

ZEOLITES: A REFINED
TOOL FOR DESIGNING
CATALYTIC SITES

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ZEOLITES: A REFINED TOOL FOR DESIGNING CATALYTIC SITES

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Edited by

Laurent Bonneviot

*Département de Chimie, CERPIC, Faculté des Sciences et de Génie, Université Laval,
Québec, Canada G1K 7P4*

Serge Kaliaguine

*Département de Génie Chimique, CERPIC, Faculté des Sciences et de Génie,
Université Laval, Québec, Canada G1K 7P4*



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FOREWORD

Once upon a time the catalytic use of zeolites was exclusively in the field of acid catalysis. Today zeolites also find applications as catalysts in a wide array of chemical reactions. These encompass base catalyzed reactions, Redox reactions and catalytic reactions on transition metals and their complexes in confined environments. The concepts of Bronsted or Lewis acid-base pairs are abundantly illustrated in the literature and better understood in terms of structural and electronic properties of zeolites. By contrast properties of chemically modified silicates, aluminosilicates and aluminophosphates are not yet fully explored. The list of oxydo-reduction reactions performed in the presence of these new materials is indeed continuously growing. For example the selective catalytic reduction of nitrogen oxides or the numerous oxidations employing hydrogen peroxide could be cited. In this context much effort is currently made in order to get a better insight into the nature of the sites involved. Thirdly, the zeolite lattice may be used as a host for encapsulated complexes or metallic clusters allowing to control the nuclearity of these active species and the steric constraints imposed on the reactants. The molecular sieve and shape selectivity effects have always constituted the most fascinating aspects of zeolite properties. The recent developments leading to increasingly large pore sizes with VPI-5, cloverite and more recently mesoporous molecular sieves have broadened the spectrum of these applications. Indeed larger and larger reactant and product molecules can be accommodated in these lattices. These new adsorbant/adsorbate systems create additional needs for experimental data and theoretical descriptions of transport properties, in particular of mono- and multi-components diffusion coefficients in the zeolite pore lattice.

All these questions represent the forefront and current trends of zeolite research. To various extents they deal with the specific factors of the zeolites which allow the fine tuning of the geometric and/or electronic properties of the active sites. It was indeed very rewarding for us, as organizers of this symposium, to realize that all these questions were actually discussed in the papers submitted to the selection committee and that they were widely represented in the selected papers.

A feature general to most of these contributions is the combined use of a variety of analytical techniques. Some of these techniques are at the frontiers of the latest analytical developments such as multiple scattering EXAFS and bidimensional MAS-NMR. It is also worth mentioning that the on-going refinements of molecular modelling can now rely on more and more accurate quantum mechanics calculations such as the density functional theory (DFT) improved by introducing high level electron correlation.

We wish to thank each and every one of the contributors to the Québec International Zeolite Symposium, who gathered coming from not less than 27 countries to share their recent findings and ideas in a research field so liable to yield future fundamental developments as well as potential technical innovations.

Laurent Bonneviot and Serge Kaliaguine

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One and two-dimensional solid-state NMR investigations of the three-dimensional structures of zeolite-organic sorbate complexes

C.A. Fyfe, H. Grondey, A.C. Diaz, G.T. Kokotailo, Y. Feng, Y. Huang, K.C. Wong-Moon, K.T. Mueller, H. Strobl and A.R. Lewis

Department of Chemistry, University of British Columbia,
2036 Main Mall, Vancouver, B.C. V6T 1Z1, Canada

1. INTRODUCTION

A most important characteristic of molecular sieve systems which is common to their applications as catalysts, sorbents and in gas separation is the size and shape selectivity toward adsorbed organic molecules conferred by the molecular dimensions of their channel and cage systems [1]. Because of their small crystallite dimensions, powder rather than single-crystal XRD techniques must be used. While it is possible to define framework topologies and structures powder X-ray diffraction, particularly if Rietveld analysis and synchrotron radiation are used [2,3], it is very difficult to reliably determine the structures of organic sorbate/framework complexes which would yield important information on the detailed nature of the interactions. Important exceptions in this regard are the single crystal XRD studies of van Koningsveld and co-workers who determined detailed high-quality structures of the high-loaded forms of *p*-xylene and *p*-dichlorobenzene in zeolite ZSM-5. These are the only reliable zeolite/sorbate structures to date [4,5].

