

## A Silicon-29 Magic Angle Spinning NMR Study of a Phillips (Chromia/Silica) Catalyst

Phillips (chromia/silica) catalyst and its modified forms are used industrially for the large-scale production of alkene polymers, the heterogeneous catalyst remaining dispersed in the product polymer (1). Typically, a chromium species is initially adsorbed from solution onto a low-density/high-surface-area silica; high-temperature calcination in air or oxygen oxidises the metal to chromium(VI), which is then activated by reduction with either carbon monoxide or the alkene itself. Despite numerous investigations, the oxidation state of the catalytically active metal, its exact mode of attachment to the silica surface and the structure of the active site have all as yet to be unambiguously established. Indeed there is much disagreement in the literature and every oxidation state from chromium(II) to chromium(VI) has been implicated as active in polymerisation (2).

In principle, high-resolution magic angle spinning NMR spectroscopy, with its ability to selectively observe nuclei affected in some way by their particular electronic environment, has the potential to answer at least some of the above questions. While most of the nuclei of atoms of chemical significance in Phillips catalysis are of low sensitivity and normally have long relaxation times, paramagnetic chromium species are present during certain stages of the catalyst preparation and, as has been recently pointed out (3), it is sometimes possible to exploit the beneficial effects of incorporating paramagnetic ions into solids. Widely used as shift and relaxation agents in solution NMR, paramagnetic ions have been little developed for similar purposes in the solid state, although, for example, the enhancement of  $^{29}\text{Si}$  relaxation rates by low

concentrations of iron and manganese homogeneously dispersed through silicate glasses (4) and cements (5) have been reported. We now find that the adsorption of paramagnetic chromium species onto a silica surface can both dramatically increase the longitudinal relaxation rates of neighbouring  $^{29}\text{Si}$  nuclei and cause changes in the appearance of the  $^{29}\text{Si}$  spectra, which are dependent on the state of the catalyst and the conditions used for the alkene polymerisation. A report of a similar improvement in spin-lattice relaxation rates for the  $^{29}\text{Si}$  nuclei of silica-supported molybdenum catalysts has appeared very recently (6).

The  $^{29}\text{Si}$  CP/MAS NMR spectrum of hydrated silica gel (Fisher-157, surface area  $750\text{ m}^2\text{ g}^{-1}$ ) has been previously reported (7) and the three observed resonances assigned to surface silicon atoms according to the number of bridging oxygens by which they are attached ( $Q^n$ ),  $Q^4$  at  $-109$  ppm,  $Q^3$  (one OH group) at  $-100$  ppm,  $Q^2$  (two OH groups) at  $-89$  ppm, relative to the silicon resonance of liquid tetramethylsilane. Our own solid-state  $^{29}\text{Si}$  NMR spectra were obtained at 59.6 MHz on a Bruker AM300WB spectrometer fitted with a Bruker HPWB73A MAS7DB solid-state probe. Magic angle spinning of the sample ( $\sim 150$  mg) was carried out typically at 4 kHz with 7-mm-o.d. zirconia rotors spun by compressed air at ambient temperature. With  $^1\text{H}$  decoupling, but without cross polarisation, the fully relaxed ( $\pi/2$  pulse, 2500-s pulse delay) 59.6-MHz  $^{29}\text{Si}\{-^1\text{H}\}$  MAS NMR spectrum of the dried ( $110^\circ\text{C}$ , 16 h) support silica of the present study (Crosfield EP10, surface area  $300\text{ m}^2\text{ g}^{-1}$ ) is the rather broad and poorly resolved envelope shown in Fig. 1a which includes the resonances of both sur-

