New insights on zeolite chemistry by advanced IR and NMR characterization tools

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ABSTRACT

New techniques and methodologies in the spectroscopic characterization of zeolites provide new insights on the complexity of zeolitic materials. In particular, emerging IR and NMR techniques shed new lights on old problems such as acidity. New, rich and quantitative information can be gathered. In particular, the ability to work under the so-called operando conditions yields much valuable data to rationally design better catalysts or zeolite based materials. The work and inspiration of Eric Derouane are often at the core of this new knowledge.

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1. Introduction: the problem of acidity

Acidity has always been a main source of interest and applications for zeolites; many processes in oil refining, petrochemistry and fine chemicals rely on solid acid catalysts. The relationships between acidity, confinement and reactivity were amongst the key focal points of Eric Derouane [1]. He was always very enthusiastic about new characterization methods and paid much attention to spectroscopic techniques. For him, this was a tool to peer ever deeper inside zeolite chemistry.

The assessment of acidity includes the quantitative description of its nature (Lewis or Brønsted), the strength of the sites, their spatial distribution. Other important parameters are related to the confinement of molecules in the pores and the accessibility of the acidic sites. These last parameters are specific to zeolites and often explain their unique catalytic properties. A good description of all these parameters is thus needed for a clear understanding of their mode of action and for an efficient design of zeolitic catalysts.

The aim of this brief overview is to highlight some of the new insights obtained in Caen with IR and NMR spectroscopy, in domains that were started when some of us were working under the guidance of Eric Derouane, or in research inspired by Eric Derouane's ideas on confinement and acidity in zeolites. It is not (another) review on zeolite acidity.

2. Accessibility of active (acid) sites

Mordenite is an excellent case study to highlight the relationship between the pore architecture and acidity of zeolites. Its Brønsted

acid sites can be located in fairly large mono-directional channels, with little or no confinement, or in small side pockets were very little space is available for reactants or probe molecules. Moreover, dealumination can create large mesopores in the solid, and thus decrease substantially the diffusion limitations while keeping the constrained local environment around the acid site. The catalytic activity of dealuminated mordenite can be enhanced by the creation of these mesopores, but the characterization of the increased accessibility of the sites is not a standard procedure. Working on the so-called Small Port Mordenite, we used pyridine and substituted pyridines to probe accessibility of Brønsted sites [2]. Even pyridine (0.57 nm) can reach only 68% of all sites in a neat small port mordenite; so we resorted to co-adsorption experiments with carbon monoxide to probe all the sites in the microporous structure. After the first dealumination step (Fig. 1), pyridine reaches 80% of the sites, leaving only 20% for carbon monoxide. After the second dealumination step, 2,6-lutidine (0.67 nm) can enter the solid and probe 60% of the sites, while 30% are left for pyridine and 10% for CO. In the end, even di-isopropyl-pyridine can enter the solid and probe 85% of the sites, while collidine (0.74 nm) and lutidine take the remaining sites and nothing is left for pyridine. These large substituted pyridines are thus very useful for probing accessibility of acid sites in hierarchical zeolites. This technique can be extended to monitor the level the dealumination required to optimize the effectiveness factor of a particular zeolite in a given reaction.

3. Size and basicity: the problem of substituted pyridines

The case described above can become more complex however. On a USY zeolite, the same series of substituted pyridines was used to check the accessibility of the many different Brønsted sites detected between 3500 and 3700 cm^{-1} in its IR spectrum (Fig. 2). Pyridine reaches nearly all sites, and only a weak intensity

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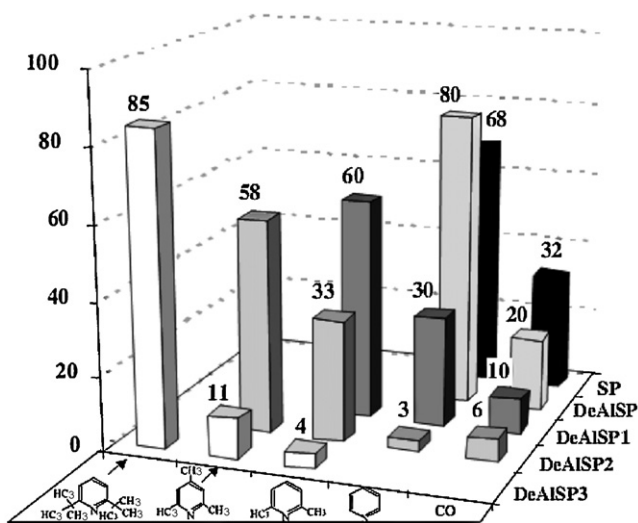 *E-mail address:* fts@ensicaen.fr (F. Thibault-Starzyk).