High resolution solid state NMR has emerged in recent years as an important complementary technique to XRD in the investigation of zeolite structures, being particularly sensitive to short to medium range geometries and orderings [6].

For some years we have worked to develop new approaches in the application of solid-state NMR techniques together with XRD studies to the investigation of zeolite structures with the aim of ultimately being able to determine the 3D structures of their complexes with sorbed organic molecules. In this paper, we outline the development of these techniques and their current standing.

2. RESULTS AND DISCUSSION

In high-resolution solid state NMR, the widths of the signals from dilute spin-1/2 nuclei are determined by the degree of crystallinity and the perfection of the local ordering. This can be achieved in the case of zeolites by investigating high-quality, completely siliceous systems where there is only the Si(4Si) local environment present. As illustrated in Figures 1A and B for ZSM-12 [7] and ZSM-5 [8], respectively, sharp resonances are observed whose numbers and relative intensities reflect the number and occupancy of the crystallographically inequivalent T-sites in the unit cell. In the case of AlPO₄ molecular sieves, there is exact alternation of Al and P, giving completely and perfectly ordered frameworks in the as-synthesized materials, as shown in Figure 1C for the ³¹P spectrum of VPI-5 [9]. This result is quite general for perfectly

crystalline and ordered solids.

These spectra may be used to monitor various structural transformations, for example, those induced by temperature as in the case of ZSM-5 [10], or in the case of AlPO_4 materials by the hydration/dehydration of octahedral Al sites. Of particular importance, they yield information on the interaction of organic sorbates with the molecular sieve framework. For example, Figure 2 shows the ^{29}Si spectrum of ZSM-5 with *p*-xylene present at a loading of two

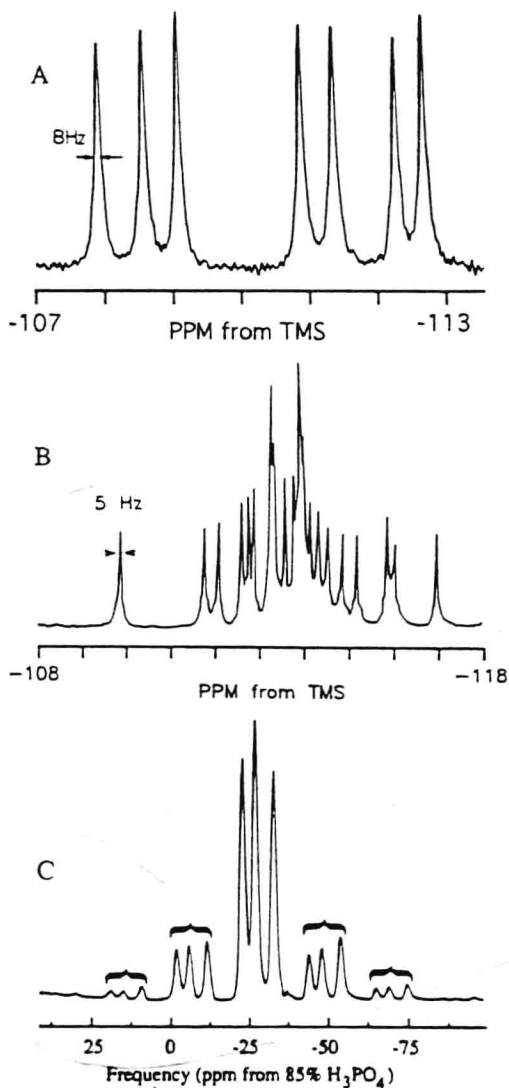


Figure 1. ^{29}Si MAS spectra of (A) ZSM-12 and (B) ZSM-5. (C) ^{31}P MAS spectrum of VPI-5 with spinning sidebands indicated by brackets.

