FROM DIOXYGEN TO SUPEROXIDE: PERIODIC DFT MODELING AND EPR STUDY OF PARAMAGNETIC Zn^{+} & Zn^{2+}–$O_2^{\bullet-}$ SPECIES IN MFI ZEOLITE

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SCOPE

$O_2^{\bullet-}$ superoxide radical anion plays an important role in catalysis, environmental chemistry, and biochemistry. One of the possible ways to generate these radicals is O_2 adsorption on low-valent transition-metal ion centers dispersed in porous materials, such as zeolites.* We present a theoretical and spectroscopic analysis of an excellent example of a system defined by monovalent **Zn^{+}** ions, which is an unusual oxidation state for this element. This work aims to support computationally and refine the experimental EPR studies involving the adsorption of isotopically labeled ^{17}O molecular oxygen on Zn+ exchanged MFI zeolite obtained by chemical vapor deposition.

*A. Oda, H. Torigoe, A. Itadani, T Ohkubo, T. Yamura, H. Kobayashi, Y. Kuroda, *J. Am. Chem. Soc.* **2013**, 135, 18481.

EXPERIMENTAL

- ✓ Zn^{+} ions were generated within commercial sample of MFI zeolite by chemical vapor deposition of metallic Zn @ 400 °C.

$$Zn_{(g)} + H^{+}_{zeol} \rightarrow Zn^{+}_{zeol} + 1/2H_{2(g)}$$

- ✓ $O_2^{\bullet-}$ were generated by the adsorption of O_2, both natural & ^{17}O enriched (70%), which allowed measurement of hyperfine coupling constants

$$Zn^{+}_{zeol} + O_{2(g)} \rightarrow (Zn^{2+} – O_2^{\bullet-})_{zeol}$$

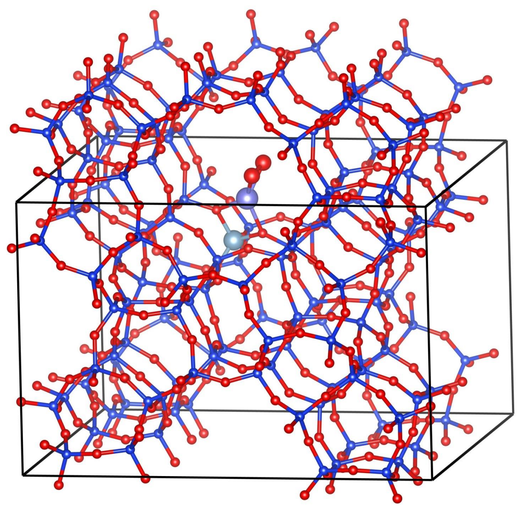
- ✓ Both Zn^{+} & $O_2^{\bullet-}$ species were monitored by EPR spectroscopy: Bruker Elexsys E580 spectrometer, X-band, 1-10 mW microwave power, frequency & amplitude modulations set to 100 kHz & 0.2 mT, respectively.

COMPUTATIONAL

- ✓ MFI unit cells with single Al^{3+}/Zn^{+} pair or (Al^{3+}/Zn^{+} & $2Al^{3+}/Zn^{2+}$) per unit cell $T_{96}O_{192}$, (T = Si, Al), Al^{3+} put in T1 &/or T7 crystallographic sites.
- ✓ Periodic models were optimized at DFT/PBE level using Turbomole code (Riper module): Γ point only, def2-TZVP basis @ Zn & dioxygen O atoms, pob-TZVP @ remaining ones.
- ✓ Cluster models consisting of of 22T atoms were constructed & employed in DFT/BHLYP calculations of EPR g and A tensors, using ZORA approach, basis sets: CP(PPP) @ Zn, EPR-III @ $O_2^{\bullet-}$ & TZVP @ remaining atoms.

