## I. Introduction to EPR

## II. EPR in heterogeneous catalysis

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## I. Introduction to EPR



- Basics of cw EPR
- One electron in the magnetic field
- Crystal field splitting and spin orbit coupling
- Interaction with nuclear spins
- Electron nuclear double resonance (ENDOR)
- Electron spin echo envelope modulation (ESEEM)

## Nuclear Magnetic Resonance Electron Paramagnetic Resonance

uses the interaction between the magnetic moments and the magnetic component of electromagnetic radiation in the presence of magnetic fields

magnetic moments through non-zero spin angular momentum of unpaired electrons and a variety of nuclei

spin angular momenta are quantized



Ms





 $U_{\alpha} = + \frac{1}{2} g_{e} \beta_{e} B$ 

### Which magnetic field strength and frequency?



NMR: 1 – 21 Tesla and 10 – 900 MHz EPR: 0.06 – 3 Tesla and 2 – 90 GHz

Low energy splitting  $\rightarrow$  low Boltzmann polarization



NMR: 10<sup>16</sup> spins per 1 ml EPR: 10<sup>10</sup>-10<sup>11</sup> spins per <1ml



### Which information?

 $B_0 = 2.34 \text{ T}$ 

Ó

 $13_{C}$ 

25.2

Atomic, molecular and lattice structure: perturbation of the magnetic moments through the neighboring electronic and nuclear spin network terce crossing borders.

 $19_{\rm F} \, {}^{1}_{\rm H}$ 

94 ioo

NMR: nuclear magnetic moments



31<sub>D</sub>

40.5



V (MHz)





### **EPR** brief

price C C C i science crossing borders.

- first EPR observation in 1945: CuCl<sub>2</sub>·H<sub>2</sub>O (133 MHz at 5 mT)
- rapid exploitation of EPR thereafter through the availability of complete 9.5 GHz ( $\lambda$ =32 mm) systems after World War (II)  $\rightarrow$  resonance at 0.35 T field
- application to chemical systems since 1970
- technological availability of magnetic fields and frequency sources limits the common EPR frequency range to 1-100 GHz
- fixed frequency and magnetic field sweep is most common
- only the electronic ground state of species is relevant for EPR
- uniquely applicable to paramagnetic state (net electron angular momentum)

- 1. free radicals in the solid, liquid or gaseous phase 1 unpaired electron
- 2. transition ions including actinide ions up to 5 or 7 unpaired electron  $V^{4+}, Ti^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+} \dots$
- 3. various point defects (localized imperfections) in solids electron trapped at a negative-ion vacancy (F center) or an electron hole



5. systems with conducting electrons semiconductors, metals

### Typical systems studied by EPR



 $H_3C$ 

Na<sup>+</sup> CI-



 $CI^{-}$ 

One electron in the magnetic field

Electron Zeeman Interaction (EZI): 2-level system

$$H = -\mu \cdot \mathbf{B} = \gamma \cdot \mathbf{S} \cdot \mathbf{B} = \mathbf{g}_{e} \cdot \beta_{e} \cdot \mathbf{S} \cdot \mathbf{B}$$

negative gyromagnetic ratio  $\gamma$ 

g-factor = 2.0023, and nearly isotropic for the simplest case

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### EPR detection: Magnetic field sweep with 100 kHz modulation



EPR  $H = g_e \cdot \beta_e \cdot \boldsymbol{B}_{eff} \cdot \boldsymbol{S}$ =  $\beta_e \cdot \boldsymbol{B}_0 \cdot \boldsymbol{g} \cdot \boldsymbol{S}$ 







### One electron in the magnetic field: 2-level systems with resonance around g = 2

- 1. Free radicals
- 2. Ti(III), <sup>98</sup>Mo(V), low-spin Fe(III)
- 3. F centers in alkali halides
- 4. Hydrogen atom trapped in crystal matrices
- 5. Conducting electrons in metals





### Much more complex EPR spectra due to ...



- effects of additional magnetic and electric fields from the unpaired electron's environment
- presence of more than one electron (e.g. transition metal ions with several unpaired d-electrons, up to 5 for high-spin Mn<sup>2+</sup> or Fe<sup>3+</sup>)
- organic molecules in triplet state