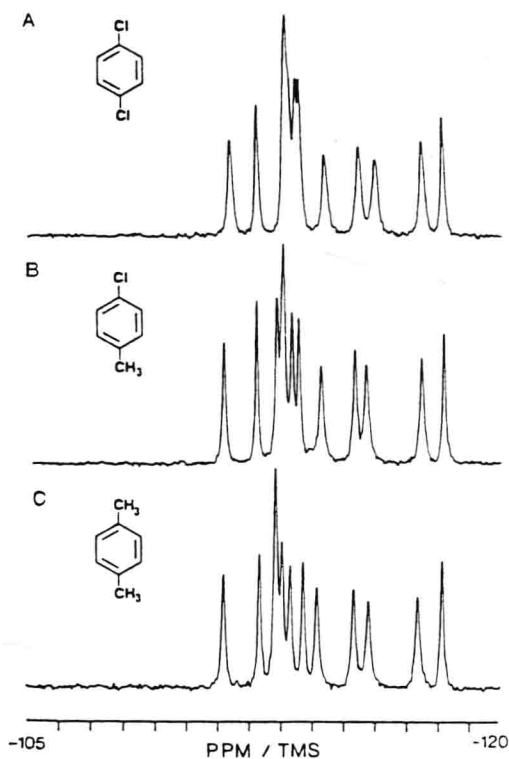


Figure 2. ^{29}Si MAS spectra of ZSM-5 loaded with 2 molecules per u.c. of (A) *p*-dichlorobenzene, (B) *p*-chlorotoluene, and (C) *p*-xylene.

molecules per unit cell (u.c.). Comparison with Figure 1B shows that the number of T-sites has decreased from 24 to 12 indicating a change in symmetry from monoclinic to orthorhombic. Further, the similarities between the spectra in the presence of *p*-xylene and *p*-dichlorobenzene and *p*-chlorotoluene (Figure 2) indicate that the interactions, at least in this case, are based on the size and shape of the organic molecule since the CH₃ and Cl substituents have the same steric factors but the molecules differ in most other aspects [11]. The difficulty in using these spectra further is that the assignment of the resonances to the different T-sites is generally not known, although there may be some information from the intensities if the site occupancies are different. In the case of ZSM-12 and ZSM-5, all of the site occupancies are the same and no assignments are possible.

This problem can be solved by using two dimensional homonuclear correlation experiments such as COSY and INADEQUATE to establish the three-dimensional (Si-O-Si) connectivity pattern with the framework when the topology is known [12]. Figure 3 shows such an experiment on ZSM-12 [7]. This yields the assignments of the resonances shown in the figures. The above experiments are based on the scalar Si/Si J-coupling which operates through the bonding network. Similar information may be obtained in the AlPO₄ systems from CP and TEDOR experiments as shown in Figure 4 [9]. Although these are based on the heteronuclear dipolar coupling which is a through-space interaction, they are selective for ³¹P-O-²⁷Al connectivities because the interaction is very strongly distance dependent and these P/Al distances are the shortest. Knowledge of the assignments may now be used to gain additional information on the details of the structures and the various changes which they can undergo. For example, zeolite ZSM-11 is found to undergo a temperature induced transition from a

