The Study on Location and Adsorbate Interaction for Vanadium Species in VO^{2+}-SAPO-5 by Electron Spin Resonance and Electron Spin Echo Modulation Spectroscopies

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Abstracts : Vanadium-incorporated aluminophosphate molecular sieve VO^{2+}-SAPO-5 was studied by electron spin resonance (ESR) and electron spin echo modulation (ESEM) spectroscopies to determine the vanadium structure and interaction with various adsorbate molecules. It was found that the main species at low concentration of vanadium is a monomeric vanadium units in square pyramidal or distorted octahedral coordination, both in oxidation state (IV) for the calcined hydrated material and in oxidation state (V) for the calcined material. After calcinations in O$_2$ and exposure to moisture, only species A is observed with reduced intensities. It is suggested as a VO(H$_2$O)$_3^{2+}$ complex coordinated to two framework oxygen bonded aluminum. When calcined, hydrated VO^{2+}-SAPO-5 is dehydrated at elevated temperature, a species loses its water ligands and transforms to VO^{2+} ions coordinated to two framework oxygens (species B). Species B reduces its intensity, significantly after treatment with O$_2$ at 600 °C for 5 h, thus suggesting oxidation of V^{4+} to V^{5+}. When dehydrated VO^{2+}-SAPO-5 contacts with D$_2$O at room temperature, the EPR signal of species A is observed. Thus species assumed as a VO^{2+}(O$_f$)$_2$(D$_2$O)$_3$, by considering two framework oxygens. Adsorption of deuterated ethanol, propanol on dehydrated VO^{2+}-SAPO-5 result in another new vanadium species E and F, respectively, which are identified as a VO^{2+}-(CH$_3$CH$_2$OD)$_3$, VO^{2+}-(CH$_3$CH$_2$CH$_2$OD)$_2$ complex. When deuterated benzene is adsorbed on dehydrated VO^{2+}-SAPO-5, another new vanadium species G, identified as a VO^{2+}-(C$_6$D$_6$) is observed. Possible coordination geometries of these various complexes are discussed.
Keyword : molecular sieve VO^{2+}-SAPO-5, VO(H$_2$O)$_3^{2+}$ complex, ESR, ESEM, VO^{2+}-(C$_6$D$_6$)

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INTRODUCTION

It is well-known that the catalytic properties of transition metal incorporated molecular sieves strongly depend on the nature and location of the metal ion on their susceptibility and coordination with adsorbate molecules.[1]

Electron spin resonance (ESR), electron spin echo modulation (ESEM), infrared spectroscopy (IR), X-ray photoelectron (XPS) spectroscopy, UV-visible diffuse reflectance spectroscopy, X-ray diffraction (XRD) and Solid NMR Spectroscopy technique have been used to characterize the properties of vanadium-exchanged zeolites such as oxidation state, location and dispersion of vanadium.[2-7]

In this study we explore the possibility of incorporating vanadium ion into SAPO-5 by adding V_2O_5 to form VO^{2+}-SAPO-5 in which vanadium is clearly in an extra-framework position. That study illustrates that V(IV) species exist as a vanadyl ion either VO^{2+},or V^{4+}. We synthesize vanadium-doped SAPO-5 by high temperature solid state ion-exchanged method between SAPO-5 and V_2O_5, and describe local symmetry of the vanadium by ESR and the nature, location and adsorbate interactions of vanadium in this material by ESEM.

EXPERIMENTAL SECTION

Preparation

The molecular sieves H-SAPO-5 was synthesized according to Union Carbide Patent with some modification made in our laboratory.[10] To synthesize SAPO-5, H_3PO_4(85 % Fluka), $Al_2O_3 \cdot H_2O$ (Vista Chemical), tripropylamine(Aldrich Chemical), fumed silica(Sigma Chemical), and de-ionized water were used to prepare a homogeneous gel with the following molar composition : $2.0Pr_3N;0.3SiO_2:Al_2O_3 \cdot P_2O_5: 40H_2O$. An aqueous solution (2.3992 g) of Catapal alumina (Vista) was prepared, after adding 8.1 ml of de-ionized water to 2.3992 g of Catapal alumina, homogenizing with continuous stirring and stirred for 1 hour at room temperature, and then 11.4 ml of de-ionized water was added and stirred at 298 K for 1 hour. Then, 2.796 ml of 85wt% H_3PO_4 was added by drop by drop to this solution. While the temperature was controlled with an ice bath at 273 k for 15 min and stirred at 298

K for 1 hour. Then, to this solution were added 0.3612 g of 99 wt% SiO_2 and 3.0 ml of H_2O successively with mixing for 30 min. Then, 7.6872 ml of 99 wt% of tripropylamine was added drop by drop. And the solution aged at room temperature for 24 h to form SAPO gel. The gel was sealed in a stainless steel pressure vessel lined with Teflon and heated at 150 °C for 48 h at autogeneous pressure. The autoclave was then cooled, and the reaction material was washed three times with de-ionized water before filtration. This product is called" as-synthesized" H-SAPO-5.

