

Magnetic Properties of Vanadium Phosphorus Oxide Catalysts Studied by Spin Echo Mapping ^{31}P NMR

M. T. Sananes and A. Tuel*

Institut de Recherches sur la Catalyse. C.N.R.S. 2, av. A. Einstein 69626 Villeurbanne Cedex, France

The magnetic properties of vanadium phosphorus oxide (VPO) catalysts are studied by variable temperature Spin Echo Mapping ^{31}P NMR.

Vanadium phosphorus oxides (VPO) have received considerable attention in recent years, particularly because of their interesting properties as catalysts in the oxidation of *n*-butane to maleic anhydride.¹ Whilst the pyrophosphate phase $(\text{VO})_2\text{P}_2\text{O}_7$ is usually recognized to be the active phase in this reaction,² industrial catalysts generally contain several phases with various P:V ratios and vanadium oxidation states, making characterization of the samples using conventional techniques difficult. Most of the phases formed during the synthesis are amorphous or poorly crystallized, which often makes X-ray diffraction unsuccessful. EPR has also been used to study paramagnetic phases but the signals were broad and difficult to interpret.³ ^{31}P and ^{51}V NMR have been shown to be powerful tools to distinguish between the various V^{5+} phases.⁴ However, when the sample contains significant amounts of V^{4+} or V^{3+} cations, interaction of the electrons of these paramagnetic centres with ^{31}P nuclei drastically broadens the observed peaks and changes the observed shift, and the ^{31}P signal is not detectable using conventional sequences.⁵

We have recently shown that it was possible to record the whole NMR spectrum by using the Spin Echo Mapping technique.^{6,7} This is done by recording a series of spectra where the irradiation frequency is varied by increments of 50 kHz above and below the ^{31}P resonance in H_3PO_4 . Because of the NMR line width in these compounds, each spectrum is obtained using an echo sequence $90^\circ_x - t - 180^\circ_y - t$ (acquisition). According to Li *et al.*,⁸ the frequency shift is due to an electron-nuclear dipolar-plus contact term. In this case, the frequency shift is related to the atomic susceptibility χ_{at} , eqn. (1),

$$\delta = (\omega - \omega_0)/\omega_0 = H_{\text{eff}} f \chi_{\text{at}} / \beta \quad (1)$$

where H_{eff} is the hyperfine field for phosphorus, β is the Bohr magneton and f is the fractional contribution of the unpaired electron spin to the ^{31}P nucleus. Therefore, the technique permits the determination of the vanadium oxidation state by measuring ^{31}P NMR spectra.

The hemihydrate $\text{VO}(\text{HPO}_4) \cdot 0.5\text{H}_2\text{O}$ and the pyrophosphate $(\text{VO})_2\text{P}_2\text{O}_7$ phases were prepared following literature procedures.^{9,10} The purity and crystallinity of the samples were determined by chemical analysis and X-ray diffraction. ^{31}P NMR spectra were recorded on a Bruker MSL 300 spectrometer, using a conventional probe head working in the temperature range 150–400 K. The 90 and 180° pulses were 9 μs and 18 μs , respectively.

We have already reported the Spin Echo Mapping ^{31}P NMR spectra of these samples.⁶ At room temperature, both samples showed a broad NMR signal at *ca.* δ 1750 for the hemihydrate and δ 2600 for the pyrophosphate. Johnson *et al.*^{9,11} reported a relatively detailed study of the magnetic properties of $\text{VO}(\text{HPO}_4) \cdot 0.5\text{H}_2\text{O}$ and $(\text{VO})_2\text{P}_2\text{O}_7$. In particular, they showed that above 100 K, the magnetic susceptibility χ could be described by a Curie–Weiss law, eqn. (2),

$$\chi = Ng^2\beta^2S(S+1)/3k(T - \Theta) \quad (2)$$

where N is the number of paramagnetic centres, g the Landé factor and Θ the Weiss temperature.

Therefore, the frequency shift δ observed by ^{31}P NMR Spin Echo Mapping is a function of temperature, eqn. (3),

$$\delta = C/(T - \Theta) \quad (3)$$

where C is the Curie constant given by eqn. (2).

Fig. 1 shows the Spin Echo Mapping spectra of $\text{VO}(\text{HPO}_4) \cdot 0.5\text{H}_2\text{O}$ recorded at temperatures between 150 and 370 K. The observed frequency shift δ decreases with the temperature from about 3200 at 370 K to about 1600 at 170 K (relative to H_3PO_4). We also observed a decrease of the NMR linewidth with increasing temperature.

