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Electron Paramagnetic Resonance Studies of Nitrogen Oxide Adsorbed on Zeolites

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Continuous wave (CW)-electron paramagnetic resonance (EPR) studies of NO adsorbed on sodium ion- and other ion-exchanged zeolites are reviewed. The EPR spectrum of NO monoradical adsorbed on zeolite can be characterized by the three different g-tensor components and the resolved y-component hyperfine coupling with the ^{14}N nucleus. Among the g-tensor components, the value of g_{zz} is very sensitive to the local environment of zeolite and becomes a measure of the electrostatic field in zeolite. The EPR spectra of NO adsorbed on alkaline metal ion-exchanged zeolite are essentially the same as those on sodium ion-exchanged zeolite. The signals assigned to $(NO)_2$ biradical were detected for EPR spectrum of NO adsorbed on Na-LTA. CW-EPR spectra as well as their theoretical calculation suggested that the two NO molecules are aligned along their N-O bond axes.

Keywords: electron paramagnetic resonance (EPR), nitrogen oxide, zeolite, adsorption.

Introduction

Nitric oxide, NO, has been recognized as an atmospheric pollutant and a potential health hazard. On the other hand, it is recently known that NO is a ubiquitous messenger molecule in the cardiovascular, nervous, and immune systems. Thus, a great number of studies on the NO molecule have been carried out in the field of environmental chemistry and biochemistry [1]. NO is an uncharged free radical possessing one unpaired electron with electronic configuration, $(K^2K^2)\text{-}(2s\sigma)^2(2s\sigma^*)^2(2p\pi)^4(2p\sigma)^2(2p\pi^*)^1$. Electron paramagnetic resonance (EPR) is the most appropriate tool for the detection of the unpaired electron and provides valuable information concerning the geometrical structure of molecules and metal ions containing unpaired electrons and the interaction between the unpaired electron and nuclei in the adjacent atoms.

The NO molecule in the ground state exhibits orbital degeneracy of the π^* orbitals. The degeneracy is removed by the interaction between the NO molecule and an electrostatic field, *e.g.* in an adsorbed state and in inorganic matrices. Theoretical studies on the g tensors for the NO adsorption complexes have been developed [2, 3] and recently, Rudolf et al. [4] proposed the following analytical expressions for the principal values of the g tensors,

$$
\begin{aligned}
g_{xx} &= g_e \frac{\Delta}{\sqrt{\lambda^2+\Delta^2}} - \frac{\lambda}{E}\left(\frac{\Delta-\lambda}{\sqrt{\lambda^2+\Delta^2}} - 1\right) \\
g_{yy} &= g_e \frac{\Delta}{\sqrt{\lambda^2+\Delta^2}} - \frac{\lambda}{E}\left(\frac{\Delta-\lambda}{\sqrt{\lambda^2+\Delta^2}} + 1\right) \\
g_{zz} &= g_e - \frac{2l\lambda}{\sqrt{\lambda^2+\Delta^2}}
\end{aligned}
\qquad (1),
$$

where λ is the NO spin-orbit coupling constant (123.16 cm^{-1}), l the effective g factor of the orbital contribution

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which equals 1 for the free NO molecule, E the energy splitting between $^2\Sigma^*$ $[(K^2K^2)\text{-}(2s\sigma)^2(2s\sigma^*)^2(2p\pi)^4(2p\sigma)^2(2p\sigma^*)^1]$ and $^2\Pi_y^*$ $[(K^2K^2)\text{-}(2s\sigma)^2(2s\sigma^*)^2(2p\pi)^4(2p\sigma)^2(2p\pi_y^*)^1]$ states, and Δ the energy splitting between $^2\Pi_x^*$ $[(K^2K^2)\text{-}(2s\sigma)^2(2s\sigma^*)^2(2p\pi)^4(2p\sigma)^2(2p\pi_x^*)^1]$ and $^2\Pi_y^*$ states. The unpaired electron resides in the $^2\Pi_y^*$ level. The energy splitting values E and Δ are affected by the local electronic structure, leading to the change in g tensors of NO adsorbed on solids. The experimentally obtained principal values of the g tensor allow the determination of the three unknown parameters, E, Δ, and l in principle.