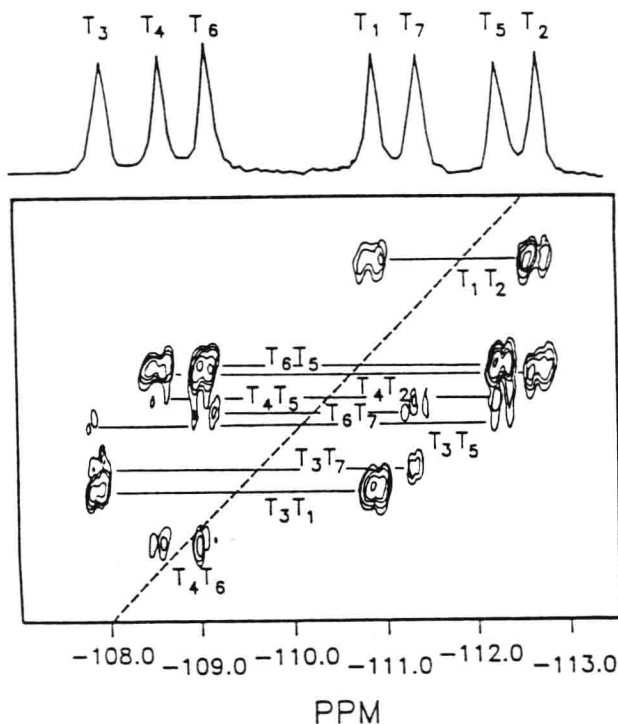


Figure 3. ²⁹Si INADEQUATE experiment on ZSM-12.

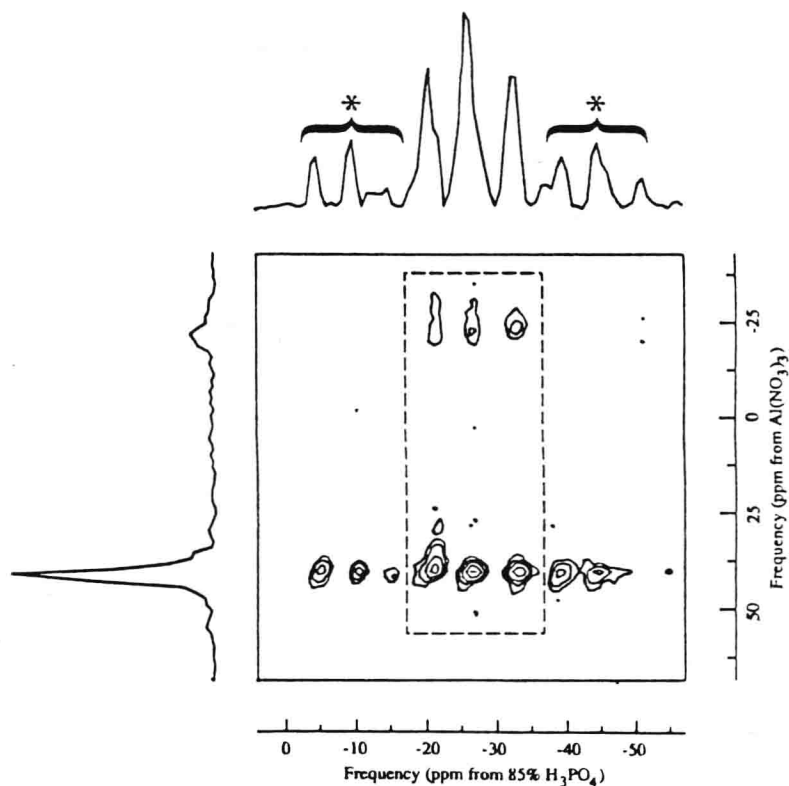


Figure 4. Two-dimensional $^{27}\text{Al} \rightarrow ^{31}\text{P}$ TEDOR experiment on VPI-5. The connectivities are displayed in the dashed box and spinning sidebands are indicated by asterisks.

high-temperature form with seven T-sites which matches the proposed framework topology (tetragonal, space group $I\bar{4}m2$) to a lower symmetry form at room temperature (twelve T-sites with equal occupancy). 2D INADEQUATE experiments on both forms yield the assignments of the resonances shown in Figure 5 (see ref. [13] for more details) and from the relationship between the two spectra it can be deduced that the space group of the room temperature form is $I\bar{4}$ (tetragonal) and that the phase transition involves the loss of the mirror plane. Information of this type is useful for further investigation of the structure by diffraction techniques.