In the working temperature range, the inverse frequency shift $1/\delta$ is a linear function of T for both samples, in agreement with eqn. (3) (Fig. 2). Extrapolation of the curves to $1/\delta = 0$ gives an estimation of the Weiss temperature, Θ .

Assuming that $\text{VO}(\text{HPO}_4) \cdot 0.5\text{H}_2\text{O}$ contains isolated $\text{V}^{4+} - \text{V}^{4+}$ dimers in which the vanadium ions are antiferromagnetically coupled, the magnetic susceptibility can be described by the Bleaney–Bowers equation,¹¹ [eqn. (4)],

$$\chi = 4C/T(3 + e^{-2J/kT}) \quad (4)$$

where C is the Curie constant of the paired V^{4+} and J/k the exchange constant between the 2 spins of the dimer. For high temperatures ($T \gg 2J/k$), the relation can be simplified, eqn. (5), with $\Theta = J/2k$.

$$\chi = C/(T - \Theta) \quad (5)$$

^{31}P NMR data gave $\Theta = -25.3$ K, in very good agreement with the values given by Johnson *et al.*⁹ and obtained by direct simulation of the susceptibility with eqn. (4).

For $(\text{VO})_2\text{P}_2\text{O}_7$, the value of Θ was approximately -75 K, slightly different from that obtained from susceptibility meas-

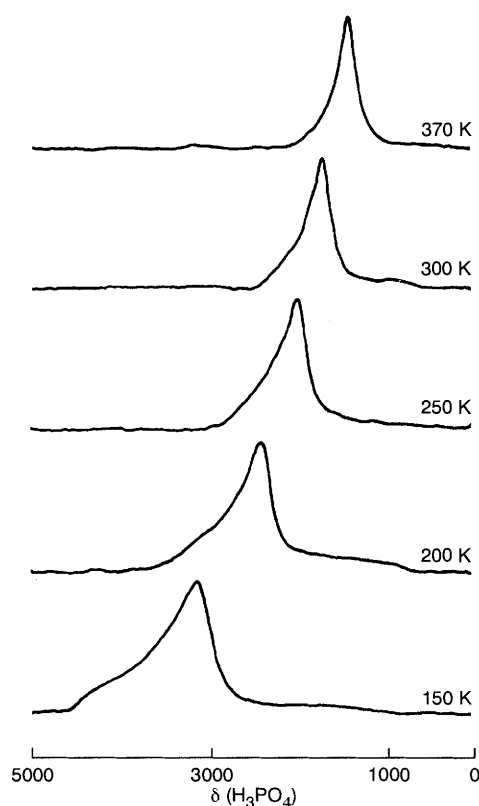


Fig. 1 Spin echo mapping ^{31}P NMR spectra of $\text{VO}(\text{HPO}_4) \cdot 0.5\text{H}_2\text{O}$ recorded at various temperatures

urements. A value of -65 K, very close to that obtained by Johnson *et al.*⁹ was obtained on a second pyrophosphate sample having a slightly lower crystallinity. It is interesting to note that the value of Θ is different from that of the hemihydrate, which can be explained by additional interactions between the dimers

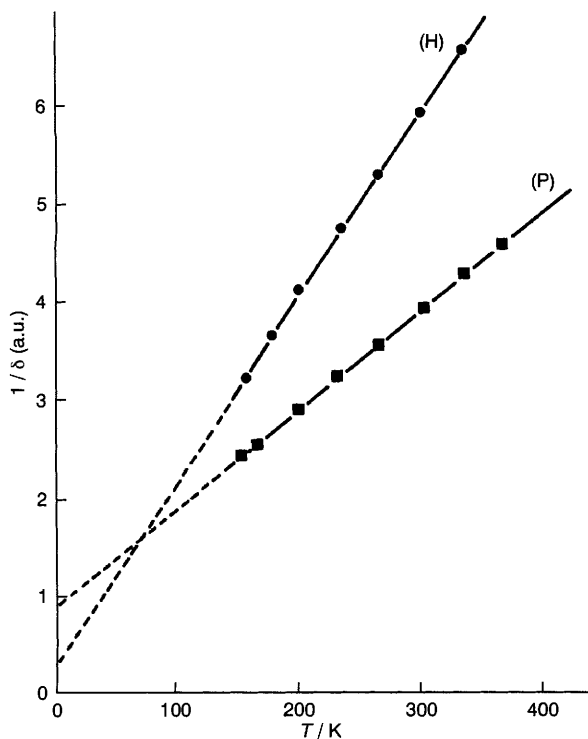


Fig. 2 Variation of the inverse frequency shift for $\text{VO}(\text{HPO}_4) \cdot 0.5\text{H}_2\text{O}$ (H) and $(\text{VO})_2\text{P}_2\text{O}_7$ (P) with temperature

