Characterization of carbon-containing catalysts by ¹³C solid-state NMR

Spectroscopic background: ¹³C nuclei have a spin of I = 1/2 and, therefore, no quadrupole moment. The ¹³C isotope has a natural abundance of 1.1 % and, in this state, a sensitivity of 1.7 x 10⁻⁴ in comparison with ¹H nuclei (1.0). Therefore, it is at the limit for solid-state NMR studies being possible to investigate without isotopic enrichment. For basic principles of solid-state NMR, see lectures "Solid-State NMR Spectroscopy" for Bachelor students or PhD seminars, accessible via the link "Lectures for Students".

¹³C NMR spectroscopy has the advantage of a **broad range of chemical shifts** with characteristic shift values for specific chemical compounds (see **Fig. 1**) [1, 2]. While the ¹³C NMR spectra of liquids consist of very narrow signals allowing the detailed identification of organic compounds, ¹³C nuclei of solids cause broad ¹³C NMR signals, mainly due to chemical shift anisotropy. Therefore, ¹³C NMR spectroscopy of solids requires application of the MAS technique to average this interaction. Furthermore, to improve the signal-to-noise ratio, often the **cross polarization (CP) technique** is utilized in combination with MAS (see "method 10"). For removing the residual dipolar ¹H-¹³C coupling, high-power ¹H decoupling is additionally applied during recording the ¹³C induction decay.



Fig. 1

In nature, **microporous silicates and aluminosilicates** are formed without any organic structure directing agent (SDA). However, most of the zeolites, synthesized in laboratories or in an industrial scale, require **organic template molecules**, which determine the sizes and shapes of the pores and cages in the final materials. Often, zeolites are hydrothermally synthesized, starting with an aqueous solution containing all inorganic agents and the organic SDAs. In some cases, the incorporation of metal atoms into the zeolite framework is limited for hydrothermally synthesized zeolites or the hydrothermal synthesis suffer from high costs due to the price of the SDA, such as for hexamethonium bromide, e.g. required for the synthesis of zeolite EU-1 (structure-type EUO). Therefore, a dry-gel synthesis route was developed, which bases on the conversion of a dry gel consisting of a non-aqueous mixture of all required inorganic and organic agents at high temperature under water vapour, delivered by a separate water bath at the bottom of the autoclave (Refs. [3-5]). With this synthesis method, no expensive SDAs are lost in an aqueous solution.

Pure **hexamethonium bromide (HMBr)** is a solid and causes ¹³C CP MAS NMR signals of methylene and methyl carbon atoms at δ_{13C} = 24.9 and 54.3 ppm, respectively (**Fig. 2, top**) [5, 6]. Due to quadrupole effects of ¹⁴N nuclei on the directly neighbored ¹³C nuclei of the methyl carbon atoms, a splitting of their ¹³C CPNMR



Fig. 2

signal occurs. The signal of methylene carbon atoms at $\delta_{13C} = 67.9$ ppm is often very broad. In the ¹³C CPMAS NMR spectrum of the dry gel (**Fig. 2, middle**), prepared for the synthesis of zeolite EU-1, signals occur at the same chemical shifts as in the spectrum of the pure template, which indicates that the SDA remain unchanged during the dry gel preparation [5]. In the ¹³C CPMAS NMR spectrum of the assynthesized zeolite EU-1 (**Fig. 2, bottom**), obtained from the above-mentioned dry gel, again the signals of the unchanged SDA appear [5]. However, an additional broad signal occurs at the chemical shift of $\delta_{13C} = 112.2$ ppm, which is due to monovalent (H₃C)₃N⁺–(CH₂)₄–CH=CH₂ cations, formed via Hofmann elimination of the bivalent hexamethonium cations. Hence, the SDA molecules are partially decomposed during the crystallization process, but both the bivalent and the monovalent hexamethonium cations remain in the channels and side pockets of the EU-1 structure [5].

