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

\[ U = \frac{1}{2} g_e \beta_e B \]

\[ \Delta U = h\nu \]
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: $10^{16}$ spins per 1 ml
EPR: $10^{10}$-$10^{11}$ spins per <1ml
Which information?

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

**NMR:** nuclear magnetic moments

\[ B_0 = 2.34 \, \text{T} \]

\[ \nu = \frac{\mu B_0}{\hbar I} = \frac{4.68 \mu}{\hbar} \]

**EPR:** electron magnetic moment
EPR brief

• first EPR observation in 1945: CuCl$_2$·H$_2$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) → 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)
Typical systems studied by EPR

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
   - \( V^{4+}, Ti^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+} \ldots \)

3. **various point defects (localized imperfections) in solids**
   - electron trapped at a negative-ion vacancy (F center) or an electron hole

4. **systems with more than one unpaired electron**
   - triplet state systems, biradicals

5. **systems with conducting electrons**
   - semiconductors, metals
One electron in the magnetic field

Electron Zeeman Interaction (EZI): 2-level system

\[ H = - \mu \cdot B = \gamma \cdot S \cdot B = g_e \beta_e \cdot S \cdot B \]

negative gyromagnetic ratio \( \gamma \)

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

\( S = 1/2, M_S = 1/2, -1/2: \)

\( |\Delta M_S| = 1, E \pm = \pm 1/2 \ g \ \beta \ B \)

\( |\Delta M_S| = 1 \) condition does not hold strictly when \( S > 1/2 \), or when hyperfine interaction is present
EPR detection:
Magnetic field sweep with 100 kHz modulation

EPR \[ H = g_e \cdot \beta_e \cdot B_{\text{eff}} \cdot S \]
\[ = \beta_e \cdot B_0 \cdot g \cdot S \]

NMR \[ H = \gamma B_{\text{eff}} \cdot I \]
\[ = \gamma B_0 \cdot (1-\sigma) \cdot I \]
One electron in the magnetic field: 2-level systems with resonance around $g = 2$

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

\[ ^1\text{H gas, } S=1/2, I=1/2 \]

\[ \text{Ge}^{3+}, S=1/2, I=9/2 \]

\[ +\frac{1}{2} \rightarrow -\frac{1}{2} \]

\[ -\frac{1}{2} \rightarrow +\frac{1}{2} \]

\[ B \quad 10\text{ mT} \]

\[ B \quad 50.0\text{ mT} \]
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$^{2+}$ or Fe$^{3+}$)
- organic molecules in triplet state

IF such terms $\gg$ electron Zeeman term due to $B_0$

- MW frequency may have too small bandwidth (e.g. in VO$^{2+}$, Mn$^{2+}$)
- 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, removing the orbital degeneracy for most transition metals. “Quenching of the orbital angular momentum” results in an effective spin $S=1/2$.

EPR spectra only through the unpaired electron in $dx^2-y^2$ orbital, potentially leading to a one electron $S=1/2$, two-level system?

**Figure:** 3d⁹ transition metal ion
Ligand field effect through second order SOC

Most molecule’s ground state undergo orbital quenching by chemical bonding (e.g. radicals) or large CF’s (e.g. transition metal ions) → $g$-factor of free electrons

But small amount of orbital angular momentum admixes to the 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 $B_0$

$$H = (g) \beta \cdot S \cdot B$$

g tensor!
**g** anisotropy

EPR spectra depend on orientation of samples in B0 in single crystals or powder samples

$$H = g_e \cdot \beta_e \cdot B_{\text{eff}} \cdot S$$

$$= \beta_e \cdot B_0 \cdot g \cdot S$$

principal values contain

| symmetric of the inner field |

$B_0$ along one of the PAS

$g = g_x, g_y$ or $g_z$

arbitrary orientation of $B_0$

$g^2 = g_x^2 \cdot I_x^2 + g_y^2 \cdot I_y^2 + g_z^2 \cdot I_z^2$

CF with axial symmetry

$g(\theta)^2 = g_{\perp} \sin^2 \theta + g^2 \cos^2 \theta$

$g_{\parallel} > g$

$B_0(g_{\parallel}) < B_0(g)$
EPR of solutions

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

Typical vanadyl solution spectrum (of VO(acac)₂)

