Location of Vanadium(IV) in VAPO-5 as Studied by Hyperfine Sublevel Correlation Spectroscopy

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(Received September 20, 2005; CL-051195)

Vanadium(IV) framework substitution in aluminophosphate molecular sieves has been explored by electron spin resonance (ESR) and hyperfine sublevel correlation (HYSCORE) spectroscopy. In both as-synthesized and hydrated materials V(IV) exists as VO^{2+} species that coordinates to two framework oxygen atoms and presumably three water molecules in a distorted octahedral geometry.

The vanadium-incorporated aluminophosphate molecular sieve (VAPO-5) is found to be catalytically active for oxidation reactions of allylic alcohols analogous and aromatic compounds.[1] Its catalytic properties are related to well-dispersed and immobilized monomeric vanadium species.[2] In as-synthesized VAPO-5 vanadium mainly exists as paramagnetic VO^{2+}. Upon calcination in oxygen the major part of the vanadium species are oxidized to V(V) but subsequent reduction converts back a substantial part of V(V) to V^{2+}.[3–8] Although essential for a deeper understanding of the catalytic activity of the material, the location of the paramagnetic vanadium species in the VAPO-5 system is still a matter of debate. Various incorporation sites have been suggested as for instance substitution for either phosphorous[3] or aluminum[4] framework atoms, and anchoring of the VO^{2+} species to the aluminophosphate framework by two framework oxygen atoms[5–8] with either two phosphorous,[6] two aluminum,[7] or one phosphorous and one aluminum atom[2] in the second coordination shell of the vanadium. In this study, we employed HYSCORE spectroscopy[9] to measure weak super hyperfine (shf) interactions of the VO^{2+} with the nuclear spins of the surrounding ^{31}P ($I = 1/2$) and ^{27}Al ($I = 5/2$) framework nuclei with the aim to confirm one of the suggested vanadium(IV) sites.

VAPO-5 has been synthesized with triethylamine as the template using the following gel composition: $1.0Al_2O_3$:$1.25P_2O_5$:$0.7Et_3N$:$20.3H_2O$:$0.05V_2O_5$. The gels were prepared as reported previously[4,10] and crystallized at 200 °C for 36 h. The as-synthesized material (sample VAPO-5(as)) was calcined at 540 °C in a flow of nitrogen for 18 h and subsequently in air for 4 h. The calcined samples were reduced in 1 bar of dry hydrogen for 8 h at 773 K and subsequently water was adsorbed at its room temperature vapor pressure (sample VAPO-5(hy)).

X-band ESR spectra of VAPO-5 materials at $T = 77\,K$ (Figure 1) revealed the existence of two paramagnetic V(IV) species A and B as reported earlier.[5–7] The spin Hamiltonian parameters for samples VAPO-5(as) (species A: $g_{xx} = 1.974$, $g_{yy} = 1.984$, $g_{zz} = 1.937$, $A_{xx/yy} = 65 \times 10^{-4}\,cm^{-1}$, $A_{zz} = 177 \times 10^{-4}\,cm^{-1}$, species B: $g_{xx} = 1.972$, $g_{yy} = 1.983$, $g_{zz} = 1.925$, $A_{xx/yy} = 66 \times 10^{-4}\,cm^{-1}$, $A_{zz} = 178 \times 10^{-4}\,cm^{-1}$) and VAPO-5(hy) (species A: $g_{xx} = 1.974$, $g_{yy} = 1.984$, $g_{zz} = 1.937$, $A_{xx/yy} = 66 \times 10^{-4}\,cm^{-1}$, $A_{zz} = 179 \times 10^{-4}\,cm^{-1}$, species B: $g_{xx} = 1.972$, $g_{yy} = 1.983$, $g_{zz} = 1.925$, $A_{xx/yy} = 68 \times 10^{-4}\,cm^{-1}$, $A_{zz} = 182 \times 10^{-4}\,cm^{-1}$), as deduced from spectral simulations using the EasySpin[11] ESR simulation package, indicate that vanadium is present as VO^{2+} species in either a distorted octahedral[6,7] or square-pyramidal[5] symmetry. The intensity ratio of the ESR signal of the two species changes slightly from A/B = 2/1 in VAPO-5(as) to A/B = 1.4/1 in VAPO-5(hy).

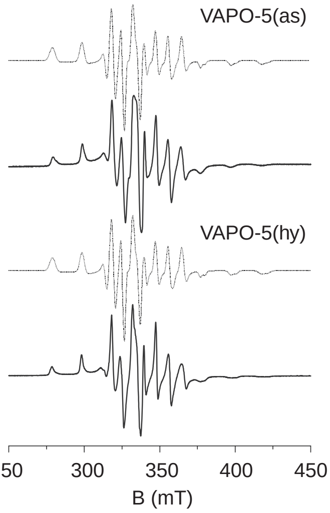

Figure 1. Experimental (—) and simulated (-----) ESR spectra of VAPO-5(as) and VAPO-5(hy) materials at $T = 77\,K$.

