Inorganica Chimica Acta, 21 (1977) 81–84

Spin Labels as a Probe in Adsorption Phenomena in Zeolites

A. RIGO, P. VIGLINO, G. RANIERI, E. F. ORSEGA, and A. SOTGIU

Istituto Chimica Fisica, Facoltà Chimica, Industriale Università di Venezia, Venezia, Italy

Received June 7, 1976

Zeolites were exchanged with spin labels carrying a cationic group. In this way useful informations on active sites and adsorbed species can be obtained by EPR spectra and NMR relaxation measurements.

Introduction

Among solids surfaces of catalytic interest, zeolites have a special importance in research on heterogeneous catalysis, based mainly on the fact that the structure of the active surface is a well defined part of the crystal structure. Zeolites, in fact, form a system of well defined channels and cavities, and the knowledge of this structure allows the use of simple models, which would simplify the basic understanding of the very complicated catalytic phenomena. In this respect one of the main problems is the correct understanding of the mechanisms by which catalysis occurs. Regarding mechanisms most informations can be deduced from surfaces studies, usually by spectroscopic means. In particular broad-line NMR and pulsed NMR have been normally used to get informations on local surface diffusion coefficients and their distribution.

On the other hand the spin labels method has been successfully applied in various fields of biological and biophysical research, owing to their capability of monitoring local changes [1, 2].

In the present work we investigate the possibility of studying absorption phenomena at molecular level in zeolites by using, as a probe, spin labels carrying a cationic group bound to the zeolites framework.

Experimental

2,2,6,6-tetramethyl-4-amino-piperidine-N-oxide, I, was prepared from 2,2,6,6-tetramethyl-4-piperidine (Fluka) according to Rozantsev [3]; 2,2,6,6-tetramethyl-piperidine-N-oxide, II, was prepared from 2,2,6,6-tetramethyl-piperidine (Fluka) [4].

Powder samples of NaX, NaY and 4A zeolites were supplied by Union Carbide. The average particle size was of the order of a few microns. In particular the NaY sample (Union Carbide batch n^0 AR 804-1; 3–5 μ) was characterized by a Si/Al ratio of 2.5 and an iron content <1 ppm.

Zeolite samples were stirred in 10^{-2}–$10^{-3}M$ spin label solutions. The pH of the solutions was kept in the range 5–5.5 by addition of high purity HCl solution. Afterwards, the labelled zeolite samples were repeatedly washed with distilled water at pH 5.5 and dried at 100 °C at 10^{-6} torr. Controlled quantities of degassed water, vaporized in several steps from a calibrated capillary tube, were added to the dried zeolites in a vacuum system.

The EPR and NMR measurements were carried out at 25 °C, after the samples had been kept at room temperature, in sealed glass vials, for about 15 hours in order to equilibrate the adsorbed water in the zeolite frame. The EPR spectra were recorded as the first derivative of the adsorption mode by using a Varian V-4500 EPR spectrometer. The spin–lattice relaxation time, T_1, of the water protons was measured by the 90°–τ–90° pulse sequence on a Polaron pulsed NMR apparatus working at 16.0 MHz.

Results and Discussion

The pk$_a$ of the $-NH_3^+$ group of spin label I resulted 9.20 at 25 °C by pH metric titration.

The spin label content of samples of 4A, NaX and NaY zeolites, stirred in solutions of I and II, are reported in Table I. The data of Table I show a relatively high content of I in NaX and NaY samples while for the same types of zeolites the content of II is at

TABLE I. Spin Label Content per Na$^+$ Ion in Exchanged Zeolite Samples, as Evaluated from the Intensity of Their EPR Line by Comparison with a Standard Reference Sample.

