

NMR Investigations of Nanostructured Ceramics

M. Edgar, M. Schubert, H.H. Limbach, and C.G. Göltner¹⁾

Institut für Organische Chemie, Freie Universität Berlin, Takustr. 3, D-14195 Berlin, Germany

¹⁾ Max-Planck-Institut für Kolloide und Grenzflächen, Kantstr. 55, D-14513 Teltow/Seehof, Germany

Key Words: Adsorption / Mesoporous / Spectroscopy, Nuclear Magnetic Resonance / Surface

Nanostructured mesoporous silicates displaying hexagonally arranged channels, templated using a liquid crystal mesophase, were investigated using H-2 and N-15 NMR spectroscopy. It is shown that N-15 MAS NMR spectroscopy allows to estimate the surface acidity of mesoporous materials by measuring the N-H bond length via the N-15 chemical shift. Further, H-2 and N-15 NMR spectroscopy identify significant differences between the structure of the surface area of H₁ silica and MCM-41. Static N-15 NMR spectroscopy was used to differentiate between pyridine located in channels perpendicular to the magnetic field from, for example, pyridine located in channels orientated parallel to the field. This observation offers the possibility of separating the NMR signals and thus pursuing the goal of "liquid phase single crystal NMR spectroscopy".

1. Introduction

A number of alternative routes to the formation of nanostructured ceramic oxides [1, 2] have been discovered since the first mesoporous silica was synthesised in 1992 [3]. One versatile, and well understood, templating approach using liquid crystal mesophases has allowed the formation of nanostructured ceramics [4], polymers [5] and metals [6]. Deuterium NMR spectroscopy has proven to be a valuable tool in determining the templating mechanism responsible for the formation of the nanostructured ceramic H₁ silica [7] (a mesoporous silica displaying a regular hexagonal array of channels, formed from a H₁ non-ionic surfactant liquid crystalline phase). In addition, deuterium NMR spectroscopy has been used to investigate the molecular motion and surface-solvent interactions of organic probe molecules adsorbed onto nanostructured ceramics [8, 9]. These investigations highlighted significant differences in the ratio of intra- to extrachannel surface area (intra: surfaces within the cylindrical channels, extra: external, defect surfaces) between H₁ silica and the classic MCM-41 material, with the latter possessing much less intrachannel surface. This finding has important repercussions for the application of nanostructured ceramics to the cracking of large hydrocarbons (which are too big to be accommodated inside microporous zeolite catalysts) as the required chemistry depends on Brønsted acid-base interactions occurring on intrachannel surface area.

In order to further understand the nature of the solvent-surface (acid-base) interactions, N-15 NMR spectroscopy has been used to investigate N-15-labelled pyridine adsorbed onto nanostructured H₁ silica and aluminium silicate. It is known that the N-15 chemical shift correlates to the N-H hydrogen bond length for a series of acid-base complexes [9]. Therefore, monitoring the N-15 chemical shift allows one to estimate the N-H distance and thus the acidity or proton-donating power of surfaces. To demonstrate this application, using two samples displaying different acidity (H₁ silica and aluminium silicate), are compared.

2. Experimental

The nanostructured ceramics were prepared according to the classic method described by Attard et al. [1]. Samples

for the NMR measurements were dried at 150 °C under high vacuum (10⁻⁷ bar) for 24 h inside a 7 mm glass MAS (magic angle spinning) NMR insert (Spintec). An exact amount of dry N-15-labelled pyridine (Chemotrade) was condensed onto the sample, and then the glass insert was flame-sealed while cooled in liquid nitrogen. An amount of 8.1 mg pyridine was adsorbed onto 70 mg H₁ silica (1), and 6.2 mg pyridine was adsorbed onto 52.5 mg aluminium silicate (2). The N-15 NMR spectra were recorded at ambient temperature on a Bruker MSL-300 instrument employing a Bruker 7 mm MAS NMR probe, with typical spinning speeds of 4 kHz.

3. Results

The N-15 MAS NMR chemical shift of pyridine adsorbed onto H₁ silica displays a high field shift of 24.5 ppm (44 Hz half height line width) from bulk liquid pyridine, while pyridine adsorbed onto aluminium silicate displays a larger high field shift of 37.2 ppm (249 Hz halfheight line width). These spectra are displayed together with the static N-15 NMR spectrum of bulk pyridine recorded with a MAS probe (Fig. 1).

