

^{129}Xe -NMR STUDY OF THE ZEOLITE MICROPOROSITY USING A BLOCKING AGENT TO AVOID THE INTERPARTICLE XENON DIFFUSION

J.-G. Kim¹, L. Ch. de Ménorval^{1*}, R. Ryoo² and F. Figueras^{1†}

¹Laboratoire de Matériaux Catalytiques et Catalyse en Chimie Organique, URA-418 CNRS, ENSCM, 8 rue de l'Ecole Normale, 34053 Montpellier Cédex 1, FRANCE.

²Department of Chemistry and Center for Molecular Science, Korea Advanced Institute of Science and Technology, Taeduk Science Town, Taejon, 305-701, KOREA.

SUMMARY

In this work we have applied the ^{129}Xe -NMR spectroscopic technique using octamethylcyclotetrasiloxane (OMCTS) as a blocking agent to avoid the interparticle xenon diffusion over different zeolite catalyst samples. We were able to extract new information about the microporosity in individual crystallite particles.

1. INTRODUCTION

^{129}Xe -NMR spectroscopy is now widely used for investigations of microporous materials, particularly zeolite catalysts [1-11]. However, a critical limitation of the ^{129}Xe -NMR method is that the NMR spectrum provides informations that are averaged over many zeolite crystallites due to a rapid exchange of xenon at room temperature (RT). The xenon diffusion may be slowed down by cooling [12], but the xenon adsorption increases at low temperature making the spectral interpretation complicated.

† Present address: Institut de Recherches sur la Catalyse, CNRS, 2 Avenue Albert Einstein, 69624 Villeurbanne Cédex. France.

* To whom correspondence should be addressed.

Recently Ryoo et al. [13] have suggested a new method to hinder the xenon intercrystalline diffusion at RT by putting liquid OMCTS in the external void volume between the NaY zeolite crystallite particles. In this work, we extended this method to other zeolites in order to extract new informations on the internal microporosity.

2. EXPERIMENTAL SECTION

NaY, CaY, mixed NaY + CaY, BEA, and KL commercial zeolites were used in this study (NaY Linde 52, BEA and KL from UETIKON). The CaY zeolite was obtained from the NaY zeolite by Ca^{2+} ion-exchange procedure [14] to give a Ca^{2+} exchange degree of 68%. The NaY and CaY zeolite samples (batch samples of 0.5 g) were dehydrated separately at 670 K and mixed in 1 : 1 ratio using an agate mortar for more than 30 m inside a glove box. The zeolite mixture was evacuated in the NMR tube at RT. The zeolite samples were put in a 10 mm NMR tube equipped with a re-sealable valve suited for attachment to a vacuum line, then evacuated for 2 h at 670 K under 10^{-5} Torr. For the samples with OMCTS the zeolites were treated within the same NMR tube with a branch (Fig. 1), followed by opening to the air in order to put liquid OMCTS into the branch, then treated again in the same conditions.