- MW frequency may have too small bandwidth (e.g. in VO<sup>2+</sup>, Mn<sup>2+</sup>)
- EPR spectra may only be observed in the ground state manifold

### Crystal-field splitting and spin-orbit coupling

cause large energy splittings in transition metal ions condensed phase

removes the orbital degeneracy for most transition metals "quenching of the orbital angular momentum" effective spin S=1/2

> EPR spectra only through the unpaired electron in *d*x<sup>2</sup>-y<sup>2</sup> orbital

 $\rightarrow$  one electron S=1/2, two-level system?

figure: 3d<sup>9</sup> transition metal ion





### Ligand field effect through second order SOC



- molecule's ground state undergo orbital quenching by Most chemical bonding (e.g. radicals) or large CF's (e.g. transition metal ions)  $\rightarrow$  g-factor of free electrons
- small amount of orbital angular momentum admixes to the But ground state through interaction with the excited states
- Therefore electron spin becomes sensitive to crystalline environment
- Leading to anisotropic g-factor, i.e. the Zeeman splitting depends on the symmetry of the ligand field and the molecular orientation in  $B_0$ S-B  $H = (\mathbf{g})$

g tensor

### **g** anisotropy

EPR spectra depend on orientation of samples in B0

in single crystals or powder samples





### EPR of solutions

Molecular motion leads to simplification of spectra due to averaging of anisotropic interactions





Typical vanadyl solution spectrum (of VO(acac)<sub>2</sub>)

### EPR at low temperature (frozen solids)

in order to increase relaxation times through freezing of molecular motion  $\rightarrow$  identical to powder spectra  $\rightarrow$  concept of anisotropy is of importance



# Interaction with nuclear spins (hyperfine interaction)



local magnetic fields by neighboring nuclear magnetic moments ( $\mu_n$ ) increasing borders.

Nuclear Zeeman interaction

NZI << EZI

$$H = g_{n} \cdot \beta_{n} \cdot \boldsymbol{B}_{eff} \cdot \boldsymbol{I}$$
$$= \gamma \cdot \boldsymbol{B}_{0} \cdot (1 - \sigma) \cdot \boldsymbol{I}$$

e.g.  $g_n$ =5.58 for proton

depend on the orientation of  $\mu_n$  with respect to  $\boldsymbol{B}_0$ 

 $\rightarrow$  splitting of each electron spin state into (2/+1) levels.





High-spin manganese (II), S=5/2

S=5/2,  $3d^5$  character in bound form; 5 line EPR spectrum I=5/2, 6-fold splitting of EPR line



 $Mn^{2+}$  in ScPO<sub>4</sub> single crystal

### Origin of hyperfine interactions



• dipole-dipole interaction between the magnetic moments

$$H_{\delta\delta} = \frac{1}{4\pi} \frac{\mu_0}{r^3 h} g_e \beta_e g_n \beta_n \left[ \mathbf{S} \cdot -\frac{3}{r^2} (\cdot )(\cdot ) \right] \quad \implies \text{ anisotropic}$$

unpaired electrons in p-, d-, or f- orbitals

• Fermi-contact interaction through finite electron spin density at the nucleus

$$H_{contact} = \frac{2}{3} \frac{\mu_0}{h} g_e \beta_e g_n \beta_n |\Psi(0)|^2 \mathbf{S} \cdot \qquad \text{isotropic}$$

unpaired electrons in mainly s- or p-,d-. f- orbitals or  $\pi$  electrons or transition metals







# Powder EPR of Cu<sup>2+</sup> coordinated to sulfur, nitrogen or oxygen



ders ...

340

# ESR observation of the formation of an Au(II) complex in zeolite Y





divalent state of gold is rare and most interesting oxidation state in transition metal chemistry

zeolites are very promising as support for stablizing cations and metalic species because of their crown-ether-like ring strcutures in their cages and channels.

first observation of square-planar Au(II) -complex with  $N_4$  in the supercage of Y-zeolite was observed via EPR

Z.Qu, L. Giurgiu, E. Roduner, Chem. Commun. (2006) 2507-2509.