Label	Zeolite		
	4A	NaX	NaY
I	EPR non detectable	~1 × 10^{-3}	~1 × 10^{-3}
II	EPR non detectable	~ 1 × 10^{-5}	~1 × 10^{-5}

least two orders of magnitude lower. In the 4A type zeolite samples no spin labels EPR signal was detectable. Since the cages of 4A are physically not accessible to both spin labels, the latter result indicates that the spin label adsorption on the zeolite crystal surface is negligible. As a consequence, the EPR signal in NaX and NaY samples can be assumed as being completely due to spin labels residing inside the zeolite cages. The different spin label content shown in Table I can be ascribed to a stronger bond of protonated form of I with the zeolite, due to the cationic exchange with Na^+ ions.

Because of the low iron content only the NaY type has been investigated by magnetic resonance spectroscopies.

The EPR spectrum of the free tumbling I in water solution consists of three sharp lines due to the nitrogen hyperfine interaction (Fig. 1a). The partial immobilization of I in NaY zeolite frame results in an asymmetric pattern of the same lines (Fig. 1b). In fact the binding of the protonated form of label I to the Na^+ sites would result in a rapid restricted rotation of the label molecule about its long molecular axis, while simultaneously tumbling within a cone. For similar motions of spin labels in biological membranes typical rotational correlation times are $<10^{-8}$sec [5]. The separation, $2A_z$, of the extreme lines is a function of the adsorbed water content and it has been suggested that these shifts should allow a convenient measure of τ_r, the spin label rotational correlation time [6]. In fact, τ_r can be calculated as a function of the measured A_z and a few other parameters whose values are dependent upon the adopted model [6]. However, independently of the adopted model, τ_r increases with increasing values of A_z and therefore faster motions correspond to lower A_z values.

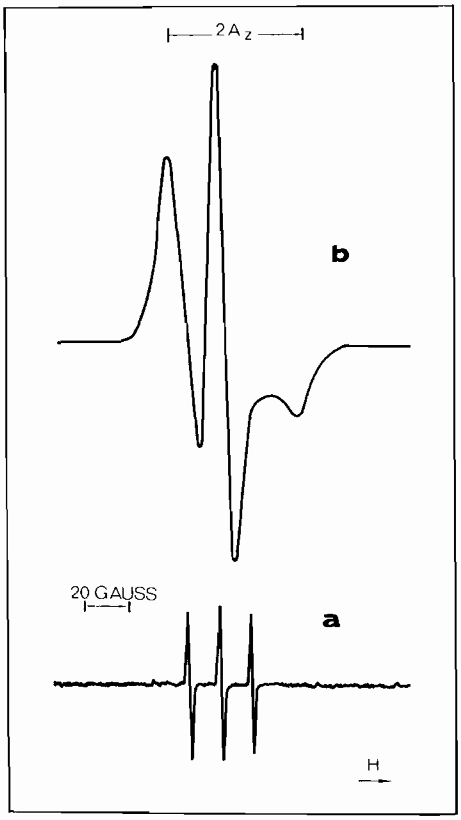

Fig. 1. EPR spectra of spin label I: a) $10^{-4}M$ water solution; b) NaY exchanged zeolite, $\theta = 0.14$.

The plot of $2A_z$ as function of the pore filling factor (θ) [7] for the adsorbed water is reported in Fig. 2, b. It appears that on increasing the degree of filling the restraint on label reorientational motion decreases until the label reaches the maximum mobility at $\theta \sim 0.6$–0.7. Further increases of the pore filling factor beyond 0.7 produce a progressive slowing down of the label motion. By substituting D_2O for H_2O and analogous but weaker effect is observed (Fig. 2a).

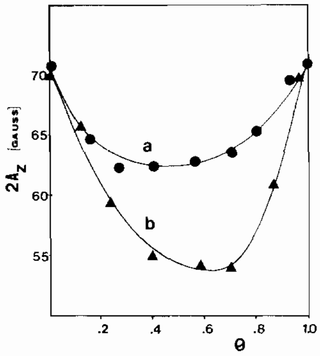

Fig. 2. $2A_z$ values of NaY zeolite exchanged with the spin label I as function of θ; a) D_2O, b) H_2O.

