SOLID-STATE NMR SPECTROSCOPY OF POROUS MATERIALS

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ABSTRACT

Zeolites and zeolite-like porous materials, known for several decades, and metal-organic framework (MOF) materials, a new type of porous materials, are two extremely interesting families of materials that exhibit promising properties for several fields of application including ion-exchange, catalysis, separation, gas and heat storage, sensing and drug delivery. Nuclear magnetic resonance (NMR) spectroscopy has in many cases played a crucial role in understanding of the formation of this type of materials, in their detailed structural description, and especially in elucidation of the interactions of the porous frameworks with the guest molecules. In this contribution fundamental characteristics of solid-state NMR spectroscopy shall be presented and application of this spectroscopy to the porous materials prepared in the Laboratory of Inorganic Chemistry and Technology at National Institute of Chemistry shall be reviewed.

Keywords: zeolites, metal-organic frameworks, solid-state NMR spectroscopy, drug-delivery, heat storage

INTRODUCTION

Microporous and mesoporous materials are materials with ordered systems of pores with diameters between several tenths of nm and several nm, are becoming more and more interesting for a variety of applications. At first they were important mostly in the field of ion-exchange and catalysis, where they were extremely efficient in oil refinement. Lately, however, also other possibilities of their applications have emerged. Microporous and mesoporous materials are investigated for their potential in drug delivery [1-5], in gas separation and storage [6-8] and in heat storage applications [9, 10].

Two of the most studied families of microporous and mesoporous materials are zeolitic porous materials [11] and metal-organic framework porous materials [12]. In the first family of materials the inorganic framework is built of SiO_4 tetrahedra (in silicates) or of alternating AlO_4 and PO_4 tetrahedra (in aluminophosphates) and is predominantly microporous and quite rigid. In the second family of materials the framework is built of metallic centers that are connected one to another through organic molecules. The diversity of coordination geometries for mostly transition metal centers and the even larger variety of organic ligands give rise to almost endless possibilities for the preparation of various metal-organic porous materials. These materials are characterized by large specific surfaces of their frameworks, by large pore volumes, and consequently by low mass densities. Unlike silicate or aluminophosphate frameworks, metal-organic frameworks are often very flexible.

On the way to application of the above described materials several difficulties are encountered. One of them is the instability of the frameworks upon the activation of materials, that is upon their preparation for application. The as-prepared porous materials namely usually contain solvent molecules or molecules that direct the formation of porous frameworks. Before application of the materials, these structure directing and solvent molecules have to be removed from the pores. Unfortunately, sometimes their removal leads

to unwanted rearrangement of the framework or even to the destruction of the porous system. The frameworks, especially the metal-organic ones, are also often very sensitive to hydration. Repeating hydration and dehydration can also lead to the destruction of the porous system. The second difficulty is that guest molecules within the pores of zeolitic or metal-organic materials, that is drug molecules within the drug-delivery systems, water molecules within the sorption-based heat-storage systems, and gas molecules within the materials for gas separation and storage, are either bonded too weakly and therefore subjected to uncontrolled release from the pores or bonded too strongly to the framework adsorption sites so that one cannot release them from the pores at required conditions. To resolve the above described difficulties, that is to be able to control the strength of the bonds between the guest molecules and the framework, detailed investigation of the location of the adsorbed molecules needs to be conducted, and the interactions of these molecules with the framework and the dynamics of the molecules have to be studied.

Very often the information about the molecules embedded within the micropores or mesopores as obtained by diffraction-based techniques is not very rich. Experimental techniques that probe the short range arrangement of atoms are usually more informative. One of the most powerful tools for studying structural properties and interactions at the atomic level, for ordered as well as disordered materials, is nuclear magnetic resonance [13]. The NMR spectra reflect the changes in local conformations of molecules and probe the couplings among the nuclei. These properties help us to study interactions between the framework and the adsorbed molecules. Advanced, more demanding NMR techniques enable the determination of distances among the constituents of the material and thus help us to locate the molecules within the pores. NMR allows also the monitoring of dynamics and diffusion of the embedded molecules.

In the following text three examples of the application of solid-state NMR spectroscopy to the above discussed problems shall be presented. In the first example NMR was used for the elucidation of the removal of solvent dimethylformamide (DMF) molecules from the Ca-based MOF. In the second example NMR measurements revealed the detailed mechanism of a step-wise removal of water from the hydrothermally stable Zn-based MOF; this MOF is stable to several tens of dehydration-rehydration cycles. The third example presents the potential of solid-state NMR spectroscopy for studying drug-delivery systems; in particular, incorporation of model drug indomethacin into two MOFs, MIL-101 and MIL-53, and into mesoporous silicate SBA-15 was studied.