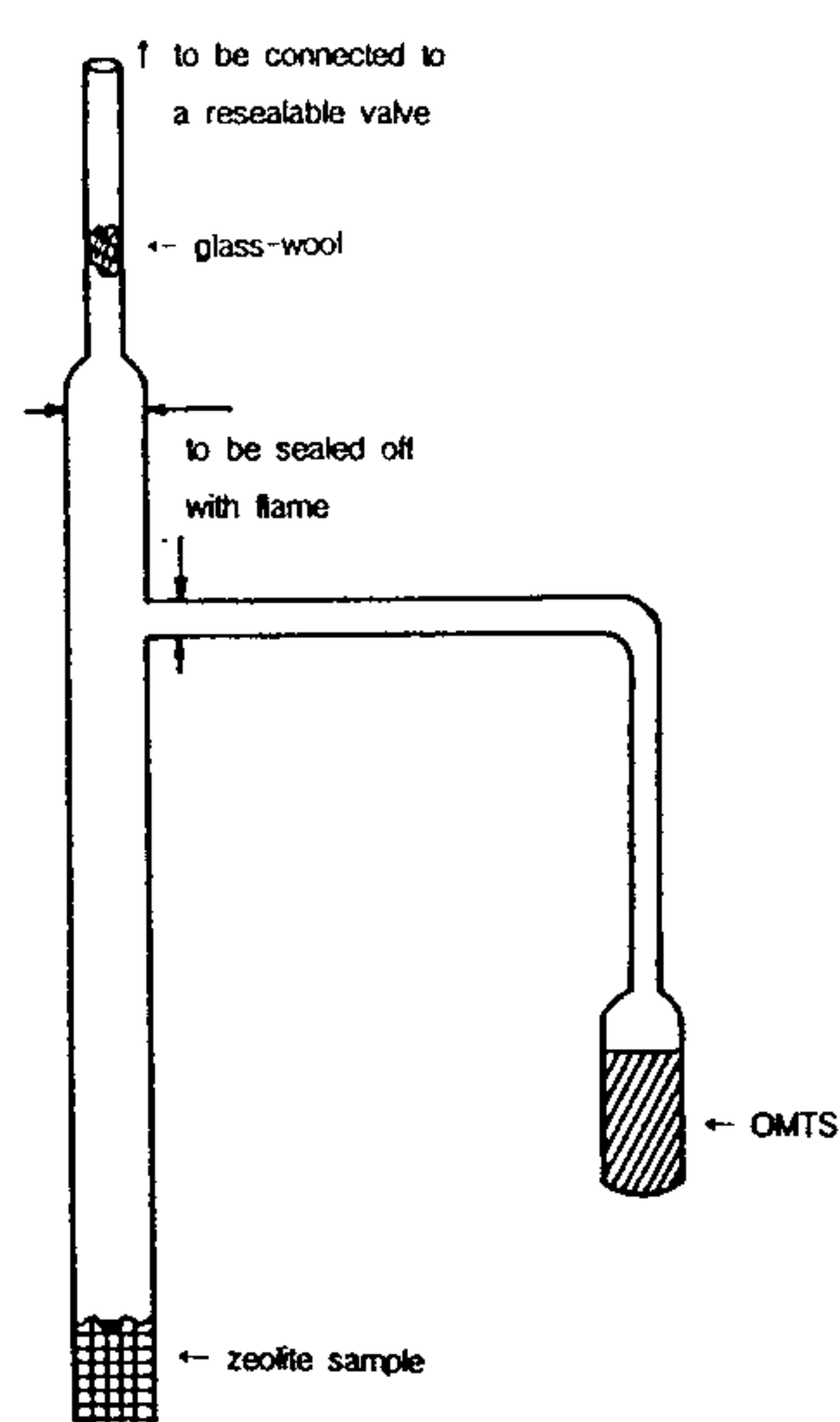


Fig.1 Schematic diagram of the NMR cell.

Finally the zeolite catalyst samples were equilibrated to a known pressure of xenon (Air Liquide, 99.995%) at RT. The NMR tube was flame-sealed after transferring the liquid OMCTS onto the sample. ^{129}Xe -NMR spectra were obtained at RT on a Bruker AC 250L spectrometer operating at a frequency of 69.19 MHz for ^{129}Xe . Typically, 2000 signal acquisitions were accumulated for each spectrum with a recycle delay of 1 s between $\pi/2$ pulses. Chemical shift measurements are precise to within 1 ppm and are expressed relative to xenon gas at zero pressure [15]. Downfield (high frequency) chemical shifts are considered to be positive.