Fig. 1. Distribution of accessibility of sites for co-adsorbed probe molecules on small port mordenite (SP) and increasingly dealuminated small port mordenite (DeAlSP, DeAlSP1, DeAlSP2 and DeAlSP3), reproduced from ref. [2].
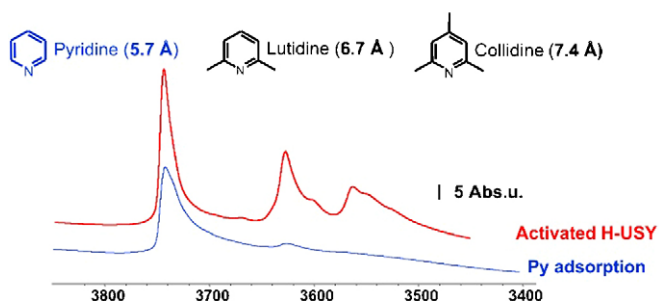

Fig. 2. IR spectra of H-USY zeolite before and after pyridine adsorption on the various OH groups observed. The bulkier and more basic lutidine and collidine probe all of the OH acidic groups, and the spectra only show flat baselines in the corresponding region (spectra not shown for the sake of clarity).
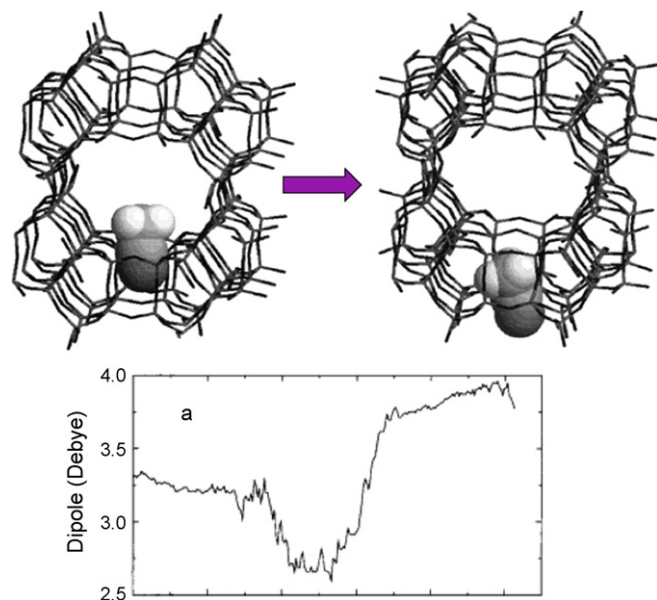

Fig. 3. Top: modeling of the introduction of acetonitrile in the confined side pocket of the mordenite structure. Bottom: changes in the molecular dipole moment of acetonitrile when going from the main channel (3.35 D) to the side pocket (3.8 D) (taken from ref. [6]).

remains for the ν(OH) vibration band around 3620 cm^{-1}. Lutidine and collidine, being bulkier, were expected to leave more sites unperturbed, but the opposite was observed. All Brønsted sites were deprotonated by lutidine and collidine as no OH groups could be detected after adsorption of the probe molecules. Substituting pyridine with methyl groups not only increases the size of the molecule, it also increases its basic strength (pKa(Py) = 5.2, pKa(Lu) = 6.75, pKa(Coll) = 7.3) [3,4] and this introduces a serious bias in the measurement of accessibility. A stronger base will deprotonate a Brønsted site from a greater distance, and will thus reach sites further away than a weaker base. Such a problem has been addressed by Onida et al. [5] with non-protonated probe molecules (only probing H-bonding). These findings suggest that the only really relevant probe molecule would be the actual reactant, quite often a weakly basic hydrocarbon molecule, which would probe its own accessibility without interference from any other molecule's basic strength.