Adsorption of NO on zeolites has been studied for more than three decades applying EPR for the characterization of adsorption and desorption behavior. Lunsford [2] was the first to report the EPR spectra of NO adsorbed on Na-FAU(Y) and NH_4-FAU(Y) zeolites. After this report, a number of EPR studies of NO adsorbed on zeolites have been reported by several authors during the 1970's. For example, Gardner and Weinberger [5] have observed EPR spectra for NO adsorbed on Na-LTA, Ca-LTA, Na-FAU(X), and H-MOR. The NO EPR spectra reported for these zeolites were very broad and ill-resolved. Kasai and Bishop [6] have noticed that the spectra for NO adsorbed on Ba-FAU(Y) and Zn-FAU(Y) zeolites become sharp after keeping the samples at room temperature for several days and demonstrated that the triplet hyperfine interaction with the ^{14}N nucleus (I=1) is clearly resolved at the y-component. These earlier EPR studies of the NO/zeolite system have been summarized in several review papers [3, 7]. Also, a large number of EPR studies of NO adsorbed on oxides such as MgO, CoO-MgO, ZnO, ZnS, and TiO_2 has been carried out in the 1970's and Che and Giamello have published a comprehensive review of the NO/oxide systems in 1990 [8]. Here the recent progress of CW-EPR studies for NO adsorption especially on zeolites is reviewed. The information of zeolite samples is summarized in Table 1.

Table 1. Information of zeolite samples

Zeolites	abbreviations	Si/Al ratio
A-type	LTA	1.0
X-type	FAU(X)	1.25
Y-type	FAU(Y)	2.75
Mordenite	MOR	7.7
ZSM-5	MFI	11.9

EPR and ENDOR study of NO adducts formed on sodium-zeolite

X-band EPR spectrum for NO (0.1 kPa) adsorbed on Na-LTA zeolite, which was recorded at 30 K, is shown in Fig. 1(a) [9]. The observed EPR spectrum of NO was characterized by the three different g-tensor components and the resolved y-component hyperfine coupling with the ^{14}N nucleus. The signals can be assigned to one NO molecule adsorbed probably on a Na cation. The EPR parameters determined by the best-fit simulation are summarized in Table 2. Non-overall symmetric g-principal values were observed. This suggests a bent structure of Na^+-N-O due to the electrostatic field associated with the zeolitic sodium ions, as pointed out by Kasai et al.[3] It is known that the g_{zz} component is more sensitive to the local environment of the zeolites than the g_{xx} and g_{yy} components, reflecting the degree of the energy separation between the π^* orbitals of NO, Δ, in accordance with eqn. (1). If l in eqn (1) is assumed to be unity, the estimation of Δ is simplified and the ordering of Δg_{zz} ($=g_e - g_{zz}$) agrees with that of the electrostatic contribution to the interaction strength between NO and the sodium ion. As can be seen in Table 2, the ordering of Δg_{zz} determined from low temperature measurement (4.0 or 5.0 K) is Na-MOR > Na-MFI > Na-LTA, suggesting that the strongest electrostatic field associated with Na^+ ions is in Na-LTA. It was experimentally demonstrated that l depends on the zeolite structure, *e.g.* 1.051±0.090 for NO/Na-LTA and 0.848±0.082 for NO/Na-MFI, respectively [4]. The Δ values calculated with these l values were 0.272±0.040 eV for NO/Na-LTA and 0.165±0.029 eV for NO/Na-MFI, being consistent with the above conclusion that the electrostatic contribution to the interaction strength between NO and sodium ion is higher on Na/LTA than on Na/MFI. Recently, the Q-band EPR spectra of NO adsorbed on Na-LTA have been carried out to determine the precise EPR parameters [10]. The results provided the EPR parameters: g_{xx} = 2.0019, g_{yy} = 1.9961, g_{zz} = 1.8856 and $A_{xx}(^{14}N) \approx A_{zz}(^{14}N) \approx 0$ mT, $A_{yy}(^{14}N)$ = 3.0 mT for NO monoradical adsorbed on Na-LTA.

