Spin-lattice and spin-spin relaxation of $^{29}$Si via paramagnetic centers in the MAS NMR of zeolites†

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The $^{29}$Si nuclear spin-lattice ($T_1$) and spin-spin relaxation ($T_2$) decays have been measured using the magic angle spinning (MAS) technique in zeolite-Y with varying amounts of Fe$^{3+}$. Analysis of $T_1$ data shows that the $^{29}$Si nuclei are dipolar-coupled to paramagnetic centers and the observed non-exponential decay of the $^{29}$Si spin magnetisation can be satisfactorily explained by a suitable theory. The $^{29}$Si transverse magnetisation, on the other hand, is both homogeneously and inhomogeneously broadened by the presence of Fe$^{3+}$ centers.

The isomorphous substitution of iron (for aluminium) in zeolite framework has emerged as an important and active area of research in view of specific catalytic properties exhibited by such materials. In such ferrisilicate zeolites, the $^{29}$Si nuclear spins experience strong dipolar fields created by the Fe$^{3+}$ paramagnetic centers. Since in high silica ferrisilicate zeolites (Si/Fe > 10) the concentration of Fe centers is small, the $^{29}$Si spectra are observable under high resolution conditions by using magic angle spinning (MAS) techniques. Measurement of the spin-lattice ($T_1$) and spin-spin ($T_2$) relaxation times from $^{29}$Si MAS NMR spectra offer considerable scope to probe the nature of $^{29}$Si-Fe$^{3+}$ interactions. We report such measurements and interpretations of the relaxation data.

Materials and Methods

Two zeolite systems were chosen for study, namely, Na-Y and ZSM-5. Iron was incorporated into them by hydrothermal synthesis. $^{29}$Si MAS NMR spectra were recorded at room temperature ($22^\circ$C) on a Bruker MSL-300 FT-NMR spectrometer at the resonance frequency of 59.6 MHz. $^{29}$Si $T_1$'s were measured using $\pi-\tau/2$ inversion recovery sequence and $T_2$ by the Hahn spin echo sequence. MAS was kept at around 3.6 kHz. The chemical analyses were performed by a combination of wet chemical, atomic absorption (Hitachi Z-800) and ICP (Jobin Yuon - JY-38 VHR) methods.

Results and Discussion

1 $^{29}$Si MAS NMR spectra

Figure 1(a) shows the $^{29}$Si MAS NMR spectra for Na-Y zeolite, where the signals due to Si(4Al), Si(3Al), Si(2Al), Si(0Al) can be distinguished and assigned. When Fe is introduced into the system, both line broadening of $^{29}$Si resonances and increase in spinning side band intensity are observed (Fig. 1, b-e). Spectra for Al-ZSM-5 and Fe-ZSM-5 are shown in Fig. 1 f and Fig. 1 g-j respectively. Spinning side bands are not shown in the figure.

![Fig. 1 — $^{29}$Si MAS NMR spectra of Na/Al-Y (a), Na/Fe-Al-Y (b-e), H/Al-ZSM-5 (f) and H/Fe-ZSM-5 (g-j). T = Al or Fe. The weight per cent of Fe$_2$O$_3$ is shown for Y-zeolite against each spectrum. All spectra were taken at spinning speed of 3.6 kHz.](image-url)
29Si MAS NMR OF ZEOLITES

Fig. 2(a)—Representative plot of the decay of 29Si longitudinal magnetisation as a function of the delay time \( t \) between \( \pi \) and \( \pi/2 \) in the inversion recovery pulse sequence.

2(b)—Plot of 29Si longitudinal magnetisation as a function of \( t^{1/2} \) for Si(2Al) signal shown in (a) at 5 wt% of Fe2O3.

2 29Si spin-lattice relaxation \((T_1)\)

The decay of the longitudinal magnetisation, as a function of the delay between the \( \pi \) and \( \pi/2 \) pulses, is shown in Fig. 2a. The decay is seen to be non-exponential. This behaviour was observed in all Fe-zeolite samples.

The observed non-exponential decay behaviour of \( M_z(t) \) can be adequately explained by considering the nuclear relaxation via paramagnetic centers under conditions of no spin-diffusion\(^9\)\(^10\). This assumption is applicable in the present case because (i) natural abundance of 29Si is low (4.7%), implying weak spin-diffusion among Si and (ii) MAS further inhibits this spin-diffusion. Hence, the rate of change of the longitudinal magnetisation is governed by interaction with paramagnetic centers only. The expression for longitudinal magnetisation is\(^9\)

\[
M(t) = \exp\left(-\frac{t}{T_1}\right)
\]

\[
= \left[<M_z>-M_0\right]/[M_z(t=0)-M_0] \quad \ldots (1)
\]

\[
\left(1/T_1\right)_{obs} = \frac{4}{3} \pi^{3/2} N_0 C^{1/2} \quad \ldots (3)
\]

\(N_0\) is the concentration of paramagnetic Fe\(^{3+}\)/cm\(^3\) and

\[
C = \frac{3}{5} N^2 \gamma_e^2 h^2 S(S+1) \tau_e \quad \ldots (4)
\]

\(\tau_e\) is the correlation time for the \( z\)-component of paramagnetic spin and other symbols have their usual meanings. According to this theory, a straight line behaviour is expected when longitudinal magnetisation is plotted as a function of \( t^{1/2} \). This is found to hold as shown by Fig. 2b where the logarithm of the magnetisation is plotted against the square root of the interpulse delay for Si(2Al). Similar behaviour was exhibited by other signals. This indicates that 29Si spin relaxation is dominated by direct electron-nuclear interactions in each case.

3 29Si spin-spin relaxation \((T_2)\)

In the presence of paramagnetic centers, the spin-spin relaxation has both a homogeneous and an inhomogeneous character for the decay of transverse magnetisation. The former is associated with the real \( T_2 \), being governed by coupling to paramagnetic centers, and the latter arises due to the bulk susceptibility of the material\(^11\). Therefore,

\[
\left(1/T_2\right)_{obs} = (1/T_2)_{intr} + (1/T_2)_{suscept. eff.} \quad \ldots (5)
\]
Evidence for susceptibility contribution to \(T_2\) is provided by Fig. 3, where the pulse sequence used is shown. The multiple signals (due to FT of echoes) arise due to the susceptibility induced inhomogeneous broadening. The same effect is also noticed in the MAS spectra (Fig. 4), where this inhomogeneous broadening gives rise to rotational echoes, which on FT lead to pronounced spinning side band patterns.

In Fig. 5 is shown the decay of the transverse magnetisation from the spin-echo sequence. Since the \(\pi\) pulse refocusses inhomogeneous part of the interaction, the observed decay is mainly determined by lifetime effects.

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