4. Confinement and basicity: acetonitrile in Si-MOR

Using the actual reactant as the probe molecule would also solve another fascinating problem arising from the specific influence of the zeolites pores. Confinement in the restricted space in the pore can alter the dipole moment of any probe molecule. Acetonitrile, for instance, has a molecular dipole moment of ca. 3.3 D in the gas phase. Modeling the behavior of acetonitrile in the pores of a purely siliceous mordenite, we have shown that the molecular dipole is

nearly unaffected in the large channel of the mordenite structure [6]. However, even without the influence of Al atoms (modeling on a purely siliceous mordenite), acetonitrile is distorted when located in the small side pocket, and its molecular dipole rises to nearly 4 D (Fig. 3).

The electron density on the nitrogen atom is therefore enhanced, and the basicity of the probe molecule is increased by confinement. If a Brønsted site was present in the side pocket, its interaction with acetonitrile would be stronger than that without confinement. Indeed, the strength of acid sites in mordenite, when measured by IR spectroscopy of adsorbed CO (too small to be influenced by the pore walls in mordenite) shows a different ranking: sites in the large channels were slightly stronger than sites in side pockets [7]. On the other hand, using acetonitrile as a probe molecule, the same sites appeared stronger in the more confined side pockets (protonation observed) than in the large channels (no protonation detected) [8]. Confinement of acetonitrile in the restrained cavity also increases its residence time in the neighborhood of the acidic proton, further favoring the proton transfer to the probe molecule. So when immersed in a microporous material containing two widely different environments, acetonitrile behaves as two molecules with different (induced) basicity. Related effects with alkylamonium cations located in different zeolitic structures were reported by Eric Derouane in 1987 [9].

5. Quantifying the IR signal

It has been established above that changing the electric dipole moment will change acido-basic properties of the adsorbed molecule. It will also probably change its IR response, and that might cause another serious problem for spectroscopy. Indeed, the intensity of the infrared absorption band is directly linked to the change in the dipole moment with the vibration ($\delta\mu/\delta q$). If the constant value of the dipole is changed, its derivative is probably also affected. Therefore, the molar extinction coefficient (the intensity of the spectroscopic response) of a probe molecule can hardly be considered the same when adsorbed on silica and when adsorbed in the confined space of the zeolites pores... For *operando* spectroscopy, the quantitative aspect of the measurement is the condition for

a reliable kinetic interpretation of catalytic data. Spectroscopists have always been paying a lot of attention to quantitative reliability of their data, by comparing transmission and diffuse reflection, using Kubelka-Munk or absorbance units, working on the linearity of the detector, estimating the role of the particle size on the ratio between diffracted, diffused and transmitted light, and by carefully measuring extinction coefficients. . . but what if the same coefficient changes with the solid catalyst, its oxidation and hydration states, its temperature? A way around that difficulty is to record the weight of the sample together with its spectrum.

By combining a microbalance and a spectroscopic cell (an operando reactor-cell), we can collect valuable information on the state of the catalyst and adsorbates on its surface (Fig. 4). This AGIR technique (Gravimetric Analysis combined with InfraRed) was set up by combining an in-house IR reactor-cell (gas flow or vacuum, 450 °C$^+$) with a Setaram SETSYS microbalance (1 µg resolution). The sample in the reactor-cell is the usual 2 cm^2 20 mg self-supporting wafer, it is attached by a Pt sample holder and a Pt wire to the balance head.

To validate this new technique, a first test was performed on an ammonium zeolite, by following its calcination (dehydration and deammoniation). Fig. 5 shows the IR spectra and the mass recorded during the drying of the sample at room temperature under dry nitrogen, and during progressive heating to 400 °C.