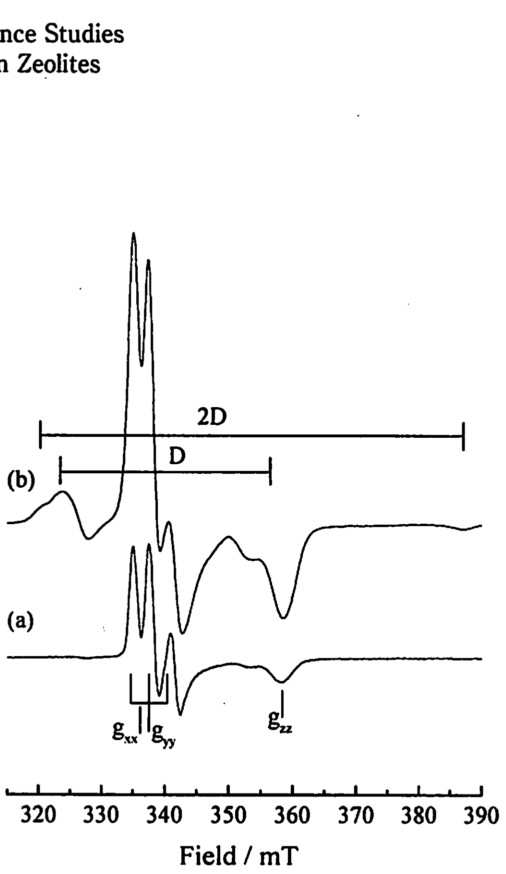

Figure 1. EPR spectra of (a) NO (0.1 kPa) and (b) NO (1.2 kPa) adsorbed on Na-LTA (30 K). The EPR parameters are given in Tables 2 and 3.

The information about adsorption site and the coordination geometry of the NO adsorption complexes formed in zeolites can be potentially obtained from super hyperfine (*shf*) interaction between the unpaired electron spin of the NO molecule and the nuclear spin of the metal ions; however, only a few cases such as $(Al_xO_y)^{n+}$-NO [2, 3, 11, 12] and Cu^+-NO [13] were studied by CW-EPR studies. No sufficient spectral resolution of the ^{23}Na *shf* coupling was obtained by CW-EPR studies on $^{23}Na^+$-NO complexes. On the other hand, pulsed ENDOR(electron nuclear double resonance) spectroscopy at W- and X-band frequencies has been successfully employed to determine the structure of NO monoradical at low temperature [14]. The bond angle of Na^+-N-O and the bond length of Na^+-N were estimated as 142 degrees and 0.21 nm from the analysis of the ^{23}Na hyperfine splittings ($^{Na(23)}A_{xx}$ = $^{Na(23)}A_{yy}$ = 6.3±0.2 MHz and $^{Na(23)}A_{zz}$ = 10.9±0.2 MHz), which were observed by pulsed ENDOR. Furthermore, the ^{23}Na nuclear quadrupole interaction was obtained. These data could provide that the Na^+-NO complex in Na-LTA zeolite is preferably formed at sodium ions at site S2 located near the six-membered rings.

EPR investigations of the adsorption-desorption behavior of the NO molecules could provide experimental

Table 2. Recently reported EPR parameters (*g*-tensors and hyperfine coupling (*hfc*) tensors) of NO monoradical formed in cation-exchanged zeolites.[a]

Zeolite type	Metal ion	Meas. Temp. /K	*g*-value			*hfc* /mT			Ref.
			g_{xx}	g_{yy}	g_{zz}	A_{xx}	A_{yy}	A_{zz}	
LTA	Na	5.0	2.0019	1.9961	1.8856	0	3.3	0	[10]
	Na	4.3	2.001	1.996	1.888	0	3.2	0	[14]
	Na	4.7	1.999	1.993	1.884	0.68	3.23	0	[15]
	Na	10	1.9993	1.9936	1.8842	0.58	3.3	0	[4]
	Na	30	2.002	1.996	1.886	0	3.3	0	[9]
	Na	80	1.980	1.989	1.906	1.19	3.06	0	[15]
	Li	16	~1.99[b]	~1.99[b]	1.780	-[b]	-[b]	0	[17]
	Li	77	1.996	1.996	1.971	0	3.0	0	[17]
MOR	Na	4.2	1.997	1.995	1.855	0	3.2	0	[26]
	Na	77	1.996	1.995	1.853	0	3.0	0	[26]
MFI	Na	4.2	1.996	1.995	1.862	0	3.2	0	[26]
	Na	10	1.9939	1.9914	1.8460	1.2	3.6	0	[4]
	Na	77	1.994	1.992	1.862	0	3.0	0	[26]