# Effect of nuclear Zeeman interaction vs. hyperfine interaction at the nucleus





weak coupling:

e.g. water protons in the first coordination sphere of copper-hexaaquo complex

strong coupling: typical for most systems



### The complete Hamiltonian

 $\mathbf{H} = \boldsymbol{\beta} \cdot \cdot \cdot \cdot + \cdot \cdot \cdot + \cdot \cdot \cdot - g_n \boldsymbol{\beta}_n$ 

1. ... so far one electron spin in magnetic fields of different origins were discussed

### 2. Zero-field splitting

- more than one electron spins (S > 1/2) in magnetic fields
- strong dipole-dipole interactions between the electrons
- e.g. transition metal ions with up to five unpaired *d*-electrons or spin triplets in organic molecules
- can be much larger than the electron Zeeman interaction
- 3. Nuclear Quadrupole Interaction
  - from nuclei with a nuclear spin quantum number  $l > \frac{1}{2}$
  - impact on EPR spectrum is usually small

### **Relaxation times and linewidths**

 $T_1$  spin-lattice relaxation: through dissipation of energy via the thermal vibration of the lattice

#### $T_2$ spin-spin relaxation:

mutual spin flips caused by dipolar and exchange interactions among the spins

1

1

linewidth determined by:

$$\frac{1}{T_{2,eff}} = \frac{1}{T_2} + \frac{1}{2T_1} \qquad (T_2 \text{ is much shorter than } 7$$

for transition metal complexes,  $T_2$  = several µs at liquid helium temperatures

### Sensitivity and resolution

e.g. for a commercial X-band spectrometer  $5 \cdot 10^{10}$  spins can be detected at a SNR of 1.5 for a 1 gauss wide line

e.g. linewidths of transition ions in crystals, present at low concentrations, or in ~1mM solutions, are typically 10–100 gauss



-1)

### A list of paramagnetic ions observed in EPR



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	1	2	3	4	5	6	7	8	9	
1st series					Cr <sup>1+</sup>		Fe <sup>1+</sup>	Co1+	Ni <sup>1+</sup>	
(Iron group)	V** Ti <sup>3+</sup>	V <sup>3+</sup> Ti <sup>2+</sup>	V <sup>2+</sup> Cr <sup>3+</sup>	Cr <sup>2+</sup>	Mn <sup>2+</sup> Fc <sup>3+</sup>	Fe <sup>2+</sup>	Co <sup>2+</sup>	Ni <sup>2+</sup>	Cu <sup>2+</sup>	
2nd series	Mo <sup>5+</sup> Nb <sup>4+</sup> Tc <sup>6+</sup>	Mo <sup>4+</sup>	Mo <sup>3+</sup> Tc <sup>4+</sup>	Ru <sup>4+</sup>	Ru <sup>3+</sup> Tc <sup>2+</sup>	Ru <sup>2 *</sup>	Rh <sup>2+</sup>	Pd <sup>2+</sup>	Ag <sup>2+</sup>	
3rd series	La <sup>2</sup> * Re <sup>6</sup> *		Re <sup>4+</sup>	Os <sup>4+</sup>	Re <sup>2+</sup> Os <sup>3+</sup> Ir <sup>4+</sup>	Pt⁴+	₽t³+	Pt <sup>2</sup> *	Au²*	

55 out of 106 elements belonging to transition-group, rare-earth and actinide ions, that is, the members of the 3d, 4d, 5d, 4f and 5f groups have been subject of EPR investigations.

\* Biologically important elements are V, Fe, Mn, Co, Cu, Mo and Ni

no. of d-electrons

### Chromium (III), S=3/2 (single crystal)



Guanidine aluminum sulfate hexahydrate (GASH) doped with 1% copper (II)

### Iron (III)



Low-spin case S=1/2



Fe<sup>3+</sup> in AgCl crystal at 20K g=2.0156, a=0.0075

low spin Fe<sup>3+</sup> in cytochrome P450 protein g=2.42, 2.25, 1.92



### High-spin iron (III), S=5/2

EZI >> ZFI

EZI << ZFI



Fe<sup>3+</sup> in AgCl crystal at 20K, cubic symmetry g-2.0156, a=0.0075

Fe (III) protein, metmyoglobin at 2K g=6, 2





### Electron Nuclear Double resonance (ENDOR)

indirect NMR detection by EPR

probe structural detail due to unresolved hyperfine structures determine both strong and weak nuclear hyperfine couplings and from more distant nuclei

solid EPR spectra are often inhomogeneously broadened





## Electron Spin Echo Envelope Modulation (ESEEM

#### indirect NMR detection by EPR



utilizing frequencies of forbidden transition that contains electronnuclear hyperfine interaction

