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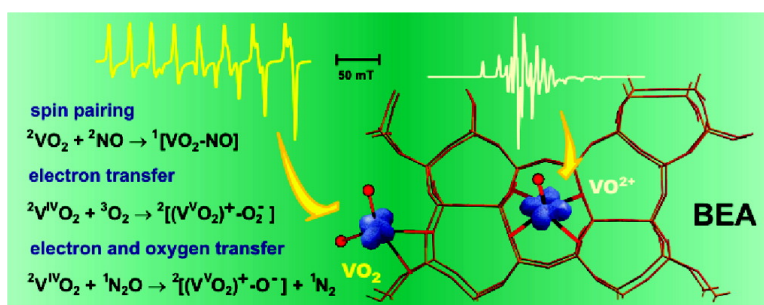
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Generation, Identification, and Reactivity of Paramagnetic VO₂ Centers in Zeolite BEA for Model Studies of Processes Involving Spin Pairing, Electron Transfer, and Oxygen Transfer

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The incorporation of transition-metal ions into molecular sieves has received a great deal of attention because of the possibility to provide the latter with redox properties leading to novel catalysts with active sites of well-defined space confinement for controlled shape selectivity.¹ Various preparation and thermal activation routes have been reported to generate specific mono- and polynuclear centers with valence and coordination states that can be tailored for particular purposes.² In this respect, vanadium introduced into zeolitic matrices can be involved in many catalytic and biomimetic reactions such as hydroxylation of hydrocarbons,³ enantioselective sulfoxidation,⁴ selective catalytic reduction of NO_x,⁵ or various photochemical processes.⁶

Depending on the preparation method, vanadium stabilized in zeolite channels typically forms oxo-complexes of V/IV oxidation state. Usually, vanadium(IV) forms complexes with one oxygen stabilized as [VO]²⁺, whereas vanadium(V) forms complexes with one or two oxygen atoms stabilized as [VO]³⁺ or [VO₂]⁺.⁷ Chelation of these cores by anionic ligands (Schiff base, EDTA, or oxalate) leads to stable molecular complexes.⁸

Contrary to frequent mono-oxovanadium,⁹ the less common di-oxo complexes almost exclusively involve diamagnetic V(V).⁷ However, Knight et al.¹⁰ have shown that vanadium atoms, produced by high-temperature vaporization or pulsed-laser ablation, can react with dioxygen to yield VO₂ radicals stabilized at 4 K in neon matrices. They provided the first EPR evidence for trapped VO₂ species, with C_{2v} symmetry and a ²A₁ ground state.

Until now, there has been no report on the generation and reactivity of VO₂ species in catalytic systems. In this paper, we describe a facile route to prepare di-oxovanadium(IV) radicals inside zeolite BEA. The discrimination between mono- and di-oxovanadium species is based on EPR and DFT investigations and on their different chemical behavior toward small molecules such as NO, O₂, N₂O, and C₃H₆.

The samples are prepared by a two-step procedure involving dealumination of zeolite BEA with nitric acid, followed by impregnation of the resulting SiBEA with aqueous NH₄VO₃ solution.¹¹

The starting zeolite BEA (Si/Al = 11) provided by RIPP (China) was treated with 13 M HNO₃ solution (4 h, 353 K) to obtain a dealuminated material (Si/Al = 1000) and then dried overnight at 353 K. In the FTIR spectra of the sample obtained, dealumination was confirmed by the disappearance of two bands at 3781 and 3665 cm⁻¹ assigned to Al–OH groups involving extraframework aluminum and of a band at 3608 cm⁻¹ due to Si–OH–Al hydroxyls involving framework aluminum. At the same time, narrow bands

at 3736 and 3710 cm⁻¹ assigned to isolated silanol groups appeared as well as an intense broad band of H-bonded Si–OH groups of the generated silanol nests at 3520–3515 cm⁻¹ revealing the presence of vacant T-sites.

The dealuminated sample was then contacted with a dilute aqueous solution of NH₄VO₃ (10⁻³ M, pH = 2.4) at room temperature. In such conditions, the prevailing VO₂⁺ cations reacted with the silanol groups of vacant T-sites of SiBEA. This reaction was ascertained by the appearance of two UV bands at 260 and 335 nm (results not shown) attributed to oxygen–vanadium(V) charge-transfer transitions involving bridging (V–O–Si) and terminal (V=O) oxygens, respectively.^{12,13} Chemical analysis of the sample, denoted as V_{0.9}SiBEA, revealed a vanadium loading of 0.9 wt %. A reference sample with 0.1 wt % of vanadium noted V_{0.1}HAIBEAL was prepared by conventional ion-exchange using a 3.5 × 10⁻² M aqueous NH₄VO₃ solution.