EXAMPLE 1: Removal of DMF from Ca-based MOF

Upon heating Ca(BDC)(DMF)(H_2O) metal-organic framework undergoes structural changes in two steps [14]. The first change occurs at 150 °C, when bonds of Ca centres with H_2O and DMF molecules are broken. At this temperature DMF is expelled from the outer shell of the crystallites and the shell is quickly transformed to non-porous DMF-free CaBDC phase. The non-porous shell prevents the diffusion of DMF from the cores of the crystallites; DMF molecules in the cores thus remain trapped within the pores of the material, but are no longer attached to Ca centres. The second change occurs at 400 °C, when also the cores of the crystallites are transformed to the CaBDC phase. The removal of DMF from the cores becomes possible due to the cracking and breaking of the crystallites. The obtained CaBDC material can be reversibly transformed to pseudo 3-dimensional Ca(BDC)(H_2O)$_3$ metal-organic framework upon exposure to humid environment. ^{1}H-^{13}C CPMAS, ^{1}H CRAMPS and 2D ^{1}H-^{1}H homonuclear correlation NMR experiments helped us to propose the mechanisms of CaBDC(RT) → CaBDC and CaBDC → Ca(BDC)(H_2O)$_3$ transformations [14]. The mechanisms include breaking of the bonds between Ca centres and carboxylate groups,

rotating of BDC ligand and re-coordination of carboxyl groups to Ca centers. Thus the decrease of Ca coordination number leads to pronounced changes in the framework connectivities. Such behavior can explain the lack of porosity in Ca-based MOFs.

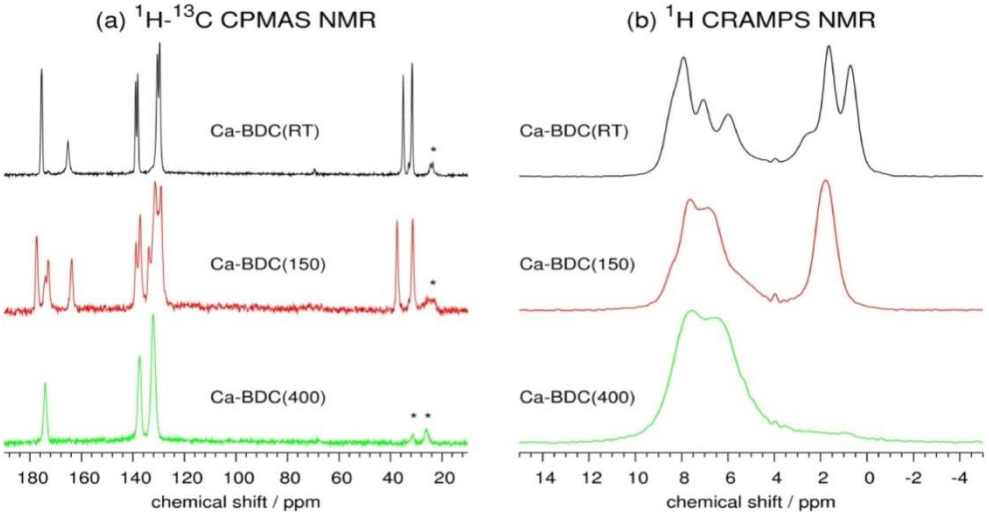

Figure 1. ^{1}H-^{13}C CPMAS (a) and ^{1}H CRAMPS (b) NMR spectra of as-prepared and thermally treated Ca-BDC material. The spectra indicate that the framework is rearranged during heating, that the environment of DMF molecules is changed upon heating to 150 °C, and that DMF is entirely removed upon heating to 400 °C. Additional information about the detachment of DMF from Ca centres was obtained by ^{1}H-^{1}H 2D NMR correlation experiment.

EXAMPLE 2: Desorption of water from Zn-based MOF

Zinc trimesate $Zn_2(BTC)(OH)(H_2O).1{,}67H_2O$ exhibits three-dimensional framework built of $[Zn_2O_6(OH)_2(H_2O)]$-based chains linked with 1,3,5-benzenetricarboxylates. The framework forms two types of parallel channels, open and closed ones. The two types of channels contain non-framework water molecules in somewhat different environments. In the closed channels the non-framework (adsorbed) water molecules are bonded with the framework (coordinated to Zn centres) water molecules through strong hydrogen-bonds. In the open channels non-framework water molecules are not involved in hydrogen bonds. The location of water molecules and the dynamics of their removal from the open and closed channels during heating was asessed by ^{1}H, ^{2}H MAS and ^{1}H-^{13}C CPMAS NMR experiments and was additionaly supported by thermogravimetric analysis [15]. The experiments showed that the removal of water from the open channels occurs below 100 °C, whereas the hydrogen-bonded water molecules and the coordinated water molecules are expelled from the pores at higher temperature of about 150 °C. ^{2}H MAS NMR showed that the removal of the latter type of water was not entirely simultaneous and that the adsorbed water begins to diffuse out of the pores at slightly lower temperature than the coordinated one. The experiments also demonstrate that structural changes of the Zn-based MOF upon dehydration/hydration are reversible up to 200 °C.

