ACTIVE SITES IN OXIDES
Because of steric and electronic reasons only a limited number of ligands or nearest neighbors can be within bonding distance of a metal atom or ion.

Surface anions and cations are coordinatively unsaturated (cus):
**ACTIVE IN BONDING WITH ADSORBATES**

$M^{n+}$ (cus) site behaves like a Lewis acid and the $O^{2-}$ (cus) ion is more basic than the bulk ions.

Such an acid-base pair can:
1. Coordinate the reagent, intermediates and products (activity, poisoning, activation procedures)
2. Participate in heterolytic dissociative adsorption

Because of **steric** and **electronic** reasons only a limited number of ligands or nearest neighbors can be within bonding distance of a metal atom or ion.

Microcrystalline samples prepared from aqueous solutions

Single crystal HV cleavage

---

**COORDINATIVE UNSATURATION: THE FIRST STEP**

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Because of **steric** and **electronic** reasons only a limited number of ligands or nearest neighbors can be within bonding distance of a metal atom or ion.

Microcrystalline samples prepared from aqueous solutions

Single crystal HV cleavage
Different cus, Different accessibility ...
Different capability in adsorbate coordination
(activation, poisoning)
Different reducibility (redox catalysts)
Different removibility (redox catalysts)

DIFFERENT REACTIVITY
Sizes and sites

Representation of MgO structure: reconstructed (111) facelet with tricoordinated oxygen

Terraced surface with steps and edges, where ions are tetracoordinated

(001) Flat surface with pentacoordinated species

a) Effect of sintering on particle dimensions

Mg$^{2+}$ ions = white
O$^{2-}$ ions = gray
Different cus, Different accessibility ...
Different capability in adsorbate coordination
  Different reducibility
  Different removibility

DIFFERENT REACTIVITY

Different Hydroxylation
Different strenght and distribution of surface active sites
THE INFLUENCE OF WATER

Water adsorbs molecularly and/or dissociatively to satisfy the coordinative unsaturation of the metal ions.

Reactivity is influenced by
1. preparation procedure
2. sample age and history
3. the activation of catalysts by heat treatment is frequently necessary
Isolated hydroxyl groups

Surface hydroxyl content of ZnO evacuated at various temperatures

\[ M^{n+}(\text{cus}) + H_2O \rightleftharpoons M^{n+}OH_2 \]

\[ O^{2-} + H_2O + M^{n+} \rightleftharpoons H_2O + M^{n+} \]
1. The surface reactivity is heavily affected by CO$_2$ whenever basic cations are present (rare earths, alkali and alkali-earth).

2. Basic cations containing oxide can be poisoned in HCs, CO etc. oxidation reactions.

Temperature Programmed Desorption - TPD - can be of some help in determining:

1. the reactivity with carbon dioxide
2. the treatments necessary to create active sites
3. the catalyst poison mechanism
Temperature Programmed Desorption - TPD - can help in determining:

1. the reactivity with carbon dioxide
2. the treatments necessary to create active sites
3. the catalyst poison mechanism

TPD-QMS for LSGF Gel (solid line) and LSGF Pec (dashed line). TCD signal (red), $H_2O$, $m/z = 18$ (blue), $CO_2$, $m/z = 44$ (—). $CO_2$ signals 5 folds magnified.
Removal of the weakly adsorbed molecular water does not necessarily activate the surface (H-bonded).

Amount of water lost per Cr$^{3+}$ upon heating from 25°C and surface area of amorphous Cr$_2$O$_3$.

Capacity for O$_2$ or CO adsorption and catalytic activity for 1-hexene hydrogenation as a function of the temperature of activation of amorphous Cr$_2$O$_3$ in H$_2$. 

INTERACTION BETWEEN MOLECULES AND SURFACES

1. **Molecular** (non-dissociative) adsorption (on single uncoordinate surface site)
   - H-bonding
   - Lewis acidic/basic interaction
   - Interaction by $\sigma$-donation and/or $\pi$-bonding interaction

2. **Dissociative** adsorption (requires anion-cation coordinatively unsaturated pair site)
   - Dissociation is usually heterolytic;
   - Homolytic dissociative adsorption is less frequent

3. **Abstractive** adsorption (requires acidic sites)
   - Usually involves protons: the adsorbed specie becomes cationic and the electrostatic interaction with the surface may be relevant