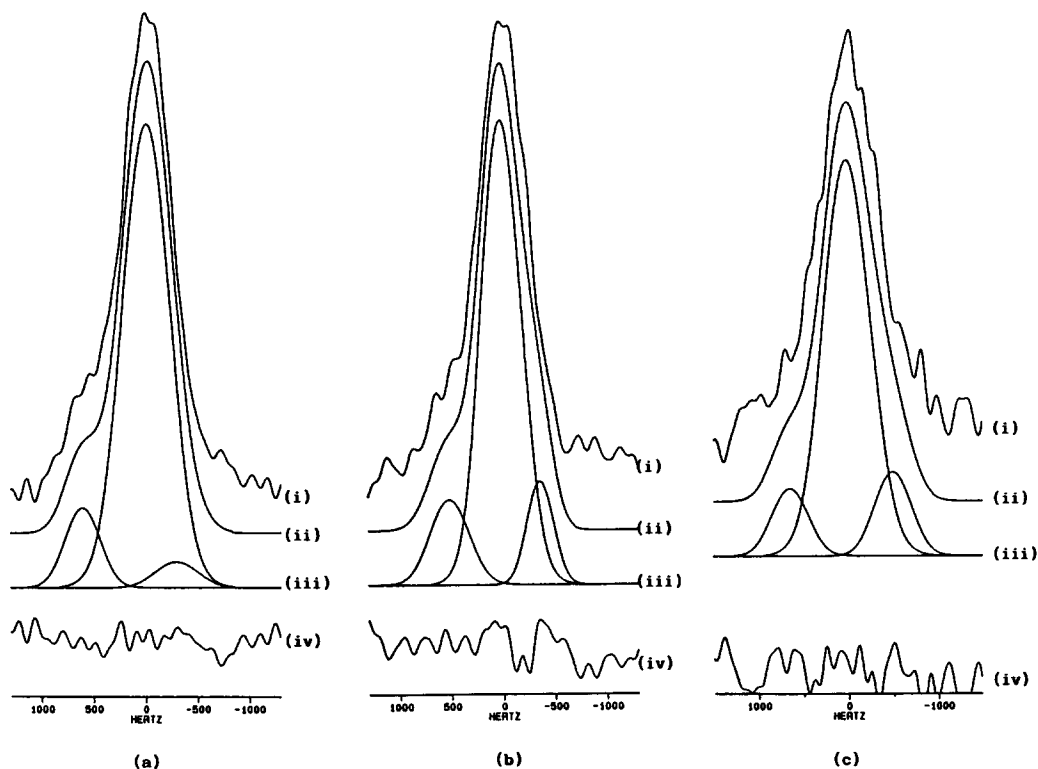


FIG. 1. Fully relaxed 59.6-MHz  $^{29}\text{Si}\{-^1\text{H}\}$  MAS NMR spectra of a Phillips catalyst at various stages in the preparation of an alkene polymer: (a) the silica support after heating in air at 110°C for 16 h; (b) the silica with 1% chromium adsorbed; (c) the catalyst, activated by calcination in air at 600°C for 16 h followed by reduction with carbon monoxide at 400°C, dispersed in ethene polymerised at 100°C and a pressure of 2.66 kN m $^{-2}$ . (i) Experimental spectrum; (ii) computer-simulated spectrum based on (iii); (iii) deconvoluted spectrum; (iv) experimental spectrum subtracted from calculated spectrum.

face (~35%) and bulk (~65%) silicon sites. The envelope was deconvoluted into three partially overlapping resonances, which can be assigned to  $Q^2$  (-90 ppm),  $Q^3$  (-100 ppm), and  $Q^4$  (-105 ppm) silicon sites.

The Phillips catalyst precursor (EP30) was produced by adsorption of basic chromium(III) acetate onto the support silica to give a loading of 1 wt% Cr. Even if it is assumed that the chromium(III) ions are adsorbed as isolated mononuclear species, with a calculated mean distance of 16 Å between chromium atoms, not all the silicon atoms of even the surface layer of EP30 can be in close proximity to a paramagnetic metal centre. Moreover, basic chromium(III) acetate adopts a trinuclear structure

$[\text{Cr}_3\text{O}(\text{CH}_3\text{CO}_2)_6(\text{H}_2\text{O})_3]^+$  in which there is an equilateral triangle of chromium atoms with an oxygen atom at the centre. Each chromium atom is coordinated octahedrally by the central oxygen atom, one from each of four acetate groups and a water molecule. The acetate groups link the vertices of the three octahedra in the complex cation (8). The absorption bands characteristic of basic chromium(III) acetate are still apparent in the infrared spectrum of EP30, indicating that the trinuclear structure is probably retained on adsorption by the silica.