VO^{2+}-SAPO-11, in which V^{4+} ions are in extra-framework positions, was prepared by solid-state ion exchange using V_2O_5 (Aldrich) and H-SAPO-5. A mixture of 0.005 g of vanadium oxide and 0.245 g of H-SAPO-5 was ground in a mortar and a pestle for 30 min. This solid mixture was then heated in an oven at 873 k in pure oxygen for 5 h and cooled slowly to room temperature. Before and after solid-state ion exchange, the sample changed from orange and to grey(species A). It forms VO^{2+}-SAPO-5 in which the framework negative charge is balanced by VO^{2+}, H$^+$ and the composition is $V_{0.01}H_{0.04}(Si_{0.1}Al_{0.49}P_{0.64})O_2$ based on the characteristic X-ray of specific element.

Sample Treatment and Measurement

Powder X-ray diffraction (XRD) patterns were recorded on a Phillips PW 1840 X-ray diffractometer using CuKα radiation. Thermogravimetric analysis was performed by the Dupon 951 thermal analyzer with heating rate of 5 °C min^{-1}. Chemical analyses of the samples were carriedout by the intensity of the characteristic X-ray with Oxford Energy dispersive X-ray spectrometer.

For ESR and ESEM measurements, VO^{2+}-SAPO-5 was loaded into 3 mm o.d. x 2 mm i.d. Suprasil quartz tube. Calcined, hydrated VO^{2+}-SAPO-5 sample was examined by ESR without any treatment (We assigned as species A). ESR spectra were recorded on a calcined, hydrated VO^{2+}-SAPO-4. This sample was then evacuated to a final pressure 10^{-4} Torr at 295 K overnight. To study the ESR behavior of the vanadium as a function of dehydration, the samples were heated under vacuum from 295 K to 873 K, this sample was oxidized by dry oxygen at 873 K for 5 h. This sample was then cooled to room temperature to give a oxidized sample (Note the ESR spectrum of Fig. 3b and we assigned as a new species B). To study the redox behavior of calcined, hydrated VO^{2+}-SAPO-5 was dehydrated at 873 K and

then contacted 1 atm of O_2 at 873 K for 5 h followed by evacuation at same temperature for 1 min to give species B. The oxygen-treated sample was then contacted with 1 atm of dry CO at 673 K for 8 h before ESR measurements we assigned as species D. The oxygen-treated sample also followed by evacuation at same temperature for 1 min and maintained under vacuum at this temperature for 18 h. To study vanadium interaction with various adsorbates the dehydrated VO^{2+}-SAPO-5 samples were exposed to the room temperature vapor pressure of EtOD, PropD (Aldrich Chemical) C_6D_6 (Aldrich Chemical), we assigned as species E, F, and G, respectively. The samples with adsorbates were sealed in liq N_2 and kept at room temperature for 24 h before ESR and ESEM measurements.

ESR spectra were recorded with a modified Varian E-4 spectrometer interfaced to a Tracer Norton TN-1710 signal averager at 77 K. Each spectrum was obtained by multiple scan to acieve a satisfactory signal-to-noice-rate. Each acquired spectrum was transferred from to signal averagerto an IBM PC/AT compatible computer for analysis and plotting. The magnetic field was calibrated with a Varian E-500 gauss meter. The microwave frequency was measured by a Hewlett-Packard HP 5342A frequency counter. The ^{2}D ESEM spectra were measured at 4.8 K with a Bruker 380 pulsed ESR spectrometer. Three pulse echoes were measured by using a $\pi/2$-τ-$\pi/2$-T-$\pi/2$ pulse sequence as a function of time T to obtain a time domain spectrum. Modulation from other nuclei in the system was minimized by choosing the τ values on the basis of the magnetic field position. The theory and simulation of ESEM are described elsewere.[25]

RESULTS

VO^{2+}-SAPO-5 sample was characterized by powder XRD, and crystallinity and phase purity was confirmed (Fig. 1). The observed XRD patterns match well with the pattern reported for the MFI structure type.[10-11] Practically no loss in crystallinity was observed when an as-synthesized sample was heated at 873K for 16 h to remain the organic template. The chemical composition of VO^{2+}-SAPO-5 was estimated by the characteristic X-ray of specific element analyzed on a number of crystals. The average chemical compositions of the sample is found to be $(V_{0.010} Al_{0.49} Si_{0.10} P_{0.64}) O_2$, which corresponds to ~1 V in 100 unit

cells. ESR spectrum of as-synthesized VO^{2+}-SAPO-5 is shown in Fig. 2. The spectrum consists of one axially symmetric signals designated here as species A with hyperfine structure. The ESR parameters are $g_{||}{}^A = 1.925$ and $A_{||}{}^A = 183$ x 10^{-4} cm^{-1} and $g_{\perp}{}^A = 1.992$ and $A_{\perp}{}^A = 64.9$ x 10^{-4} cm^{-1}. Because of overlap with the parallel components, the ESR parameters of the perpendicular components, through resolved, are less accurate than the parallel components. These parameters are typical of VO^{2+} with distorted octahedral coordination.[1-2] The spectrum shows hyperfine structure due to interaction of the unpaired $3d^1$ electron with the ^{51}V nucleus whose spin is 7/2 and that is present in 99.76 % abundance and by second-order effect that to produce an asymmetric hyperfine patterns with unequal separations of the lines. The well-resolved hyperfine structure supports a high dispersion of the VO^{2+} ions in SAPO-5. Moreover, no abroad background signal due to polynuclear oxidized vanadium, which is normally present in samples prepared with high vanadium contents, is observed. Immediately after calcinations in dry oxygen, VO^{2+}-SAPO-5 does not show any signal suggesting the complete oxidation of VO^{2+} to V^{5+} during calcinations. A calcined sample is normally exposed to room-temperature humidity before evacuation and dehydration treatments and thus, is hydrated. This calcined, hydrated sample shows weak ESR signal. However, calcined sample after oxidation treatment at 773 K for 5 h shows ESR spectrum that is very weak from that of a calcined, hydrated sample.
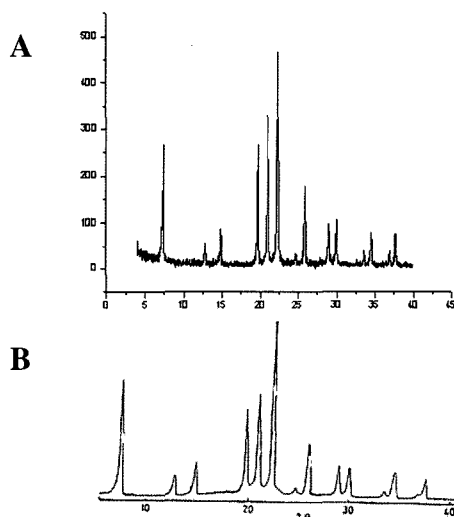