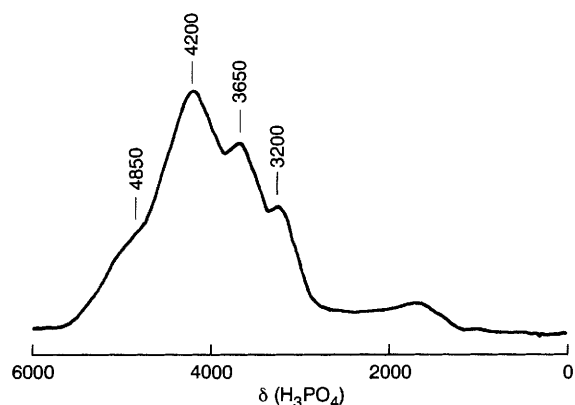


Fig. 3 Spin echo mapping ^{31}P NMR spectrum of $(\text{VO})_2\text{P}_2\text{O}_7$ recorded at 150 K

in the structure. However, the measurement of δ for $(\text{VO})_2\text{P}_2\text{O}_7$ is difficult because of the linewidth, particularly at low temperatures. Indeed, the spectrum was split into four lines, which is particularly evident in Fig. 3, $T = 150$ K. These lines are not due to different crystallographic environments in the structure, indeed, changes in the ^{31}P chemical shifts due to structural differences in diamagnetic samples do not generally exceed 100 ppm for phosphorus, and are not temperature dependent. They are more likely to be related to variations in the oxidation state of vanadium atoms. It has been reported that each pair of sharing octahedra in $(\text{VO})_2\text{P}_2\text{O}_7$ could be considered as a redox system inside the crystalline matrix itself. The oxidation state of vanadium cations is not 4 but 3.69 and 4.19 for one of the pairs and 3.79 and 4.44 for the other.¹² Therefore, the electron density of each phosphorus atom depends on its location in the structure and may explain the presence of four lines in the ^{31}P NMR spectrum.

Concerning the variation of the linewidth with temperature, we have observed that the inverse width varied almost linearly with T in the working temperature range. However, if the paramagnetic shift can be theoretically calculated, this is not the case for the linewidth. Moreover, lines are often complex and unsymmetrical with respect to the irradiation frequency, which makes the measurement of the width relatively difficult. More details about the variation of the line shape and width with temperature will be given in a forthcoming paper.

We have shown that ^{31}P NMR spectra of paramagnetic VPO catalysts could be obtained using the Spin Echo Mapping technique. The evolution of the NMR shift with temperature gives direct information about the magnetic susceptibility of the sample, particularly the Weiss temperature when dimers are present in the structure.

Received, 15th March 1995; Com. 5/01664I

References

- 1 *Vanadyl Pyrophosphate Catalysts, Catalysis Today*, ed. G. Centi, 1993, vol. 16, No. 1, Elsevier, Amsterdam.
- 2 F. Cavani, G. Centi and F. Trifiro, *Appl. Catal.*, 1984, **9**, 191.
- 3 G. Martini, F. Trifiro and A. Vaccari, *J. Phys. Chem.*, 1981, **86**, 1573.
- 4 F. Ben Abdelouahab, R. Olier, N. Guilhaume, F. Lefebvre and J. C. Volta, *J. Catal.*, 1992, **134**, 151.
- 5 J. C. Vedrine, J. M. Millet and J. C. Volta, *Faraday Discuss. Chem. Soc.*, 1984, **87**, 207.
- 6 M. T. Sananes, A. Tuel and J. C. Volta, *J. Catal.*, 1994, **145**, 251.
- 7 M. T. Sananes, A. Tuel, G. J. Hutchings and J. C. Volta, *J. Catal.*, 1994, **148**, 395.
- 8 J. Li, M. E. Lashier, G. L. Schrader and B. C. Gerstein, *Appl. Catal.*, 1991, **73**, 83.
- 9 J. W. Johnson, D. C. Johnston, A. J. Jacobson and J. F. Brady, *J. Am. Chem. Soc.*, 1984, **106**, 8123.
- 10 E. Bordes, P. Courtine and G. Pannetier, *Ann. Chim.*, 1973, **8**, 105.
- 11 D. C. Johnston and J. W. Johnson, *J. Chem. Soc., Chem. Commun.*, 1985, 1720.
- 12 E. Bordes, *Catal. Today*, 1987, **1**, 495.