3. RESULTS AND DISCUSSION

Fig.2 shows the ^{129}Xe -NMR spectra for NaY, CaY and their 1:1 mixture obtained after mixing of NaY + CaY zeolite samples, before and after adding OMCTS (after 1 h equilibrium time). The NaY and CaY samples gave simple signals with the chemical shifts at 85 and 114 ppm (Fig. 2a, b) The observation of a single coalescent NMR peak from the NaY-CaY mixture in Fig. 2c, situated at 97 ppm is consistent with rapid intercrystalline xenon diffusion on the NMR Time scale [12, 16] The fact that the NMR line corresponding to the mixture is resolved in two lines after the addition of OMCTS means that xenon is now diffusing only inside NaY or CaY in the characteristic NMR time scale and consequently the chemical shift, δ_{Xe} , is only coming from contributions from inside of the NaY or CaY zeolite crystallites. The line appearing at 190 ppm is due to xenon dissolved in liquid OMCTS. Thus, the addition of OMCTS in situ into the NaY-CaY mixture resolved the NMR signals by blocking the intercrystal xenon diffusion. The chemical shifts of the two resolved lines (at 93 and 106 ppm) increases gradually with time after the OMCTS addition[13]. This observation indicates that OMCTS filled the zeolite microporosity from the outer rim of the individual zeolite crystallites toward the centers, compressing gradually with time the xenon in the zeolite matrix

The addition of OMCTS to a BEA zeolite does not modify its $\delta_{\text{Xe}}(\text{BEA}) = 113$ ppm, nor its line width, $\Delta H = 4.3$ ppm for an equilibrium xenon pressure of 600 T, whatever the interval between the moment at which the OMCTS is added and the ^{129}Xe NMR spectrum recorded. up to 6 months later (Figure not shown). This observation indicates :