Fig. 1. XRD patterns of synthesized samples (A) SAPO-5, (B) H-SAPO-11[10].

On the other hand, the ESR spectrum of $(VO)^{2+}$-SAPO-5 after dehydration at 873 K for 18 h after previously oxidized sample, shows only a single axially symmetric signal with hyperfine structure, designated here as species C (Fig. 2c). The ESR parameters are $g_{||}^C = 1.942$ and $A_{||}^C = 183 \times 10^{-4}$ cm^{-1}, and $g_{\perp}^C = 2.038$ and $A_{\perp}^C = 60.1 \times 10^{-4}$ cm^{-1}. These parameters are significantly different from those of species A. Possible impurities, like e.g., a vanadium (IV) pentoxide are expected to contain dimeric or polymeric vanadyl units which give rise to a broad singlet at room temperature.[3] In the calcined material, most vanadium ions are oxidized to state(V), as can be concluded from the presence of a single weak ESR signal(ca. 1 % of the original intensity).
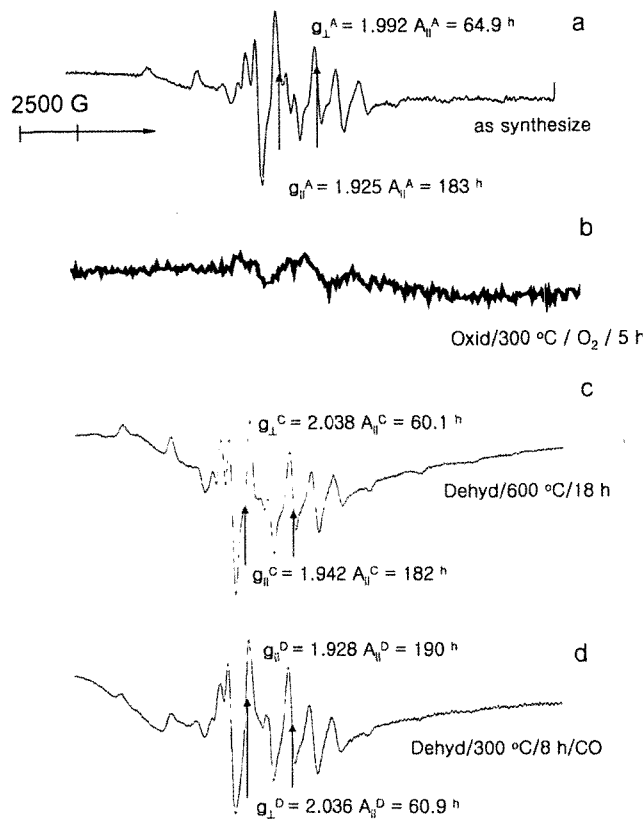
Fig. 2. ESR spectra at 77 K of (a) as-prepared VO^{2+}-SAPO-5 and (b) as-prepared VO^{2+} after O$_2$ oxidation at 673 K for 5h (c) dehydration at 873 K for 18 h of as-prepared VO^{2+} (d) after CO treatment at 673 K for 8 h of previously oxidized sample. *^{h} x 10^{-4} cm^{-1}

The reduction behavior of CO, when calcined VO^{2+}-SAPO-5, after dehydration at 873 K, O_2 treatment same temperature for 5h, and the evacuation, is treated with 1 atm of CO at temperature > 673 K for 8 h. the resultant spectrum shows a vanadium species, denoted as species D, with parameters $g_{||}^D$ = 1.928 and $A_{||}^D$ = 190 x10^{-4} cm^{-1}, and $g_{\perp}^D$ =2.036 and $A_{\perp}^D$ = 60.9 x 10^{-4} cm^{-1}(Fig. 3d). The ESR parameters of the species correspond to those of VO^{2+} with distorted octahedral site symmetry.