S=1/2, I=7/2

EPR at low temperature (frozen solids)

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

S=1/2, I=0

1st derivative
Interaction with nuclear spins (hyperfine interaction)

local magnetic fields by neighboring nuclear magnetic moments ($\mu_n$) depend on the orientation of $\mu_n$ with respect to $B_0$ → splitting of each electron spin state into $(2I+1)$ levels.

**Nuclear Zeeman interaction**

$$H = g_n \cdot \beta_n \cdot B_{\text{eff}} \cdot I = \gamma \cdot B_0 \cdot (1-\sigma) \cdot I$$

e.g. $g_n=5.58$ for proton

Nuclear Zeeman interaction ($NZI$) ≪ Electronic Zeeman Interaction ($EZI$)

$^1$H, S=1/2, I=1/2

nitrooxide radical, S=1/2, I=1
Cobalt (II), 3d⁷ (single crystal)

Co(II), V(IV), VO(II)

S=1/2, I=7/2

8 lines

Co²⁺ in Mg(CH₃COO)₂·4H₂O crystal
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$_4$ single crystal
Origin of hyperfine interactions

- **dipole-dipole interaction** between the magnetic moments

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

\[ \text{anisotropic} \]

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

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

\[ H_{\text{contact}} = \frac{2}{3} \frac{\mu_0}{\hbar} g_e \beta_e g_n \beta_n |\Psi(0)|^2 \mathbf{S} \cdot \]

\[ \text{isotropic} \]

unpaired electrons in mainly *s*- or *p*-, *d*-, *f*- orbitals or *\pi* electrons or transition metals
The hyperfine interaction matrix $A$

$$H = H_{FS} + \beta \cdot \cdot \cdot + \cdot \cdot + \cdot \cdot + \cdot \cdot + \cdot \cdot - g_n \beta_n \cdot$$

$$= \begin{bmatrix} \delta & \delta \\ \delta & \delta \end{bmatrix} = 1a_{iso} + \begin{bmatrix} \delta \\ \delta \end{bmatrix}$$

- isotropic EZI and HFI for $I=3/2$ (e.g. Cu$^{2+}$)
- selection rule: $\Delta m_s = \pm 1$ and $\Delta m_I = 0$
- 4 allowed transition
- centered around $g_{iso}$ and split by $a_{iso}$
Powder and single crystal EPR spectra of Cu$^{2+}$ complexes $S=1/2$, $I=3/2$

$g_{||}$ is larger than $g_{\perp}$

$g$, A values: copper ion is surrounded by oxygen

Cu$^{2+}$ doped into CaCd(CH$_3$COO)$_4$·6H$_2$O
Powder EPR of Cu$^{2+}$ complexes

powder EPR spectrum for an axially elongated copper complex
Powder EPR of Cu$^{2+}$ coordinated to sulfur, nitrogen or oxygen

coordination to close nuclei through $g_{\parallel}$ and $A_{\parallel}$ values by CW X-band EPR

(a) copper (II) diethyldithiocarbamate
(b) copper (II) tetrapyridyl porphyrazine
(c) copper (II) in calcium cadmium acetate hexa
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 stabilizing cations and metallic species because of their crown-ether-like ring structures in their cages and channels.

first observation of square-planar Au(II) complex with N₄ in the supercage of Y-zeolite was observed via EPR.