4. **Reductive** adsorption in which the adsorbed molecule is oxidized while the surface is reduced; it may also be abstractive (es an example when lattice oxygen is involved in oxidation)
MODEL CHEMISORPTIONS

\[
\text{H}_2 + \text{Zn}^{2+} - \text{O}^2- \rightleftharpoons \text{H}^- \text{H}^+ - \text{Zn}^{2+} - \text{O}^2-
\]

\[
\text{C}_3\text{H}_6 + \text{Zn-O} \rightleftharpoons \text{CH}_2-\text{CH}-\text{CH}_2^- \text{H}^+ \text{Zn}\text{O}
\]

\[
\text{CH}_3\text{CCH}_3 + \text{M-O} \rightleftharpoons (\text{CH}_3\text{C}=\text{CH}_2)^- + \text{H}^+ \text{O}\text{M}
\]

\[
\text{ROH} + \text{Zn-O} \rightarrow \text{RO} \text{H} \text{Zn} - \text{O}
\]
CHEMISORPTION ON REAL SURFACES: ALCOHOL CHEMISORPTION AND SURFACE HYDROXYLATION

Dehydroxylated surface

Dissociative interaction (I)

Molecular interaction (II) through the interaction with the Lewis acid and base sites.
CHEMISORPTION ON REAL SURFACES: 
ALCOHOL CHEMISORPTION AND SURFACE 
HYDROXYLATION

Hydroxylated surface

Esterification with surface hydroxyl groups (III)

Replacement of molecular water present on the surface (IV)

Reversible adsorption on the surface hydroxyl groups or methoxy groups through hydrogen bonds (V).
**IR SPECTROSCOPY: AN EASY AND POWERFUL TOOL TO INVESTIGATE CHEMISORPTION - CO**

CO tends to interact through the C end to the cationic center; this interaction is usually weak and reversible by outgassing.

Polarization = blue shift

\[ \sigma \text{-Donation and } \pi \text{-backdonation} \]

metal to CO = red shift

\[
\begin{align*}
\text{CoOx/La}_2\text{O}_3 & \quad \text{LaCoO}_3 & \quad \text{La}_2\text{O}_3 \\
\end{align*}
\]

RT (black line), 373 K (blue line), 423 K (green line), 473 K (yellow line), 523 K (pink line), 573 K (turquoise).
IR SPECTROSCOPY: AN EASY AND POWERFUL TOOL TO INVESTIGATE CHEMISORPTION NO

Linear nitrosyl form over cationic sites = blue shift (> 1850 cm⁻¹) = > shift > acidity

Bent nitrosyl mainly forms over reduced center = red shift

Adsorption in pairs on $M^{n+}$ ion shows in IR as a pair of absorption bands (symmetric and antisymmetric stretches).

Absorption frequencies depend on the oxide.

Separation between peaks is constant for a given cation and varies less from sample to sample.

<table>
<thead>
<tr>
<th>Cation</th>
<th>Peak Positions, cm⁻¹</th>
<th>Peak Separation, cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Cr^{2+}, Cr^{3+}$</td>
<td>1745-1775, 1865-1895</td>
<td>120 - 130</td>
</tr>
<tr>
<td>reduced MoOₓ</td>
<td>1695-1713, 1800-1817</td>
<td>100</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>1810, 1910</td>
<td>100</td>
</tr>
<tr>
<td>Co²⁺</td>
<td>1765-1795, 1840-1875</td>
<td>80 - 90</td>
</tr>
<tr>
<td>reduced WOₓ</td>
<td>1685, 1795</td>
<td>110</td>
</tr>
</tbody>
</table>
SURFACE ACTIVE SITES:

- Acid/Base Sites
- Redox Sites

Different role for different sites
SURFACE ACIDITY

A solid acid shows a tendency to donate a proton or to accept an electron pair, whereas a solid base tends to accept a proton or to donate an electron pair.

Lewis acidic sites: coordinatively unsaturated cations

\[ M^{n+}(\text{cus}) + :\text{B}(\text{g}) \rightleftharpoons M^{n+}:\text{B} \]

Brønsted acidic sites: hydroxyl groups

\[ \text{B} + \text{HO}^* \rightleftharpoons \text{BH}^+ + \text{O}^- \]

Basic sites: coordinatively unsaturated oxygen ions

Lewis \rightleftharpoons Brønsted acidic sites

\[ -M^{n+}-\text{O}^2- + \text{H}_2\text{O} \rightleftharpoons -M^{n+}-\text{O}^2- \]
## Solid acids

**Table 1. Solid acids**

1. Natural clay minerals: kaolinite, bentonite, attapulgite, montmorillonite, clarit, fuller's earth, zeolites

2. Mounted acids: $\text{H}_2\text{SO}_4$, $\text{H}_3\text{PO}_4$, $\text{CH}_2(\text{COOH})_2$ mounted on silica, quartz sand, alumina or diatomaceous earth

3. Cation exchange resins

4. Charcoal heat-treated at 573 K

5. Metal oxides and sulfides: ZnO, CdO, Al$_2$O$_3$, CeO$_2$, ThO$_2$, TiO$_2$, ZrO$_2$, SnO$_2$, PbO, As$_2$O$_3$, Bi$_2$O$_3$, Sb$_2$O$_5$, V$_2$O$_5$, Cr$_2$O$_3$, MoO$_3$, WO$_3$, CdS, ZnS

