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Evidence for a new type of vanadyl pairs in $(VO)_2P_2O_7$: an ESR and magnetisation study [*]

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ESR and magnetisation experiments have identified a new type of antiferromagnetic pairing of vanadyl groups in the butane oxidation catalyst vanadylpyrophosphate. This pairing is an order of magnitude weaker than the coupling predominantly found in crystalline $(VO)_2P_2O_7$.

Keywords: vanadylpyrophosphate, butane oxidation, maleic anhydride, catalyst, pairing of vanadyl groups, ESR spectroscopy, magnetic susceptibility, Curie–Weiss behaviour, Curie constant, Weiss temperature

1. Introduction

Catalysts based on vanadium–phosphorus–oxide (V–P–O) are industrially used for the production of maleic anhydride (MA) from n-butane. Although the V–P–O system has been under intense investigation for the last three decades, still little is known about the exact structure of the active site [1–3]. Nevertheless, it is widely accepted that vanadylpyrophosphate, $(VO)_2P_2O_7$, is the main component in the active catalyst [1–3].

In the literature, the catalytic activity of the V–P–O catalysts has been related to the local structure of vanadyl groups in vanadylpyrophosphate. The structure of crystalline vanadylpyrophosphate consists of pairs of edge-sharing pseudo-octahedrally co-ordinated vanadium ions at a distance of ∼3.2 Å, which are isolated by pyrophosphate groups [4]. This structural unit is often used to model the active sites in V–P–O catalysts [2,5,6]. However, various other models have been proposed, viz., interfaces between different $VOPO_4$ phases and $(VO)_2P_2O_7$ [7], V^{5+} sites on the surface of $(VO)_2P_2O_7$ [2], V^{5+} species in interaction with $VO(PO_3)_2$ [8], and amorphous V^{4+} and/or V^{5+} phases supported on crystalline $(VO)_2P_2O_7$ [9,10]. To study the amorphous phase we have applied ESR spectroscopy and magnetisation experiments to gain more insight in the magnetic interactions between possible different VO^{2+} ions in an equilibrated currently used bulk V–P–O catalyst. Both, ESR and magnetic measurements, are selective for (amorphous) V^{4+} (d^1) ions and do not detect non-magnetic V^{5+} species.

In principle, a single isolated VO^{2+} ion ($S = 1/2$, $I = 7/2$) has a characteristic octet ESR spectrum showing the hyperfine coupling to the ^{51}V nuclear magnetic moment. Upon pairing of two vanadyl ions, the two electron spins may combine to a non-magnetic spin singlet ($S = 0$) or a paramagnetic spin triplet state ($S = 1$). Only the latter is ESR detectable. The superexchange interaction between the two vanadium ions leads to a situation in which the two electron spins have an antiferromagnetic character, i.e., the singlet state is energetically favoured. The hyperfine interactions with the ^{51}V ($I = 7/2$) nucleus, being orders of magnitude weaker than the exchange interaction, are averaged out and do not manifest themselves in the ESR spectrum of the spin triplet state. Therefore the ESR spectrum of strongly coupled pairs has the form of a single broad line with inhomogeneous broadening due to g-tensor anisotropy.

The probability (P_t) that a given pair exists in the paramagnetic triplet state depends on temperature and is given by equation (1):

$$P_t(T) \propto \frac{4\,e^{2J/kT}}{1 + 3\,e^{2J/kT}}. \qquad (1)$$

Here $2J$ is the energy difference between the spin singlet and triplet states of the pair. For temperatures below $2J/k$ this factor decreases to zero rapidly, and the population of the triplet state is thermally depleted.

To study the exchange interactions between pairs of vanadyl ions in a bulk V–P–O catalyst we have applied ESR spectroscopy and magnetisation experiments at low temperatures.

2. Experimental

The catalyst used for this study was prepared [11] in organic environment (i-butanol/cyclohexanol) according to a well known procedure [12] and equilibrated in the C_4