Fig. 3 shows spectrum after D_2O are adsorbed on dehydrated VO^{2+}-SAPO5 at room temperature for 20 min. A single vanadium species, whose parameters are sample as those of species A, is observed on adsorbtion of D_2O on VO^{2+}-SAPO-5. This results suggest that species A is an aquo-vanadyl complex. The ESR spectrum recorded on VO^{2+}-SAPO-5 after adsorbed deuterated ethanol shows a new vanadium species E characterized by $g_{||}^E$ = 1.916 and $A_{||}^E$ =196 x 10^{-4} cm^{-1} and $g_{\perp}^E$ = 1.986 and $A_{\perp}^E$= 69.5 x 10^{-4} cm^{-1} is observed (Fig. 4e). Also when deuterated propanol is adsorbed on dehydrated VO^{2+}-SAPO-5, a new species F, with ESR parameters $g_{||}^F$ = 1.930 and $A_{||}^F$ = 194 x 10^{-4} cm^{-1}, and $g_{\perp}^F$ =1.988 and $A_{\perp}^F$ = 70.5x 10^{-4} cm^{-1} is observed. Also, when deuterated benzene is adsorbed on dehydrated VO^{2+}-SAPO-5, a new species G, with ESR parameters $g_{||}^G$ = 1.918 and $A_{||}^G$ = 193 x 10^{-4} cm^{-1}, and $g_{\perp}^G$ = 1.980 and $A_{\perp}^G$ = 64.9 x 10^{-4} cm^{-1} is observed.
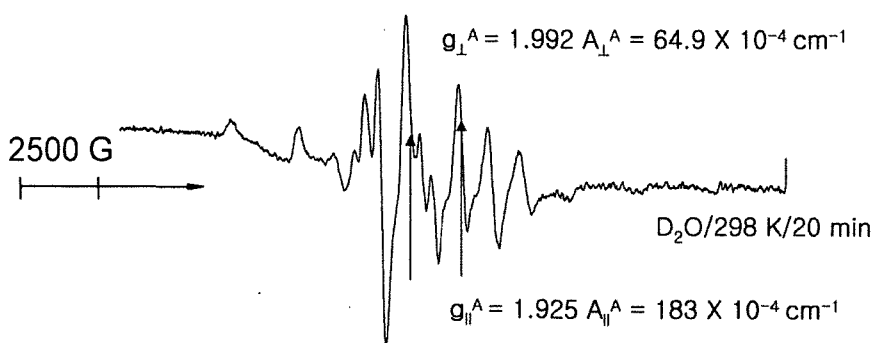
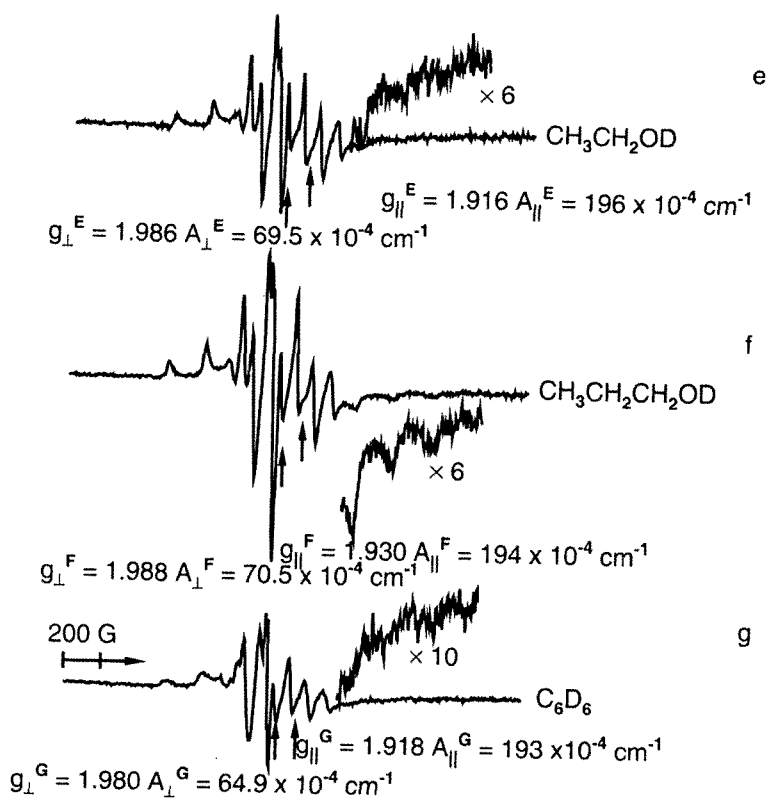Fig. 3. ESR spectrum at 77 K of VO^{2+}-SAPO-5 after D_2O adsorption on a dehydrated sample at 298 K for 20 min.

Fig. 4. ESR spectra at 77 k of VO^{2+}-SAPO-5 (e) after CH_3CH_2OD adsorption on dehydrated at 298 K for 20 min (f) after $CH_3CH_2CH_2OD$ adsorption on a dehydrated sample at 298 K for 20 min (g) after C_6D_6 adsorption on a dehydrated sample at 298 K for 20 min.

Three-pulse ^2D ESEM spectra were recorded at around a magnetic field of 3400 G and at a microwave frequency of 9.854 GHz for various VO^{2+} species. The echo signal was maximum around this field. The delay between the first and second pulses (τ) was selected so as to minimize modulation from other magnetic nuclei present in the system. Fig. 5a is given the experimental and simulated ^2D ESEM spectrum of VO^{2+}-SAPO-5 after adsorbing deuterated ethanol. The interpulse time τ was selected as 0.26 μs. Simulation of the spectrum gives three deuterium at 3.1 Å. These values are consitent with three CH_3CH_2OD molecules directly coordinating with VO^{2+} ions in species E. Fig. 5b shows the experimental and simulated ^2D ESEM spectrum of VO^{2+}-SAPO-5 after deuterated propanol adsorption.