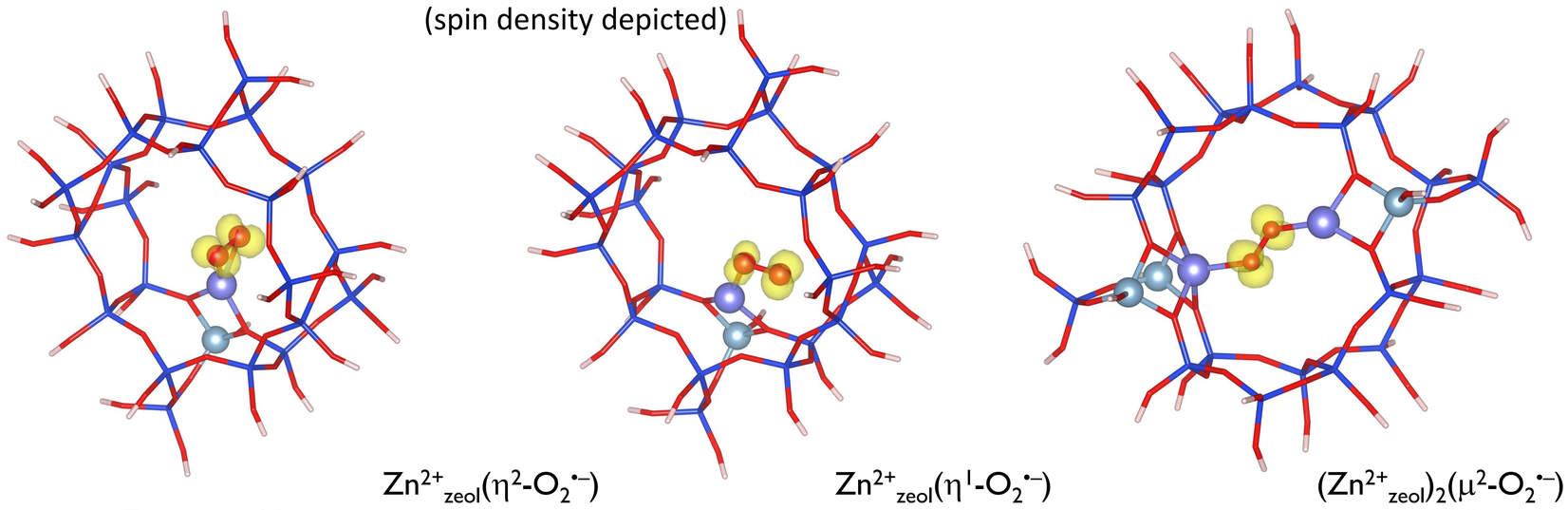
DFT/PBE optimized periodic MFI model

($O_2^{\bullet-}$)-$Zn^{+}AlSi_{95}O_{192}$



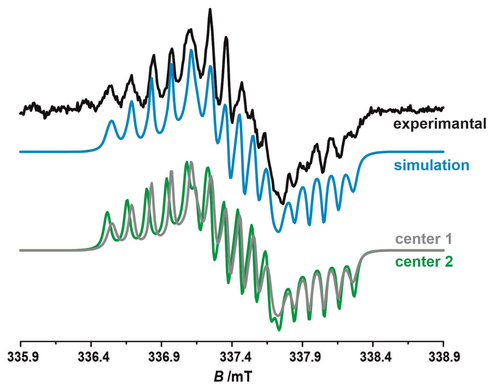
Cluster models

(spin density depicted)