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

\[ H = \beta \cdot \cdot \cdot + \cdot \cdot \cdot + \cdot \cdot \cdot + \cdot \cdot \cdot - g_n \beta_n \cdot \]

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 \(I > ½\)
   - 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

Linewidth determined by:
\[
\frac{1}{T_{2,\text{eff}}} = \frac{1}{T_2} + \frac{1}{2T_1}
\]
($T_2$ is much shorter than $T_1$)

For transition metal complexes, $T_2 = \text{several } \mu\text{s at liquid helium temperatures}$

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 $\sim 1\text{mM}$ solutions, are typically 10–100 gauss
A list of paramagnetic ions observed in EPR

<table>
<thead>
<tr>
<th>1st series (Iron group)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
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<td>V^{4+}</td>
<td>V^{3+}</td>
<td>V^{2+}</td>
<td>Cr^{2+}</td>
<td>Cr^{1+}</td>
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<td>Ni^{2+}</td>
<td>Cu^{2+}</td>
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<tr>
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<td>Mo^{4+}</td>
<td>Mo^{5+}</td>
<td>Ru^{4+}</td>
<td>Ru^{3+}</td>
<td>Ru^{2+}</td>
<td>Rh^{2+}</td>
<td>Pd^{2+}</td>
<td>Ag^{2+}</td>
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<td>Tc^{4+}</td>
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<td>Tc^{6+}</td>
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<table>
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<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
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<tbody>
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<td>Re^{2+}</td>
<td>Os^{4+}</td>
<td>Os^{3+}</td>
<td>Ir^{4+}</td>
<td>Pt^{4+}</td>
<td>Pt^{3+}</td>
<td>Pt^{2+}</td>
<td>Au^{2+}</td>
</tr>
<tr>
<td>Re^{6+}</td>
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<tr>
<td></td>
<td>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.</td>
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* Biologically important elements are V, Fe, Mn, Co, Cu, Mo and Ni
Chromium (III), $S=3/2$ (single crystal)

$S=3/2 \rightarrow$ four electronic energy levels

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

High-spin case
S=5/2, 3d⁵ character in bound form
5 line EPR spectrum

Low-spin case
S=1/2

Fe³⁺ in AgCl crystal at 20K
\( g=2.0156, a=0.0075 \)

low spin Fe³⁺ in cytochrome P450 protein
\( g=2.42, 2.25, 1.92 \)
High-spin iron (III), $S=5/2$

**EZI >> ZFI**

Fe$^{3+}$ in AgCl crystal at 20K, cubic symmetry

$g=2.0156, a=0.0075$

**EZI << ZFI**

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

EPR saturation  NMR saturation frequency sweep

EPR detection

CW EPR  EPR frequency  CW ENDOR  NMR frequency
Electron Spin Echo Envelope Modulation (ESEEM)

indirect NMR detection by EPR

electron-nuclear coupled system

two allowed transitions ($\Delta m_S=\pm 1$, $\Delta m_I=0$)  
two forbidden transitions ($\Delta m_S=\pm 1$, $\Delta m_I=\pm 1$)

utilizing frequencies of forbidden transition that contains electron-nuclear hyperfine interaction

$\rightarrow$ echo modulation
ESEEM to the study of bonding between Cu(II) ions and hydrated metal oxide surfaces in the presence of phosphates

Cu(II) (pyrophosphate)$_2$

Cu(II) (pyrophosphate)$_2$ adsorbed on $\delta$-Al$_2$O$_3$

Cu(II) NTP adsorbed on $\delta$-Al$_2$O$_3$
Dynamic Nuclear Polarization

sensitivity enhancement of NMR by EPR

utilizing higher $\gamma$
low temperature of electron spins

$\psi_1 = |2m_s,2m_I\rangle$ : nucleus (I=1/2) coupled to an electron (s=1/2)
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, $^{14}$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.