EXAMPLE 3: Characterization of drug-delivery systems with indomethacin

Solid-state NMR spectroscopy provides a unique tool for studying the structural properties of the mesoscopically confined drug, and for studying the drug-drug and drug-matrix interactions. We demonstrated this in model drug-delivery systems prepared from non-functionalized and functionalized SBA-15 mesoporous silicate matrices [15,16], Cr-, Fe-, and Al-based MIL-101 metal organic frameworks, and Al-based MIL-53 metal organic frameworks, loaded with different amounts of indomethacin molecules.

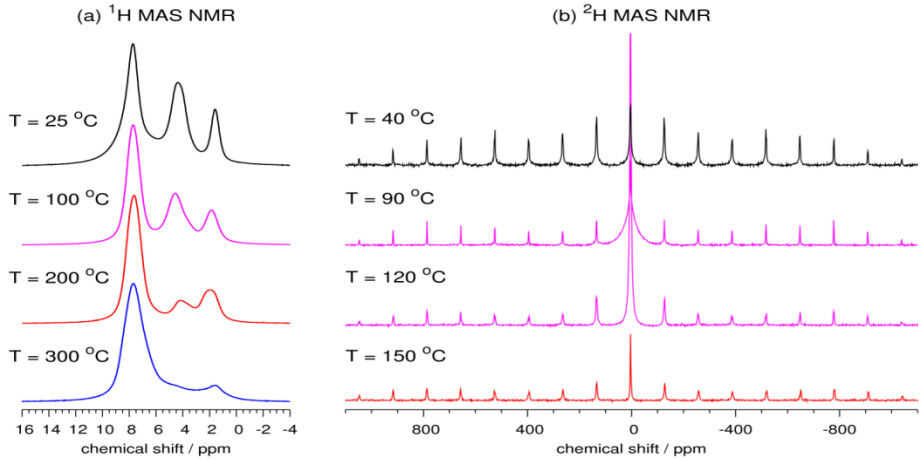

Figure 2. ^{1}H (a) and ^{2}H (b) MAS NMR spectra of $Zn_2(BTC)(OH)(H_2O)\cdot 1{,}67H_2O$. Thermal treatment of the sample for the ^{1}H MAS NMR measurement was performed ex-situ and thermal treatment of the sample for the ^{2}H MAS NMR was carried out in-situ within the NMR probe. ^{1}H NMR spectra provide quantitative information about the removal of water molecules. ^{2}H NMR spectra, exhibiting typical quadrupolar sideband pattern, provide additional information on the dynamics of water molecules.

In the SBA-15-based drug-delivery systems ^{1}H MAS and ^{1}H-^{13}C CPMAS NMR spectroscopy indicated that only when concentration of indomethacin within the mesopores becomes sufficiently high (when the mass fraction of indomethacin within the sample exceeds 0.15), hydrogen bonds between the drug molecules become abundant. Nitrogen sorption analysis and comparison of ^{1}H spin-lattice relaxation times in progressively loaded SBA-15 matrices suggested that at low loading concentrations indomethacin forms a layer on the silicate walls of the mesopores, and that at moderate or high loading concentrations rigid nanoparticles that extend throughout the entire mesopore cross-section are formed. ^{1}H-^{13}C CPMAS NMR spectrum of indomethacin embedded within the mesopores of SBA-15 closely resembled the spectrum of the bulk amorphous indomethacin and did not allow to draw firm conclusions about the molecular conformation and the packing of the drug molecules within the pores. On the contrary, variable-temperature ^{1}H spin-lattice relaxation measurements showed that the mesoscopically confined indomethacin is significantly different from the bulk amorphous indomethacin. It does not become rubbery and it exhibits a solid-solid transition at 363 K that is similar to the phase transition of the crystalline indomethacin solvate with tetrahydrofuran. In MIL-101- and MIL-53-based drug-delivery systems, in addition to the structural and dynamical information about the incorporated indomethacin molecules, ^{1}H MAS and ^{1}H-^{13}C CPMAS NMR experiments provided a very convenient way for the determination of the amount of the loaded drug (Figure 3).