The static N-15 NMR spectrum of pyridine adsorbed onto H₁ silica (Fig. 2) displays two signals: i) a Lorentzian line shape, ii) a signal which can be fitted with a CSA line shape (note: this line shape is an ensemble of shifts arising from pyridine-located channels which are orientated between perpendicular and parallel to the magnetic field, and thus displaying a different average shielding or deshielding shift anisotropy). The static N-15 NMR spectrum of pyridine adsorbed onto MCM-41 (Fig. 2) displays an intense Lorentzian line shape and a very low intensity CSA line shape.

4. Discussion

4.1 The Influence of Surface Acidity on N-15 NMR Chemical Shifts

The N-15 chemical shift difference between bulk liquid pyridine and its protonated form covers a range of 105 ppm [11], as such it serves as a sensitive indicator of acidity. This property, which was first used by Haw and Maciel et al. in

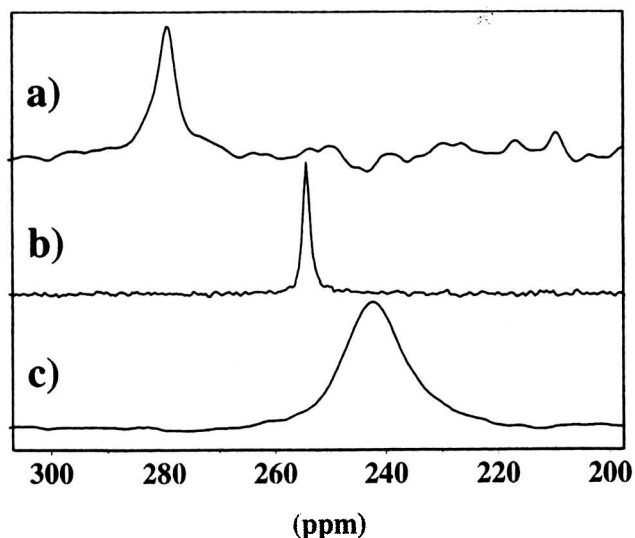


Fig. 1
Comparison of the MAS N-15 NMR chemical shifts of N-15-labelled pyridine: a) bulk liquid (static), b) 8.1 mg pyridine adsorbed onto 70 mg H_1 silica, c) 6.2 mg pyridine adsorbed onto 52.5 mg aluminium silicate

1981 [12a], has been used extensively in several NMR spectroscopy surface investigations of zeolites [12b–d], and is covered in a number of general reviews [13a–c]. In the present work, MAS N-15 NMR spectra of pyridine adsorbed on to H_1 silica are compared with those of pyridine adsorbed onto aluminium silicate (Fig. 1).

Pyridine forms a hydrogen bond with the Si-OH groups on the surface of H_1 silica via the nitrogen lone pair of electrons (N–H–O). At room temperature these hydrogen bonds are readily broken and reformed as a result of rapid jumps of the pyridine molecules between Si-OH sites, thus the spectra represent the rapid exchange regime. Therefore, a single N-15 NMR chemical shift is obtained representing an ensemble average over a range of acidic Si-OH sites. For H_1 silica the 24.5 ppm high field chemical shift, relative to pyridine, shows that a weak hydrogen bond is formed with the surface Si-OH groups. In principle, it is possible to measure the N-15 MAS chemical shifts of pyridine, permanently bound to Si-OH sites (slow exchange regime), by cooling the sample. Such spectra will directly display the range of Si-OH acidities. It has not been possible to measure low temperature MAS NMR spectra due to difficulties involved in obtaining stable sample spinning for the long experiment times required to acquire a sufficient signal-to-noise ratio. Nevertheless, useful qualitative indications of the surface acidity have been gained from room temperature measurements.