1. The ESEEM method is particularly well adapted for studying powder spectra in molecular sieves and other oxide solids.

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 $^{13}$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 bandwidth: ~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
  - 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 defects, e.g. anion or cation vacancies and surface colour centers (F$_{S}^{+}$) 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 $^{25}$Mg$^{2+}$ cations

3. detection of radical anion formed through absorption and electron transfer

\[ \text{Cl}^{-} \quad \text{Na}^{+} \quad \text{Cl}^{-} \]

\[ \text{Na}^{+} \quad \text{e}^{-} \quad \text{Na}^{+} \]

\[ \text{Cl}^{-} \quad \text{Na}^{+} \quad \text{Cl}^{-} \]
Reversible formation of $\text{N}_2^-$ radical anion by $\text{N}_2$ adsorption into surface color centers of MgO

Finding through EPR, ENDOR and Theory:

- Defects are formed and stabilized in very low coordinated surface vacancies.
- The unusual electronic structure of these color centers, consisting of free electrons in a surface vacancy accounts for their high chemical activity as reducing sites.

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$_2$ or ZrO$_2$

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
Photoreduction of CO\textsubscript{2} with H\textsubscript{2} over ZrO\textsubscript{2}:

\[ \text{ZrO}_2 + 13\text{CO}_2 + \text{H}_2 \rightarrow \text{ZrO}_2 + \text{HCOO}^- + \text{F}_\text{center} \]

\[ \text{ZrO}_2 + \text{uv} \rightarrow \text{ZrO}_2 + \text{CO}_2 \]

1\textsuperscript{3}\text{CO}_2^- radical anion (I=1/2)

doublet splitting

the excitation of adsorbed CO\textsubscript{2} to form the CO\textsubscript{2}^- radical seems to be a localized surface process; long-lived species

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)/CeO$_2$ catalyst material**
– coprecipitation from aqueous solutions containing Cu$^{2+}$ and Ce$^{4+}$ ions
– sorption of Cu$^{2+}$ ions onto ceria gel
Copper (II) in promoting cerium (IV) oxide catalysts

![Graph showing EPR spectra at different temperatures (333K, 573K, 873K, 1073K, 1273K).]

- $g_{\text{iso}} \sim 2$
- Amorphous Cu(II) aggregates on ceria surface (polymeric Cu(OH)$_2$ and hexaaqua {Cu(H$_2$O)$_6$}$^{2+}$) with axial symmetry: $g_{||} = 2.248$, $g_{\perp} = 2.092$, $A_{||} = 120$G, $A_{\perp} = 28$G
- Isolated Cu$^{2+}$ ions in tetragonally distorted octahedral sites with $g_{||} = 2.195$, $g_{\perp} = 2.031$, $A_{||} = 85$G, $A_{\perp} = 12$G
- From the coupling between two Cu$^{2+}$ ions ($I=3/2$) triplet signal from Cu(II) dimer, 7 lines through hsf
- Interionic distance: 3.1Å
- $g_{\text{iso}} = 2.098$ due to CuO crystallite particles

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

forbidden transition due to triplet states of Cu(II) dimer

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

Isolated monomeric Cu\textsuperscript{2+} ions are located in sites on the ceria surface similar to those of dimers and are precursors for the dimer formation

Exposure of Cu(II)/CeO$_2$ catalysts to CO

calcination at 873K, no CO

evacuation at 573K

RT, CO

373K, CO

473K, CO

573K, CO

673K, CO

673K, O$_2$

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

removal of Cu(II) dimer signal

removal of monomeric Cu$^{2+}$ signal

appearance of Ce$^{3+}$ signal

reoxidation at 673K under O$_2$ atm.