6. Metal salts: MgSO$_4$, CaSO$_4$, SrSO$_4$, BaSO$_4$, CuSO$_4$, ZnSO$_4$, CdSO$_4$, Al$_2$(SO$_4$)$_3$, FeSO$_4$, Fe$_2$(SO$_4$)$_3$, CoSO$_4$, NiSO$_4$, Cr$_2$(SO$_4$)$_3$, KHSO$_4$, K$_2$SO$_4$, (NH$_4$)$_2$SO$_4$, Zn(NO$_3$)$_2$, Ca(NO$_3$)$_2$, Bi(NO$_3$)$_3$, Fe(NO$_3$)$_3$, CaCO$_3$, BPO$_4$, AIPO$_4$, CrPO$_4$, FePO$_4$, Cu$_2$(PO$_4$)$_3$, Zn$_3$(PO$_4$)$_2$, Mg$_2$(PO$_4$)$_2$, Ti$_2$(PO$_4$)$_3$, Zr$_2$(PO$_4$)$_3$, Ni$_3$(PO$_4$)$_2$, AgCl, CuCl, CaCl$_2$, AlCl$_3$, TiCl$_3$, SnCl$_2$, CaF$_2$, BaF$_2$, AgClO$_4$, Mg(ClO$_4$)$_2$

# Solid bases

## Table 2. Solid bases

1. Mounted bases: NaOH, KOH mounted on silica or alumina; alkali metal and alkaline earth metal dispersed on silica, alumina, carbon, K₂CO₃ or in oil; NR₃, NH₃, KNH₂ on alumina; Li₂CO₃ on silica

2. Anion exchange resins

3. Charcoal heat-treated at 1173 K or activated with N₂O, NH₃ or ZnCl₂ - NH₄Cl - CO₂

4. Metal oxides: BeO, MgO, CaO, SrO, BaO, ZnO, Al₂O₃, Y₂O₃, La₂O₃, CeO₂, ThO₂, TiO₂, ZrO₂, SnO₂

5. Metal salts: Na₂CO₃, K₂CO₃, KHCO₃, KNaCO₃, CaCO₃, SrCO₃, BaCO₃, (NH₄)₂CO₃, Na₄WO₄ • 2 H₂O, KCN

6. Mixed oxides: SiO₂ - MgO, SiO₂ - CaO, SiO₂ - SrO, SiO₂ - BaO, SiO₂ - ZnO, SiO₂ - Al₂O₃, SiO₂ - ThO₂, SiO₂ - TiO₂, SiO₂ - ZrO₂, SiO₂ - MoO₃, SiO₂ - WO₃, Al₂O₃ - MgO, Al₂O₃ - ThO₂, Al₂O₃ - TiO₂, Al₂O₃ - ZrO₂, Al₂O₃ - MoO₃, Al₂O₃ - WO₃, ZrO₂ - ZnO, ZrO₂ - TiO₂, TiO₂ - MgO
## Acid and Basic Oxides

**Tab. 1.1 Ossidi “acidi”**

<table>
<thead>
<tr>
<th>Puri</th>
<th>CdO, PbO, As₂O₅, Bi₂O₃, Sb₂O₅, V₂O₅, Cr₂O₃, MoO₃, WO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Misti</td>
<td>SiO₂⁻SnO₂, SiO₂⁻BeO, SiO₂⁻Ga₂O₃, SiO₂⁻Y₂O₃, SiO₂⁻La₂O₃, SiO₂⁻V₂O₅,</td>
</tr>
<tr>
<td></td>
<td>Al₂O₃⁻ZnO, Al₂O₃⁻CdO, Al₂O₃⁻B₂O₅, Al₂O₃⁻V₂O₅, Al₂O₃⁻Cr₂O₃, Al₂O₃⁻Mn₂O₃,</td>
</tr>
<tr>
<td></td>
<td>Al₂O₃⁻Fe₂O₅, Al₂O₃⁻Co₂O₄, Al₂O₃⁻NiO, TiO₂⁻CuO, TiO₂⁻ZnO, TiO₂⁻CdO,</td>
</tr>
<tr>
<td></td>
<td>TiO₂⁻SnO₂, TiO₂⁻Bi₂O₅, TiO₂⁻Sb₂O₅, TiO₂⁻V₂O₅, TiO₂⁻Cr₂O₃, TiO₂⁻MoO₃,</td>
</tr>
<tr>
<td></td>
<td>TiO₂⁻WO₃, TiO₂⁻Mn₂O₃, TiO₂⁻Fe₂O₅, TiO₂⁻Co₂O₄, TiO₂⁻NiO, ZrO₂⁻CdO,</td>
</tr>
<tr>
<td></td>
<td>ZnO⁻MgO, ZnO⁻Fe₂O₅, MoO₃⁻CoO⁻Al₂O₃, MoO₃⁻NiO⁻Al₂O₃, TiO₂⁻SiO₂⁻MgO,</td>
</tr>
<tr>
<td></td>
<td>MoO₃⁻Al₂O₃⁻MgO</td>
</tr>
</tbody>
</table>