The magnetic field and τ values are the same as for adsorbed CH_3CH_2OD. Simulation of the spectrum gives two deuteriums at 3.2 Å.

These parameters are consistent with two propanol molecules directly coordinating with VO^{2+} ions in species F. Fig. 6 shows the experimental and simulated ^2D ESEM spectrum observed for VO^{2+}-SAPO-5 after adsorbing C_6D_6. Simulation of the spectrum gives six deuteriums at 3.9 Å. These parameters indicate that one molecule of benzene coordinates with VO^{2+} in species G.
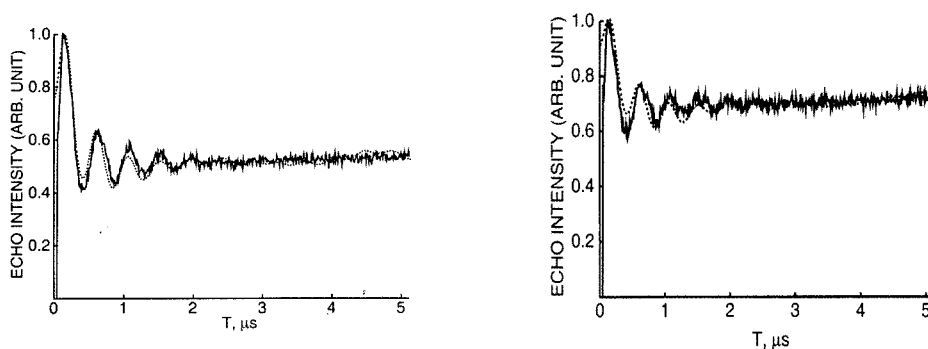
(a)   (b)

Fig. 5. Experimental(-) and simulated(----) three pulse ESEM spectra at 4 K of a dehydrated VO^{2+}-SAPO-5 with (a)CH_3CH_2OD (N=3, R=3.08Å, A=0.05MHz) (b) $CH_3CH_2CH_2OD$ (N=2, R=3.23Å , A=0.067MHz)
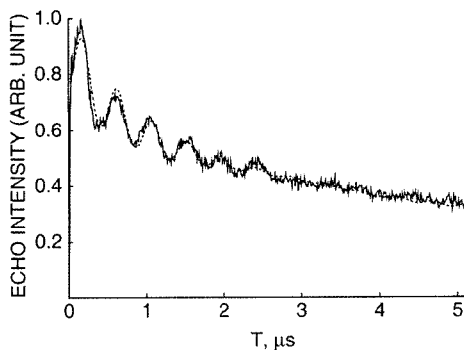

Fig. 6. Experimental(-) and simulated(----) three pulse ESEM spectra at 4 K of a dehydrated VO^{2+}-SAPO-5 with C_6D_6 (N=6, R=3.88Å, A=0.097MHz).

DICUSSIONS

Tetravalent vanadium normally enters into compounds and various host lattices as V^{4+} more and more after as the stable oxovanadium molecular ion VO^{2+} exhibiting paramagnetic resonance absorption due to a single unpaired electron. The electronic state of VO^{2+} is normally dependent on the $3d^1$ electron of vanadium and therefore the energy levels of VO^{2+} are similar to those of V^{4+} ion. However, there are differences from the paramagnetic behavior of these two ions. The ionic V^{4+} usually has tetrahedral coordination and, because of low lying excited state, has a very short spin-lattice relaxation time. So, ESR spectra can only be observed at or below 77 K. On the other hand, the vanadyl species VO^{2+} normally has square pyramidal or distorted octahedral coordination and has a longer spin-lattice relaxation time,[12] as a consequence, its ESR spectra can be observed at room temperature.

The spin Hamiltonian parameters of VO^{2+} change from lattice to lattice. The g and A values depend on several molecular parameters and the crystal field splliting. The g and A values depend on several molecular parameters and the crystal field splitting. The properties of a ligand such as its elecronegativity, π-bonding ability, and ligand field strength, will also influence the g and A values.[13] In generally isotropic parameters g_{iso} {=(1/3)($g_{||}$ + 2 $g_{||}$) and A_{iso} {=(1/3)($A_{||}$ + 2 $A_{\perp}$) vary ligand bond strength. For a ligand with strong covalent bonding, the delocalization of the unpaired electron of vanadium onto the ligand orbital is large, which reduces the spin-orbit coupling and thereby increases g_{iso}. This situation results in smaller hyperfine coupling and thereby increases g_{iso}, because the interaction of the electron with the vanadium nucleus decreases. ESR studies has been reported for several systems in which vanadium enters as VO^{2+} ion, doped into aluminophosphate five. For example, the VO^{2+} ion in VAPO-5 exhibits an ESR signal with parameters $g_{||}$ = 1.932, $g_{\perp}$ = 1.983, and $A_{||}$ = 185 x 10^{-4} cm^{-1} $A_{\perp}$ = 73 x 10^{-4} cm^{-1}.[6] Similarly, the parameters from the sample of VO^{2+} doped into ZSM-5 are $g_{||}$ = 1.930 and $g_{\perp}$ = 1.984, and $A_{||}$ = 187 x 10^{-4} cm^{-1} and $A_{\perp}$ = 76 x 10^{-4} cm^{-1}.[12] The VO^{2+} ions in these systems have distorted octahedral site symmetry with ground state being d_{xy}, and ESR signals can be observed at 300 K. Similar values have been reported for VO^{2+} in several other crystal lattice.[14] For example, VO^{2+} ions in VAPO-5 shows an ESR signal with parameters $g_{||}$ = 1.934 and $g_{\perp}$ = 1.993,and $A_{||}$ = 189.8 x 10^{-4} cm^{-1} and $A_{\perp}$ = 72 x 10^{-4} cm^{-1}.[15]