In Fig. 3a is shown the proton spin–lattice relaxation rate of water molecules, adsorbed in the NaY

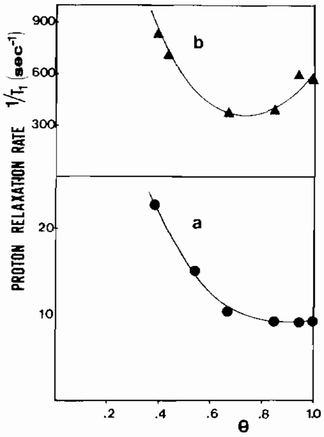

Fig. 3. Plot of $1/T_1$ as function of adsrobed H_2O: a) NaY zeolite; b) NaY zeolite exchanged with the spin label I.

zeolite, as a function of θ; in Fig. 3b the same quantity is reported for the NaY exchanged zeolite. Due to the given value of the signal to noise ratio, it has been practically possible to make measurements of T_1 starting from $\theta \sim 0.4$.

The T_1 values shown in Fig. 3a can be considered typical of an unlabelled zeolite with a very low iron concentration; we note in particular that our T_1 value (about 110 msec) at $\theta = 1$ (~30 H_2O molecules per cage) agrees quite well with the value of about 100 msec given by Resing and Thompson [8] for a similar zeolite. The paramagnetic impurities content of the unlabelled iron free sample is sufficiently low so that the proton relaxation is mainly due to the nuclear dipolar field of the adsorbed molecules, modulated by rotation and transational diffusion [8, 9].

The $1/T_1$ data reported in Fig. 3b for the spin labelled zeolite look quite different when compared with the corresponding values given in Fig. 3a, the main difference being that they are much higher (at least of a factor 40). This is a direct evidence that the proton relaxation is now mainly controlled by the dipolar interaction between the ^1H nuclei and the electron spin of the spin labels.

We are in this case measuring the spin–lattice relaxation for a system in which the nuclei exchange between two environments: i) in a spin label free cage; ii) in a cage where the spin label I is exchanged in a Na^+ site. Due to the low value of the spin label concentration (about 10^{-3} spin label per Na^+ ion), we are observing the relaxation of the magnetization due to the protons in the former environment, and the observed relaxation rate, $1/T_1$, is given by [10]:

$$\frac{1}{T_1} = \frac{1}{T_{10}} + \frac{f}{\tau_M + T_{1s}} \qquad (1)$$

where T_{1s} and T_{10} are the longitudinal relaxation times of the nuclei interacting and not interacting with spin label, respectively; τ_M is the lifetime of the H_2O protons in the paramagnetic environment and f is the fractional number of protons interacting with the spin label. According to the T_1 values obtained for the water protons in the unlabelled zeolite, $1/T_{10}$ is negligible in eq. 1.

Spot measurements of T_1 at different temperatures (not reported here) show that $1/T_1$ decreases with increasing temperatures, which is just the opposite of $1/\tau_M$. Therefore we are in the situation where $\tau_M \ll T_{1s}$ (fast exchange) and as a consequence $1/T_1$ results proportional to $1/T_{1s}$. T_{1s} is controlled by the dipolar interaction between the proton nuclear spin and the unpaired electron of the spin label, the spin hyperfine interaction being negligible for such compounds [11].

Without making any assumption about the specific motion modulating such interaction, following the usual BPP theory [12], we just define a parameter τ_c which gives an unambiguous and most general description for the averaging of the local magnetic field and need not be a molecular model. Then, neglecting the hyperfine interaction, we have:

$$\frac{1}{T_1} - \frac{1}{T_{10}} = \frac{Af}{r^6}\left[\frac{3\tau_c}{1+(\omega_I\tau_c)^2} + \frac{7\tau_c}{1+(\omega_s\tau_c)^2}\right] \qquad (2)$$

where ω_I and ω_s (with $\omega_I \ll \omega_s$) are the Larmor frequencies of the nuclei and the electrons respectively, r is their separation and A is a constant [13]. In the range we have applied the eq. 2 f can be safely assumed as independent of θ since for $\theta > 0.4$ the water molecules are weakly and aspecifically adsorbed in the zeolite cages [14].