**Tab. 1.2 Ossidi “basici”**

<table>
<thead>
<tr>
<th>Puri</th>
<th>BeO, MgO, CaO, SrO, BaO, Y₂O₃, La₂O₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Misti</td>
<td>SiO₂⁻BaO, ZrO₂⁻ZnO</td>
</tr>
</tbody>
</table>

**Tab. 1.3 Ossidi “anfoteri”: presentano contemporaneamente siti sia acidi che basici**

<table>
<thead>
<tr>
<th>Puri</th>
<th>ZnO, Al₂O₃, CeO₂, ThO₂, TiO₂, ZrO₂, SnO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Misti</td>
<td>SiO₂⁻Al₂O₃, SiO₂⁻TiO₂, SiO₂⁻ZrO₂, SiO₂⁻MgO, SiO₂⁻CaO, SiO₂⁻SrO, SiO₂⁻</td>
</tr>
<tr>
<td></td>
<td>ZnO, SiO₂⁻MoO₃, SiO₂⁻WO₃, SiO₂⁻ThO₂, Al₂O₃⁻MgO, Al₂O₃⁻ThO₂, Al₂O₃⁻TiO₂,</td>
</tr>
<tr>
<td></td>
<td>Al₂O₃⁻ZrO₂, Al₂O₃⁻MoO₃, Al₂O₃⁻WO₃, TiO₂⁻CuO, TiO₂⁻MgO, TiO₂⁻ZrO₂</td>
</tr>
</tbody>
</table>
SURFACE vs SOLUTION

- No dynamic equilibrium (as in solution)
- No levelling effect of the solvent
- Both acidic and basic sites can be contemporaneously present
- Sites characterized by different strength and type (no complexes formation)
Surface acidity vs hydroxilation: generation of acidity and basicity

Surfaces characterized by a different degree of hydroxyl condensation: 30%; 67.8% and 90.4%

Different types of isolated hydroxyls
(+ = Al$^{3+}$ cations of the next lower plane)
From basic (A) highly negative - to acidic (C) highly positive

Al-O distance and angle = surface distortions,
Preparation procedures

Alogenation, K or Na doping

γ-alumina surface
ACID STRENGTH of a SOLID

ability of the surface to convert an adsorbed neutral molecule into its conjugate acid

<table>
<thead>
<tr>
<th>relative acidity order on oxide surfaces</th>
<th>pK_a</th>
<th>$\Delta H^\circ_{\text{acid}}$ kcal/mol</th>
<th>$\Delta H^\circ_{\text{B-H}}$ kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. C_6H_5SH</td>
<td></td>
<td>331.8</td>
<td>83.3</td>
</tr>
<tr>
<td>2. HCOOH</td>
<td>3.7</td>
<td>345.2</td>
<td>106</td>
</tr>
<tr>
<td>3. CH_3COOH 1. CH_3COOH</td>
<td>4.8</td>
<td>348.5</td>
<td>105.8</td>
</tr>
<tr>
<td>4. HCN</td>
<td>9.3</td>
<td>353.1</td>
<td>123.8</td>
</tr>
<tr>
<td>5. C_6H_5OH 2. C_6H_5OH</td>
<td>9.9</td>
<td>351.4</td>
<td>86.5</td>
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<tr>
<td>6. CH_3SH 3. CH_3SH</td>
<td>12.0</td>
<td>359.0</td>
<td>90.7</td>
</tr>
<tr>
<td>7. CH_3OH 4. CH_3OH</td>
<td>15.5</td>
<td>379.2</td>
<td>104.4</td>
</tr>
<tr>
<td>8. C_2H_5OH 5. C_2H_5OH</td>
<td>17.0</td>
<td>376.1</td>
<td>104.2</td>
</tr>
<tr>
<td>9. C_6H_5CCH 6. C_6H_5CCH 7. HCCCH</td>
<td>18.5</td>
<td>370.3</td>
<td>132</td>
</tr>
</tbody>
</table>

water

Gas phase
Hematite: the crystal structure

The primitive cell is rhombohedral ($R3c$) with two formula units (distortion of the cubic perovskite structure along the $[111]$ direction). The transition metal atoms lie along the $c$-axis (the body diagonal). Each Fe has six nearest O neighbors within a distorted octahedral configuration.