Table 1 ESR Parameters and Possible Assignments of Various Vanadium Species Observed in VO^{2+}-SAPO-5 Molecular Sieve

Treatment	Species	assignment	$g_{||}$	$A_{||}{}^a$	$g_{\perp}$	$A_{\perp}{}^a$
Calcined hydrated	A	VO^{2+}-$(H_2O)_3$	1.925	183	1.992	64.9
Oxidized	B					
Dehydrated	C	VO^{2+}	1.942	183	2.038	60.1
CO	D	VO^{2+}-$(CO)_2$	1.928	190	2.036	60.9
D_2O	A	VO^{2+}-$(D_2O)_3$	1.925	183	1.992	64.9
CH_3CH_2OD	E	VO^{2+}-$(CH_3CH_2OD)_3$	1.916	196	1.986	69.5
$CH_3CH_2CH_2OD$	F	VO^{2+}-$(CH_3CH_2CH_2OD)_2$	1.930	194	1.988	70.5
C_6D_6	G	VO^{2+}-(C_6D_6)	1.918	193	1.979	64.9

^{a} x 10^{-4} cm^{-1}

Tetravalent V^{4+}, ion on the other hand, has different values for the ESR parameters. For example, V^{4+} in $ThGeO_4$ shows an ESR signal with $g_{||}$ = 1.831 and $g_{\perp}$ = 1.980, and $A_{||}$ = 166 x 10^{-4} cm^{-1} and $A_{\perp}$ = 32 x 10^{-4} cm^{-1} at 77 K.[19] Vanadium has tetrahedral site symmetry with a ground state of d_{xy} in these systems. Even in systems where V^{4+} has octahedral site symmetry, the ESR parameters are markedly different from those of VO^{2+}. This ion has a short relaxation time because the spectrum is observed only at 77 K but not at 300 K.[24]

Calcined hydrated VO^{2+}-SAPO-5 shows single species, A. ESR parameters are very similar to the values reported for VO^{2+} with octahedral site symmetry in various other systems. Thus, species A can be assigned to VO^{2+} with distorted octahedral coordination.

The observed ESEM results on VO^{2+}-SAPO-5 support the model suggested by Montes et al.[6] wherein the vanadyl species neutralize two Al-O⁻ groups from the framework, leaving two additional Al-O⁻ to be neutralized by protonated template species or by H_3O^+. A different VO^{2+} species, which are characterized by species E with ESR parameters parameters $g_{||}{}^E$ = 1.916, and $A_{||}{}^E$ = 196 x 10^{-4} cm^{-1} and species F with ESR aparameters $g_{||}{}^F$ = 1.930, and $A_{||}{}^F$ = 194 x 10^{-4} cm^{-1} are generated from ethanol, and propanol, respectively. Adsorption of propanol onto a dehydrated sample of VO^{2+} complex generates a VO^{2+} complex which has a different stereochemistry from the complex produced after the adsorp-

tion of ethanol. It is possible, due to the size of propanol, that the tail portion of the molecule project through a 12-membered ring and the hydroxyl end lies in the six-ring window into the vanadyl ion. In CuH-SAPO-5 it is reported that univalent cations are distributed near six-ring windows in the site II.[16] Only a single species is observed in a dehydrated sample and after adsorption of various adsorbates on dehydrated sample. If species A is indeed the same vanadium species located at different framework sites, one would expect two signals after adsorption of various adsorbates. Moreover, species A in calcined hydrated sample is the same species observed after adsorption of D_2O on dehydrated sample. This observation clearly supports the idea that species A is aquavanadyl complex with additional coordination from framework oxygens. VO^{2+}-SAPO-5 molecular sieve is synthesized by solid-state ion-exchanged method. Thus, formation of complex for vanadyl ions with water interaction is likely under such basic conditions. So, we assign vanadyl species A to $VO(H_2O)_3^{2+}$ based on the number of water molecules interacting with VO^{2+} ion species and octahedral symmetry after adsorption of D_2O on dehydrated sample. This analogy is justified by the fact that the ESR parameters observed for species A in calcined hydrated sample are the same as those observed after adsorption of D_2O on the dehydrated sample.

It would be interesting to compare the structure of vanadium in dehydrated sample VO^{2+}-SAPO-5 with that in vanadium aluminophophate materials such as VAPO-5. In our earlier study on a VO^{2+}-SAPO-11 molecular sieve, we observed a single paramagnetic vanadyl species with distorted octahedral coordination in a calcined hydrated sample. This species is suggested as $VO(H_2O)_2^{2+}$ based on ESR results.[20] However, in the earlier study on a VAPO-5 molecular sieve, one of these species is identified as $VO(H_2O)_3^{2+}$ based on ESEM results.[1] The absence of any vanadyl species in calcined hydrated VO^{2+}-SAPO-5 is indicative of complete oxidation of VO^{2+} ion to V^{5+} ion during calcinations in O_2. On evacuation and dehydration at 873 K, a new species C, characteristic of a vanadyl ion, is observed. Reduction of metal ion such as Mo^{5+}, Pd^{2+} during dehydration at elevated temperature has been reported earlier in several systems. For example in Pd^{2+}-exchanged SAPO-34, we have reported that dehydration at temperature >873 K causes a elevation of ESR intensity. This increase in ESR intensity was attributed to the change Pd^{2+} to Pd^{1+} by residual water decomposition.[17] A similar mechanism is possible here in VO^{2+}-SAPO-5 wh-