Figure 1b shows the fully relaxed 59.6-MHz  $^{29}\text{Si}\{-^1\text{H}\}$  MAS NMR spectrum of EP30. Despite the presence of paramagnetic chromium species causing an inevitable re-

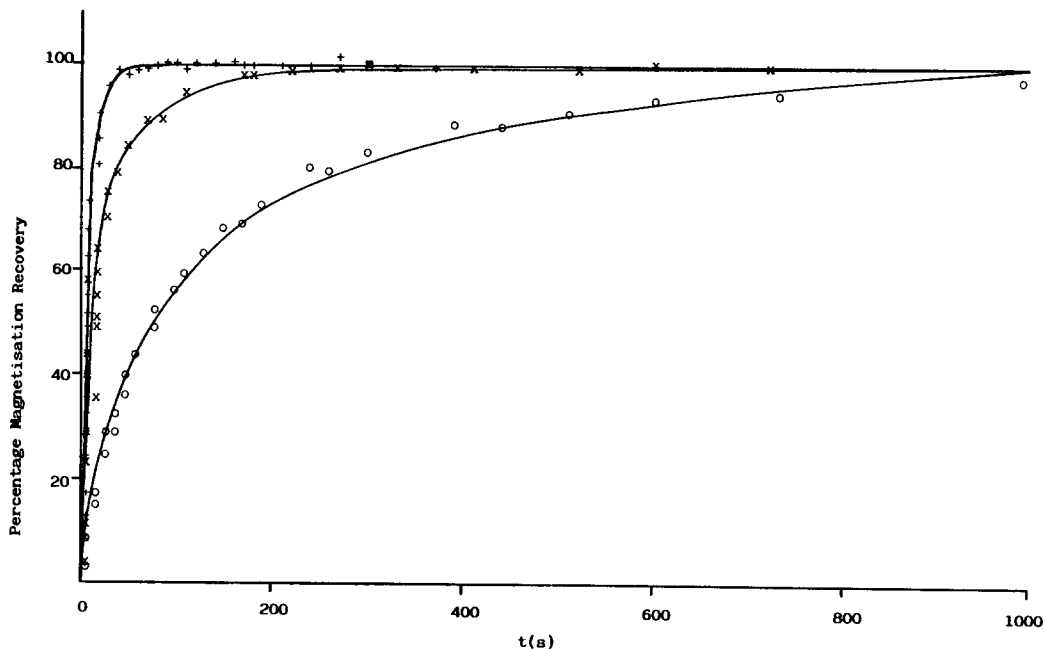


Fig. 2. 59.6-MHz  $^{29}\text{Si}$  MAS  $T_1$  measurements for the spectra shown in Fig. 1; (a)  $\circ$ ; (b)  $\times$ ; (c)  $+$ . Illustrated are the magnetisation recovery curves obtained from the saturation recovery Fourier-transform method (SRFT)  $[\pi/2-(\pi/2)_{30}-t-\pi/2-\text{acq.}-(\pi/2)]_{52}$ .

duction in  $^{29}\text{Si}$  spin-spin relaxation times  $T_2$ , there appears to be relatively little additional line broadening (the half-height width of the spectral envelope remained at about 500 Hz) in the spectrum, which was again deconvoluted into three resonances assigned to  $Q^2$  (-91 ppm),  $Q^3$  (-100 ppm), and  $Q^4$  (-107 ppm) sites. Figure 1c shows the fully relaxed  $^{29}\text{Si}-\{^1\text{H}\}$  MAS NMR spectrum of the catalyst, activated by calcination in air at 600°C for 16 h, followed by reduction with carbon monoxide at 400°C, and dispersed in ethene polymerised at 100°C and a pressure of 2.66 kN m $^{-2}$ . The spectral envelope in this case is somewhat broader (the half-height width of the spectral envelope increased to about 700 Hz) than in 1a and 1b, although this appears to result from a rather greater chemical shift dispersion of the three  $Q^n$  sites than from significantly reduced  $T_2$  values.