With a coupled on-line analysis of the gases evolved from the reactor, a true operando technique is obtained, and catalytic activity and selectivity can be measured in real time. In the present simple observation of a decomposition and desorption, the advantages of the set-up are clearly visible, and the new technique has more value than the sum of three separate techniques. Fig. 6 shows an enlargement of the domain of interest in the three types of data, weight vs. temperature, on-line gas analysis, and spectra of the surface species. The weight loss for a 20 mg wafer was 2.5 mg, in two separate steps. The on line MS of the gases shows that the first step is only desorption of water, while ammonium is decomposed into ammonia in a second step, with some overlap, but not at the beginning of the experiment, when only water comes out.
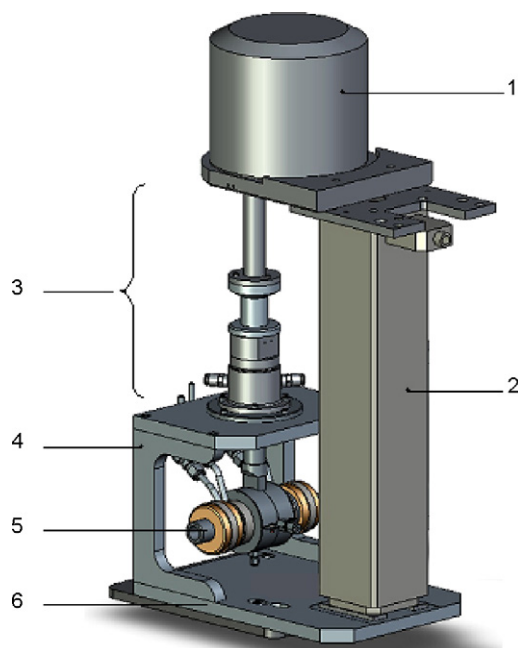

Fig. 4. General view of the AGIR system: 1, Setaram microbalance; 2, telescopic column; 3, connectors between the IR cell and the balance; 4, IR cell support; 5, IR cell; 6, stand.

Interestingly, the infrared spectrum shows that a band assigned to NH_4^+ is deeply modified even during the very first step, when only water leaves the zeolite channels. This shows that water is also adsorbed on the ammonium ion itself. The overall integrated intensity of the $\delta(NH_4^+)$ vibration band might only be slightly affected, but the position of the maximum intensity is very different, and adsorbed water thus influences greatly the extinction coefficient of the ammonium band. This is critical for operando spectroscopy. In the case of co-adsorbed species, especially when polar compounds
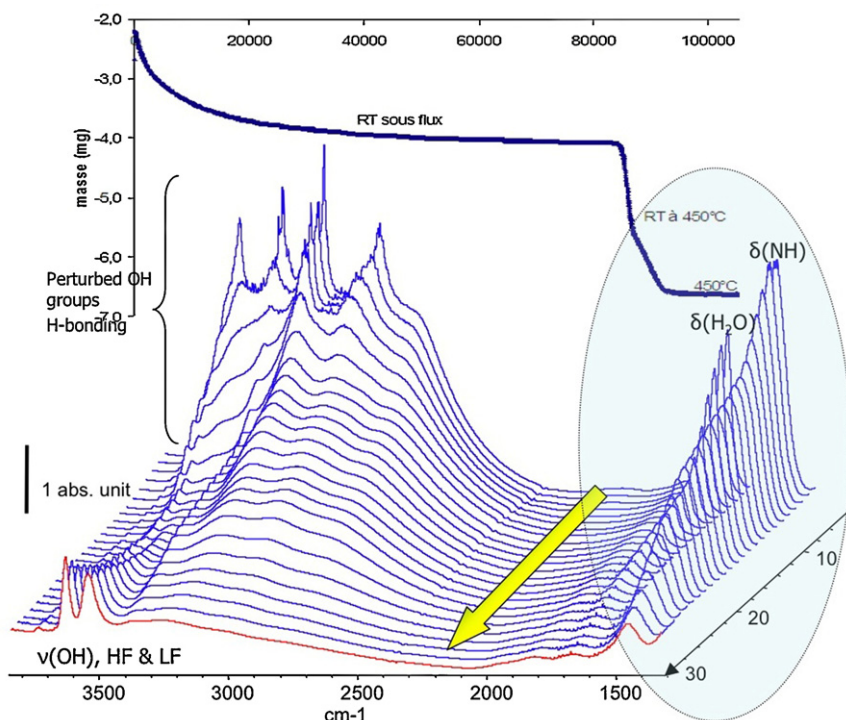