The last step in the extension of these solid state NMR techniques is to apply them to the investigation of the three dimensional structures of zeolite-sorbate complexes. This can be done by using experiments such as cross-polarization and REDOR which are based on the through-space dipolar interaction. Because of the strong distance dependence, the distances between the T-sites in the framework (whose identities are now known) and nuclei on suitably isotopically substituted substrates may be determined, yielding the 3D structure of the zeolite-sorbate complex. To test the validity of this approach we have investigated a number of such experiments applied to the high-loaded form of zeolite ZSM-5 containing p-xylene where the answer is known from the high-quality single crystal structure of van Koningsveld and co-workers [4].

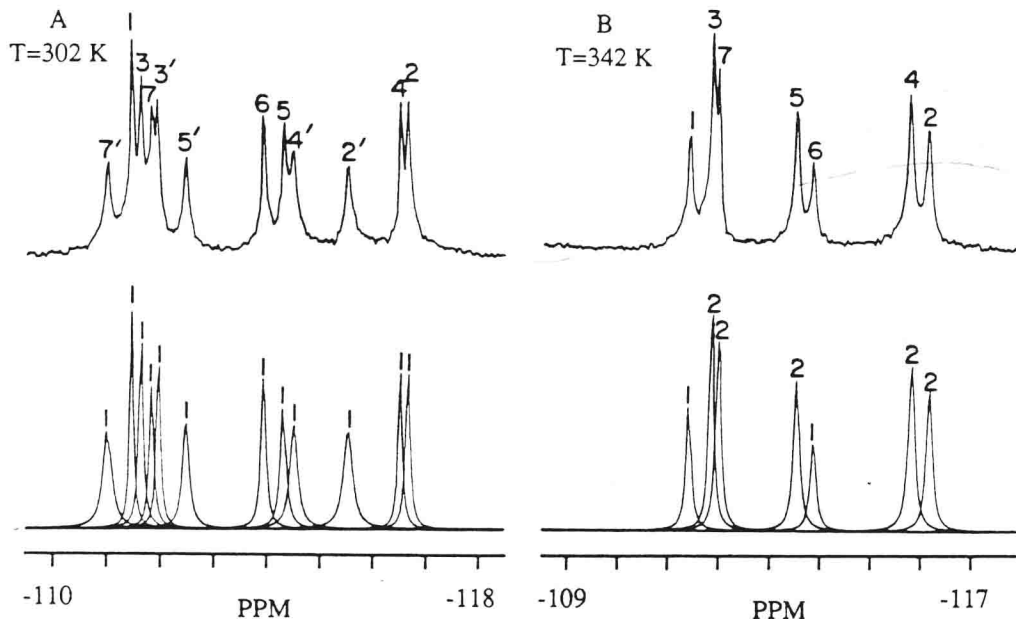
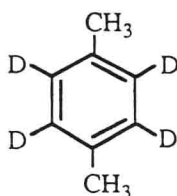
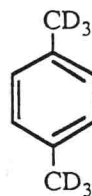


Figure 5. ^{29}Si MAS spectra of ZSM-11 at (A) 302 K and (B) 342 K. Below each spectrum is the deconvolution in terms of Lorentzian curves.

In the present paper, the application of the CP technique with protons as the source nuclei will be described as representative of this class of experiments. In order to localize the polarization source as much as possible, experiments were carried out with the two specifically deuterated *p*-xylenes (1) and (2).



(1)



(2)

Since the CP process is greatly dependent on molecular motions, these must be well understood for the system being studied. In the present work, these were investigated by wide line deuterium NMR of the sorbed organics. It was found that at 6 molecules/u.c., the methyl groups in the organic substrate have rapid C_{3v} rotational motion while the aromatic rings are essentially rigid but a proportion show some low frequency "ring-flips" around the 1,4-axis.