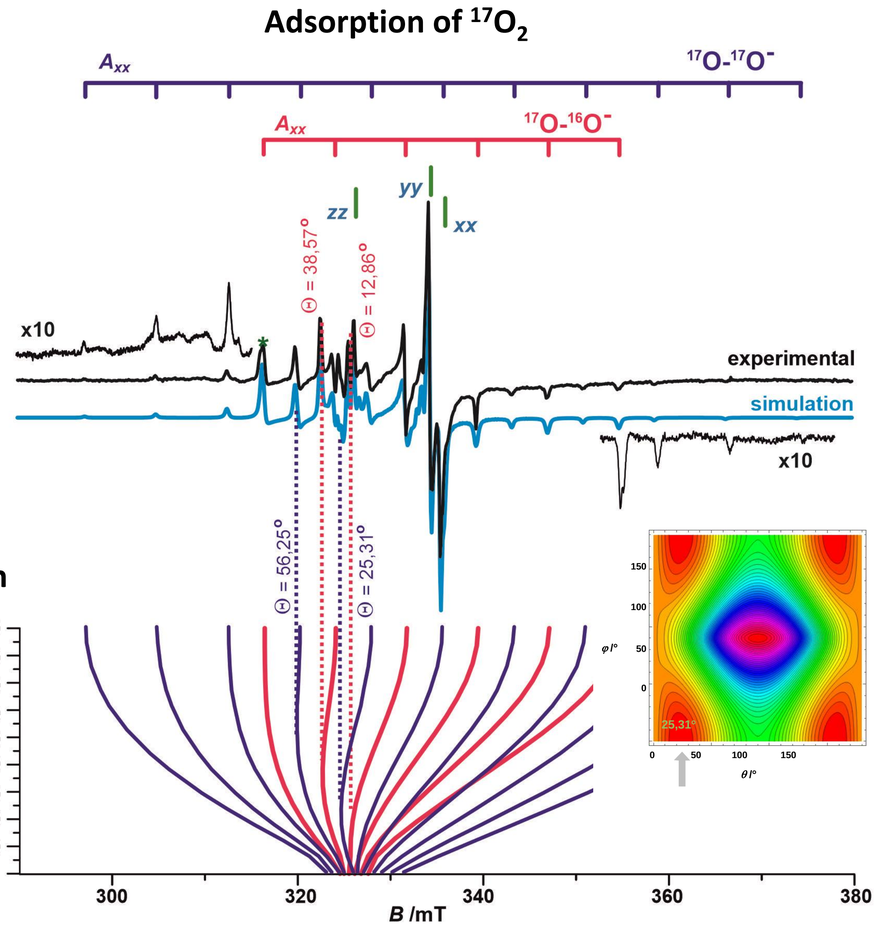


	$Zn^{2+}_{zeol}(\eta^2\text{-}O_2^{\bullet-})$	$Zn^{2+}_{zeol}(\eta^1\text{-}O_2^{\bullet-})$	$(Zn^{2+}_{zeol})_2(\mu^2\text{-}O_2^{\bullet-})$
$E_{DFT/PBEads}$(kJ/mol)	-111	-109	-208

EPR spectra of Zn(I) centers in ZSM-5 zeolite

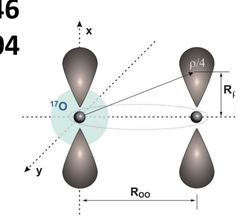


Adsorption of $^{17}O_2$



Analysis of spin density distribution (*A* tensor)

$\rho(2s) = 0.01$
$\rho(2\pi^*_x) = 0.46$
$\rho(2\pi^*_y) = 0.04$



Comparison of experimental EPR data and DFT/CAM-B3LYP results

Center			g_{xx}	g_{yy}	g_{zz}	A_{xx} / MHz	A_{yy} / MHz	A_{zz} / MHz
						^{27}Al shf (I = 5/2)		
Zn(I)/ZSM-5	EPR		1.994	1.998	2.002	2.88	2.80	3.89
	DFT		1.988	2.003	2.010	2.82	3.06	4.06
$Zn(II)O_2^-$/ZSM-5							^{17}O hf (I = 5/2)	
	EPR	56.5%	2.003	2.010	2.061	215.3	16.9	17.3
		43.5%	2.002	2.009	2.037	213.0	12.5	16.0
η^2-O_2^- (side-on)	DFT		2.001	2.014	2.060	257.0	20.2	15.7
						257.5	20.1	15.6
η^1-O_2^- (end-on)			1.993	2.005	2.069	176.1	8.7	0.2
						320.9	36.8	27.4
μ^2-(O,O) (bridge)			1.992	2.010	2.033	220.3	12.6	2.1
						297.9	23.9	16.9

RESULTS

- ✓ The best agreement between exp. & DFT found for $O_2^{\bullet-}$ radical adsorbed on Zn^{2+} site in η^2-$O_2^{\bullet-}$ side-on manner with two equivalent O atoms, where Zn^{2+} ion is tetrahedrally coordinated by radical & zeolite O atoms.
- ✓ η^1-$O_2^{\bullet-}$ end-on coordination slightly less stable (we cannot exclude possible saddle point), worse g_{xx} & ***A*** values agreement (2 non-equivalent O atoms)with EPR data.
- ✓ The strongest O_2 binding predicted for bridging, but the presence of Zn^{+}/Zn^{2+} pairs is unlike in low Al zeolite, again poor agreement of g_{xx} & **A** values with EPR data.

ACKNOWLEDGEMENTS

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