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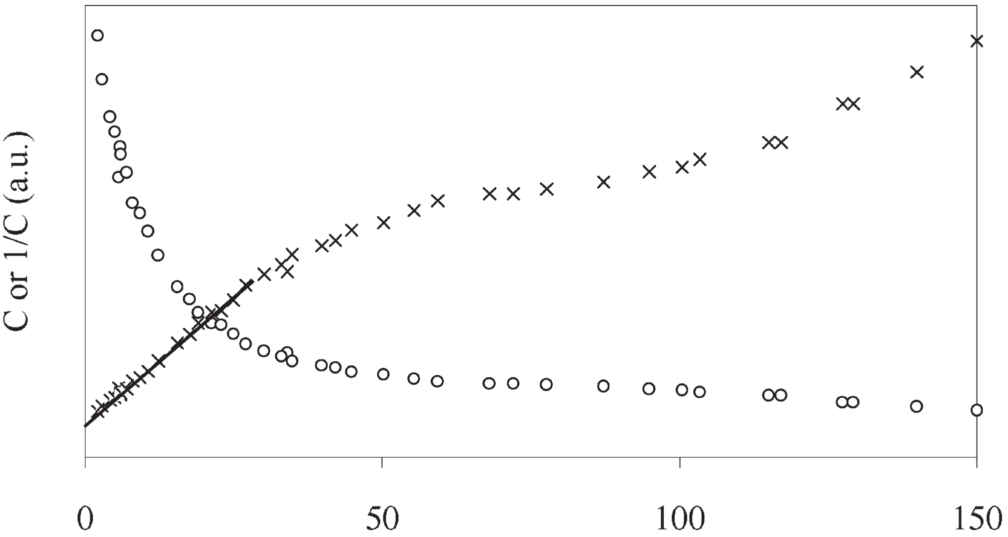

Figure 1. Magnetic susceptibility from magnetisation experiments as a function of temperature (open circles) and inverse susceptibility (crosses). The shoulder near 80 K indicates the existence of vanadyl pairs with antiferromagnetic spin exchange interaction. The straight line below 20 K is extrapolated to a Weiss temperature θ of 7 K.

oxidation reaction for more than 100 h. Results of the catalytic performance testing as well as a detailed description of the characterisation (N_2-physisorption/XPS/TGA/DSC/(HT)XRD/DRIFTS) have been published elsewhere [11, 13].

The ESR experiments were performed on an X-band Bruker ESP300 spectrometer equipped with a EN801 resonator (operating in TM110 cylindrical mode with unloaded $Q = 1000$). The microwave power was 1 mW, far below saturation levels for the samples considered here. The magnetic field was modulated with a frequency of 12.5 kHz and an amplitude of 1 G. The cavity was equipped with a thermostat to prevent frequency drift. The sample temperature was adjusted in the range of 3.7–300 K with an Oxford ESR900 helium flow cryostat under control of an Oxford ITC503 temperature controller (temperature stability of 0.5 K).

The magnetisation experiments were performed on a vibrating sample magnetometer (Princeton Applied Research model 155) using a Janis Research helium bath cryostat (model 153). After a temperature change sufficient time was taken for temperature equilibration. No indications for thermal or magnetic hysteresis have been observed in the ESR or magnetisation data.

3. Results

Figure 1 shows the magnetic susceptibility χ (open circles) of the equilibrated bulk catalyst as measured with the magnetometer as a function of temperature between 2 and 150 K. The crosses show $1/\chi$ (same data) on an inverted scale. The data show a clear deviation from a Curie–Weiss law, $\chi(T) \propto 1/(T-\theta)$, for temperatures near 80 K. This deviation is indicative of a substantial quantity of V–P–O complexes existing as pairs with a strong antiferromagnetic coupling, which favours antiparallel alignment of the electronic spins into a non-magnetic spin singlet state (*vide infra*). The coupling originates from spin exchange interactions with $J/k = -65.7$ K, and has been reported in the literature before [14,15]. In the following we will refer to these pairs as strongly interacting pairs.

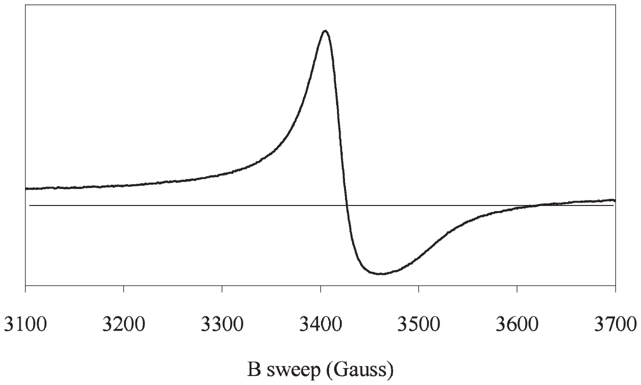

Figure 2. X-band ESR spectrum of the equilibrated organic bulk V–P–O catalyst at room temperature. The single broad line does not show hyperfine couplingto the ^{51}V nucleus ($I = 7/2$). The magnetic field is centered at 3400 G, and swept over 600 G. The spectrum has been taken at a microwave frequency of 9.437 GHz.

Between 4 and 30 K, the strongly interacting pairs contribute only very little to the total χ, as the spin triplet state is thermally depleted. In this temperature range the magnetisation data show a typical Curie–Weiss behaviour for antiferromagnets with a Curie–Weiss temperature $\theta = 7$ K. For antiferromagnetically coupled pairs this temperature is related to the coupling parameter J as $k\theta = -(3/2)J$.