Figure 2 illustrates HYSCORE spectra recorded at 335.9 mT for the as-synthesized VAPO-5(as) and calcined and subsequently hydrated VAPO-5(hy) materials. Both VO^{2+} species A and B contribute to the HYSCORE spectra at this field position. The spectra are comparable except for the fact that the signal to noise ratio for VAPO-5(hy) was lower and more scans had to be accumulated. Intense cross peak ridges due to ^{31}P, ^{27}Al, and ^{1}H nuclei are observed which are indicative for substantial ligand shf couplings of the VO^{2+} species with framework phosphorous and aluminum atoms. Assuming an axially symmetric phosphorous shf interaction tensor, we estimate from the maximum curvatures $\Delta\nu_{max} = 0.29\,MHz$ for VAPO-5(as) and $\Delta\nu_{max} = 0.32\,MHz$ for VAPO-5(hy) of the ^{31}P cross peak ridges an anisotropic shf coupling parameters $T_\perp = 2.1$ and $T_\perp = 2.2\,MHz$,[12] respectively. Then, the $T_\perp$ parameters together with the cross-peak positions lead to isotropic shf coupling parameters A_{iso} of about 6 MHz which correspond to a spin density in the phosphorous s atomic orbitals (AO's) of $\rho_s = 0.04\%$. On the basis of the point dipole approximation[12] the $T_\perp$ parameters would translate into a V(IV)–P distances of 2.5 Å which seems to be underestimated in the present case of an phosphorous atom in the second or higher coordination sphere presumably because of unpaired spin density contributions in the phosphorous p AO's. In case of the ^{27}Al peaks shf parameters

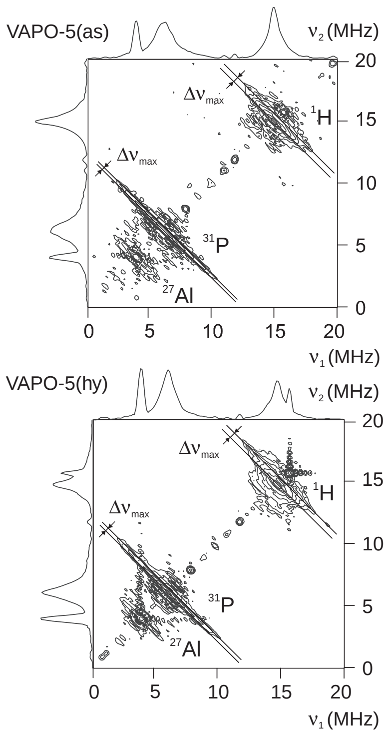

Figure 2. HYSCORE spectra of VAPO-5(as) and VAPO-5(hy) materials measured at the powder position (335.9 mT) of the V(IV) ESR spectra at $T = 6$ K with a pulse delay $\tau = 88$ ns (optimized for ^{31}P) between first and second microwave pulse. The diagonal peak at (15.7, 15.7) MHz is an instrumental artifact.

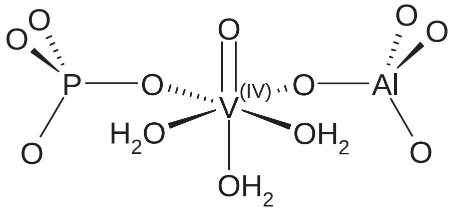

Figure 3. Proposed structure of V(IV) species in VAPO-5.

$T_\perp = 0.9$ MHz and $A_{\rm iso} = 2$ MHz have been deduced from the position and width of the cross peak ridges for both samples leading to $\rho_s = 0.05\%$ and again an underestimated V(IV)–Al distance of 2.7 Å. The expected V(IV)–P/Al distances for P or Al in the second coordination sphere are about 3 Å:[7] Thus, both the magnitude of the anisotropic ^{31}P and ^{27}Al shf coupling parameters and the comparable spin densities at the two atoms imply that the VO^{2+} species coordinate equatorially to two framework oxygen atoms with phosphorous and aluminum framework atoms in the second coordination shell (Figure 3). A comparable VO^{2+} coordination has been already suggested on the basis of quantum chemical calculations in combination with X-ray absorption and Raman spectroscopic studies.[2] Further bonds of the vanadium to framework oxygen atoms can be excluded because of the observed substantial ^{1}H shf couplings. The parameters estimated from the pronounced proton cross peak ridges (VAPO-5(as): $\Delta\nu_{\rm max} = 0.62$ MHz, $T_\perp = 4.8$ MHz, $A_{\rm iso} \approx 4$ MHz and VAPO-5(hy): $\Delta\nu_{\rm max} = 0.67$ MHz, $T_\perp = 4.9$ MHz, $A_{\rm iso} \approx 4$ MHz) are typical for equatorially coordinating water molecules of VO^{2+}(H$_2$O)$_n$ type complexes.[13] The less pronounced ^{1}H cross peaks near the proton nuclear Larmor frequency with parameters $\Delta\nu_{\rm max} = 0.27$ MHz and $T_\perp = 3.1$ MHz are presumably due to an axially coordinated water molecule in accordance with a distorted octahedral VO^{2+} environment.[6,7,14]

The observed presence of a both phosphorous and aluminum framework atoms in the second coordination shell of the VO^{2+} excludes isomorphous substitution of the V(IV) ions into the aluminophosphate framework. The HYSCORE data rather support an anchoring of the vanadyl ions to the framework by two framework oxygen atoms as previously suggested by Cheng et al.[2] In as-synthesized as well as in calcined and subsequently hydrated VAPO-5 the open coordination sites are then saturated by water molecules as depicted in Figure 3. Calcination of the molecular sieve does not seem to have a significant influence on the sitting of the VO^{2+} ions in the VAPO-5 system and their specific coordination to the framework oxygen atoms. Finally, it is worth to mention that two potential different anchoring sites for VO^{2+} with phosphorous and aluminum atoms as second next neighbors have been identified in the VAPO-5 structure by DFT studies[2] which might explain the formation of two VO^{2+} species A and B with slightly different ESR parameters. Further orientation selective HYSCORE experiments are in progress to verify this assignment of the two species A and B.

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Published on the web (Advance View) October 29, 2005; DOI 10.1246/cl.2005.1614