ere V^{5+} is reduced to VO^{2+} by residual water with water decomposition. A possible reaction mechanism is shown in eq (1), where M represents the molecular sieve VO^{2+}-SAPO-5:

$$[V^{5+} = O, H_2O]M \rightarrow [V^{4+} = O, H^+, OH^-]M \rightarrow [V^{4+} = O \ (OH---H^+)M \ ------------------(1)$$
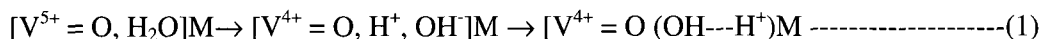
The appearance of species A after O_2 treatment at 873 K is due to oxidation of the VO^{2+} ions to V^{5+}. Dehydration of hydrated VO^{2+}-SAPO-5 produces species C, whose g and A parameters are slightly different from those of species A. These changes can be related to a change in the ligand nature between species C and species B. In VO^{2+} exchanged SAPO-11 these changes have been described as VO^{2+} ions localized with a supercage having coordination with three framework oxygens.[20] Because the 4-ring and 6-ring channels of SAPO-5 are too small for the large VO^{2+} ion to enter, the location of these ions in the main 12-ring seems likely. The smaller hyperfine coupling of species C in comparison with that of species A could be due to greater covalent bonding between vanadium and framework oxygens in VO^{2+}-SAPO-11. We have studied on the oxidation-reduction behavior of vanadium in VO^{2+}-SAPO-11. ESR signal with parameters $g_{||} = 1.927$ and $g_{\perp} = 1.990$, and $A_{||} = 180 \times 10^{-4}$ cm^{-1} and $A_{\perp} = 79 \times 10^{-4}$ cm^{-1} was reported for a VO^{2+} species in its calcined hydrated.[20] After calcinations this signal disappeared completely due to complete conversion of to V^{5+}.

On the reduction in CO at 673 K for 6 h, an ESR signal with parameters with $g_{||}^D = 1.928$ and $g_{\perp}^D = 2.036$, and $A_{||}^D = 190 \times 10^{-4}$ cm^{-1} and $A_{\perp}^D = 60.9 \times 10^{-4}$ cm^{-1} is observed showing the reversible redox behavior of vanadium in VO^{2+}-SAPO-5. Similar to results have been reported for VAPO-5 with parameters with $g_{||} = 1.934$ and $g_{\perp} = 1.993$, and $A_{||} = 189.8 \times 10^{-4}$ cm^{-1} and $A_{\perp} = 72 \times 10^{-4}$ cm^{-1}.[21] The ESR parameters of species D observed in VO^{2+}-SAPO-5 after reduction by CO are somewhat different from these of species A. This result suggests that the coordination environments of VO^{2+} in species are somewhat different from those for species A or C. The ESR parameters of species D are close to those of species A. Species A, however, has lower A values. The lowering of A parameter indicates that the axial components becomes more covalent. Species D is therefore more likely a square pyramidal complex compare to octahedral symmetry observed for species A. This difference in symmetry may account for the observed difference in the ESR parameters

for species D compared to species A.

Lower oxidation states of vanadium are also possible after reduction. It has been reported using temperature-programmed reduction that in VAPO-5 reduction of $V^{4+} \rightarrow V^{3+}$ takes place at temperature above 1073 K and is associated with the collapse of the molecular sieve framework.[2] Since the reduction temperature used into the present study (673-873 K) is much lower than this temperature, we do not show any further of V^{4+} to V^{3+}. Species D, hence, suggests that all of vanadium exist as V^{4+} after reduction with CO, a possible model that is consistent with various observations on the location and redox behavior of vanadium in VO^{2+}-SAPO-5 is shown schematically in Fig. 7. Although several studies have been studied on the nature of vanadium, especially its oxidation state and the location in molecular sieve, studies on the interaction of this ion with external adsorbates are limited. To describe the redox behavior of vanadium incorporated in AlPO-5, these materiel have been studied by ESR and ESEM. They suggested that the vanadium ion is located at sites near to framework aluminum than to phophorus. They reported that on calcinations, V^{4+} species are converted to V^{5+} species.[1] In the present study, the fact that the ESR parameters of VO^{2+} changes significantly after adsorption of various molecules indicates direct insertion of these molecules into the first coordination sphere of vanadium ion. This is further confirmed by the ^2D ESEM spectra observed for the these complexes.

With adsorbed ethanol, VO^{2+}-SAPO-5 shows a new VO^{2+}- species, E. ^2D ESEM of three deuteriums at 3.1 Å are consistent with three ethanol molecules coordinating with vanadium with their polar axes pointing toward the metal ion. The first coordinating sphere of vanadium species E involves only oxygen ligand atoms of both the framework and the ethanol molecules. Thus, species E is more likely octahedral symmetry compared to square pyramid. Adsorption of CH_3OD on VAlPO-5 generates a complex in which two methanol molecules coordinate with VO^{2+} ions[1] in CuH-SAPO-5, only two molecules of methanol are found to coordinate with Cu^{2+} ions.[18]

With adsorbed C_3H_7OD, VO^{2+}-SAPO-5 shows a new vanadium species F. ^2D ESEM parameters of two deuterium at 3.2 Å are consistent with two propanol molecule coordinating with V^{4+}. A possible geometry for this complex is one in which the vanadyl ion has σ-bond coordination with a oxygen atom to form square pyramidal. Adsorption of C_3H_7OD on CuH-Chabazite generates a complex in which three propanol molecule coordin-

ate with Cu^{2+} ions.[22] This suggests that the size of the alcohol does not after the stereochemistry of the VO^{2+} ions in SAPO-5 samples.