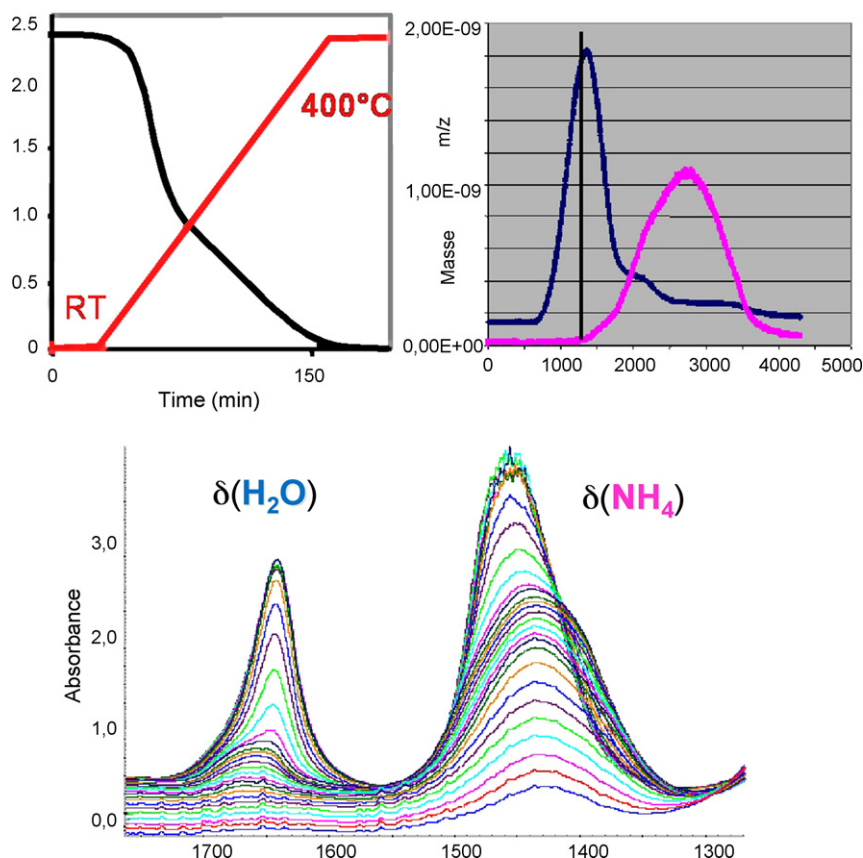**Fig. 5.** Mass loss and IR spectra recorded during the calcination of NH$_4$-Y zeolite between RT and 400 °C.

Fig. 6. AGIR data collected during the calcination of NH_4-Y zeolites. Top left: temperature and weight loss of the sample vs. time. Top right: on line MS analysis of the gases coming out of the reactor. Bottom: IR spectra in the H_2O and NH_4 region.

are present, the extinction coefficient of one surface species can vary strongly with the coverage of other surface species. This shows how much more care is needed for a quantitative interpretation of operando results, and AGIR could be a systematic test for a reliable description of a catalyst surface in working conditions.

Such an AGIR set-up has other interesting applications, and a great potential for catalysis. Coke for example does not lead to clear spectroscopic features in IR, but valuable information can be gained by a close and quantitative monitoring of the coking and decoking. Another potential application could be the quantitative monitoring of CO_2 mineralization, as well as complex co-adsorptions and desorptions. . .

6. IR operando spectroscopy [10]

Deactivation of acidic zeolites and coke formation can be studied by operando techniques and, although coke gives very little signal in infrared, valuable information can be obtained [11]. Two broad bands were identified at 1390 and 1595 cm^{-1}, depending on the nature of the coke laid down during ortho-xylene isomerization on an MFI zeolite. 2D-COS-IR (correlation spectroscopy, where synchronous and asynchronous spectra are recorded [12]) was used in this reaction to detect the formation of trace amounts of coke [13,14]. On the one dimension spectra, at high temperature, the signal becomes noisy, and no change is visible with time on stream (Fig. 7, top). The 2D-COS analysis reveals a change in the "coke" bands. This change is completely obscured by the intense xylenes bands in the same region, but is clearly detected in 2D correlation spectroscopy. Interestingly, this coke band has no correlation with the bands of the Brønsted acid sites, and no cross peak exists between 1596 and 3600 cm^{-1} on the 2D map. The intense cor-