[a] EPR parameters reported earlier were summarized in Ref. [7]. [b] Precise values could not be determined.

information about the adsorption energies of the NO probe molecules at the Lewis acid sites [15, 16]. The desorption temperatures of NO molecule from Na-LTA, Na-MFI, and H-MFI were estimated from the temperature-dependence EPR studies to be 150, 190, and 240 K, respectively. Thus obtained desorption temperature can be considered as a measure of the acid strength of the Lewis acid site; sodium cations in sodium-zeolite and aluminum defect centers in proton-zeolite are known as weak and strong Lewis sites, respectively. The desorption of the NO molecule from the adsorption sites leads to the corresponding decrease in the EPR signal intensity of the NO adsorption complexes. At the same time the EPR signals were accompanied by a strong increase in the homogeneous linewidth δB^{hom} with rising temperature. The homogeneous linewidth can be expressed as a function of temperature and follows an Arrhenius behavior,

$$\delta B^{\mathrm{hom}}(T) = b_1 \exp\left(-\frac{E_A}{k_B T}\right) \tag{2}$$

with the preexponential factor b_1 and the Boltzmann constant k_B. The activation energies, E_A, of NO desorption were determined using both eqn. (2) and the temperature dependence of the linewidths as 4.1±1.5 kJmol^{-1} for Na-MFI, 7.1±2.1 kJmol^{-1} for Na-LTA, and 20.2±7.3 kJmol^{-1} for H-MFI. The obtained values of E_A are consistent with the expectation that the activation energy of H-MFI with strong Lewis acidity is larger than that of Na-MFI with weak Lewis acidity.

EPR study of NO adducts formed on zeolites containing other cations

The EPR parameters of NO introduced to fully lithium ion-exchanged LTA zeolite, Li-LTA, are listed in Table 2 [17]. The *g*-tensors of NO monoradical for Li-LTA (16 K) were compared with those for Na-LTA (5 K). Δg_{zz} ($=g_e - g_{zz}$ =2.0023-1.780 = 0.2223) of Li-LTA was larger than that (2.0023-1.8856 = 0.1167) of Na-LTA. This means that the Δ value is smaller for the former than for the latter system; the electrostatic field associated with Li^+ ions in LTA zeolites may be weaker than that with Na^+ ions.

When NO was introduced into H-MFI activated at 1073 K, the EPR spectrum exhibited an anisotropic *g* tensor and a *shf* splitting of about 1.1 mT into six lines due to the magnetic interaction of the unpaired electron at the nitric oxide molecule with one ^{27}Al(I=5/2) nuclear spin [16]. Although the *shf* in the CW-EPR spectrum was ill-resolved, the assignment of the *shf* splitting was proved by pulsed ENDOR spectroscopy [12]. Thus, NO was successfully employed to study the structure of aluminum centers, so-called "true" Lewis sites, in proton-exchanged zeolites such as H-MFI [11, 12, 16] and H-FAU(Y) [18].