The as-prepared samples, V_{0.9}SiBEA and V_{0.1}HAIBEAL, were not EPR active, indicating a diamagnetic pentavalent state of vanadium (*d*⁰). By contrast, evacuation (~10⁻⁵ Pa) at 773 K for 2 h of the samples led to the reduction of V(V) to V(IV) (*d*¹), as shown by the corresponding EPR spectra (Figure 1). In the EPR spectrum of V_{0.9}SiBEA, two types of signals can be distinguished. A weak one, present solely in the V_{0.1}HAIBEAL sample, is pseudoaxial with |A_{||}| ~ 20 mT, and characteristic of the V^{IV}O₂⁺ species.^{6,9} The second one, with orthorhombic symmetry, exhibits a much larger hyperfine constant (|A_i| ~ 30 mT). It is observed for the first time to the best of our knowledge for zeolites and any other catalytic materials. Computer simulation of the spectra using EPRsim32 program¹⁴ for the V_{0.1}HAIBEAL sample gave the following values: *g*_x = 1.987, *g*_y = 1.983, *g*_z = 1.927, |A_x| = 8.4, |A_y| = 7.7, and |A_z| = 20.7 mT, typical of the mono-oxovanadium(IV), proving definitely its nature.⁹ The spin-Hamiltonian parameters of the new signal, *g*_x = 1.803, *g*_y = 1.942, *g*_z = 1.968, |A_x| = 26.8, |A_y| = 32.8, and |A_z| = 31.8 mT, dramatically differ from those assigned to mono-oxo complexes. On the basis of DFT calculations (vide infra) and earlier literature data,¹⁰ we assign this signal to the VO₂ radicals stabilized inside zeolite BEA. The decomposition of the EPR spectrum of V_{0.9}SiBEA into the mono- and di-oxovanadium components is shown in Figure 1. In order to ascertain the attribution of the mono-oxo and di-oxovanadium(IV) complexes, relativistic DFT calculations of their EPR parameters (*g* and *A* tensors) were carried out within the ZORA approximation.¹⁵ We used a VO[Al₂Si₄O₆(OH)₁₂] cluster to model the vanadyl complexes in exchangeable sites in V_{0.1}HAIBEAL and a (SiH₃)₂O₂Si(OH)₂ cluster for hosting the VO₂ molecule in the V_{0.9}SiBEAL sample (Figure 1).

As shown by simulation of the EPR spectra, the *g* and *A* tensors of both vanadium species are sufficiently structure-sensitive to clearly distinguish them. In particular, the isotropic hyperfine constant (⁵¹*a*_{iso}) appears to be extremely sensitive to the number of

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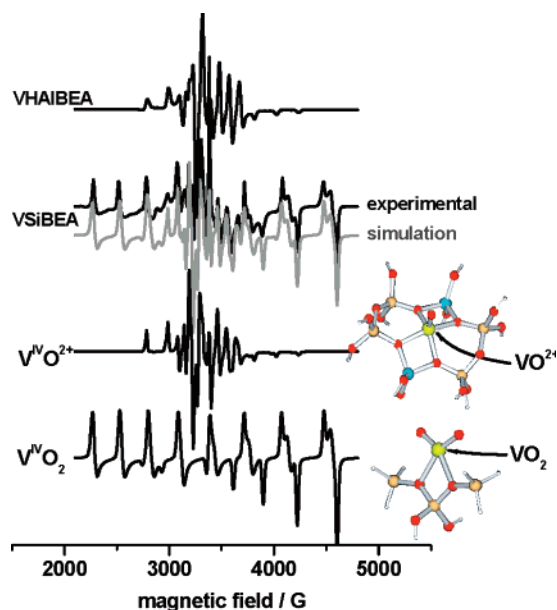


Figure 1. X-band EPR spectra of $V_{0.1}$ HAIBEA and $V_{0.9}$ SiBEA samples along with the corresponding signal components assigned to $V^{IV}O^{2+}$ and $V^{IV}O_2$. The structures represent DFT optimized clusters of the $VO[Al_2Si_4O_6(OH)_{12}]$ and $VO_2[(SiH_3)_2O_2Si(OH)_2]$ complexes.

oxo ligands and, therefore, can be used as a simple diagnostic for resolving the oxo-dioxo dichotomy of vanadium(IV). In the case of the mono-oxo $V^{IV}O^{2+}$ complex, the semi-occupied molecular orbital (SOMO) assumes mainly a metal $3d_{xy}$ character, and the local pseudoaxial symmetry imposed by the dominant $V=O$ bonding does not allow for $4s$ admixing. The value of $\nu_{a_{iso}}$ is then entirely determined by the spin-polarization mechanism,¹⁶ which results in a negative value of $\nu_{a_{iso}} = -12.3$ mT qualitatively reproduced by DFT calculations.