relation peak at 1596 cm^{-1} is rather linked to the weak band at 3656 cm^{-1} (which at 300 °C corresponds to the room temperature peak at 3670 cm^{-1} for extraframework OH groups) and to a silanol ν(OH) vibration band at a fairly low frequency (3727 cm^{-1} at 300 °C, 3735 cm^{-1} at RT). These OH groups were shown to be due to silanols
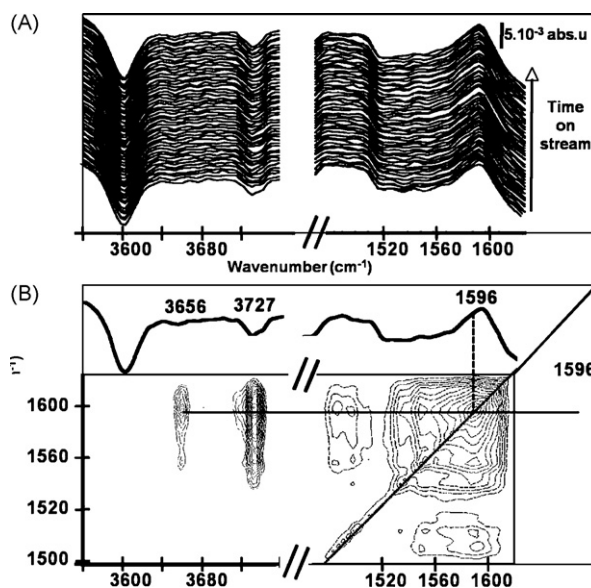

Fig. 7. 2D-COS (correlation spectroscopy) map of the spectra recorded during xylenes isomerization of xylenes on H-MFI zeolites at 300 °C. (A) 1D spectra recorded during 90 min at steady state. (B) 2D-COS analysis of the spectra on top, showing a diagonal peak at 1596 cm^{-1} (indicating a change in intensity) with cross peaks at 3656 and 3727 cm^{-1}.

in defect sites (silanol nests). 2D-COS-IR has thus allowed the detection of traces of coke formed on defect sites. This coke fills up the void created by the defect, and restores the perfect pore shape, inducing a high para-xylene selectivity on the catalyst, as observed during the full operando study [14].

7. Xenon NMR

Solid state NMR is the other spectroscopic technique often used in zeolite characterization. One of the very exciting developments of NMR is its ability to probe many fine features of zeolite porosity by ^{129}Xe NMR [15]. However, the intrinsically low sensitivity of ^{129}Xe NMR spectroscopy prevents the monitoring of fast processes such as diffusion.

The advent of operando NMR probes (flow through) and its combination with hyperpolarized ^{129}Xe [16] allows to combine higher spectral resolution and faster acquisition of the NMR signal. This in turn opens the door to more sophisticated NMR techniques, such as 2D exchange experiments; these allow the monitoring in a time scale between a few milliseconds to a few seconds. Some diffusion phenomena take place during such a time scale and can now be probed.

Fig. 8 illustrates the power of the technique on a typical Ferrierite zeolite. At room temperature and with a relatively modest spinning rate (3 kHz), the two environments of Xe are clearly identified, namely in the cavities (100 ppm) and inside the channels (135 ppm). The difference with the static or slow spinning samples is evident as well as the fact that most of the Xe detected is located inside the zeolite samples.