Figure 2 shows the ESR spectrum of the equilibrated bulk V–P–O catalyst. It consists of a single asymmetric line centered around $g = 1.96$, without resolved hyperfine structure. In particular, the hyperfine coupling to the nearby ^{51}V ($I = 7/2$) nucleus is not observed. The absence of V hyper-

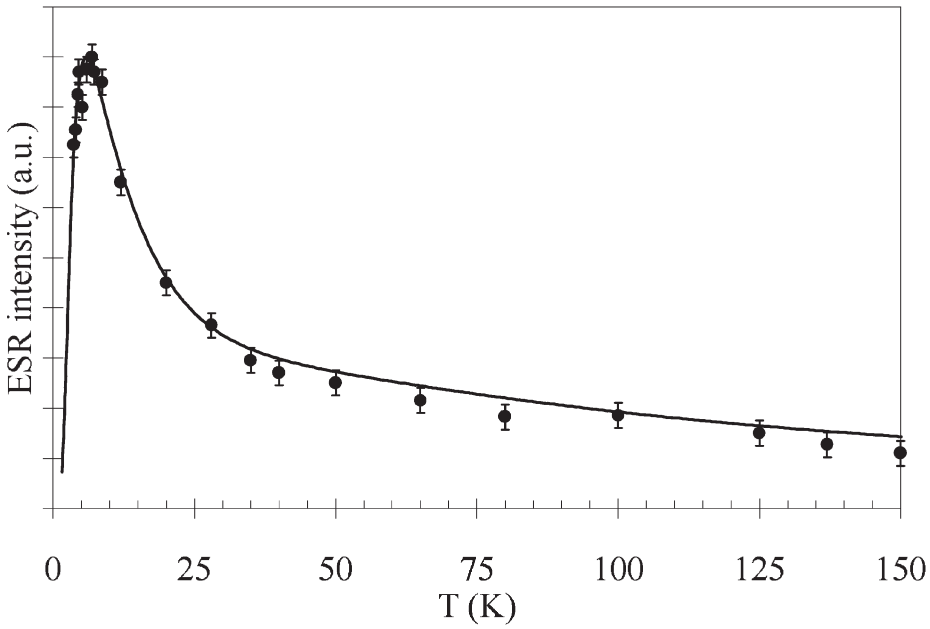

Figure 3. ESR intensity as a function of temperature (dots). The solid curve represents a fit of the data according to equation (2). The fit parameters are given in the text.

fine coupling is common in solid state V–P–O samples [16] and is attributed to the simultaneous flipping of neighbouring electron spins [17], which averages out the interaction with the nuclei. The shape of the ESR spectrum corresponds to the powder spectrum of a paramagnetic species with axially symmetric g-tensor. A fit of the line shape gives axial g-tensor parameters of $g_{//} = 1.935 \pm 0.008$ and $g_{\perp} = 1.970 \pm 0.005$. These values agree with the g-tensor parameters reported for isolated VO^{2+} ions [18,19].

Figure 3 shows the total integrated ESR intensity as a function of temperature (data points). Just as with the magnetisation data, the ESR intensity exhibits a shoulder around 80 K as caused by the presence of a substantial number of pairs with a strong antiferromagnetic exchange coupling ($J/k = -65.7$ K). At even lower temperatures, the ESR intensity does not exhibit Curie–Weiss behaviour but shows a well defined maximum near 7 K. This behaviour is not manifest in the magnetisation data and proves that a substantial number of vanadyl groups must exist as pairs with a weaker antiferromagnetic exchange coupling. Therefore, we have fitted the ESR intensity as the superposition of signals originating from strongly interacting vanadyl pairs and weakly interacting vanadyl pairs. Within the accuracy of the ESR measurements, one strong interaction is sufficient to mimic the behaviour of strongly interacting pairs. The ESR intensity $I(T)$ has been fitted with equation (2):

$$I(T) \propto \frac{w_1}{T} \cdot \frac{4\,\mathrm{e}^{2J_1/kT}}{1 + 3\,\mathrm{e}^{2J_1/kT}} + \frac{w_2}{T} \cdot \frac{4\,\mathrm{e}^{2J_2/kT}}{1 + 3\,\mathrm{e}^{2J_2/kT}}. \qquad (2)$$

The factors (w_i/T) give the Curie approximation to the ESR intensity $I(T)$ for a given triplet state, the other factors give the Boltzmann probability to find a vanadyl pair in the spin triplet state as defined in equation (1). The solid line in figure 3 shows the results from a fit with $w_1/w_2 = 1.5 \pm 0.3$, and two types of pairs, i.e., strongly interacting ($J_1/k = -65.7$ K, fixed), and weakly interacting ($J_2/k = -4.7 \pm 0.5$ K).