Among various transition metal ion-exchanged zeolites, the copper ion-exchanged zeolites are the most extensively studied using EPR because they showed high catalytic activity for NO decomposition [19]. Copper(II) ions possess a d^9 electron configuration (S=1/2) appropriate for EPR study. When NO was introduced in zeolites with partially reduced copper ions, copper nitrosyl complexes were formed in the zeolite [20, 21]. It is reported that the mode of coordination of the NO species is essentially controlled by the relative energies and the symmetry match between the π^* and n orbitals of the NO ligand and orbitals of the d manifold of the copper ion. Two types of copper nitrosyl complexes formed in Y-type zeolite were discussed in earlier studies, Cu-NO$^{\delta+}$ with electron transfer from NO to Cu^{2+} and Cu-NO$^{\delta-}$ with that from Cu^+ to NO. The cationic nitrosyl ligand results in a nearly linear Cu-NO bond, while an anionic nitrosyl ligand is characterized by a bent end-on coordinated NO. Since the latter nitrosyl compound is active for EPR, the analysis of its structure is one of the potential subjects debated for copper-zeolite system. Recently, Sojka et al.[13] have reported the details of structure of the Cu-NO$^{\delta-}$ adduct formed in Cu-MFI zeolite. When the Cu(II) ion was reduced to Cu(I), introduction of NO into the zeolite caused reappearance of EPR signals which were characteristic of the unpaired electron essentially residing on NO. The reported parameters of the Cu-NO$^{\delta-}$ adduct formed in MFI zeolite are $g_{xx} = 1.999$, $g_{yy} = 2.003$, $g_{zz} = 1.889$, $|^{Cu(63,65)}A_{xx}| = 16.0$ mT, $|^{Cu(63,65)}A_{yy}| = 15.5$ mT, $|^{Cu(63,65)}A_{zz}| = 20.5$ mT, $|^{N(14)}A_{xx}| = 3.0$ mT, $|^{N(14)}A_{yy}| = 0.43$ mT, and $|^{N(14)}A_{xx}| = 0.55$ mT. Based on the experimental EPR parameters, an end-on η^1 bent structure was proposed for this adduct in which the unpaired electron resides mainly on the coordinated NO and the copper *shf* splittings arise from delocalization of the unpaired electron density onto Cu orbitals. The spin density was estimated to be 0.2 on copper, 0.55 on nitrogen, and 0.25 on oxygen.

Triplet state of NO adducts formed in zeolite

Kasai and Gaura [22] have first reported that the EPR spectrum of NO in Na-LTA consists of two signals, one due to Na-NO complex and the other due to an unusual NO-NO species (henceforth abbreviated as $(NO)_2$ biradical) with a triplet state. They observed an X-band EPR signal due to the forbidden transition, $|\Delta Ms|=2$, at *ca.* 170 mT ($g \cong 4$), when the corresponding allowed transitions, $|\Delta Ms|=1$, were observed for the same sample at *ca.* 340 mT ($g \cong 2$). This verified the presence of a triplet biradical species. In this section, details of $(NO)_2$ biradical with triplet state will be presented on the basis of recent results.

X-band EPR spectrum for NO adsorbed on Na-LTA is shown in Fig. 1(b). In Fig. 1(b), it is clear that the signals of the NO monoradical and the NO biradical were superimposed. The comparison of Figs. 1(a) and 1(b) showed that the NO monoradical dominates when the pressure is low, while the NO biradical becomes dominant at higher NO pressure [7]. Q-band EPR measurements were carried out for the same system at 5 K to evaluate the precise EPR parameters of the $(NO)_2$ biradical [10]: $g_{xx} = 2.0042$, $g_{yy} = 1.9770$, and $g_{zz} = 1.9120$ and D and E parameters ($|D| = 33.1$ mT and $|E| = 2.8$ mT) of the zero field splitting (ZFS). Both NO and $(NO)_2$ radicals were also observed for NO adsorbed on partially lithium ion-exchanged Na-LTA [17] and sulfated zirconia [23].

The EPR parameters of the $(NO)_2$ biradical obtained from the best fit simulation are shown in Table 3. It is well established that the zero-field splitting tensors (ZFS) of radical pairs generally originate from the dipolar-dipolar interaction between the two unpaired electrons of the radical units. The D-parameter of ZFS depends on the average distance between two radicals, R, according to the following equation derived from a point-dipole approximation [24],

$$D = \frac{3g\beta}{2R^3} \quad (3),$$

where g and β are the spectroscopic g-factor and the Bohr magneton, respectively. The values of R, evaluated from the experimental D values, are listed in Table 3.

The g- and D-tensors need not always to be parallel with each other, and test simulations were performed trying to reproduce in particular the experimental EPR powder lineshape of the biradical [10]. The biradical lineshape was very sensitive with respect to the relative orientations of the g and the D tensors. Best agreement

Table 3. g tensors and zero-field splitting (ZFS) tensor for $(NO)_2$ biradical.