With adsorbed C_6D_6, VO^{2+}-SAPO-5 shows a new vanadium species G. ^{2}D ESEM parameters of six deuteriums at 3.9 Å are consistent with one benzene molecule coordinating with V^{4+}. A possible geometry for this complex is one in which the vanadyl ion has weak σ-bond coordination with a ring of benzene molecules to form a distorted tetrahedral complex.

When deuterated benzene is adsorbed onto PdH-SAPO-5, Pd^{1+} is found to have π-bond coordination with one molecule of benzene.[23] On the basis of the ESR and ^{2}D ESEM results, possible coordination geometry of the vanadium species observed are given in Fig. 8 It should be noted that unlike V ions present into the framework of VAPO$_4$-5 ion, which includes a vanadyl oxygen, incorporated into the extra-framework.

CONCLUSION

Electron spin echo modulation spectroscopy, when coupled with spectroscopy has been shown to be very effective in obtaining informative about the geometry and location of vanadium in VO^{2+}-SAPO-5 and its coordination with various adsorbates. Calcined, hydrated VO^{2+}-SAPO-5 is suggested as a $VO(H_2O)_3^{2+}$ complex coordinate to two framework oxygen with distorted octahedral coordination. During calcinations of $VO(H_2O)_3^{2+}$, most of VO^{2+} ions are oxidized to V^{5+}. Cacined, hydrated $VO(H_2O)_3^{2+}$, after dehydration at elevated temperature, shows a vanadyl species suggested to be a VO^{2+} ions with no water ligands. Adsorption of CH_3CH_2OD on dehydrated VO^{2+} sample generates a new VO^{2+} species, which is identified as $VO(CH_3CH_2OD)_3^{2+}$. Adsorption of $CH_3CH_2CH_2OD$ on dehydrated sample generates a new vanadyl species, F identified as $VO(C_3H_7OD)_2^{2+}$. When deuterated bezene is adsorbed on the dehydrated sample generates a new vanadyl species G identified as $VO(C_6D_6)_2^{2+}$. ·

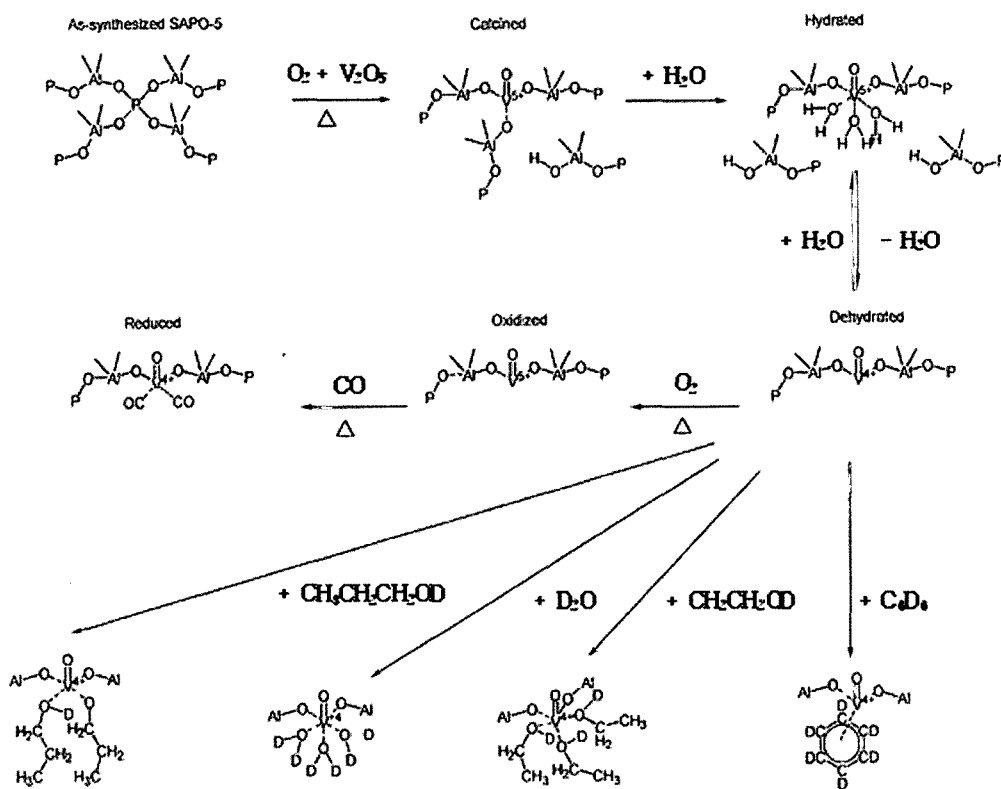Fig. 7. Possible structures of vanadium species in VO^{2+}-SAPO-5 and their reaction with adsorates

Acknowledgement

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