Hematite: the IR spectra

Heating in $O_2$ at increasing temperatures (400 to 800°C)

Heating in $O_2$/evacuation at 440°C

Heating in $O_2$ flow at increasing temperatures (350 to 645°C)

<table>
<thead>
<tr>
<th>$\tilde{\nu}_{OH}$</th>
<th>$\tilde{\nu}_{OD}$</th>
<th>($\tilde{\nu}<em>{OH}/\tilde{\nu}</em>{OD}$)</th>
<th>$\tilde{\nu}_{OH}$</th>
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<tbody>
<tr>
<td>3720</td>
<td>2745</td>
<td>1.355</td>
<td>3490</td>
<td>2560</td>
<td>1.363</td>
</tr>
<tr>
<td>3700</td>
<td>2730</td>
<td>1.355</td>
<td>3435</td>
<td>2530</td>
<td>1.358</td>
</tr>
<tr>
<td>3675</td>
<td>2705</td>
<td>1.359</td>
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<tr>
<td>3635</td>
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<td>1.359</td>
<td>3405</td>
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<td>2500</td>
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<tr>
<td>3515</td>
<td>2580</td>
<td>1.362</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Hematite: the IR spectra

Two layers of hexagonally close packed oxygen atoms are shown with iron atoms filling 2/3 of the available octahedral holes.

Array of iron (small circles) and oxygen (large circles) atoms in the \{0001\} faces of haematite.

- Only one type of surface hydroxyl group
- OH are sufficiently close together for H-bonds between adjacent groups

<table>
<thead>
<tr>
<th>$\tilde{\nu}_{\text{OH}}$</th>
<th>$\tilde{\nu}_{\text{OD}}$</th>
<th>($\tilde{\nu}<em>{\text{OH}}/\tilde{\nu}</em>{\text{OD}}$)</th>
<th>$\tilde{\nu}_{\text{OH}}$</th>
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<td>2580</td>
<td>1.362</td>
<td></td>
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</tbody>
</table>

Fig. 9.—Possible configurations of cyclic structures, consisting of triads of surface hydroxyl groups and each containing three hydrogen bonds, on the \{0001\} exposed faces of haematite.

Hematite: the IR spectra

![Diagram of hematite structure](image)

**Fig. 10.—Section of the (0112) surface planes of haematite.**

**A** = Liganded to a single iron atoms  
**B, C** = Bridged between two iron atoms  
**D** = Liganded to three iron atoms

<table>
<thead>
<tr>
<th>(\bar{v}_{OH})</th>
<th>(\bar{v}_{OD})</th>
<th>(\bar{v}<em>{OH}/\bar{v}</em>{OD})</th>
<th>(\bar{v}_{OH})</th>
<th>(\bar{v}_{OD})</th>
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</tr>
</tbody>
</table>

Chemisorption of probe molecules

Table 1
Basic probes, their pKₐ's and the position of their diagnostic vibrational bands

<table>
<thead>
<tr>
<th>Base</th>
<th>Conjugated acid</th>
<th>pKₐ</th>
<th>PA</th>
<th>Sensitive bands (base)</th>
<th>Diagnostic band (acid)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Piperidine</td>
<td>C₅H₁₀NH</td>
<td>C₅H₁₀NH₂⁺</td>
<td>11.1</td>
<td>933</td>
<td>δNH₂⁺</td>
</tr>
<tr>
<td>n-Butylamine</td>
<td>n-C₄H₁₀-NH₂</td>
<td>n-C₄H₁₀-NH₃⁺</td>
<td>10.9</td>
<td>846</td>
<td>δₚₚₚ NH₃⁺</td>
</tr>
<tr>
<td>Ammonia</td>
<td>NH₃</td>
<td>NH₄⁺</td>
<td>9.2</td>
<td>846</td>
<td>δₚₚₚ NH₃</td>
</tr>
<tr>
<td>Pyridine</td>
<td>C₅H₅N</td>
<td>C₅H₅NH⁺</td>
<td>5.2</td>
<td>912</td>
<td>ν₁₉₈</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>ν₁₉₉</td>
</tr>
<tr>
<td>Acetone</td>
<td>(CH₃)₂C=O</td>
<td>(CH₃)₂C=OH⁺</td>
<td>−7.2</td>
<td>816</td>
<td>νC=O</td>
</tr>
<tr>
<td>Pivalonitrile</td>
<td>t-C₄H₉-C≡N</td>
<td>t-C₄H₉C≡NH⁺</td>
<td>−10</td>
<td>783</td>
<td>νCN</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>CH₃-C≡N</td>
<td>CH₃-C≡NH⁺</td>
<td>−10.4</td>
<td>783</td>
<td>νCN</td>
</tr>
<tr>
<td>Nitric oxide</td>
<td>NO</td>
<td>[HNO]⁺</td>
<td></td>
<td>598</td>
<td>νN=O</td>
</tr>
<tr>
<td>C monoxide</td>
<td>CO</td>
<td>[HCO]⁺</td>
<td></td>
<td>598</td>
<td>νC=O</td>
</tr>
</tbody>
</table>
## Chemisorption of probe molecules