Material	*g*-tensor			ZFS/mT		Distance of radical pairs / nm	Ref.
	g_{xx}	g_{yy}	g_{zz}	$\|D\|$	$\|E\|$		
Na-LTA	2.0042	1.9770	1.9120	33.1	2.8	0.45	[10]
Na-LTA	1.976	1.976	1.912	28.8		0.45	[22]
LiNa-LTA[a)]	1.989	1.989	1.900	41.0		0.42	[17]
Sulfated Zirconia	1.993	1.993	1.994	19.5		0.52	[23]

[a)] The exchange level of lithium ion is 66%.

was obtained when g_{ZZ} and D_{ZZ} are parallel to each other. Complementary lineshape simulations using small deviations from complete coincidence were also carried out using the model in Fig. 2. The system was described by a spin Hamiltonian involving the Zeeman terms of each NO unit and a dipolar coupling between the two unpaired electrons. The principal values of the g-tensors of each molecule were the experimental ones for the biradical with the principal axes parallel and perpendicular to the NO bond and along the common x-axis (g = 2.0042). The direction of D_{ZZ} was taken along the line connecting the midpoints of the two N-O bonds. It is concluded that the principal axes of g_{ZZ} and D_{ZZ} cannot deviate by more than 30 degrees from each other in this model.

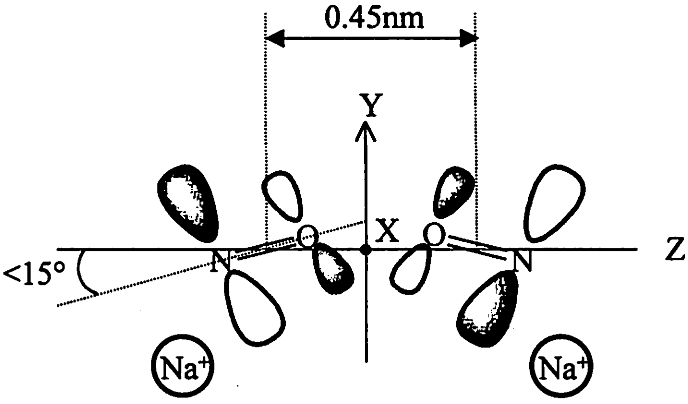

Figure 2. Proposed model of $(NO)_2$ biradical formed in Na-LTA.

Refinement of the above geometric model of the $(NO)_2$ biradical formed in Na-LTA was achieved by pulsed EPR measurement [25]. The experimental data of pulsed EPR clearly indicated that triplet state $(NO)_2$ biradical interacts with sodium ions in the Na-LTA zeolite. Theoretical MO calculations have been performed with UHF/6-31+G(d) to obtain the optimized geometrical structure and with B3LYP/6-31+G(d) to obtain the spin densities and the dipolar coupling. The plots of energy vs. the angle (O)N-Na-N(O), θ, showed that at 150 degree < θ < 180 degree, the triplet state is more stable than the singlet state, supporting the small deviation of the principal axes of $(NO)_2$ biradical as mentioned above.

Conclusions and outlooks

In this review, the recent CW-EPR studies have been summarised for NO adsorbed on metal ion- and proton-exchanged zeolites. CW-EPR measurements of NO adsorbed on Na ion-exchanged zeolite gave spectra with the anisotropic g-factors, which can be assigned to the NO monoradical. In order to determine the precise EPR parameters, measurements at higher frequencies have been made for NO in Na-zeolites. Only one component of the ^{14}N hyperfine coupling tensor could be resolved by EPR, but the smaller couplings perpendicular to the N-O axis have been determined with ENDOR. It was also possible to observe an interaction with Na^+ ions by ENDOR, and from this a geometric model of the NO-Na^+ complex was constructed. EPR investigations of the adsorption-desorption behavior of the NO molecules could provide the adsorption energies of the NO probe molecules.

A large number of EPR studies have been carried out for NO adsorbed on cation-exchanged zeolites, in particular, proton- and copper ion-exchanged zeolites. In the former case, the magnetic interaction of the unpaired electron at the NO molecule with one ^{27}Al nuclear spin was observed by CW-EPR measurement, demonstrating that NO was successfully employed to study the structure of aluminum center: "true" Lewis sites. The latter study is interesting from the catalytical point of view because copper ion-exchanged zeolite shows an activity for NO decomposition.