The N-15 MAS NMR chemical shift of pyridine adsorbed onto aluminium silicate displays a single broad signal 37.2 ppm high field from bulk liquid pyridine. As this represents the ensemble average of chemical shifts over all the acidic surface sites, it clearly reveals a wider range of acidic sites, relative to H_1 silica, with a significant contribution from strongly acidic Si-OH and Si-OH(Al) groups. It was not possible to determine whether Brønsted acid sites were

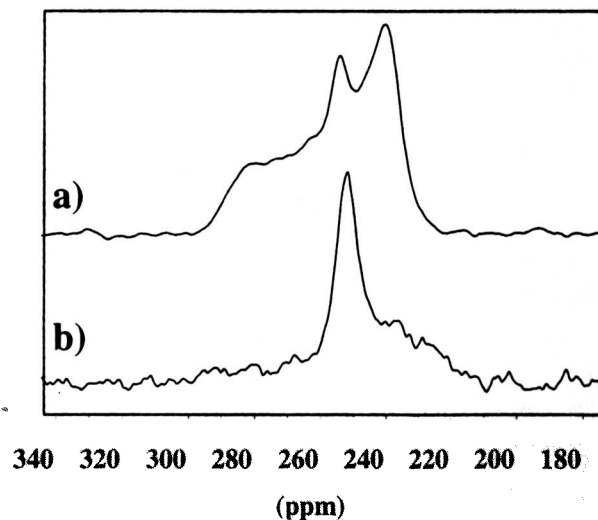


Fig. 2
Comparison of the static N-15 NMR spectra of N-15-labelled pyridine adsorbed onto: a) H_1 silica, b) MCM-41

present in this sample. Although, the Al-27 MAS NMR spectra revealed only tetrahedrally coordinated aluminium to be present in this sample [14]. Further evidence for the formation of stronger hydrogen bonds at the surface of aluminium silicate is available from the halfheight width of the N-15 MAS NMR signal. Even at room temperature this signal is broad (compared to H_1 silica) and thus reflects the reduction in the rate of jumping from acidic site to acidic site, and so indicates that molecular motion is closer to the slow exchange regime.

A tentative extrapolation of the available N-15 NMR data, combined with the known correlation between N-15 chemical shift and N–H hydrogen bond length [10], provides N–H distances in the range of $2.0 \pm 0.3 \text{ \AA}$ for H_1 silica and $1.6 \pm 0.3 \text{ \AA}$ for this aluminium silicate.

4.2 The Influence of Confinement Within Nanoscale Channels

Static H-2 NMR spectra of an organic solvent adsorbed onto the surface of H_1 silica (Fig. 3) clearly identify two distinct molecular motions. Molecules adsorbed onto intrachannel surface undergo anisotropic rotation coupled with translational diffusion and give rise to a Pake pattern, while molecules adsorbed onto extrachannel surfaces undergo isotropic rotation coupled with translational diffusion and give rise to a Lorentzian line (Fig. 4). As expected, basic molecules such as pyridine- d_5 display a stronger interaction with the surface and therefore a more anisotropic motional behaviour than less basic molecules such as benzene- d_6 [8]. A comparison between the static H-2 NMR spectra of pyridine- d_5 adsorbed onto H_1 silica and MCM-41 shows that the intrachannel surface area of H_1 silica, as displayed by the Pake pattern, is dominant (Fig. 3a), while it is the extrachannel surface area of MCM-41, as displayed by the isotropic signal, which is dominant (Fig. 3b).

The N-15 static NMR spectrum of N-15 labelled pyridine adsorbed onto H_1 silica (Fig. 2) displays two signals, arising