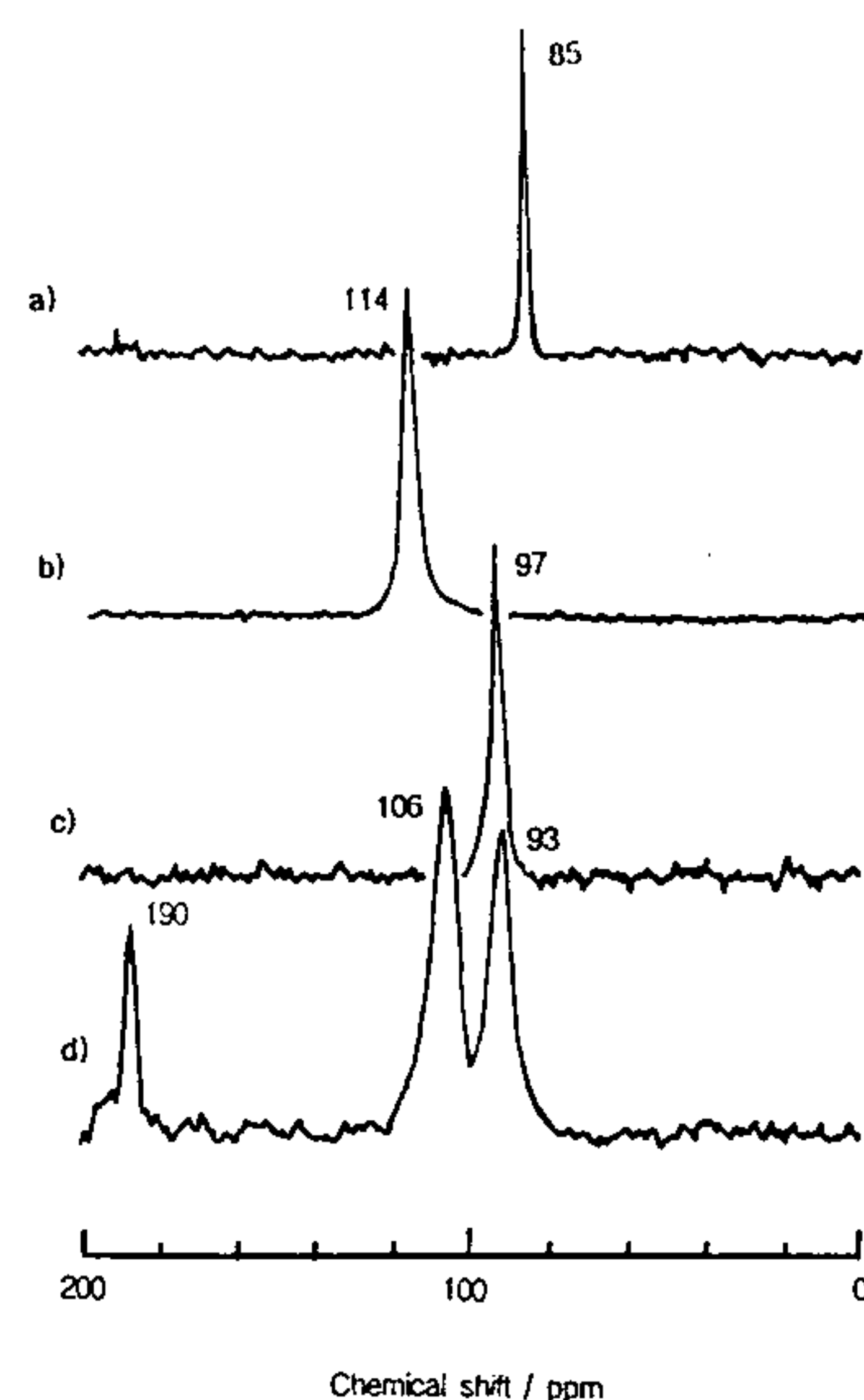


Fig.2 ^{129}Xe -NMR spectrum under 400 Torr of Xe at RT: a) mixture of NaY and CaY; b) Diffusion-blocked (OMCTS) mixture of NaY and CaY.

first, that OMCTS can not penetrate at all in the microporosity of zeolite BEA (pores of 7.5×5.7 and 6.5×5.6 Å) contrary to Y zeolite (pores of 7.4 Å) where OMCTS slowly penetrates in the microporosity; second, the aperture of the Y zeolite porosity is definitely larger for the admission of the OMCTS molecule than for BEA zeolite.

We expected that for a KL zeolite (pores of 7.1 Å), the OMCTS normally cannot penetrate. We have observed before adding OMCTS, the existence of two lines for the ^{129}Xe NMR spectrum (Fig. 3a), one narrow line, $\delta_{\text{Xe}} = 128$ ppm and $\Delta H = 7$ ppm and one broad one, $\delta_{\text{Xe}} = 112$ ppm and $\Delta H = 15$ ppm, contrary to a precedent work [1] where only one line existed and according to the expected X-ray powder diffraction patterns of the KL zeolite. The existence of two separated xenon lines means that the diffusion of the xenon atoms between the two different microporosity regions must be much slower than the characteristic NMR time scale. The addition of OMCTS destroys the broad line situated at high magnetic fields, indicating that the OMCTS can penetrate into the microporosity of a part of the sample and this observation can be interpreted if we consider the existence of defects in some channels of the KL zeolite crystallites, leading to a larger porosity (Fig. 3b). The narrow line remained at the same position, with the same ΔH as before

when OMCTS is added. In this case the OMCTS molecule cannot penetrate at all in the internal microporosity of the normal KL channels, even after repeating the experiment 6 months later. X-ray results on this sample don't show any particular sign of zeolite damage. The ^{129}Xe -NMR spectroscopic technique using blocking agent molecules like OMCTS distinguished the existence of defects in the microporosity of the KL zeolite.