 $\rightarrow$  echo modulation



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## ESEEM to the study of bonding between Cu(II) ions and hydrated metal oxide surfaces in the presence of phosphates



### **Dynamic Nuclear Polarization**

sensitivity enhancement of NMR by EPR





Nuclear spin coordination around the electron spin through hyperfine coupling

### • cw ENDOR

strong hyperfine coupling

insensitive

### • ESEEM

peaks at same position as in ENDOR

weak hyperfine coupling (e.g. far nuclei, <sup>14</sup>N)

sensitive

only applicable to radicals and transition metal with narrow EPR lines

### • 2D HYSCORE

weak hyperfine coupling and connectivity to electron spin resonance

only applicable to radicals and transition metal with narrow EPR lines

effect increases at lower magnetic field X-band is a good compromise



CW EPR and ESEEM are powerful tools for analyzing catalytically important oxide systems containing paramagnetic ions



- 2. Paramagnetic species can be located with respect to various surface or framework atoms via weak electron-nuclear dipolar hyperfine interactions with surrounding magnetic nuclei to distances of about 0.6 nm.
- 3. By using deuterated or <sup>13</sup>C-labeled adsorbates it is possible to determine the number of adsorbed molecules and their distance to a catalytically active center.



### CW EPR

S-band (2-4 GHz), X-band (8-10 GHz), Q-band (~35 GHz) and W-band (~90 GHz).



reflected MW power as a function of  $B_0$  with 100kHz amplitude modulation at constant frequency, <200mW power, high sensitivity

### Pulsed EPR

- small excitation bandwith: ~100MHz through 10 ns pulse (30 Gauss at g=2)
- low sensitivity due to low Q/high power/long deadtime ~100ns
- low temperature in order to prolong relaxation time
- sophisticated technical equipment and theoretical treatment needed
- fast acquisition of entire EPR spectrum (a few microseconds)
- additional information about weakly coupled nuclei
- direct measurements of relaxation rates



## II. EPR in heterogeneous catalysis

- Defects and radical processes on oxide surfaces
  - Color centers on oxides
  - Photocatalytic reactions on oxides
  - Interfacial coordination chemistry
- Metal centers in microporous materials
- In situ EPR ("operando" EPR)





# What can we learn from EPR in heterogeneous catalysis studies?

- explore the nature of active sites
- identify reaction intermediates
- follow the coordination of supported transition metal ions
- follow the oxidation states of supported transition metal ions
- understand electron transfer reactions



# Strengths of EPR for heterogeneous catalysis studies

- direct detection of paramagnetic states
- unambiguous identification, low background signal
- high sensitivity (compared to NMR)
- surface and bulk species can be distinguished
- non-invasive technique
  - $\rightarrow$  in-situ catalytic studies on bulk catalysts materials possible

### Colour centers on oxides

the adsorption and catalytic behaviour of simple binary oxides (e.g. MgO) depend on the morphology and defectivity of the oxide itself

the study of localized point detefcts, e.g. anion or cation vacancies and surface colour centers (F<sub>s</sub><sup>+</sup>) created by doping anion vacancies with an excess electron is of great interest

#### EPR is a unique tool:

- 1. detection of colour centers of <0.02% of the entire surface area
- 2. location through superhyperfine interaction with surrounding protons from the surface hydroxyls and lattice <sup>25</sup>Mg<sup>2+</sup> cations
- 3. detection of radical anion formed through absorption and electron transfer





## Reversible formation of $N_2^-$ radical anion by $N_2$ adsorbtion into surface colour centers of MgO





B/Gauss

Finding through EPR, ENDOR and Theory:

defects are formed and stabilized in very low coordinated surface vacancies

the unusual electronic structure of these colour centers, consisting of free electrons in a surface vacancy accounts for their high chemical activity as reducing sites

E. Giamello, M.C. Paganini, M. Chiesa, D.M. Murphy, *J. Phys. Chem. B* 104 (2000) 1887-90

### Photocatalytic reactions on oxides



#### Motivation:

find detailed information on photogenerated paramagnetic species in the bulk or surface of photocatalytic materials