Because under our experimental conditions τ_M and τ_s should be $> 10^{-7}$ sec [14, 15] we can identify τ_c with τ_r, which was evaluated $< 10^{-8}$ sec for similar systems [5]. Consequently $1/T_1$ will result always proportional to τ_c since $\omega_s \sim 10^3\ \omega_I$ and $\omega_I = 10^8$ sec^{-1}. According to this hypothesis, which could be verified for instance by NMR relaxation times measurements at different frequencies, the T_1 data would reflect the rotational motion of the spin labels inside the zeolite cages. Such a conclusion is supported by the strong correlation between EPR and NMR data (see Fig. 2 and 3).

Therefore a plausible interpretation of the experimental facts might be the following: as the zeolite cages begin to be occupied by the water molecules, the electrical field due to the zeolite framework experimented by the spin label is weakened. As a consequence the spin label mobility increases as it is reflected by the narrowing of the EPR spectra (A_z decreases). As the θ value approaches 0.6, the interaction between the water molecules increases, since they tend to form clusters of hydrogen bonded water molecules, which will in turn hinder the spin label motion [16]. This effect at $\theta \sim 0.6$ overcomes the effect of the electrical field shield offered by the water molecules and the spin label motion drops. The weaker effect observed on substituting D_2O for H_2O could be ascribed to the stronger hydrogen bonds formed by the D_2O molecules.

As a conclusion it can be said that the spin labelling technique is potentially helpful to give informations on the adsorption phenomena on surfaces of catalytic interest, but more investigations are necessary to ascertain the limits of the method.

Acknowledgments

We should like to thank dr. J. A. Rabo of Union Carbide for kindly providing the zeolites and for the helpful discussions on their properties.

References

1 H. McConnel and B. McFarland, *Quart. Rev. Biophys., 3,* 91 (1970).

2 L. J. Berliner in: "Progress in Biorganic Chemistry", Vol. 3; ed. E. T. Kaiser, F. J. Kezdy, Wiley, New York, 1974.

3 E. Rozantsev and Yu Kokhanov, *Izv. Akad. Nauk. SSSR Ser. Khim., 8,* 1477 (1966).

4 R. Briere, H. Lemaire and A. Rassat, *Bull. Soc. Chim. Fr., 11,* 3273 (1965).

5 J. Israelchvili, J. Sjosten, L. E. Goran Erikson, M. Ehrstrom, A. Graslund and A. Ehremberg, *Biochim. Biophys. Acta, 339,* 164 (1974).

6 A. T. Bullock, C. G. Cameron and P. M. Smith, *J. Polymer Sci., 11,* 1263 (1973).

7 V. A. Astakhov and M. M. Dubinin, *Izv. Akad. Nauk. SSSR Ser. Khim., 17,* 3 (1971).

8 M. A. Resing and J. K. Thompson, *Proc. of the 15th Coll. Ampère,* Amsterdam, 1969, p. 237.

9 H. Pfeifer in: "NMR Basic Principles and Progress", ed. P. Diehl, E. Fluck, R. Kosfeld, Springer Verlag, Berlin, 1972, Vol. 7, p. 53.

10 Z. Luz and S. Meiboom, *J. Chem. Phys., 40,* 2686 (1964).

11 A. S. Mildvan and J. L. Engle in: "Methods in Enzymology", Academic Press, 1972, Vol. 26.

12 N. Bloembergen, E. M. Purcel and R. V. Pound, *Phys. Rev., 73,* 679 (1948).

13 I. Solomon, *Phys. Rev., 99,* 559 (1955).

14 J. P. Cohen-Addad and J. P. Farges, *J. Physique, 27,* 739 (1966).

15 T. R. Krugh in: "Spin Labeling Theory and Applications", ed. L. Berliner, Academic Press, 1976.

16 A. Z. Sarakhov, V. F. Konoyuk and M. M. Dubinin in: "Advances in Chemistry Series", Vol. 121, American Chemical Society, 1973, p. 403.