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Ion distribution in copper exchanged zeolites by using Si-29 spin lattice relaxation analysis ☆

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ABSTRACT

Transition metal-containing zeolites, particularly those with smaller pore size, have found extensive application in the selective catalytic reduction (SCR) of environmental pollutants containing nitrogen oxides. We report these zeolites have dramatically faster silicon-29 (Si-29) spin lattice relaxation times (T_1) compared to their sodium-containing counterparts. Paramagnetic doping allows one to acquire Si-29 MAS spectra in the order of tens of seconds without significantly affecting the spectral resolution. Moreover, relaxation times depend on the method of preparation and the next-nearest neighbor silicon $Q_n(m\mathrm{Al})$ sites, where $n = 4$ and $m = 0$–4, respectively. A clear trend is noted between the effectiveness of Cu exchange and the Si-29 NMR relaxation times. It is anticipated that the availability of this tool, and the enhanced understanding of the nature of the active sites, will provide the means for designing improved SCR catalysts.

1. Introduction

Zeolites are microporous aluminosilicates having applications as adsorbents, catalysts, separation materials, etc. [1]. Recently, transition metal containing zeolites have found extensive application in diesel emission control [2,3]. The transition metal ions act as coordination centers for adsorbed molecules and also act as catalytically active centers. The nature of these metal ions and their interaction with the zeolite framework is of paramount importance, dictating the efficiency in the conversion of harmful nitrogen oxides. Also, the specific locations of these ions impart structural stability during the standard function of the vehicle emission system, often at very high temperature and/or in the presence of water. Advanced characterization tools are necessary to understand the nature of the catalyst, and there have been several recent reports on the application of spectroscopic techniques [4,5].

Nuclear magnetic resonance spectroscopy in the solid state (SSNMR), often combined with elemental analysis, powder X-ray diffraction, and infrared spectroscopy, is a powerful tool for the structural characterization of zeolites and other microporous materials [6–9]. Si-29 is a particularly versatile nucleus that can be used to probe many structurally relevant properties, such as zeolite framework type, silicon-to-aluminum ratio, and hydroxylation. It has even been shown that, in model systems with optimized local order and Si-29 isotope enrichment, *de novo* structure solving employing Si-29 based detection schemes is possible [10].

An inherent drawback of Si-29 detection, at least in context of non-enriched samples from industrial catalyst production and pre-production testing, is the typically low signal-to-noise in a given experiment time. It results from an interplay of Si-29 isotope natural abundance, gyromagnetic ratio, structural line broadening, and, in case of direct detection, long relaxation times T_1 which are typically on the order of tens to hundreds of seconds.

Alternative routes to solution may involve direct spectroscopy of other nuclei, e.g. Al-27, assuming that spectroscopy is performed under suitable conditions [6,7,11], or H-1, after complete removal of all residual H_2O [12]. However, Si-29 spectra can add significant additional information such as precise determination of next-nearest neighbors and framework connectivity.

In recent years, sensitivity enhancement by Dynamic Nuclear Polarization (DNP) [13,14] has become a viable tool for the characterization of microporous materials [15]. DNP involves the transfer of large thermal polarization of electron spins to nuclear spins, enabling solid-state NMR experiments to be performed with significant increase in signal-to-noise ratio and savings in time.

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Sophisticated instrumentation (e.g., a gyroton), extensive sample preparation processes and very low temperatures (e.g., 100 K) are required. A critical evaluation of the absolute sensitivity enhancement has been recently addressed [16].

Many high-performance catalysts incorporate dopants in their active sites, such as vanadium or tin, which may have isotopes that are relatively well accessible by direct SSNMR spectroscopy [17,18]. However, this is not always the case, as for example with copper, which has NMR-detectable isotopes, but mandates tailored methodology [19] and is thus not a very common choice for NMR spectroscopy.

On the other hand, a system doped with a paramagnetic species provides interesting means of structural characterization in terms of NMR relaxation, as has been noted for example in the solid state for biomolecules [20–26], zeolites [27,28], and other inorganic systems [29]. The most apparent benefit of such treatments is to rapidly improve signal-to-noise ratio through faster scan recycling [20,21]. Notably, it is also possible to indirectly obtain information about local species, such as interatomic distances [24,30].

In this contribution, we propose a method to estimate the effectiveness of Cu-ion-exchange in the industrially important zeolite Cu-SSZ-13 by determining the spin lattice relaxation time T_1 of Si-29. This method makes use of a very favorable but general condition of paramagnet incorporation that enables a rapid measurement (savings in time by a factor of 400–600 compared to non-doped systems) without sacrificing spectral resolution. The process of ion exchange in Cu-SSZ-13 is elucidated by Si-29 T_1 measurements after exchanging varying levels of Cu content.

2. Theory

Paramagnetic centers within a system of nuclei affect both the resonance frequencies as well as the relaxation times of nearby nuclei due to the presence of unpaired electrons. When considering the shifts of the NMR signal frequencies, two main effects are of note: the Fermi Contact Shift (CS) and the Pseudocontact Shift (PCS).