Table 2

Position ($\nu$, cm\(^{-1}\)) of the vibrational bands of pyridine and pyridinium ion as compared to those of benzene

<table>
<thead>
<tr>
<th>Point group $D_{6h}$</th>
<th>Point group $C_{2v}$</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Benzene C(_6)H(_6)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sym</td>
<td>Notation</td>
<td>Act</td>
</tr>
<tr>
<td>$A_{1g}$</td>
<td>1</td>
<td>R</td>
</tr>
<tr>
<td>$E_{2g}$</td>
<td>8</td>
<td>R</td>
</tr>
<tr>
<td></td>
<td>8b</td>
<td>$B_{1}$</td>
</tr>
<tr>
<td>$E_{1u}$</td>
<td>19</td>
<td>IR</td>
</tr>
<tr>
<td></td>
<td>19b</td>
<td>$B_{1}$</td>
</tr>
</tbody>
</table>

\[\text{G. Busca; Catalysis Today 41 (1998) 191-206}\]
Chemisorption of probe molecules

G. Busca; Catalysis Today 41 (1998) 191-206
Alumina: Lewis and Brønsted acid sites by pyridine

Lewis acid site  Brønsted acid site

H-bond

Before exposure

After exposure

After outgassing 100°C

After outgassing 100°C
Hematite: the chemisorption of probe molecules: pyridine

(973 K 17h O₂ flow)
Adsorption of py = formation of H bonds between the isolated hydroxyl groups and the nitrogen atoms
Py rapidly desorbed by evacuation of the sample at beam temperature = weakness of surface-adsorbate interaction

(713 K 19h O₂ flow)
Evacuation has little effect = stronger interaction than the H-bond Lewis acid/base interaction

a = after heat treatment
b = after exposure to pyridine
c = after subsequent evacuation

C.H. Rochester, S.A. Topham; Faraday 1259
Hematite: the chemisorption of probe molecules: ammonia

Isolated OH groups form H-bonds with ammonia

Ammonia is rapidly desorbed by evacuation

= weakness of surface-adsorbate interaction

Partial desorption after short times; complete desorption after long times

= stronger H-bond than pyridinete

Weaker interaction Lewis acid/base interaction

C.H. Rochester, S.A. Topham; Faraday 1259
FORMATION OF ACIDIC SITES: FROM BINARY TO COMPLEX OXIDES

Mixing oxides new acidic sites can be created.
FORMATION OF ACIDIC SITES: FROM BINARY TO COMPLEX OXIDES

Tanabe’s model: a local model

The generation of new acid sites is caused by an excess of negative or positive charge in a model structure of a binary oxide

**MODEL STRUCTURE**

1. The coordination number of a cation in the component oxide is maintained in the binary oxide
2. The coordination number of the oxygen ion in the binary oxide is the same as in the major component oxide
FORMATION OF ACIDIC SITES: FROM BINARY TO COMPLEX OXIDES

Problems of the Tanabe’s model

😊 Easy to be applied

😊 The coordination number is sometime not unique, and not easy to be determined exactly

😊 The use of formal oxydation states may be not accurate (with respect to the real charge)

😊 The model cannot predict the acid strenght
FORMATION OF ACIDIC SITES: 
FROM BINARY TO COMPLEX OXIDE

Kung’s model: a delocalized model

The generation of new acid sites is related to the electrostatic potential experienced by the substituting cation due to all the ions in the matrix oxide

\[ \Delta V = \sum_{i} \left( \frac{q_i}{r_i} \right)_{BOz} - \sum_{i} \left( \frac{q_i}{r_i} \right)_{AO} \]

Electrostatic potential experienced by a cation A in a matrix BOz and AO
FORMATION OF ACIDIC SITES: FROM BINARY TO COMPLEX OXIDE

Kung’s model: a delocalized model

1) Substituting cation A is of a lower formal oxidation state than the matrix cation B: \( y < z \)

2) Substituting cation A is of a higher formal oxidation state than the matrix cation B: \( y > z \)
Kung's model

Substituting cation A is of a lower formal oxidation state than the matrix cation B: $y < z$

Oxygen excess:

1) Development of anion vacancies
   = formation of Lewis acid sites

2) Adsorption of protons on the surface
   = formation of Brønsted acid sites

Mechanisms 1 and 2 are strictly connected and related to the surface hydroxilation and thermal history

3) Development of interstitial cation defects
   = difficult prevision
Kung’s model