The effect of the distance dependence can be seen qualitatively from a comparison of the CP spectra with that from a simple one-pulse experiment as shown in Figure 6. The structure is orthorhombic with 24 T-sites of equal occupancy and the assignments of the resonances come as previously from 2D INADEQUATE experiments [14]. In the CP spectrum some signals are obviously enhanced compared to the others. The resonances due to the T-sites 1, 2, 10, 12 and 16 are quite well resolved and these were used in the study.

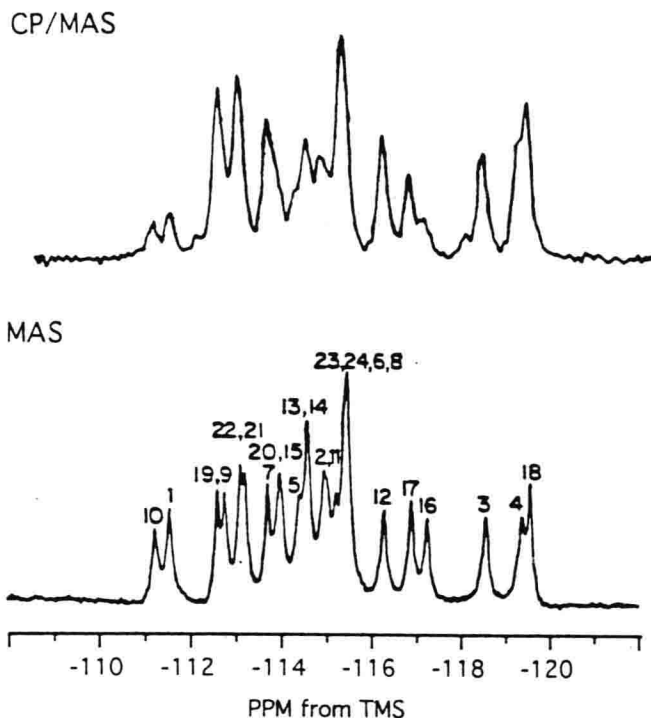


Figure 6. (a) ^{29}Si CP/MAS spectrum of the complex of p-xylene (2) in ZSM-5 at a loading of 6 molecules per u.c. The contact time was 5 ms, with a recycle delay of 5 s. (b) ^{29}Si MAS spectrum of the complex of p-xylene in ZSM-5 at a loading of 8 molecules per u.c.

The spin-dynamics of the cross-polarization process from I to S nuclei as a function of time are described by Equation (1) [15].

$$S(t) = S_{\max} (1 - T_{\text{CP}}/T_{1\rho(\text{H})})^{-1} (\exp(-t/T_{1\rho(\text{H})}) - \exp(-t/T_{\text{CP}})) \quad (1)$$

S_{\max} represents the theoretical maximum signal intensity obtainable from the polarization transfer, $T_{1\rho(\text{H})}$ the proton $T_{1\rho}$ value and T_{CP} the cross-polarization time constant. Thus the S signal intensity as a function of time should consist of an exponential growth controlled by the cross polarization transfer and an exponential decay due the $T_{1\rho}$ process. Of particular interest, T_{CP} can be related to the second moment of the IS dipolar interaction, $(\Delta\omega^2)_{\text{IS}}$, as in Equation (2) and is proportional to r_{IS}^6 as in Equation (3), [16].

$$\frac{1}{T_{\text{CP}}} = \frac{C (\Delta\omega^2)_{\text{IS}}}{\sqrt{(\Delta\omega^2)_{\text{II}}}} \quad (2)$$

$$\frac{1}{T_{\text{CP}}} \propto (\Delta\omega^2)_{\text{IS}} \propto \frac{\gamma_{\text{I}}^2 \gamma_{\text{S}}^2}{\sum r_{\text{IS}}^6} \quad (3)$$