#### EPR is a unique tool:

for the characterization of photocatalytic materials based on polycrystalline semiconductor oxides, such as TiO<sub>2</sub> or ZrO<sub>2</sub>

- 1. detect charge carrier states such as trapped electrons or trapped holes on the surface
- 2. identify the nature of photoproduced radicals
- 3. monitor their reactivity under various conditions



Y. Kohno, T. Tanaka, T. Funabiki, S. Yoshida, Phys. Chem. Chem. Phys. 2 (2000) 2635-2639.

## Transition metal ions dispersed on solid surfaces: role of copper in promoting host metal oxides

#### Motivation:

to understand synergy between copper promoter and host oxide (e.g.  $CeO_2$ ,  $SnO_2$ ,  $ZrO_2$ ,  $TiO_2$ ) metal ion in NO reduction and CO or hydrocarbon oxidation

#### EPR is a unique tool:

to probe the changes in the inner and outer coordination sphere and oxidation state of paramagnetic transition metal oxide or ion during a catalytic reaction

- 1. structure of the surface complex
- 2. mechanisms of their interaction with small molecules

Example: Cu(II)/CeO2 catalyst material

- coprecipitation from aqueous solutions containing Cu<sup>2+</sup> and Ce<sup>4+</sup> ions
- sorption of Cu<sup>2+</sup> ions onto ceria gel



## Copper (II) in promoting cerium (IV) oxide catalysts



Field / Gauss

 $g_{iso} \sim 2$ amorphous Cu(II) aggregates on ceria surface (polymeric Cu(OH)<sub>2</sub> and hexaaqua {Cu(H<sub>2</sub>O)<sub>6</sub>}<sup>2+</sup>

axial symmetry: g\_=2.248, g\_=2.092, A\_=120G, A\_=28G isolated Cu<sup>2+</sup> ions in tetragonally distorted octahedral sites

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g||=2.195, g $\perp$ =2.031, A||=85G, A $\perp$ =12G from the coupling between two Cu<sup>2+</sup> ions (I=3/2) triplet signal from Cu(II) dimer, 7 lines through hsf interionic distance: 3.1Å

g<sub>iso</sub>=2.098 due to CuO crystallite particles

P.G. Harrison, I.K. Ball, W. Azelee, W. Daniell, D. Goldfarb, Chem. Mater. 12 (2000) 3715-3725.

### Copper (II) in promoting cerium (IV) oxide catalysts



## Copper (II) in promoting cerium (IV) oxide catalysts

(A) 1 DPPH 333K (a) 573K (b)873K  $\{0\}$ 1073K (d) 1273K (e). 2000 2500 3000 3500 4000

isolated monomeric Cu<sup>2+</sup> ions are located in sites on the ceria surface similar to those of dimers and are precursors for the dimer formation

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### Exposure of Cu(II)/CeO<sub>2</sub> catalysts to CO





removal of broad isotropic signal due to amorphous Cu(II) clusters

removal of Cu(II) dimer signal

removal of monomeric Cu<sup>2+</sup> signal appearance of Ce<sup>3+</sup> signal

reoxidation at 673K under O<sub>2</sub> atm.

P.G. Harrison, I.K. Ball, W. Azelee, W. Daniell, D. Goldfarb, Chem. Mater. 12 (2000) 3715-3725.

### Exposure of Cu(II)/CeO<sub>2</sub> catalysts to CO





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#### Order of reduction

1. amorphous copper(II) dispersed

on the ceria surface

- 2. dimer species
- 3. isolated Cu<sup>2+</sup> ions
- 4. CeO<sub>2</sub> support (Ce<sup>3+</sup> appears)

isolated copper(II) is located within the growing crystallites of ceria and its accessibility limited

## copper(II) is reduced in preference to cerium(IV) by CO

P.G. Harrison, I.K. Ball, W. Azelee, W. Daniell, D. Goldfarb, Chem. Mater. 12 (2000) 3715-3725.