Substituting cation A is of a higher formal oxidation state than the matrix cation B: \( y > z \)

**Oxygen deficiency**

1) Adsorption of negatively charged oxygen species

2) Adsorption of OH-

   = coordinative unsaturation of A is removed
   = electrostatic potential on A is removed

No significant acid sites

3) Formation of cation vacancies

   = new basic sites
DETERMINATION OF SURFACE ACIDITY

1) Adsorption of probe molecules

2) Isoelectric point

3) Titration with indicators
Adsorption of probe molecules

1) $\text{NH}_3$

2) pyridine

3) Lutidine (2,6-dimethyl pyridine)

4) $\text{CO}$ Polarization = blue shift

5) $\text{CO}_2$

$\text{NH}_3 + \text{HO}^- \rightarrow \text{NH}_4^+ + \text{O}^--$

$\text{C}_5\text{H}_5\text{N} + \text{HO}^- \rightarrow \text{C}_5\text{H}_5\text{NH}^+ + \text{O}^---$


Coordination of Carbonates

$v_3$ splitting (cm$^{-1}$) | Type of coordination
---|---
zero | symmetric
100 | monodentate
300 | bidentate or bridged

symmetric
monodentate
bidentate
bridged
Adsorption of probe molecules

Figure 5-3 Relative amounts of a: Lewis acid; b: Brønsted acid sites of a sample of Nb$_2$O$_5$·nH$_2$O as a function of pretreatment temperature as determined by the IR absorption peak intensity of adsorbed pyridine after evacuation at: 1, room temperature; 2, 100°C; 3, 200°C; and 4, 300°C. The surface areas of the sample after pretreatments at various temperatures are: 100°C, 164 m$^2$/g; 300°C, 126 m$^2$/g; and 500°C, 42 m$^2$/g. (From Bull. Chem. Soc. Jpn., 56, 2927 (1983), copyright Chemical Society of Japan.)

Table 5-3 Acid Sites on Various Transition Metal Oxides Determined by Ammonia or Pyridine Adsorption

<table>
<thead>
<tr>
<th>Oxide$^a$</th>
<th>Mode of Bonding</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H-bonding</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>+</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>+</td>
</tr>
<tr>
<td>V$_2$O$_5$</td>
<td></td>
</tr>
<tr>
<td>Nb$_2$O$_5$</td>
<td>+</td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>+</td>
</tr>
<tr>
<td>Cr$_2$O$_3$/Al$_2$O$_3$</td>
<td>+</td>
</tr>
<tr>
<td>MoO$_3$</td>
<td>+</td>
</tr>
<tr>
<td>Mo$_2$O$_3$/Al$_2$O$_3$</td>
<td>+</td>
</tr>
<tr>
<td>WO$_3$/Al$_2$O$_3$</td>
<td>+</td>
</tr>
<tr>
<td>Re$_2$O$_7$/Al$_2$O$_3$</td>
<td>+</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>+</td>
</tr>
<tr>
<td>NiO</td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td>+</td>
</tr>
</tbody>
</table>

$^a$Oxides used in the study.
Solid oxide particles in aqueous suspensions are often electrically charged:

- Imbalance between the densities of adsorbed H+, OH-, and ionized OH- groups
- Adsorption of charged species (hydrolysis products of material dissolved from the solid \([M^{z+}(OH)_{n}]^{z-n}\)

The net charge can be observed by electrophoresis.

The surface charge depends on the pH of the solution:
- The pH at which there is no net surface charge = isoelectric point (zero point charge):
- The suspended particles do not move in an electric field
Very sensitive function of the sample history

IEP of numerous oxide have been determined

Correlation between IEP of components in a composite

Figure 5-4 Zeta-potential at 22.5°C as a function of pH. Curve 1: NiAl₂O₄ and CoAl₂O₄; curve 2: Co₃O₄; curve 3: Al₂O₃; and curve 4: NiO. (From J. Catal., 83, 225 (1983), copyright Academic Press).
Very sensitive function of the sample history:

- Impurities (cationic or anionic)
- Defects (vacancies, dislocations)
- Ions in the aqueous phase