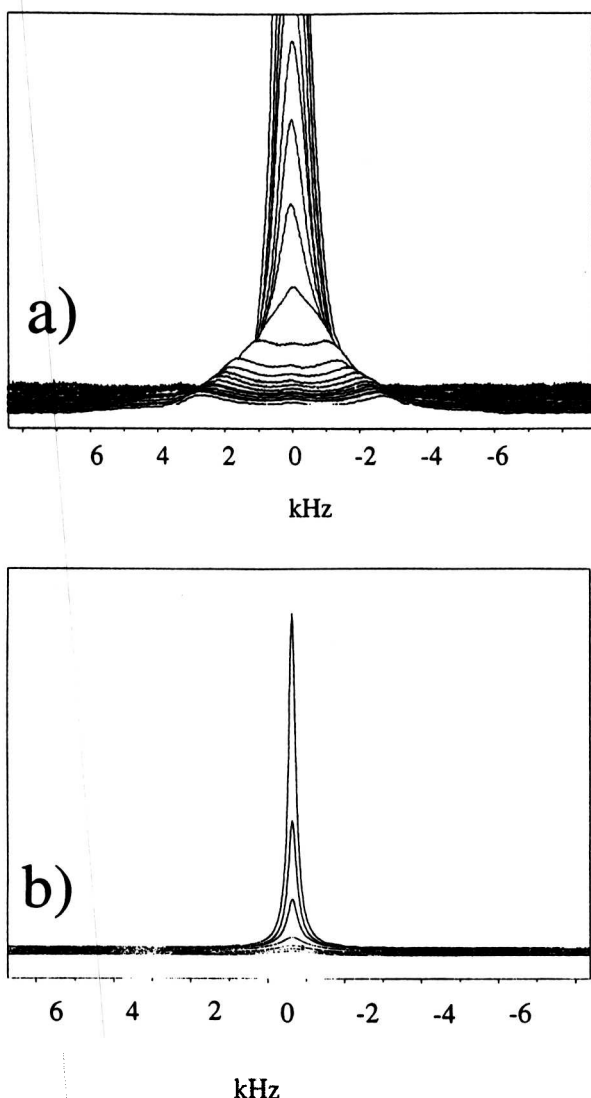


Fig. 3
A comparison of the deuterium NMR spectra of pyridine- d_5 adsorbed onto: a) H_1 silica, b) MCM-41

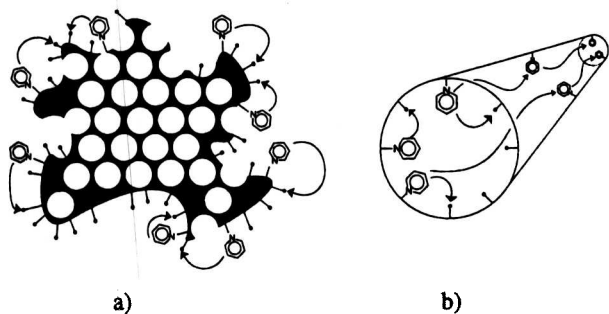


Fig. 4
A scheme showing the jump motion of pyridine: a) on extrachannel surface, which gives rise to an isotropic NMR signal, b) on intrachannel surface, which gives rise to an anisotropic NMR signal

om intra- and extrachannel solvent-surface interactions. This supports the results from the deuterium NMR investigations and also provides additional information. The distinct 'CSA' line shape reflects the anisotropic rotational

motion coupled with translational diffusion, however, this line shape is an ensemble of many signals and is not a single CSA pattern. The origin of these multiple signals are explained using the following argument, which assumes that there is a limited number of molecular orientations possible within any given channel. Take for example a single channel, orientated perpendicular to the external magnetic field [15], and observe only the shielding tensor lying along the N-H-O hydrogen bond. Jumping of pyridine molecules from one acidic site to the next, around the circumference of the channel, will average the tensor, while translational diffusion along the channel will have no net effect on the magnitude of the tensor. Identical jumping and translational diffusion behaviour within a channel orientated parallel to the magnetic field will, for the shielding tensor lying along the N-H-O bond, produce no net averaging of the tensor at all. Despite the simplicity of this argument, which assumes smooth surfaces and ignores the complicating influence of transition states, as well as 'free' (non-bound) pyridine and the orientation of the pyridine molecules to the surface, it shows how the averaging of the shielding tensors of nitrogen depend on the relative orientation of the channel to the magnetic field.

Fig. 2 displays the N-15-static NMR spectrum of pyridine adsorbed onto MCM-41. Despite the reported similarity of the nanostructures of H_1 silica and MCM-41, the spectra are in stark contrast to one another. The dominant feature of the latter spectrum is an intense Lorentzian line shape produced as a result pyridine moving on extrachannel surface. Underlying this signal is a very weak CSA line shape. The reason behind the differences observed between these NMR spectra is the relative ratio of intra- to extrachannel surface area. The H-2 and N-15 NMR results show conclusively that the proportion of intrachannel surface area in MCM-41 is significantly less than for H_1 silica.

5. Conclusion and Outlook

The acidity of the surface of two materials have been estimated in terms of an N-H bond distance determined using the N-15 MAS NMR chemical shift as a measure. More favourable probe molecules are currently being investigated which should enter the slow exchange regime at more readily accessible temperatures, yet also display the same N-15 chemical shift dependence on the acidity.