There are, however, major differences in the spin-lattice  $T_1$  relaxation behaviour of the silica atoms of the Phillips catalyst at

various stages in the preparation of an alkene polymer. Silicon-29 has a spin-lattice relaxation time  $T_1$  of about 2 h in high-purity silica (9), although in less well-ordered silicas such as EP10 this value should be substantially reduced (6). Figure 2 shows the magnetisation saturation recovery curves for the three spectra illustrated in Fig. 1, indicating the dramatic effect that paramagnetic species adsorbed on the surface of the silica have on the rates of longitudinal relaxation of the  $^{29}\text{Si}$  nuclei. For example, recovery to 90% of the equilibrium magnetisation requires about 500 s for the support silica EP 10 alone, reducing to about 70 s for EP30, and only 16 s for the catalyst dispersed in gas-phase polymerised ethene. Samples were freely handled in air and the MAS rotors were spun by compressed air. Saturation with atmospheric molecular oxygen was therefore common to all three samples and, while perhaps being a major contributor to relaxation in EP10, cannot be responsible for the increases observed in the

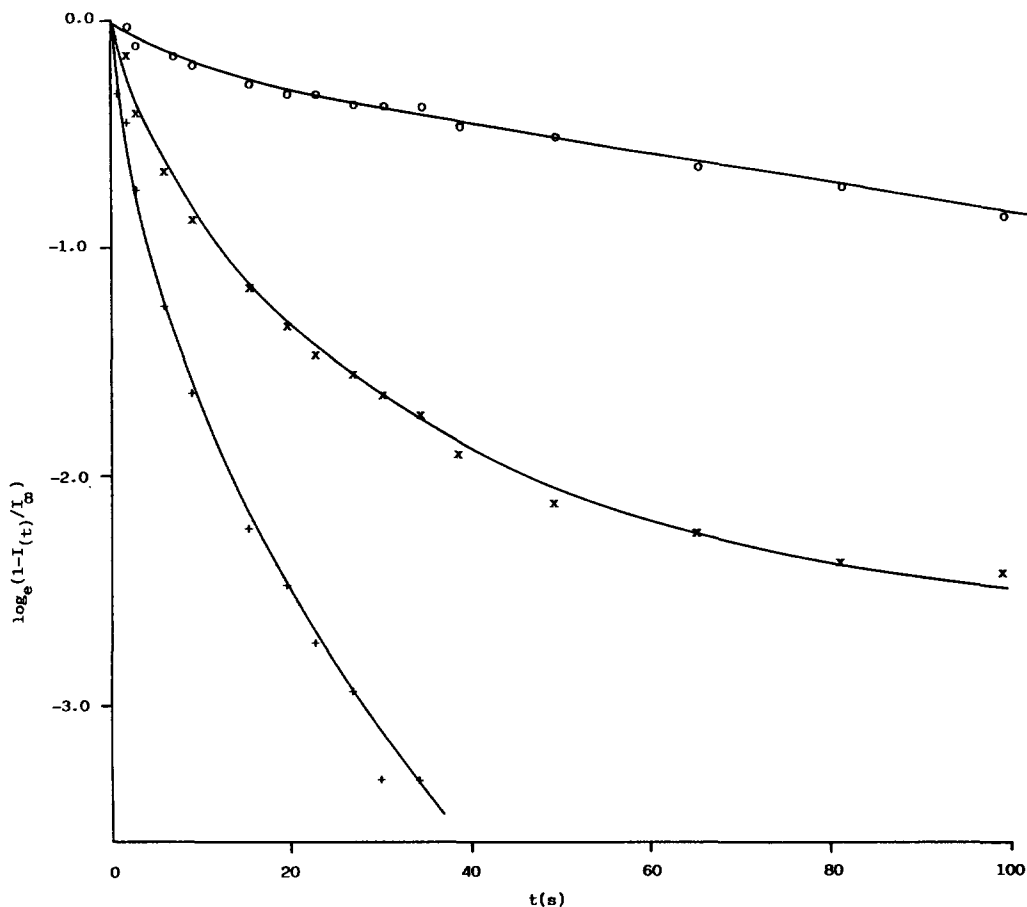