The potential of 2D exchange experiments is illustrated in Fig. 9, on an ITQ-6 sample, a delaminated zeolite of the Ferrierite family [16]. In these spectra, the presence of cross peaks after a given mixing time indicates that the exchange takes place between the gas phase and the inter-lamellar space, between cavities and inter-lamellar space, and finally between Xe in channels and the cavities. This gives a clear indication of the path followed by the Xe molecules: from the gas phase to the inter-lamellar space, to the surface cavities ("cups") en route to the microporous channels. On the one hand, a closer look at the experimental data can lead to more quantitative information on the dynamics of guest molecules in the host framework. On the other hand, the technique can also be broadened to characterize coked samples, or other strongly adsorbed molecules such as templates in the pores, the connectivity in unknown microporous structure, the creation of
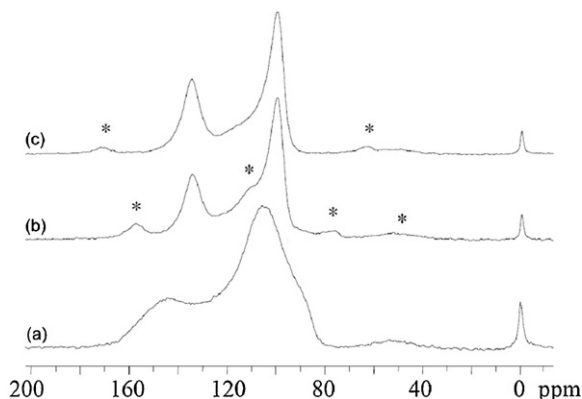
Fig. 9. ITQ-6 hyperpolarized Xe 2D-exchange spectrum obtained for a mixing time of 50 s. The sample was spun at a speed of 3 kHz. For each of the 256 increments 8 scans were acquired with a 2 s repetition delay. Cross peaks appear at positions characteristic of an exchange between (a) Xe adsorbed in inter-lamellar space and Xe gas in the free space of the rotor, (b) Xe adsorbed in cavities and in inter-lamellar space, and (c) Xe adsorbed in channels and cavities.

mesoporosity by various techniques, the effect of shaping on the accessibility of micropores...

8. Future needs and challenges

Such a brief survey can only give a glimpse of the potential of deeper insights in zeolite science in general. It can however be stated that a quantitative exploitation of these techniques will lead to a better characterization of zeolite catalysts or materials and in turn to an ever more rational design of these nanomaterials.

In addition, many challenges lie also ahead, such as:

- the recording of IR spectra of guest molecules in a working zeolitic catalysts with a better spatial and time resolution enabling for instance better kinetic analysis (SSITKA methodology combined with IR
- the parallel monitoring of the working zeolitic catalyst with complementary techniques (IR, Raman, NMR...) or the direct coupling of these techniques on the same material
- the characterization of shaped catalysts and the identification of its physical and chemical consequences

activation of molecules with non-traditional sources (laser, microwaves, plasma...). These are very demanding challenges, but even a partial and a slow success has the potential to bring new and sharper tools to the next generation of zeolitic scientists. Eric Derouane would have loved to participate in such endeavors, helped by his formidable intellect and innate creativity and also challenged us to go even further than thought feasible. He was not afraid of launching controversial concepts [17,18] but proved right long after [19]. He will be sorely missed.

Fig. 8. Hyperpolarized Xe spectra on ferrierite obtained with the MAS probe under a flow of 200 cm³ min⁻¹ of a 1% Xe mixture. The 128 scans were acquired with a 5 s repetition delay: (a) static sample, (b) at 2 kHz, (c) at 3 kHz. Isolated Xe atoms in cavities appear around 100 ppm, and Xe atoms in channels appear at 135 ppm. The line close to 0 ppm is due to the gas phase. Spinning sidebands are marked with asterisks.
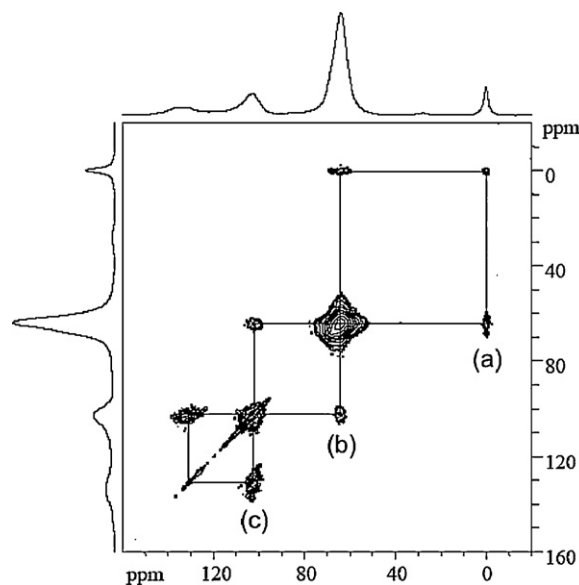
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