#### e Exposure of Cu(II)/CeO<sub>2</sub> catalysts to CO and reoxidation with NO (a)(a)**(b)** RT (b) (c)isolated Cu<sup>2+</sup> ions (d) NO 323K CO $(\mathbf{e})$ 373K (0)(f) (e) (f)(g)I DPPH Cu(II) ion dimers (h) **O**<sub>2</sub> 2000 3000 4000 5000 2000 3000 4000 Field / Gauss Field / Gauss

# Exposure of $Cu(II)/CeO_2$ catalysts to CO and reoxidation with NO





lack of Cu-NO signal indicates that NO does not bind to Cu sites but rather to the ceria surface

## Copper (II) in promoting cerium (IV) oxide catalysts in CO oxidation

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- isolated monomeric Cu<sup>2+</sup> ions are located in the same sites on the ceria surface as those of the dimers and are precursors
- 2. dispersed amorphous copper and copper dimers seem most active
- 3. Cu(II) gets more readily reduced than Ce(IV) by CO
- 4. during reoxidation, NO does not bind to Cu sites but to Ce surface

P.G. Harrison, I. K. Ball, W. Azelee, W. Daniell, D. Goldfarb, Chem. Mater. 12 (2000) 3715-3725.

- 1. true  $Ce_{1-x}Cu_xO_{2-\delta}$  oxide solution was found to be the active phase
- 2. Cu(II) is built into the lattice creating a neighboring oxygen vacancy
- 3. Cu(II) dimers have distances shorter than the Cu-Ce lattice sites
- P. Bera et al, Chem. Mater. 14 (2002) 3591-3601.

## hypothesis: absorption of a second Cu<sup>2+</sup> ion onto the oxygen defect and its reduction (electron transfer) next to the isolated Cu<sup>2+</sup> site

# Metal centres in (silico-)aluminophosphate microporous materials



- 1. Aluminophosphate (AIPO-n) and silicoaluminophosphate (SAPO-n) molecular sieves
- 2. Al and/or P can be replaced by metals to form MeAPO-*n* or MeAPSO-*n* materials
- 3. Me = Ti(III), V(IV), Cr(III), Mn(II), Fe(III), Co(II), Ni(I), Pd(I), Cu(II), Mo(V),
- 4. The **location** and **structure** of the reactive metal ion site and its **interaction** with different adsorbated and reactants is of importance
- 5. The **incorporation of transition metal ions into framework sites** of the ALPO-*n* and SAPO-*n* is of particular interest for the design of novel catalysts.
- 6. A variety of metals can be incorporated into the aluminophosphate structure, but actual incorporation into the tetrahedral framework is difficult to prove.



M. Hartmann, L. Kevan, Chem Rev. 99(3) (1999) 635-663.



#### <sup>31</sup>P and <sup>2</sup>D ESEM spectroscopy provides detailed information about coordination and can therefore discriminate between ion-exchanged and synthesized Ni materials

NiH-SAPO-5: Ni(I) is located in the center of a hexagonal prism (site SI)

<u>Ni-APSO-5</u>: Ni(I) replaces framework phophorous according to nearest phosphorous coordination and distance

methanol or ethylene absorbed on NiH-SAPO-5 and Ni-APSO-5



# Incorporation of Mn(II) into framework sites in the aluminophosphate zeotype $AIPO_4$ -20

Unlike lattices of typical zeolites, AIPO<sub>4</sub>-20 lattice is neutral. Substitution with transition metal provides ion-exchange ability or acidity



MnAIPO<sub>4</sub>-20 possess specific catalytic activity in hydrocarbon cracking



cw EPR: presence of a single Mn(II) site with a <sup>55</sup>Mn hyperfine coupling of 8.7mT

D. Arieli, D.E.W. Vaughan, K.G. Strohmaier, D. Goldfarb, J. Am. Chem. Soc. 121 (1999) 6028-6032.

# Incorporation of Mn(II) into framework sites in the aluminophosphate zeotype $AIPO_4$ -20



ESEEM: detection of weak superhyperfine coupling

<sup>1</sup>H, <sup>14</sup>N, <sup>27</sup>AI (5.44 Å), <sup>31</sup>P

#### ENDOR: detection of strong superhyperfine coupling

<sup>31</sup>P doublet: strong hyperfine interarction (3.14 Å) <sup>27</sup>Al no doublet: weaker hyperfine interaction (4.44 Å)