FIG. 3. Plots of  $\log_e(1 - I(t)/I_\infty)$  vs  $t$  from the SRFT experiments for the spectra shown in Fig. 1, (a)  $\circ$ ; (b)  $\times$ ; (c)  $+$ .  $I(t)$  represents the intensity of the  $^{29}\text{Si}$  resonance for the delay  $t$  and  $I_\infty$  the same value for an infinite delay. For a single-exponential relaxation a straight line plot should be obtained with an inverse slope equal to  $-T_1$ .

rates of longitudinal relaxation of EP30 and the catalyst dispersed in polymerised ethene.

Figure 3 shows that all three samples exhibit non-single-exponential spin-lattice relaxation behaviour. It has been suggested that an  $\exp[-(t/T_1)^{1/2}]$  law can arise in some systems where the paramagnetic relaxing species are randomly distributed throughout the system (10, 11). However, in the present case, where the paramagnetic chromium species are distributed only on the surface of the silica, a better fit is given by a multiexponential decay involving about four different  $T_1$ 's. A more detailed account of the

longitudinal relaxation behaviour will be given elsewhere.

Magnetic susceptibility measurements by the Gouy technique show that at 291 K both EP30 and the sample of catalyst dispersed in polymerised ethene have a small net bulk paramagnetism despite their low chromium content. After correcting for the diamagnetic susceptibilities of the support silica and ethene polymer (12) both samples have approximately the same specific susceptibility ( $\chi_g \sim 40 \times 10^{-6}$  cgs), indicating the same number of unpaired electrons per chromium atom in each case. This quite clearly suggests