The CS is caused by direct contact of a free electron from the paramagnetic center with the nucleus being studied, and can cause extreme shifts in resonance frequency, often by as much as a few thousand ppm [29]. In order for this shift to occur, the free electron must overlap with the S orbital of the studied nucleus. When this occurs, the shift is defined by Eq. (1), derived rigorously in [31] where A is proportional to the probability of the electron being at the center of the nucleus, S is the electron spin, γ_I is the nuclear gyromagnetic ratio, and $\bar{g}$ is the electron gyromagnetic ratio.

$$\delta^{CS} = \frac{A}{\hbar}\frac{\bar{g}\mu_B S(S+1)}{3kT\gamma_I} \tag{1}$$

The PCS is caused by two factors: the distance r between the paramagnetic center and the studied nucleus, and the magnetic susceptibility tensor χ of the paramagnetic center. The shift itself is defined by Eqs. (2)–(4) [23] which are derived in detail by Bertini et al. [31], and is generally on the order of a few to a few tens of ppm. More isotropic paramagnetic species, such as Cu^{2+}, will have smaller shifts. In a study by Jaroniec, ^{13}C nuclei in a protein system had PCS of approximately −3 to +3 ppm when introduced to a Co^{2+} paramagnetic center [23], while in the study described here, Si-29 nuclei exhibit no discernable shift due to nearby Cu^{2+} ions.

$$\delta^{PCS} = \frac{1}{12\pi r^3}\left[\Delta\chi_{ax}(3\cos^2\theta - 1) + \frac{3}{2}\chi_{rh}\sin^2\theta\cos 2\varphi\right] \tag{2}$$

$$\Delta\chi_{ax} = \chi_{zz} - \frac{\chi_{xx}+\chi_{yy}}{2} \tag{3}$$

$$\Delta\chi_{rh} = \chi_{xx} - \chi_{yy} \tag{4}$$

The paramagnetic relaxation enhancement (PRE) is caused by the dipolar coupling with the free electrons, which inherently have a much more rapid relaxation with correlation time τ_e of 10^{-7}–10^{-13} s. Relaxation rates can be increased by several orders of magnitude depending on the distance between the nucleus and paramagnetic center, the electron correlation time, and the Larmor frequencies ω_I and ω_S of the nucleus and electron. The PRE of the relaxation times T_1 and T_2 are defined by the Solomon-equations [32] with derivation and constants defined in multiple studies [26,29,32], with T_1 being shown by Eq. (5).

$$\frac{1}{T_1} = \frac{2k\gamma_I^2 S(S+1)}{r^6}\left(\frac{\tau_e}{1+(\omega_I-\omega_S)^2\tau_e^2} + \frac{3\tau_e}{1+\omega_I^2\tau_e^2} + \frac{6\tau_e}{1+(\omega_I+\omega_S)^2\tau_e^2}\right) \tag{5}$$

In an ideal system with efficient spin diffusion, relaxation would follow a single exponential decay. However, with further deviations from an ideal system, stretched exponential models become more accurate [33]. In particular, this study focuses on materials with low abundance Si-29 nuclei coupled with paramagnetic centers. Systems similar to this have been studied, and show that relaxation follows a stretched exponential with β equal to 0.5 in the ideal case with no spin diffusion [27,34]. In the study presented here, we fit the stretched exponential with an unconstrained stretching parameter β according to Eq. (6).

$$M(t) = M_{eq}(1 - \exp(-t/T_1)^{\beta}). \tag{6}$$

3. Experimental/methods

Na–Y (Si/Al = 2.6) was a commercial sample from Zeolyst. Copper exchange was carried out using $Cu(CH_3COO)_2$ at 60 °C for 1 h. Cu-SSZ-13 was synthesized by hydrothermal methods. Cu exchange was carried out in similar fashion as described for zeolite Y [2]. Cu doping in SSZ-13 was also carried out by a precipitation method using oxalic acid. Chemical analyses were conducted using ICP-MS, and Cu content is expressed as weight percent.

NMR experiments were performed on a Varian Unity Inova 400 MHz (9.4 T) spectrometer using a 7.5 mm magic-angle spinning (MAS) assembly. Additional data for 7 T and 14.1 T are given as supplementary material. Si-29 NMR MAS spectra were measured using a 45° tip angle and a relaxation delay of 60–150 s. Spin–lattice relaxation times were measured using the saturation recovery method, with staggered recovery delays to remove influence from any field drifts. Different saturation delays were used for Na and Cu forms.

Data were processed using ACD/Labs® to output intensities and fitted using Origin Pro®. The signal intensities were plotted as a function of the saturation recovery delay times using a stretched exponential function.

4. Results and discussion

The spin lattice relaxation times of Si-29 vary significantly for different materials. For example, recycle delays on the order of hours are not uncommon in glasses [35]. The relaxation in pure materials is shortened by the addition of paramagnetic ions such as Eu^{3+}, or Gd^{3+} [8]. The reduction in T_1 is due to the very large magnetic moment ($\mu_s = -g_e\beta_e S$) and the short spin–lattice relaxation time of electron. The silicon atoms which are close to the paramagnetic center are affected while those located far away are influenced to a lesser extent.