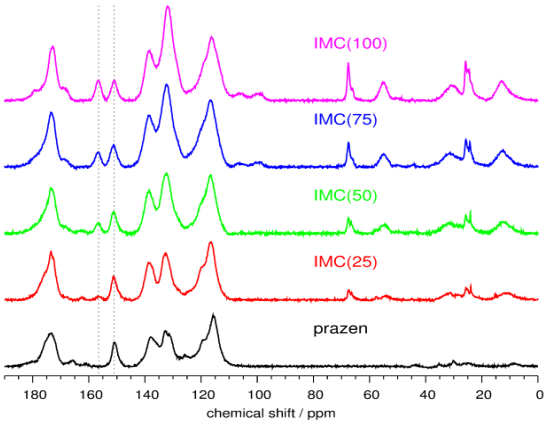

Figure 3. ^{1}H-^{13}C CPMAS NMR spectra of Al-MIL-101/IMC drug-delivery systems. The systems contain different amounts of drug (IMC). The dotted lines denote two well-resolved signals of IMC (the left signal) and

Al-MIL-101framework (the right signal). The spectra show that the fraction of the drug within the drug-delivery system can be very well controlled. Quantitative analysis of the spectra allowed us to determine the fraction of IMC within the Al-MIL-101/IMC drug-delivery systems.

CONCLUSION

We hope that this short contribution shows that solid-state NMR spectroscopy is a powerful technique for the characterization of porous materials. In addition to structural details about the framework, solid-state NMR spectroscopy can often yield the information about the structural properties of the guest molecules embedded within the pores and about the interactions of these molecules with the framework.

REFERENCES

[1] M. Vallet-Regi, *Chem. Eur. J.*, 2006, **12**, 5934-5943.

[2] M. Vallet-Regi, F. Balas, and D. Arcos, *Angew. Chem. Int. Ed.*, 2007, **46**, 7548-7558.

[3] P. Horcajada, T. Chalati, C. Serre, B. Gillet, C. Sebrie, T. Baati, J. F. Eubank, D. Heurtaux, P. Clayette, C. Kreuz, J.-S. Chang, Y. K. Hwang, P.-N. Bories, L. Cynober, S. Gil, G. Férey, P. Couvreur, and R. Gref*et al.*, *Nature Mater.*, 2010, **9**, 172-178.

[4] A. C. McKinlay, R. E. Morris, P. Horcajada, G. Ferey, R. Gref, P. Couvreur, and C. Serre, *Angew. Chem. Int. Ed.*, 2010, **49**, 6260-6266.

[5] R. C. Huxford, J. Della Rocca, and W. Lin, *Curr. Opin. Chem. Biol.*, 2010, **14**, 262-268.

[6] Z.-S. Bae and R. Q. Snurr, *Angew. Chem. Int. Ed.*, 2011, **50**, 11586-11596.

[7] J.-R. Li, J. Sculley, and H.-C. Zhou, *Chem. Rev.*, 2012, **112**, 869-932.

[8] P. Nugent,Y. Belmabkhout, S. D. Burd,A. J. Cairns, R. Luebke, K. Forrest,T. Pham, S. Ma, B. Space, L. Wojtas, M. Eddaoudi, and Michael J. Zaworotko, *Nature*, 2013, 495, 80-84.

[9] S. K. Henninger, F. Jeremias, H. Kummer, and C. Janiak, *Eur. J. Inorg. Chem.*, 2012, 2625-2634.

[10] A. Ristić, N. Zabukovec Logar, S. K. Henninger, and V. Kaučič, *Adv. Funct. Mater.*, 2012, **22**, 1952-1957.

[11] M. E. Davis and R. F. Lobo, Chem. Mater, 1992, 4, 756-768.

[12] G. Ferey, *Chem. Soc. Rev.*, 2008, **37**, 191-214.

[13] A. Sutrisno and Y. Huang, *Solid State Nucl. Magn. Reson.*, 2013, **49-50**, 1-11.

[14] M. Mazaj, G. Mali, M. Rangus, E. Žunkovič, V. Kaučič, and N. Zabukovec Logar, submitted to *J. Phys. Chem. C*, 2013.

[15] T. Ukmar, A. Godec, O. Planinšek, V. Kaučič, G. Mali, and M. Gaberšček, *Phys. Chem. Chem. Phys.*, 2011, **13**, 16046-16054.

[16] T. Ukmar, T. Čendak, M. Mazaj, V. Kaučič, and G. Mali, *J. Phys. Chem. C*, 2012, **116**, 2662-2671.