4. Discussion

We will discuss our results for two different temperature ranges separately, i.e., 3–40 K and 40–150 K. Furthermore, we will follow the suggestion of Johnston et al. [14,15], who supposed that their magnetisation data include two separate contributions. The first contribution is originating from strongly interacting pairs ($J/k = -65.7$ K), and passes through a maximum at around 80 K. The other contribution comes from defects in the vanadylpyrophosphate structure and is monotonously increasing as the temperature is lowered. Although these paramagnetic defects account for just a few percent of the total amount of vanadyl groups in the sample only, they dominate the magnetic susceptibility at low temperature [14].

It is interesting to note that the ESR data on the hydrated precursor, $VO(HPO_4)\cdot 0.5H_2O$ [20] can be explained without invoking the presence of defects. Powder diffraction data [7,14,15,20] reveal that the hydrated precursor contains less defects than the dehydrated catalyst. The amount of defects in the final catalyst depends on the details of the pre-treatment (heating rate, final temperature and annealing time).

Analogous to Johnston et al. [14,15] we also find a contribution to the magnetisation originating from both weakly interacting vanadium atoms, and from strongly interacting pairs. This holds for our results measured either with the magnetometer or with ESR spectroscopy.

Starting from 150 K and going down in temperature, the magnetisation initially increases down to 100 K, and between 100 and 70 K, where the strongly interacting pairs have a maximum (80 K), χ is much less dependent on the temperature. Below 70 K, the contribution from the strongly interacting pairs rapidly falls to zero as the triplet state is substantially depleted. The dominant part of the magnetisation is now due to weakly interacting vanadium atoms and the total magnetisation starts to increase again. The weak interactions are still strong enough to average out the hyperfine structure and no structural change in the ESR spectrum is observed. In principle the ESR spectrum of a single isolated spin triplet state ($S = 1$) should have characteristic weak $\Delta m = \pm 2$ transitions at reduced magnetic field values (forbidden half-field transitions). In our sample the half-field transitions were unobservable, which suggests the presence of additional magnetic interactions between the pairs in the sample [20].

In the temperature range of 3–40 K, the strongly interacting pairs contribute very little to the total magnetisation; at 40 K the contribution from these pairs is 15% and falls rapidly to zero as the temperature is decreased. The magnetisation follows very well a Curie–Weiss law for an antiferromagnetic compound with a Weiss temperature θ of 7 K. The agreement is good for both the ESR intensity measurements and the magnetisation experiments. However, the two different techniques show discrepancies at lower temperatures. At around 6 K the ESR intensity starts falling off rapidly, whereas the magnetisation data show a monotonous increase of the susceptibility $\chi(T)$. We consider the rapid drop of the ESR intensity as a manifestation of the thermal depopulation of the triplet state of weakly interacting vanadyl pairs. The antiferromagnetic coupling of these pairs is estimated at $J/k = -4.7$ K. In contrast to the ESR data, the magnetic susceptibility follows the Curie–Weiss law at temperatures below 7 K. A possible explanation for this observation is the fact that ESR selects only those paramagnetic species that obey the conditions for microwave resonance. Therefore, the contribution of the weakly interacting pairs with a narrow ESR spectrum can be identified at low temperatures. Magnetisation experiments, on the contrary, will also reflect the contribution from the strongly relaxing paramagnetic defects, which are broadened beyond detection in the ESR background.

Both, ESR and magnetisation data, are assumed to be compatible, and therefore the magnetic susceptibility as a function of temperature was fitted with equation (3). In this equation the strong pairs (w_1, $J/k = -65.7$ K), the weak pairs (w_2, $J/k = -4.7$ K) and the antiferromagnetic defects (w_3) are included. The defects are supposed to be isolated VO^{2+} ions and have spin $S = 1/2$. The weight factors (w_i) are directly proportional to the number of vanadyl ions involved.

$$\chi(T) \propto \frac{w_1}{T} \cdot \frac{4\,e^{2J_1/kT}}{1 + 3\,e^{2J_1/kT}} + \frac{w_2}{T} \cdot \frac{4\,e^{2J_2/kT}}{1 + 3\,e^{2J_2/kT}} + \frac{w_3}{T}. \quad (3)$$

Combining the results from ESR and magnetisation experiments the relative numbers of VO^{2+} ions existing in strong pairs ($J/k = -65.7$ K), weak pairs ($J/k = -4.7$ K), and defects in our sample is estimated to be $10:7:2$, respectively.

In conclusion, this work has revealed the presence of substantial non-crystalline contributions of V^{4+} phases in an equilibrated organic bulk V–P–O catalyst. This contribution would not have been observed with magnetisation experiments only, but manifests itself prominently in low-temperature ESR data. It will be interesting to correlate the presence of these amorphous V^{4+} species with the catalytic performance of bulk V–P–O catalysts.

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