D. Arieli, D.E.W. Vaughan, K.G. Strohmaier, D. Goldfarb, J. Am. Chem. Soc. 121 (1999) 6028-6032.

Probe host-guest interactions at the molecular level in zeolite and molecular sieve materials

science crossing borders... 1. ZSM-5, NaY Cu(II) exchanged zeolites 2. MCM-4 large-pore molecular sieve materials for adsorptive and catalytic applications involving large molecules **2D HYSCORE**  $\omega \sqrt{2\pi}(MHz)$ solution MCM-41 H-Cu(II) distance: 3.05 Å NaY ZSM-5 MCM-41  $\Delta \omega_{max}^{S}$ 3000 3500 15 20 2500 10 3000 3500 2500 B/G 

 $Cu(py)_2$ 

Cu(en)<sub>2</sub>

W. Böhlmann, A. Pöppl, D. Michel, Colloids and Surfaces 158 (1999) 235-240.

 $Cu(py)_{4}^{2+}$  complexes

### In situ EPR



spectroscopic measurements of catalysts under working conditionscience crossing borders...

### **Operando EPR**

in situ EPR in combination with other spectroscopic analysis and simultaneous on-line product analysis (e.g. EPR/UV-vis/laser-Raman)

Example: operando studies of transition metal oxide catalysts, e.g. of supported  $VO_x$  and  $CrO_x$  catalysts in oxidative and non-oxidative dehydrogenation of propane.

... while EPR detects sensitively paramagnetic transition metal ions such as V<sup>4+</sup>, Cr<sup>5+</sup> and Cr<sup>3+</sup>, UV-vis isa powerful monitor for diamagnetic TMI such as V<sup>5+</sup> and Cr<sup>6+</sup> since the latter give rise to intense charge-transfer transitions



# In situ EPR on vanadium oxide based catalysts at 673K

Motivation:

catalysts based on vanadium oxide belong to the most important active phase for heterogeneously catalyzed reactions involving surface reduction and reoxidation cycles

vanadium oxide is not applied as pure phase but in form of mixed bulk oxides such as vandium phospates (VPO) or highly dispersed on support materials such as TiO<sub>2</sub>

of great interest is the role of crystalline and amorphous phases in the catalytic process

#### EPR is a unique tool:

- capable of identifying the structural environment of isolated VO<sup>2+</sup> species in supported catalysts
- 2. characterizing VO<sup>2+</sup> sites in bulk oxides (so far only possible with EPR)
- 3. in situ observation under reaction condition



# EPR exchange line narrowing: sensitive monitor for disorder-related sensitivity

 $(NH_4)_2(VO)_3(P_2O_7)_2$  (VPO catalysts) during ammoxidation of toluene: amorphous VO<sup>2+</sup> containing phases are active components

EPR line shape analysis <B<sup>4</sup>>/<B<sup>2</sup>><sup>2</sup> characterizes exchange coupling between neighboring VO<sup>2+</sup> : increases with exchange interaction

perturbation of spin-spin exchange upon contact with reactant increases with exchange interaction

certain degree of structural disorder correlates with catalytic activity







### EPR in heterogeneous catalysis

#### TOOL

- CW EPR spectroscopy
  - g, A tensor analysis, spectral fitting: oxidation state, intermediates, hint about structure
- ESEEM, ENDOR and 2D HYSCORE spectroscopy
  - direct measurement of hyperfine coupling tensor terms: structure information
- EPR Line shape analysis
  - crystalline vs. amorphous phase

#### **APPLICATIONS**

- Defects and radical processes on oxide surfaces
- Metal centers in microporous materials
- In situ EPR ("operando" EPR)

### EPR literature used in this presentation

Books & Reviews:

- J. Weil, J.R. Bolton, J.E. Wertz, "Electron paramagnetic resonance", Wiley Interscience, New York, 1994
- J. R. Pilbrow, "Transition ion electron paramagnetic resonance", Clarendon Press, Oxford, 1990.
- A. Schweiger, "Pulsed Electron Spin Resonance spectroscopy", Angew. Chem. Int. Ed. Engl. 30 (1991) 265-292.

Journal Papers:

- D. M. Murphy, C.C. Rowlands, Current Opinion in Solid State and Materials Science 5 (2001) 97-104.
- E. Giamello, M.C. Paganini, M. Chiesa, D.M. Murphy, J. Phys. Chem. B 104 (2000) 1887-90
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