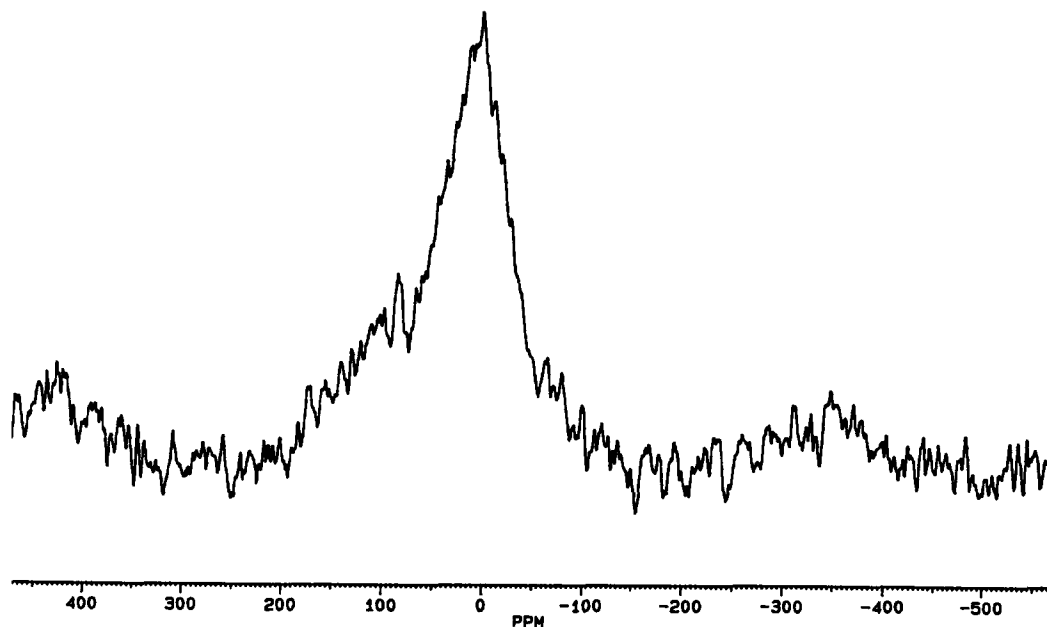


FIG. 4. 59.6 MHz  $^{29}\text{Si}\{-^1\text{H}\}$  NMR spectrum of catalyst dispersed in an ethene polymer produced industrially using high ethene pressures and with the catalyst dispersed in a liquid hydrocarbon.

that chromium(III) is the final oxidation state attained by the metal of the Phillips catalyst in the low-pressure, low-temperature ethene polymerisation. The local effect of the chromium(III) magnetic moment should thus be very similar in both samples, yet the  $^{29}\text{Si}$  nuclei of the catalyst dispersed in the ethene polymer are being relaxed more efficiently.

Two explanations come to mind: either (i) the paramagnetic chromium species become closer to the same number of silicon atoms of the surface layer of the silica as in EP30 or (ii) the trinuclear structure of chromium acetate is broken down during processing of the catalyst and the resulting individual mononuclear chromium species are dispersed over the silica surface, bringing a greater proportion of the  $^{29}\text{Si}$  nuclei into the close proximity of a paramagnetic centre. We prefer the latter explanation but what has been established is that the  $^{29}\text{Si}$  NMR spectrum of the support silica is markedly affected by both the magnetic moment of the paramagnetic species and their distribution over its surface.

By deliberately choosing a spectrum recy-

cle time too short for full relaxation to occur, it is possible to selectively enhance that part of the spectrum arising from the more rapidly relaxing  $^{29}\text{Si}$  nuclei. The spectrum of EP30 obtained using a  $\pi/2$  pulse, but only a 0.2-s pulse delay, has a strong resonance at about  $-109$  ppm (with a shoulder at about  $-99$  ppm) with a linewidth comparable to that reported for the individual resonances of the surface silicon atoms of silica gel (Fisher-157) (7). Under the same conditions, the spectrum of the sample of catalyst dispersed in polymer showed an even more enhanced resonance at  $-110$  ppm, although a downfield shoulder was no longer observed. Substantial spinning side bands for this resonance were observed, indicating an asymmetry at the silicon site. In solution NMR chromium(III) ions are normally regarded as shiftless relaxing agents (13) and if the lack of significant induced shift also applies to solid-state spectra, then it is the upfield resonances (i.e., those arising from  $Q^3$  and  $Q^4$  sites) that are being selectively relaxed.

Figure 4 shows the very different

59.6-MHz  $^{29}\text{Si}\{-^1\text{H}\}$  MAS NMR spectrum (rotation rate 4 kHz) of this catalyst dispersed in an ethene polymer produced industrially using high ethene pressures and with the catalyst suspended in a liquid hydrocarbon. At the high pressures used in the industrial process the carbon monoxide reduction step is not necessary for catalyst activation. The peaks at the wings of the spectrum are too far from the large centre resonances to be due to spinning side bands (which would appear at about 67.1 ppm from the central resonance). We are presently unable to interpret this spectrum but it would seem that the final oxidation states and speciation of the chromium at the silica surfaces lead to the major spectral differences between laboratory and industrially prepared ethene polymer samples.

It therefore appears that, notwithstanding its low natural abundance and normally poor sensitivity, the  $^{29}\text{Si}$  nucleus can act as a sensitive and noninvasive NMR probe of the nature of catalytically active paramagnetic metal ions adsorbed onto a silica surface.

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