The abnormally large $|A_i|$ components of the hyperfine tensor obtained for $V_{0.9}$ SiBEA can only be accounted for by direct delocalization of the spin density onto the $4s$ orbital of vanadium, leading to a positive $\nu_{a_{iso}}$ value. Indeed, the DFT calculations revealed the following composition of the spin density: 19% ($4s$), 67% ($3d_{x^2-y^2}$), and 13% ($3d_{z^2}$). The experimental value of $\nu_{a_{iso}}(\text{exp}) = 30.5$ mT (calculated assuming all $|A_i|$ components are positive) fits well the theoretical $\nu_{a_{iso}}(\text{theo}) = 36.6$ mT value calculated for the $VO_2(SiH_3)_2O_2Si(OH)_2$ model. Thus, we can definitely attribute the new signal to the unusual VO_2 radical molecule well-dispersed and stabilized inside the BEA zeolite.

Owing to the particular molecular structure of the di-oxovanadium(IV) complex, both the spin density repartition and the SOMO exhibit sizable lobes along the sterically accessible directions. The SOMO can therefore overlap more effectively with the relevant orbitals of the ligands as compared with mono-oxo complexes. In addition, because its low ionization potential (0.77 eV below VO^{2+} level) and lability of the di-oxo moiety, VO_2 acts as a well-defined electron and oxygen donor center. To substantiate this prediction, the reactivity of VO_2 with small molecules was assessed. The corresponding reactions of $V_{0.9}$ SiBEA with NO (3 Torr), O_2 (2 Torr), N_2O (10 Torr), and C_3H_6 (10 Torr) were monitored by EPR at 298 and 77 K.

At 298 K, the di-oxovanadium(IV) species easily reacted with NO via a spin pairing mechanism, $^2VO_2 + ^2NO \rightarrow ^1[VO_2-NO]$, forming a diamagnetic mononitrosyl adduct, whereas the distinctly less reactive $V^{IV}O^{2+}$ mono-oxo species remained intact during this

reaction. Because the energy of the SOMO of VO_2 species is situated above the $2\pi^*$ level of the NO ligand, a bound nitroside ($NO^{\delta-}$) group is formed, providing an excellent model for sharpening the details of the outer-sphere mechanism of the N–N bond formation step in NO reduction or $deNO_x$ reaction.¹⁷

Interaction of VO_2 with dioxygen resulted in immediate formation of a new monoclinic EPR signal (with $g_x = 2.0054$, $g_y = 2.0113$, $g_z = 2.0239$, $|A_x| = 0.54$, $|A_y| = 0.68$, and $|A_z| = 0.98$ mT), according to the electron-transfer reaction $^2V^{IV}O_2 + ^3O_2 \rightarrow ^2[(V^{VO_2})^+-O_2^-]$. This signal is consistent with the superoxide radical attached to vanadium core,¹⁸ forming a bent $(V^{VO_2})^+-O_2^-$ complex of potential relevance for mimicking the haloperoxidase catalytic activity of enzymes.

The interaction of N_2O with VO_2 is more complex, transforming the di-oxo species via a vanadyl intermediate into the vanadium-(V) bound O^- radical¹⁸ with $g_x = 2.0202$, $g_y = 2.0173$, $g_z = 2.0284$, $|A_x| = 1.65$, $|A_y| = 1.58$, and $|A_z| = 1.49$ mT and involving oxygen and electron transfer. In turn, single oxygen transfer leading to the rupture of the double C=C bond was observed in the case of propene adsorption.

In conclusion, the nature of the di-oxovanadium(IV) VO_2 centers generated and stabilized by evacuation at 773 K inside the VSiBEA zeolite is definitely ascertained by EPR and DFT methods. Preliminary studies of their reactivity revealed that they constitute a promising functional system for model studies of many elementary chemical processes. VO_2 species exhibit high reactivity toward NO and O_2 (via spin pairing and electron-transfer reactions), in the decomposition of N_2O (via oxygen transfer coupled with electron transfer), as well as in oxygen insertion to the double bond of preadsorbed olefins.

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Supporting Information Available: Computational and experimental details, and structures of the VO^{2+} and VO_2 complexes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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