In the structure of **metal-organic frameworks (MOFs)**, organic molecules act as linkers between metal atoms (see e.g. Refs. [7-9]). In the case of **MOF-5**, **1,4-benzoldicarboxyl (BDC)** is used as linker molecules (Fig. 3, top) between Zn atoms. Fig. 3, bottom, displays the high-resolution ¹³C CPMAS NMR spectrum of MOF-5 in comparison to the broad and featureless static ¹³C NMR spectrum, which demonstrates the advantage of the MAS NMR technique [7]. The main reason of the broadening of static ¹³C NMR signals of solids is the chemical shift anisotropy of ¹³C



Fig. 3

nuclei. The line widths of the ¹³C CPMAS NMR signals of MOF-5 are often in a range of 10 to 20 Hz. Larger line widths hint at a distribution of the isotropic chemical shift due to structure defects of the MOF-5 material [7].

Conversion of reactants at **active surface sites of zeolites** can lead to the formation of chemically bound organic compounds, such as **alkoxy groups**. Often, these surface alkoxy species contribute to the mechanism of heterogeneously catalyzed reactions (**Fig. 4**) [10]. Therefore, numerous ¹³C CPMAS NMR studies focused on the formation of surface alkoxy groups and their properties [11-15].



The interesting ¹³C NMR spectroscopic parameters of surface alkoxy groups are their isotropic chemical shift δ_{13C} and their chemical shielding anisotropy $\Delta \sigma$. As an example, **Fig. 5** shows the ¹³C CP MAS NMR spectrum of ethoxy groups formed by ethanol with ¹³C-enriched methylene groups (CH₃¹³CH₂OH) at Broensted acid sites of zeolite H-Y [12]. The ¹³C CPMAS NMR spectrum is dominated by a signal at δ_{13C} = 72.6 ppm with spinning sidebands characteristic for strongly bound surface species. The signal at δ_{13C} = 72.6 ppm was, therefore, assigned to surface ethoxy species (SiO(¹³CH₂CH₃)AI), while the signal at $\delta_{13C} = 61.7$ ppm is due to terminal ethoxy species (SiO(¹³CH₂CH₃)) and/or strongly bonded ethanol [12]. The asterisks assign spinning sidebands. By simulation of the sideband patterns, the chemical shielding anisotropies $\Delta \sigma$ were determined. For methoxy species on H-SAPO-34, a $\Delta\sigma$ value of 50 to 45 ppm was found [15], which is very close to the $\Delta\sigma$ values of 52 and 43 ppm, determined for the ¹³C CPMAS NMR signals at δ_{13C} = 72.6 and 61.7 ppm, respectively, in Fig. 5. This finding supports the assignment of the abovementioned two signals to carbon atoms in the methylene groups of ethoxy species, rigidly bound at the zeolite surface.



Catalyst preparation: In the most cases, ¹³C solid-state NMR studies are performed without a specific pretreatment of the sample materials, such as for the above-mentioned investigations of template molecules in as-synthesized zeolites or of

linkers in metal-organic frameworks. Another situation exists for the study of catalytically active surface species, such as alkoxy groups, which may react, e.g. with water molecules to other organic compounds. In this situation, a pretreatment and handling of the sample materials, like for ¹H MAS NMR studies (see "method 1"), must be performed.

¹³C solid-state NMR studies: The ¹³C CPMAS NMR study of the hexamethonium bromide in Fig. 2 was was performed at a Bruker MSL-400 spectrometer with a resonance frequency of $v_0 = 100.6$ MHz and a 7 mm Bruker MAS NMR probe, with a contact time of 5 ms, and a sample spinning rate of $v_{rot} = 4$ kHz. The spectrum of the ethoxy species at zeolite H-Y in Fig. 5 was recorded at the same spectrometer with a 7 mm DSI-740 MAS NMR probe of Doty Scientific Instruments, a contact time of 5 ms, and a sample spinning rate of $v_{rot} = 2.2$ kHz. See Ref. [9] for the details of obtaining the ¹³C solid-state NMR spectra in Fig. 3. Tetramethylsilane (TMS) was used as chemical shift standard ($\delta_{13C} = 0$ ppm)

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