Significant and important differences were observed between the NMR spectra of pyridine adsorbed onto the surfaces of H_1 silica and MCM-41. These indicate that the relative intrachannel surface area of MCM-41 is very much smaller than for H_1 silica. As such, this has important consequences for the application of these mesoporous materials as catalysts, which depend directly on the quality and quantity of nanostructured surface area.

The NMR results may now enable a new technique to be developed. As it is possible to differentiate between pyridine located in channels orientated, for example, parallel and perpendicular to the magnetic field, then it should also be possible to separate their NMR signals. This represents an

unique opportunity to pursue the goal of "liquid phase single crystal NMR spectroscopy".

The Alexander von Humboldt Fellowship is gratefully acknowledged for providing a Humboldt Stipendium (M.E.). In addition, we would like to take this opportunity to thank G. S. Attard and J. W. Emsley for their useful and encouraging discussions throughout the course of this piece of work.

References

- [1] G.S. Attard, J.C. Glyde, and C.G. Göltner, *Nature* **378**, 366–368 (1995).
- [2] M. Antonietti and C.G. Göltner, *Angew. Chem. Intl. Ed. Engl.* **36**, No. 9 (1997).
- [3] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, and J.S. Beck, *Nature* **359**, 710–712 (1992).
- [4] M.C. Weissenberger, C.G. Göltner, and M. Antonietti, *Mesopore Monolithe aus Polymeren Flüssigkristalltemplaten*, Bunsentagung, Darmstadt 8th–10th May 1997.
- [5] H. Hentze, C.G. Göltner, and M. Antonietti, *Herstellung von Polymergelen in Lyotropen Mesophasen und Mikroemulsionen*, Bunsentagung, Darmstadt 8th–10th May 1997.
- [6] G.S. Attard, C.G. Göltner, S. Henke, J. Corker, and R. Templer, *Angew. Chem.* in press, 1997.
- [7] G.S. Attard, M. Edgar, J.W. Emsley, C.G. Göltner, *The True Liquid Crystal Approach to Mesoporous Silica*, in: *Liquid Crystals for Advanced Technologies*, MRS, Proc. 425 (1996).
- [8] G.S. Attard, M. Edgar, J.W. Emsley, C.G. Göltner, *Deuterium NMR Spectroscopy of Solvents Adsorbed to the Surface of Mesoporous Silica*, in: *Liquid crystals for Advanced Technologies*, MRS Proc. 425 (1996).
- [9] G.S. Attard, C.G. Göltner, and M. Edgar, *Acta Mater.* accepted, 1997.
- [10] Private communication: H.H. Limbach, N.S. Golubev, and P. Lorente, Institut für Organische Chemie, Freie Universität Berlin, D-14195 Berlin, Germany.
- [11] S. Berger, S. Braun, and H. Kalinowski, *NMR-Spektroskopie von Nichtmetallen*, NMR Spektroskopie, Georg Thieme, Stuttgart, 1992.
- [12] a) G.E. Maciel, J.F. Haw, I. Chuang, B.L. Hawkins, T.A. Early, D.R. McKay, and L. Petrakis, *J. Am. Chem. Soc.* **105**, 5529 (1983); b) J.A. Ripmeester, *J. Am. Chem. Soc.* **105**, 2925 (1983); c) P.D. Majors and P.D. Ellis, *J. Am. Chem. Soc.* **109**, 1648 (1987).
- [13] a) H. Pfeifer, W. Meiler, and D. Deininger, *Annual Reports of NMR Spectroscopy*, Vol. 15, ed. by G.A. Webb, 1983; b) E. Brunner, *J. Mol. Struct.* **355** (1995); c) J.M. Griffiths and R.G. Griffin, *Analytica Chim. Acta* **283**, 1081 (1993); d) J. Klinowski, *Analytica Chim. Acta* **283**, 929 (1993).
- [14] M. Edgar, J.W. Emsley, G.S. Attard, and C.G. Göltner, unpublished results.
- [15] D. Schweitzer and H. W. Spiess, *J. Mag. Reson.* **15**, 529 (1974).

Presented at the 96th Annual Meeting of the Deutsche Bunsen-Gesellschaft für Physikalische Chemie "Physikalisch-chemische Eigenschaften nanostrukturierter Systeme" in Darmstadt, May 8th to 10th, 1997 E 9671