11–15]. Because of its high basic strength (TMP strength is about 1000 times greater than that of pyridine) and its rather small size, this probe is able to be adsorbed on a large amount of the solid acid sites. On the other hand, because of its air sensitivity, all experiments should then be done under controlled atmosphere. In this paper, we describe the characterization of surface acid properties of γ-alumina and chlorinated γ-alumina by ^{31}P MAS NMR of adsorbed TMP.

2. Experimental

2.1. Sample preparation

A γ-Al_2O_3 sample (specific surface area of about 200 $m^2\ g^{-1}$) is used. This alumina is first calcined at 530°C under flowing dry air for 2 h.

The γ-Al_2O_3/Cl (1.1 wt%) sample is obtained by oxychlorination with a H_2O–HCl–air stream. Gaseous HCl is a result of the decomposition in air of 1,2-dichloropropane at 500°C in CO_2, H_2O and HCl. The sample is then calcined at 530°C under dry air for 2 h. At this step, the chlorine content is about 1.4 wt%. Then the chlorine content is lowered to 1.1 wt% by calcining the sample at 530°C for 20 min under air that contains ca. 20000 weight ppm H_2O.

Samples are then pretreated for 2 h under flowing helium at 530°C. The samples are transferred into an adsorption cell in an air-free glove box. Vacuum is maintained in the cell at 7.5×10^{-5} Torr overnight. Trimethylphosphine (Aldrich) is introduced from vapor phase at room temperature up to saturation and allowed to equilibrate for 0.5 h. Samples are degassed under vacuum at 25, 100, 200 and 350°C. Samples are then transferred into a 4 mm ceramic zirconia NMR rotor in an air-free glove box. The spectra are recorded immediately to minimize oxidation.

In order to simplify the presentation, samples are identified according to the following example: Al_2O_3/Cl/200, which indicates that the alumina is chlorinated, subsequently exposed to TMP and then degassed at 200°C.

2.2. NMR measurement

^{31}P MAS NMR spectra were recorded using a Brüker MSL 400 spectrometer. In such apparatus, the ^{31}P resonance frequency is 162 MHz. ^{31}P chemical shifts were reported relative to 85% H_3PO_4. Direct 90° pulses were used with a pulse width of 4 μs. ^{31}P MAS NMR spectra were recorded with proton inverse gated decoupling [16]. A typical spinning rate was 12 kHz. The phosphorus T_1 (which is the longitudinal relaxation time) for adsorbed species is relatively short, less than 1 s, and the repetition rate is 5 s, thus spectra were recorded under these appropriate conditions for direct quantification. The number of scans per acquisition was 1000.

2.3. XRF measurement

The amounts of phosphorus and chlorine are determined by X-ray fluorescence (XRF) using a Philips PW 1480 spectrometer.

3. Results

The ^{31}P NMR spectra of TMP adsorbed on γ-alumina and chlorinated γ-alumina pretreated at 530°C are shown in fig. 1. The ^{31}P spectra contain two main peaks: a large one with a maximum close to -50 ppm attributable to Lewis acid sites, and a smaller one located at about -5 ppm due to Brønsted acid sites [15]. Weak resonances between 20–30 and 50–70 ppm are detected. They are due to oxidised TMP [8,13].

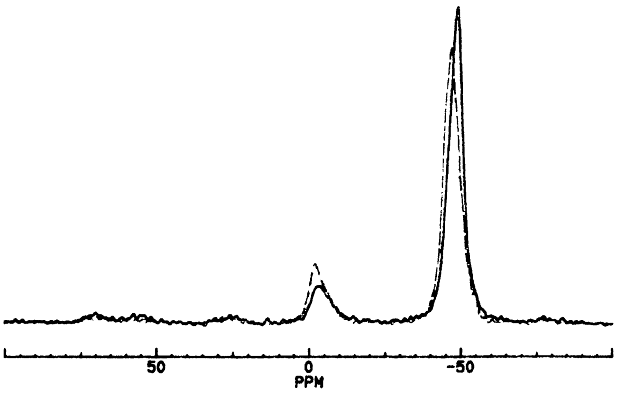

Fig. 1. ^{31}P MAS NMR spectra of $(CH_3)_3P$ on Al_2O_3/25 (——) and on Al_2O_3/Cl/25 (– – –).