A peculiar property of the NO/Na-LTA system is the formation of $(NO)_2$ biradical separated by about 0.45 nm. Q-band CW-EPR spectra as well as their theoretical calculation suggested that the two NO molecules are aligned along their N-O bond axes. A confirmation of this model is complicated by the difficulty of simulating the EPR spectra when the axes are not aligned. Pulsed EPR studies was made to overcome this difficulty and gave the important information that the stability of the triplet state structure was attributed to an unusual geometric structure imposed by the zeolite matrix, with the N-O bonds along a line.

References

[1] T. Nagano and T. Yoshimura, *Chem. Rev.*, 102 (2002) 1235.

[2] J. H. Lunsford, *J. Phys. Chem.*, 72 (1968) 4163.

[3] P. H. Kasai and R. J. Bishop Jr., in *Zeolite Chemistry and Catalysis*, ed. J. A. Rabo, ACS Monograph 171, Washington DC (1976) p. 350.

[4] T. Rudolf, A. Pöppl, W. Hofbauer, and D. Michel, *Phys. Chem. Chem. Phys.*, 3 (2001) 2167.

[5] C. L. Gardner and M. A. Weinberger, *Can. J. Chem.*, 48 (1970) 1317.

[6] P. H. Kasai and R. J. Bishop Jr., *J. Am. Chem. Soc.*, 94 (1972) 5560.

[7] D. Biglino, H. Li, R. Erickson, A. Lund, H. Yahiro, and M. Shiotani, *Phys. Chem. Chem. Phys.*, 1 (1999) 2887.

[8] M. Che and E. Giamello, *Stud. Surf. Sci. Catal.*, 57 (1990) B265.

[9] H. Yahiro, A. Lund, N. P. Benetis, and M. Shiotani, *Chem. Lett.*,2000 (2000) 736.

[10] H. Yahiro, A. Lund, R. Assa, N. P. Benetis, and M. Shiotani, *J. Phys. Chem. A*, 104 (2000) 7950.

[11] A. Gutsze, M. Plato, H. Karge, and F. Witzel, *J. Chem. Soc. Faraday Trans.*, 92 (1996) 2495.

[12] A. Pöppl, T. Rudolf, and D. Michel, *J. Am. Chem. Soc.*, 120 (1998) 4879.

[13] Z. Sojka, M. Che, and E. Giamello, *J. Phys. Chem.*, 101 (1997) 4831.

[14] A. Pöppl, T. Rudolf, P. Manikandan, and D. Goldfarb, *J. Am. Chem. Soc.*, 122 (2000) 10194.

[15] T. Rudolf, A. Pöppl, W. Brunner, and D. Michel, *Magn. Reson. Chem.*, 37 (1999) 93.

[16] T. Rudolf, W. Böhlmann and A. Pöppl, *J. Mag. Reson.*, 155 (2002) 45.

[17] H. Yahiro, K. Kurohagi, G. Okada, Y. Itagaki, M. Shiotani, and A. Lund, *Phys. Chem. Chem. Phys.* , 4 (2002) 4255.

[18] A. Seidel, A. Gutsze and B. Boddenberg, *Chem. Phys. Lett.*, 275 (1997) 113.

[19] H. Yahiro and M. Iwamoto, *Appl. Catal. A*, 222 (2001) 163.

[20] C. Naccache, M. Che, and Y. Ben Taarit, *Chem. Phys. Lett.*, 13 (1972) 109.

[21] C. C. Chao and J. H. Lunsford, *J. Phys. Chem.*, 76 (1972) 1546.

[22] P. H. Kasai and R. M. Gaura, *J. Phys. Chem.*, 86 (1982) 4257.

[23] A. Volodin, D. Biglino, Y. Itagaki, M. Shiotani, and A. Lund, *Chem. Phys. Lett.*, 327 (2000) 165.

[24] T. Gillbro and A. Lund, *J. Chem. Phys.*, 61 (1974) 1469.

[25] D. Biglino, M. Bonora, A. Volodin, and A. Lund, *Chem. Phys. Lett.*, 349 (2001) 511.

[26] H. Yahiro, N. P. Benetis, A. Lund, and M. Shiotani, *Stud. Surf. Sci. Catal.*, 135 (2001) 348.