

An Atomic View of Catalysts Using Solid-State NMR

Raynald Giovine¹, Julien Trébosc¹, Frédérique Pourpoint¹, Jean-Paul Amoureux^{1,2}, Olivier Lafon^{1,3}

¹ Univ. Lille, CNRS, ENSCL, UCCS, Lille, France. ² Bruker BioSpin, Wissembourg, France. ³ Institut Univ. de France, Paris, France. *Corresponding author : olivier.lafon@univ-lille.fr

The development of improved heterogeneous catalysts can be undertaken in a rational way by a better understanding of their atomic-level structures. Solid-State NMR spectroscopy is very well suited to the study of heterogeneous catalysts because it can give information on the local structure. However, the lack of sensitivity and resolution poses a limit for the characterization of surface sites, notably when they are occupied by isotopes with low gyromagnetic ratio, low natural abundance (¹⁵N...), slow longitudinal relaxation (²⁹Si...) or subject to large anisotropic interactions, such as chemical shift anisotropy (¹⁹⁵Pt...) or quadrupolar interaction (¹⁷O, ²⁷Al, ⁴⁵Sc, ^{47,49}Ti, ⁶⁷Zn...).

We have in recent years developed and applied innovative NMR techniques to circumvent this issue and obtain new insights into the structure of heterogeneous catalysts. We have notably introduced efficient and robust techniques to probe connectivities and proximities involving quadrupolar nuclei. Correlation experiments involving ²⁷Al nuclei at high magnetic field have notably been employed to probe the structure of Brønsted acid sites at the surface of amorphous silica alumina and report, for the first time, the presence of Brønsted acid sites based on pentacoordinated Al sites in these solid acid catalysts widely used in chemical processes (see Fig. 1).¹ Furthermore, the estimate of dipolar couplings between ⁶⁷Zn nuclei and protons has permitted to understand the synergistic effects between Zn²⁺ ions and Brønsted acid sites in Zn-modified zeolites used for the activation of methane.² More recently we have used magnetization transfer from protons to oxygen-17 nuclei to selectively observe the ¹⁷O signals of silanol groups at the surface of fumed silica catalyst support.³

We have also employed solid-state NMR to understand the functionalization of dendritic fibrous silica nanoparticles (DFNS) (see Fig. 2). The sensitivity gain provided by Dynamic Nuclear Polarization (DNP) has permitted the identification of surface amine sites produced by the reaction of DFNS with ammonia. ¹H, ²⁹Si and ^{47,49}Ti solid-state NMR experiments at high fields have also been used to prove the formation mechanism of DFNS-supported TiO₂ photocatalysts.⁴

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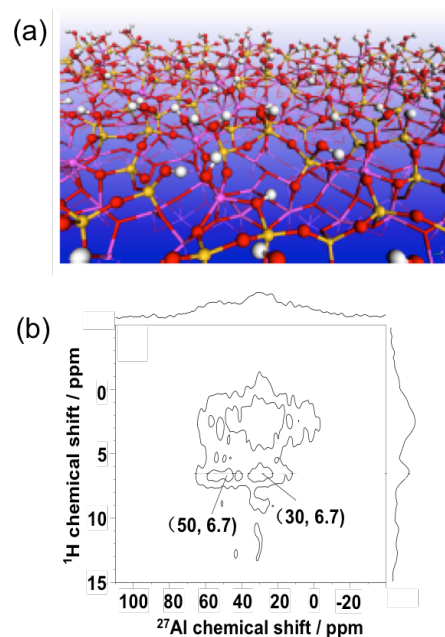


Figure 1. Structure of ASA, which contains Brønsted acid sites based on pentacoordinated Al sites, as proved by the ²⁷Al{¹H} D-HMQC spectra of ASA loaded with ammonia at 18.8 T.

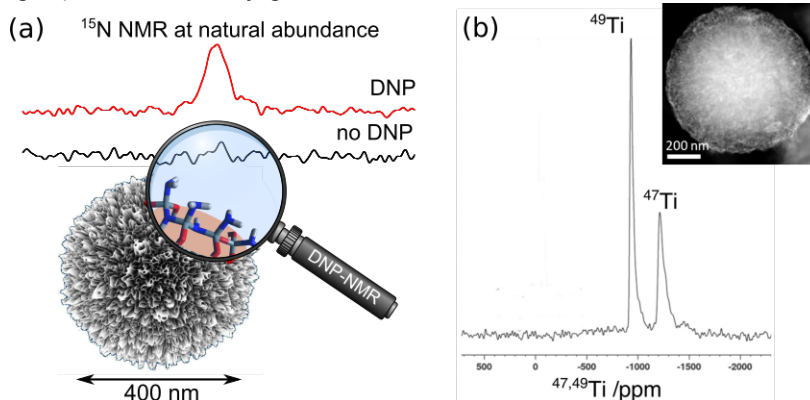


Figure 2. DFNS-supported catalysts: (a) Observation of the surface sites of nitridated DFNS using DNP-enhanced ¹⁵N NMR; (b) ^{47,49}Ti NMR spectrum of DFNS-supported TiO₂ photocatalysts, the TEM image of which is shown as inset.