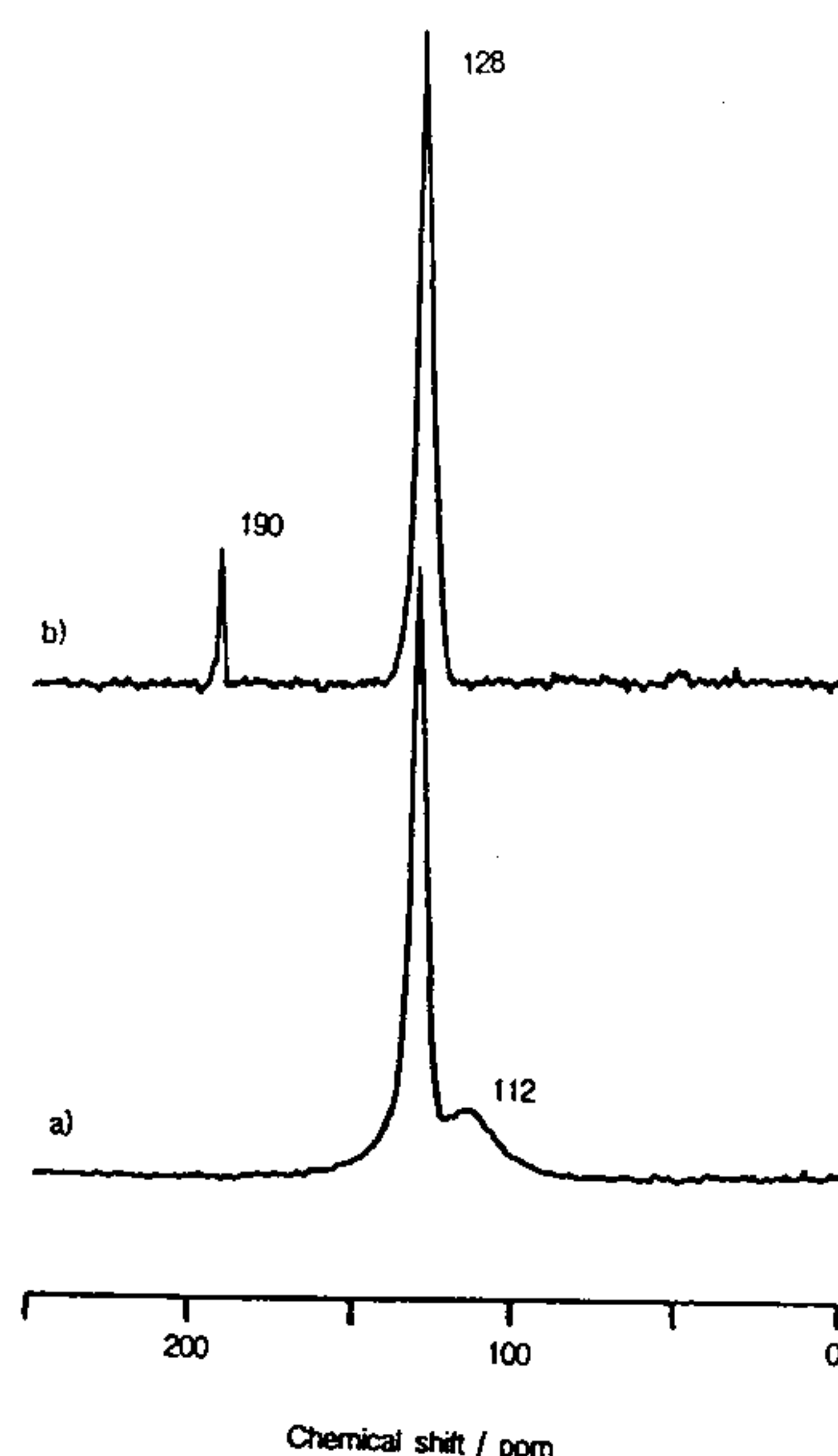


Figure 3. ^{129}Xe -NMR under 560 Torr of xenon at RT : a) KL zeolite; b) KL zeolite after addition of OMCTS.

4. CONCLUSIONS

The spectroscopic technique using ^{129}Xe -NMR together with OMCTS as a blocking agent allows the study of individual crystallite microporous volume of different zeolites. The xenon as an internal probe can discriminate if a molecule penetrates or not in a given zeolite microporosity. Furthermore the xenon probe can follow the diffusion of other molecules in the internal zeolite microporosity and finally is very sensitive to the existence of defects that cannot be characterized by other techniques like X-rays.

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