### Table 5-4 Isoelectric Points of Transition Metal Oxides and Hydroxides

<table>
<thead>
<tr>
<th>Oxide</th>
<th>IEP</th>
<th>MnO₂</th>
<th>IEP</th>
<th>Mn(OH)₂</th>
<th>IEP</th>
<th>MoO₃</th>
<th>IEP</th>
<th>NiO</th>
<th>IEP</th>
<th>Ni(OH)₂</th>
<th>IEP</th>
<th>TiO₂</th>
<th>IEP</th>
<th>V₂O₅</th>
<th>IEP</th>
<th>WO₃</th>
<th>IEP</th>
<th>ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr₂O₃ (hydrous)</td>
<td>7.0</td>
<td>4 to 4.5</td>
<td></td>
<td></td>
<td></td>
<td>6.2</td>
<td></td>
<td>8.3</td>
<td>11 to 12</td>
<td>4.5 to 6.3</td>
<td>1.4</td>
<td>&lt;0.5</td>
<td>8.7 to 9.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co(OH)₂ (solid)</td>
<td>11 ± 0.2</td>
<td>7.0</td>
<td></td>
<td></td>
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<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co₃O₄</td>
<td>7.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>CuO</td>
<td>9.5 ± 0.4</td>
<td>6.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>8.3</td>
<td>to 10.3</td>
<td>4.5 to 6.3</td>
<td>1.4</td>
<td>&lt;0.5</td>
<td>8.7 to 9.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(OH)₂ (hydrous)</td>
<td>7.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(OH)₂</td>
<td>12 ± 0.5</td>
<td>4.5 to 6.3</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe₃O₄</td>
<td>6.5 ± 0.2</td>
<td>1.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>α-Fe₂O₃</td>
<td>5.2 to 8.5</td>
<td>&lt;0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>γ-Fe₂O₃</td>
<td>6.7 ± 0.2</td>
<td>8.7 to 9.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 5-5 Isoelectric Points of Oxides Supported on Alumina

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Co₃O₄</th>
<th>CoAl₂O₄</th>
<th>Ni-Al³⁺</th>
<th>NiO</th>
<th>NiAl₂O₄</th>
<th>Mo-Al⁶⁺</th>
<th>MoO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure γ-Al₂O₃</td>
<td>0.6</td>
<td>1.0</td>
<td>1.6</td>
<td>4.4</td>
<td>5.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IEP</td>
<td>8.30</td>
<td>8.30</td>
<td>8.05</td>
<td>7.65</td>
<td>7.95</td>
<td>8.05</td>
<td>7.30</td>
</tr>
<tr>
<td>pure Co₃O₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pure CoAl₂O₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-Al³⁺</td>
<td>2.3</td>
<td>4.5</td>
<td>6.0</td>
<td>9.0</td>
<td>pure NiO</td>
<td>NiAl₂O₄</td>
<td></td>
</tr>
<tr>
<td>IEP</td>
<td>8.80</td>
<td>8.15</td>
<td>8.00</td>
<td>7.80</td>
<td>7.60</td>
<td>8.30</td>
<td>2.65</td>
</tr>
<tr>
<td>pure NiO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiAl₂O₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo-Al⁶⁺</td>
<td>1.1</td>
<td>4.1</td>
<td>8.8</td>
<td>11.4</td>
<td>13.8</td>
<td>pure MoO₃</td>
<td></td>
</tr>
<tr>
<td>IEP</td>
<td>8.30</td>
<td>8.65</td>
<td>8.50</td>
<td>8.30</td>
<td>8.00</td>
<td>7.85</td>
<td>6.25</td>
</tr>
<tr>
<td>pure MoO₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
1) Adsorption onto the solid of an indicator which changes color on protonation
If the surface possesses hydroxyl groups more acidic than the $pK_a$ of the indicator, the indicator becomes protonated and undergoes a change in color

2) The solid is titrated with a strong base such as n-butylamine to completely deprotonate the indicator
The amount of n-butylamine needed to completely deprotonate the indicator is the amount of surface hydroxyl groups more acidic than the $pK_a$ of the indicator
Using indicators with different pKₐ the distribution of acid strength of an oxide can be determined.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Surface Area m²/g</th>
<th>Acid Amounts (mmol/g) at different pKₐ's</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>+4.8</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>190</td>
<td>-</td>
</tr>
<tr>
<td>TiO₂</td>
<td>38.5</td>
<td>0.057</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>72.0</td>
<td>-</td>
</tr>
<tr>
<td>TiO₂-ZrO₂</td>
<td>230</td>
<td>-</td>
</tr>
<tr>
<td>TiO₂-Al₂O₃</td>
<td>204</td>
<td>0.422</td>
</tr>
<tr>
<td>ZrO₂-Al₂O₃</td>
<td>320</td>
<td>-</td>
</tr>
</tbody>
</table>
Titration with Indicators

😊 Exposure to moisture, $CO_2$, must be avoided

😊 Long time required to attain equilibrium between the surface and the indicator

😊 Very accurate values of $pK_a$ of indicators are needed
BASIC STRENGTH

Benzoic acid titration method using indicators

1) Adsorption onto the solid of an indicator which changes color on deprotonation

2) The solid is titrated with an acid (benzoic acid)
For the reaction of an acid indicator, BH, with a solid base

The basic strength:

\[ H = pK_a + \log \frac{[\text{B}^-]}{[\text{BH}]} \]