Additional experiments, performed on γ-alumina with different levels of hydroxylation, provided evidence that these oxidised species were only located on Lewis acid sites. The ^{31}P NMR spectrum of TMP adsorbed on completely dehydroxylated γ-alumina contains only one peak at -50 ppm, attributable to Lewis acid sites. After one night under air, this peak completely disappears and resonances between 20–30 and 50–70 ppm appear. The area sum of these resonances is equal to the area of the peak at -50 ppm, which was present before the oxidation. So, the NMR total area does not change. The oxidation of TMP adsorbed on γ-alumina, containing both Lewis and Brønsted acid sites, involves a disappearance of peaks at -5 and -50 ppm and an appearance of resonances between 20–30 and 50–70 ppm. On the contrary, the oxidation is characterized by a loss of the NMR total area. This loss accurately corresponds to the peak area at -5 ppm, attributable to Brønsted acid sites. These experiments suggest that TMP initially adsorbed on Brønsted acid sites is desorbed when it is oxidised, and resonances between 20–30 and 50–70 ppm are attributable to oxidised TMP adsorbed on Lewis acid sites.

Figs. 2 and 3 show the evolution of ^{31}P NMR spectra for different desorption temperatures, for alumina and chlorinated alumina. NMR peak areas corresponding to the different sites are reported in table 1. A narrow structure appears for samples degassed at high temperature. This behaviour has been demonstrated to be characteristic of a *J*-coupling between aluminium and phosphorus [17,18].

The amount of phosphorus on each sample has been determined by X-ray fluorescence (XRF). Samples have been put under air during the XRF quantitative analysis. Consequently, the only measured phosphorus correspond to oxidised trimethylphosphine species adsorbed on Lewis acid sites. A good linear correlation appears between the phosphorus content and the resonance area sum, which are assigned to oxidised and non-oxidised TMP species adsorbed on Lewis acid centers (fig. 4).

The equation of the linear regression straight line is the following:

$$\text{P (wt\%)} = 3.724 \times 10^{-3}(\text{oxidised area} + \text{Lewis area}),$$

$$\text{correlation coefficient: } r^2 = 0.986\,.$$

This equation enables the calculation of the number of TMP molecules that is equivalent to the amount of acid sites per area unit. The number of Brønsted and Lewis

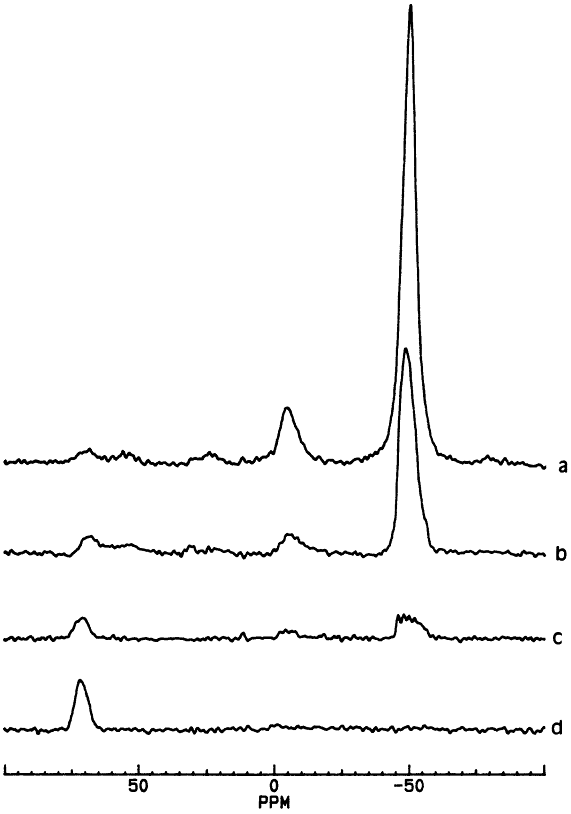

Fig. 2. Effect of the desorption temperature on the ^{31}P MAS NMR spectra of $(CH_3)_3P$ in γ-alumina: $Al_2O_3/25$ (a), $Al_2O_3/100$ (b), $Al_2O_3/200$ (c), $Al_2O_3/350$ (d).

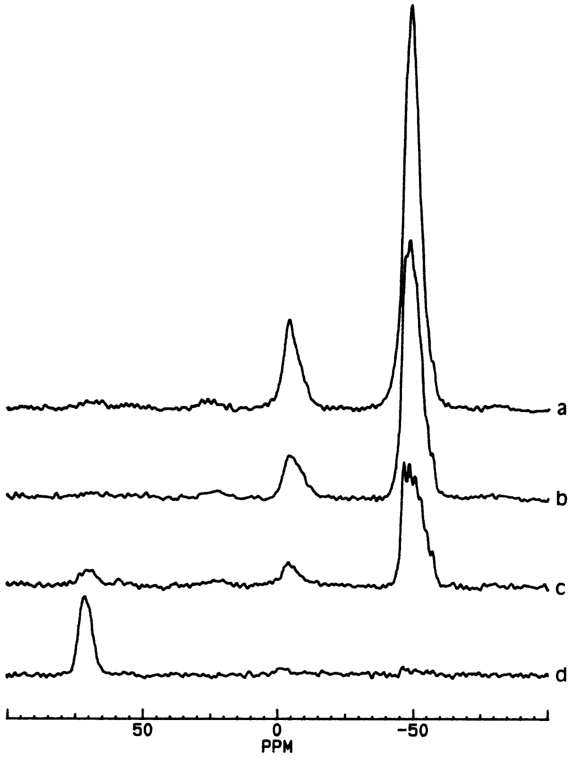

Fig. 3. Effect of the desorption temperature on the ^{31}P MAS NMR spectra of $(CH_3)_3P$ in chlorinated γ-alumina: $Al_2O_3/Cl/25$ (a), $Al_2O_3/Cl/100$ (b), $Al_2O_3/Cl/200$ (c), $Al_2O_3/Cl/350$ (d).

acid sites per nm^2, for each desorption temperature, on alumina and chlorinated alumina are shown in table 2.

4. Discussion

The results of the NMR and XRF quantitative studies show that the γ-alumina and chlorinated γ-alumina have the same total number of acid sites (0.59 site/nm^2 for γ-alumina and 0.58 site/nm^2 for chlorinated γ-alumina). Results show that the number of Lewis acid sites is six and five times as high as the number of Brønsted acid sites respectively on γ-alumina and chlorinated γ-alumina.

Previous studies by Knözinger and Ratnasamy [19] were done on the surface acid–base properties modelisation of alumina. They show that there are as many Lewis acid sites as Brønsted acid sites on γ-alumina previously pretreated between 500 and 550°C. Their model forecasts between three and four Lewis or Brønsted acid sites per nm^2, that is a total number of acid sites between six and eight per nm^2. Facing these results, it seems that TMP is only adsorbed on about 10% of the acid sites. The 90% remaining acid sites are not acidic enough to be revealed by TMP. Moreover, according to Knözinger and Ratnasamy [19], only 1 to 10% of sites are catalytically active. Their activities closely depend on their acid strength. The 10% of sites revealed by TMP could be therefore the active ones.

Experimentally, the total number of Lewis acid sites revealed by TMP is higher than the total number of Brønsted acid sites. The model of Knözinger and Ratnasamy [19] forecasts the same numbers on γ-alumina previously pretreated between 500 and 550°C. So, the difference between the numbers of Lewis and Brønsted acid sites, observed by ^{31}P MAS NMR of TMP, suggests that most of Brønsted acid sites are weaker than the Lewis acid sites.

If the total amount of acid sites does not change when 1.1 wt% chlorine is added, the distribution of Lewis and Brønsted acid sites seems to be modified. The addition of chlorine involves an increase of about 25% of Brønsted acid sites and a decrease of about 6% of Lewis acid sites.

Table 1
NMR areas and phosphorus content

Samples	NMR areas in arbitrary unit (±5%)			P (wt%) by XRF (±3%)
	Brønsted	Lewis	total	
$Al_2O_3/25$	22	135	157	0.48
$Al_2O_3/100$	8	74	82	0.26
$Al_2O_3/200$	3	16	19	0.07
$Al_2O_3/350$	0	12	12	0.07
$Al_2O_3/Cl/25$	28	127	155	0.50
$Al_2O_3/Cl/100$	16	91	107	0.33
$Al_2O_3/Cl/200$	7	52	59	0.20
$Al_2O_3/Cl/350$	3	20	23	0.11

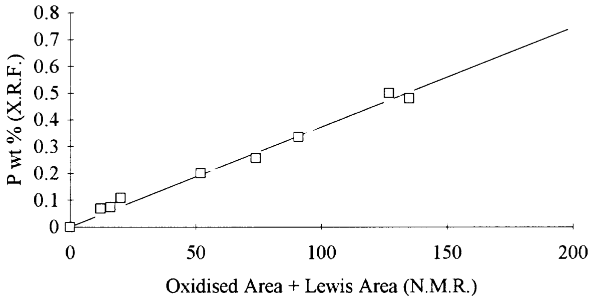

Fig. 4. Correlation between the phosphorus content and the resonance area sum assigned to oxidised and non-oxidised TMP species adsorbed on Lewis acid centers.

Table 2
Concentration of Brønsted and Lewis acid sites

Samples	Number of acid sites/nm^2		
	Brønsted	Lewis	total
Al_2O_3/25	0.08	0.51	0.59
Al_2O_3/100	0.03	0.28	0.31
Al_2O_3/200	0.01	0.06	0.07
Al_2O_3/350	0	0.04	0.04
Al_2O_3/Cl/25	0.10	0.48	0.58
Al_2O_3/Cl/100	0.06	0.34	0.40
Al_2O_3/Cl/200	0.03	0.19	0.22
Al_2O_3/Cl/350	0.01	0.08	0.09

Even though the increase of Brønsted acid sites per nm^2 seems to be low (from 0.08 to 0.10 site/nm^2) after chlorine addition, it is significant because of NMR measurement accuracy (table 1). By contrast, the decrease of the total amount of Lewis acid sites remains in the NMR measurement error.

The spectra of the Al_2O_3/25 and Al_2O_3/Cl/25 samples (fig. 1) show that the ^{31}P resonance characteristic of Lewis and Brønsted acid sites shift downfield, by 1 and 1.4 ppm respectively, with the addition of chlorine onto the alumina. This suggests that chlorine increases the acid strength of Lewis and Brønsted sites, because of increasing deshielding of the ^{31}P nucleus. Indeed, quantum-chemical calculations show that the increase of the acid strength of Lewis and Brønsted sites results in an increase of the atomic charge [20,21], respectively on hydrogen and aluminium. The more the electron density transfer from phosphorus to either Lewis or Brønsted acid sites, the more the aluminium or hydrogen atomic charge. An increase of this transfer involves a decrease of the phosphorus electronic shield facing magnetic field and consequently an increase of the chemical shift.

In addition, the acid strength can be followed by thermodesorption of the TMP adsorbed on the catalyst surface. The TMP has been eliminated by vacuum treatments at several temperatures. The amount of adsorbed base that is left on catalyst (measured by NMR and XRF), enables to evaluate Lewis and Brønsted site distributions owing to their acid strength.

The site distributions of alumina and chlorinated alumina are presented in fig. 5. For both acidity types (Lewis and Brønsted), four categories of sites are proposed. Each of them corresponds to a desorption temperature interval of TMP. The modification of the strength distribution of Brønsted acid sites on chlorinated γ-alumina is mainly due to an increase of the number of acid sites that keep TMP adsorbed beyond 200°C. For Lewis acid sites, the chlorination increases the number of sites adsorbing TMP beyond 200°C and decreases the number of sites desorbing the TMP up to 200°C.

We will call "strong sites" the ones TMP is desorbed from above 200°C and "weak sites" up to 200°C.

In summary, the alumina chlorination first increases the numbers of strong Lewis and strong Brønsted acid sites, and second, decreases the number of weak Lewis acid sites.

The increase of the number of strong Lewis acid sites (0.13/nm^2) is in the same order of magnitude as the decrease of the number of weak Lewis acid sites (0.16/nm^2). Thus, the increase of the number of strong Lewis acid sites could be due to strengthening of the acidity of weak Lewis sites (inductive effect exerted by the adjacent Cl^- ions).

If some of the weak Lewis acid sites are transformed into strong sites upon alumina chlorination, it is likely that some weaker sites can become acidic enough to be revealed by TMP. So, the decrease of the number of weak Lewis acid sites, due to a strengthening of their acidity, could be compensated to a certain extent by an increase of the acid strength of initially weaker sites. As the number of weak Lewis acid sites decreases, this hypothesis seems incorrect. But it must not be rejected if the decrease of the number of weak Lewis acid sites is not

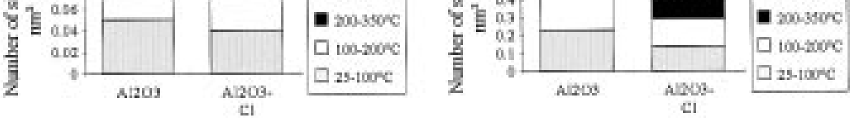

Fig. 5. Distributions of Brønsted and Lewis sites owing to their acid strength on alumina and chlorinated alumina.

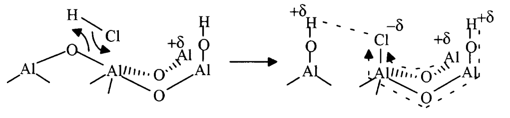

Fig. 6. Dissociative adsorption of HCl on the surface bridges of γ-alumina.

only due to a strengthening of their acidity. Indeed, the partial decay of weak Lewis acid sites can suggest an adsorption of chlorine on the latter. This observation suggests that chlorine adsorption is made by dissociative adsorption of HCl on the surface Al–O–Al bridges of γ-alumina. The dissociative adsorption of HCl, that was previously reported by Tanaka [22], Melchor [23] and Thomson [24] is pictured in fig. 6.

The coordinatively unsatured Al^{3+} of Al–O–Al bridges, which adsorb the Cl^- ions, would be weak Lewis acid sites. Therefore, the number of weak Lewis acid sites would decrease when 1.1 wt% of chlorine is added on γ-alumina. But, we can assume that chlorine is first adsorbed on the strongest Lewis acid sites of γ-alumina because of its strong electronegativity. When all the strongest Lewis acid sites are coordinated to chlorine, chlorine is then adsorbed on less strong Lewis acid sites. But because of its electronegative character, chlorine increases the strength of adjacent Lewis acid sites by inductive effect. Consequently, the number of strong Lewis acid sites increases while the number of weak Lewis acid sites decreases. The addition of HCl on the surface Al–O–Al bridges also leads to the creation of Brønsted acid sites. According to Tanaka [22], the OH groups produced by adsorbed HCl are more acidic than the initially present ones. These are supposed to form a coulombic hydrogen bond with adjacent chlorine. So, the increase of the number of Brønsted strong acid sites, observed by NMR, would be due to the creation of such sites and to strengthening of the acidity of sites by the inductive effect exerted by the adjacent Cl^- ions.

Some infrared studies [23,25] have shown that the gaseous HCl treatment of γ-alumina involves a disappearance of the high-frequency band, assigned to type I OH groups and the appearance of characteristic bands of H_2O molecules. According to Knözinger and Ratnasamy [19], the type I groups are the more basic hydroxyls on γ-alumina. The chlorination mechanism that accounts for these observations is represented in fig. 7.

In this case, the chlorine increases the strength of adjacent Lewis and Brønsted acid sites by inductive effect. So, the increase of numbers of strong Lewis and Brønsted acid sites could to some extent result from this adsorption type.

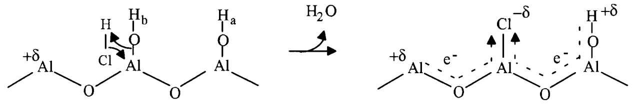

Fig. 7. Substitution of basic hydroxyls.

5. Conclusion

In this paper, we have demonstrated that ^{31}P MAS NMR combined with thermodesorption is a powerful method for the study of surface acid properties of γ-alumina. XRF measurements have shown that NMR is quantitative, and if combined with thermodesorption, NMR is able to determine the strength distribution of the acid sites, either Brønsted or Lewis acid sites.

Moreover, this work has demonstrated that the total amount of acid sites revealed by TMP does not change when 1.1 wt% chlorine is added on γ-alumina. The total number of acid sites is 0.6 site/nm^2.

Chlorine induces a strong modification of the acid sites distribution. The increase of the number of "strong" Lewis acid sites is due to strengthening of acidity of weaker Lewis sites (inductive effect exerted by the adjacent Cl^- ions).

The decrease of the number of "weak" Lewis acid sites can result not only from a strengthening of their acidity, but also from the adsorption of chlorine on these sites, which are not revealed by TMP any more.

The increase of the number of "strong" Brønsted acid sites is due to an increase of the strength of Brønsted acid sites by inductive effect and the creation of such sites by adsorption of HCl on Al–O–Al bridges.

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References

[1] B.C. Gates, J.R. Katzer and G.C.A. Schuit, *Chemistry of Catalytic Processes* (McGraw-Hill, New York, 1979).
[2] J. Kijenski and A. Baiker, Catal. Today 5 (1989).
[3] W.L. Earl, P.O. Fritz, A.A.V. Gibson and J.H. Lunsford, J. Phys. Chem. 91 (1987) 2091.
[4] J.A. Ripmeester, J. Am. Chem. Soc. 105 (1983) 2925.
[5] G.E. Maciel, J.F. Haw, I.S. Chuang, B.L. Hawkins, T.E. Early, D.R. McKay and L. Petrakis, J. Am. Chem. Soc. 105 (1983) 5529.
[6] J.F. Haw, I.S. Chuang, B.L. Hawkins and G.E. Maciel, J. Am. Chem. Soc. 105 (1983) 7206.
[7] J.H. Lunsford, W.P. Rothwell and W.X. Shen, J. Am. Chem. Soc. 107 (1985) 1540.
[8] J.H. Lunsford, P.N. Tutunjian, P.J. Chu, E.B. Yeh and D.J. Zalewski, J. Phys. Chem. 93 (1989) 2590.
[9] A. Bendada, E.F. De Rose and J.J. Fripiat, J. Phys. Chem. 98 (1994) 3838.

[10] H. Yong, D. Coster, F.R. Chen, J.G. Davis and J.J. Fripiat, in: *New Frontiers in Catalysis*, Studies in Surface Science and Catalysis, Vol. 75 B, eds. L. Guczi, F. Solymosi and P. Tétényi (Elsevier, Amsterdam, 1993) p. 1159.
[11] L. Baltusis, J.S. Frye and G.E. Maciel, J. Am. Chem. Soc. 109 (1987) 40.
[12] D. Coster, A. Bendada, F.R. Chen and J.J. Fripiat, J. Catal. 140 (1993) 497.
[13] T.C. Sheng, P. Kirszensztejn, T.N. Bell and I.D. Gay, Catal. Lett. 23 (1994) 119.
[14] T.C. Sheng and I.D. Gay, J. Catal. 145 (1994) 10.
[15] H. Sang, H.Y. Chu and J.H. Lunsford, Catal. Lett. 26 (1994) 235.
[16] S. Brau, H.O. Kalinowski and S. Berger, *100 and More Basic NMR Experiments, A Practical Course* (VCH, New York, 1996) ch. 4.
[17] P.J. Chu, J.H. Lunsford and D.J. Zalewski, J. Magn. Reson. 87 (1990) 68.
[18] P.J. Chu, A. De Mallman and J.H. Lunsford, J. Phys. Chem. 95 (1991) 7362.
[19] H. Knözinger and P. Ratnasamy, Catal. Rev. Sci. Eng. 17 (1978) 31.
[20] H. Pfeifer, J. Chem. Soc. Faraday Trans. 84 (1988) 3777.
[21] M.B. Fleisher, L.O. Golender and M.V. Shimanskaya, J. Chem. Soc. Faraday Trans. 87 (1991) 745.
[22] M. Tanaka and S. Ogasawara, J. Catal. 16 (1970) 157.
[23] A.E. Melchor, Thesis No. 83-60, Université Lyon I, France (1983).
[24] J. Thomson, G. Webb and J. M. Winfield, J. Mol. Catal. 67 (1991) 117.
[25] J.B. Peri, J. Phys. Chem. 70 (1966) 1482.