Exposure of Cu(II)/CeO$_2$ catalysts to CO

Order of reduction
1. amorphous copper(II) dispersed on the ceria surface
2. dimer species
3. isolated Cu$^{2+}$ ions
4. CeO$_2$ support (Ce$^{3+}$ 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

Exposure of Cu(II)/CeO₂ catalysts to CO and reoxidation with NO

- CO
- NO
- O₂

RT
323K
373K

isolated Cu²⁺ ions

Cu(II) ion dimers
Exposure of Cu(II)/CeO$_2$ catalysts to CO and reoxidation with NO

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

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isolated Cu$^{2+}$ ions

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Cu(II) ion dimers
Copper (II) in promoting cerium (IV) oxide catalysts in CO oxidation

1. isolated monomeric Cu\(^{2+}\) 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


1. true Ce\(_{1-x}\)Cu\(_x\)O\(_{2-\delta}\) 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


hypothesis: absorption of a second Cu\(^{2+}\) ion onto the oxygen defect and its reduction (electron transfer) next to the isolated Cu\(^{2+}\) site
Metal centres in (silico-)aluminophosphate microporous materials

1. Aluminophosphate (AlPO-\textit{n}) and silicoaluminophosphate (SAPO-\textit{n}) molecular sieves

2. Al and/or P can be replaced by metals to form MeAPO-\textit{n} or MeAPSO-\textit{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 \textit{location} and \textit{structure} of the reactive metal ion site and its \textit{interaction} with different adsorbed and reactants is of importance

5. The \textbf{incorporation of transition metal ions into framework sites} of the ALPO-\textit{n} and SAPO-\textit{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.

Nickel species have been studied intensively in SAPO materials because of their catalytic importance. It is of particular interest that Ni(I) can be stabilized. Isolated Ni(I) species with axial symmetry ($g_{||} = 2.49$, $g_{\perp} = 2.11$) in NiH-SAPO-11 through thermal or hydrogen reduction, the $g$ values are not sufficiently discriminatory to find the location of nickel(I) Ni-APSO-5: Ni(I) replaces framework phosphorous according to nearest phosphorous coordination and distance.

$^{31}$P and $^{2}$D ESEEM 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).

Ni-APSO-5: Ni(I) replaces framework phosphorous 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 AlPO$_4$-20

Unlike lattices of typical zeolites, AlPO$_4$-20 lattice is neutral. Substitution with transition metal provides ion-exchange ability or acidity

MnAlPO$_4$-20 possess specific catalytic activity in hydrocarbon cracking

cw EPR: presence of a single Mn(II) site with a $^{55}$Mn hyperfine coupling of 8.7mT

Incorporation of Mn(II) into framework sites in the aluminophosphate zeotype AlPO$_4$-20

ESEEM: detection of weak superhyperfine coupling

$^1$H, $^{14}$N, $^{27}$Al (5.44 Å), $^{31}$P

ENDOR: detection of strong superhyperfine coupling

$^{31}$P doublet: strong hyperfine interaction (3.14 Å)

$^{27}$Al no doublet: weaker hyperfine interaction (4.44 Å)

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

Incorporation of organic copper complexes (pyridine, ethylenediamine):

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 HYSORE](image)

**Cu(en)$_2$**, **Cu(py)$_2$**, **Cu(py)$_4^{2+}$** complexes

In situ EPR

spectroscopic measurements of catalysts under working conditions.

**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\textsubscript{x} and CrO\textsubscript{x} catalysts in oxidative and non-oxidative dehydrogenation of propane.

... while EPR detects sensitively paramagnetic transition metal ions such as V\textsuperscript{4+}, Cr\textsuperscript{5+} and Cr\textsuperscript{3+}, UV-vis is a powerful monitor for diamagnetic TMI such as V\textsuperscript{5+} and Cr\textsuperscript{6+} 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 phosphates (VPO) or highly dispersed on support materials such as TiO$_2$

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

**EPR is a unique tool:**

1. capable of identifying the structural environment of isolated VO$^{2+}$ species in supported catalysts
2. characterizing VO$^{2+}$ 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\(^{2+}\) containing phases are active components

EPR line shape analysis \(\frac{\langle B^4 \rangle}{\langle B^2 \rangle^2}\) characterizes exchange coupling between neighboring VO\(^{2+}\):
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:

Journal Papers: