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Full paper / Mémoire

Efficiency of dipolar and *J*-derived solid-state NMR techniques for a new pair of nuclei $\{^{31}P,^{29}Si\}$. Towards the characterization of Si–O–P mesoporous materials

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Abstract

Solid-state NMR methods based on dipolar and *J*-derived experiments such as CP, MAS-*J*-HMQC and MAS-*J*-INEPT MAS have been developed in the frame of the $\{^{31}P,^{29}Si\}$ spin pair. The potential of these techniques has been demonstrated using model compounds including crystalline silicophosphate phases ($Si_5O(PO_4)_6$ and various SiP_2O_7 polymorphs). *Spatial* interactions as well as *through-bond* connectivities were established. Evaluation of isotropic $^2J_{P-O-Si}$ coupling constants has been established by careful analysis of the HMQC and INEPT build-up curves under fast MAS. The efficiency of the $^{31}P \rightarrow {}^{29}Si$ CP MAS experiment for the detailed characterization of Si–O–P mesoporous materials (at low temperature) was demonstrated. The incorporation of P atoms in the silica network has been proved unambiguously. Such materials could be appropriate for biocompatibility purposes. ***To cite this article: C. Coelho et al., C. R. Chimie 11 (2008).***

Résumé

Des méthodes de RMN en phase solide fondées sur l'interaction dipolaire (polarisation croisée en rotation à l'angle magique) et l'interaction de couplage *J* (MAS-*J*-HMQC et MAS-*J*-INEPT) ont été développées dans le cadre de la paire de spins $\{^{31}P,^{29}Si\}$. La mise au point de ces séquences a été effectuée à l'aide de composés modèles, comme $Si_5O(PO_4)_6$ et certains polymorphes de SiP_2O_7. Les *proximités spatiales* ainsi que les *connectivités chimiques* sont ainsi mises en évidence. L'évaluation des constantes isootropes de couplage $^2J_{P-O-Si}$ a été permise grâce à l'analyse détaillée des courbes d'évolution HMQC et INEPT. L'efficacité de la séquence $^{31}P \rightarrow {}^{29}Si$ CP MAS est démontrée dans le cadre de l'étude de matériaux mésoporeux de type Si–O–P. L'incorporation des atomes de phosphore au sein du réseau de silice est ainsi prouvée. Ces composés sont des candidats potentiels dans le cadre des matériaux biocompatibles. ***Pour citer cet article : C. Coelho et al., C. R. Chimie 11 (2008).***

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Mots-clés : Silicophosphate ; RMN en phase solide ; Polarisation croisée ; Couplage *J* ; Matériaux mésoporeux

1. Introduction

In the last few years, mesoporous materials attracted much attention due to their potential applications in several fields, including catalysis, polymerization, photochemistry…[1]. The silica-based MCM-41 structure is known to act as a bioactive material. Indeed, the intrinsic porosity of such material offers a wide range of possibilities for hosting molecules and the ability for drug delivery [2,3]. Recently, several researchers have been interested in the incorporation of bisphosphonates [4] in the pores of mesostructured silica, which may inhibit bone resorption. Confinement of such molecules could offer new opportunities such as bone reconstruction. The direct synthesis of Si–O–P mesoporous materials has been very rarely reported in the literature [5,6] and has received little attention.

In the field of materials, the local structure of nuclei can be probed efficiently by solid-state NMR spectroscopy. A large panel of techniques can be implemented for establishing *connectivities* between nuclei. It includes cross-polarization and *J*-derived experiments. The CP MAS (cross-polarization magic-angle spinning) sequence [7] relies on *dipolar* interaction. Such experiment establishes *spatial* proximities between X and Y nuclei. For X = ^{31}P and Y = ^{29}Si, very few results have been reported so far in the literature. These results are related to silicon phosphide (involving direct ^{31}P–^{29}Si bonds) [8] and silicophosphates involving ^{31}P–O–^{29}Si groups [9]. *J*-derived experiments based on the isotopic scalar *J* coupling constants establish X–Y *through-bond* connectivities. In the early 1990s, such solid-state NMR sequences were implemented successfully by Fyfe et al. [10] and Eckert et al. [11]. More recently, several groups showed that a large number of *J* experiments could be easily transposed to solid-state NMR. Among these, we find the HMQC (heteronuclear multiple quantum coherence) sequence, which has been adapted for the following spin pairs: ^{1}H/^{13}C, ^{1}H/^{15}N, ^{31}P/^{27}Al, ^{27}Al/^{17}O, ^{31}P/^{29}Si and ^{31}P/^{71}Ga [11–17]. The INEPT (insensitive nuclei enhanced by polarization transfer) sequence [18] is one of the most important pulse blocks in modern solution state experiments [19]. In solid-state NMR, the INEPT sequence was adapted for the study of mobile [20] and rigid [21] organic and hybrid systems. Examples related to inorganic components have been rarely reported in the literature [22–26].

In this paper, the complete study of silicophosphate phases such as $Si_5O(PO_4)_6$ and various SiP_2O_7 polymorphs is presented. The efficiency of ^{31}P → ^{29}Si CP MAS, MAS-*J*-HMQC and MAS-*J*-INEPT experiments involving the {^{31}P,^{29}Si} spin pair is demonstrated. The ^{31}P → ^{29}Si CP MAS experiment has been then successfully applied for the structural characterization of Si–O–P derived mesoporous materials. Such materials were obtained via an aerosol process. The incorporation of phosphorus in the silica network at atomic level was clearly demonstrated.

2. Experimental: syntheses and solid-state NMR

Solid-state NMR experiments were performed on a Bruker Avance 300 spectrometer at $B_0 = 7$ T with ν_0 (^{31}P) = 121.49 MHz and ν_0 (^{29}Si) = 59.63 MHz, using a 4-mm triple resonance Bruker MAS probe. Samples were spun at the magic angle using ZrO_2 rotors (5–14 kHz). ^{31}P chemical shifts were referenced to 85% aqueous H_3PO_4. ^{29}Si chemical shifts were referenced to TMS. In the case of mesoporous materials, all experiments were obtained at low temperature ($T = 238$ K), thanks to a cooling unit (BCU-X), a control temperature unit, and a DVT probe. The calibration of the temperature was performed using lead nitrate, $Pb(NO_3)_2$. Full experimental details are given in the figure captions. The X-ray diffraction patterns of mesoporous materials were obtained using a D8 Advance Bruker diffractometer (Cu Kα radiation: $\lambda = 1.54718$ Å, 1–6° in 2θ with a step size of 0.02° in 2θ, scan rate: 5 s/step). For TEM experiments (Philips Technai 12), samples were dispersed in ethanol and dropped onto a copper grid covered with carbon.

The synthesis protocols are the following: *$Si_5O(PO_4)_6$*: TEOS ($Si(OCH_2CH_3)_4$), ethanol and distilled water were used as precursors (TEOS/EtOH/H_2O = 1:4:3). The phosphorus precursor H_3PO_4 (85%) was added (Si/P = 1:1) at room temperature. The reaction was slightly exothermic. The addition of 1% (molar ratio) of a paramagnetic complex ($NiCl_2 \cdot 6H_2O$) was performed for NMR relaxation purposes, leading to a slightly green solution. After stirring at 25 °C, a transparent green wet gel was obtained (2 h). The final powder was