Supported Nanoparticles: Catalysis and Characterization

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IMPRS “Complex Surfaces in Materials Science”
Block Course SS 07
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Three Way Converter

Conversion in %

Pt and Rh: CO 90, HC 95, NOx 81
Pt only: CO 60, HC 80, NOx 40
Rh only: CO 53, HC 60, NOx 75
Precious Metal Content in Three Way Converter

Conversion in %

- Pt: 41.7 g/ft³
  - Rh: 8.3 g/ft³

- Pt: 40 g/ft³
  - Rh: 0 g/ft³

- Pt: 0 g/ft³
  - Rh: 8.3 g/ft³
Outline

1. Introduction into Heterogeneous Catalysis
2. Motivation for the Use of Nanoparticles
3. Properties of Nanoparticles
4. Catalyst Preparation Methods
5. Characterization of Supported Metals
6. Characterization of Supported Metal Oxides
How to Prepare Supported Nanoparticles

- molecularly dispersed species (ions or clusters in solution)
- gas phase species
- bulk solid species
Steps of Catalyst Preparation (IUPAC)

1. Preparation of the primary solid
   associating all useful components (impregnation or coprecipitation,
or, in the case of zeolites, crystallization)

2. Processing of that primary solid to obtain the catalyst precursor,
   for example by heat treatment

3. Activation of the precursor to give the active catalyst:
   reduction to metal, formation of sulfides, deammoniation
Supports & Reactants

Supports
- High surface area oxidic compounds: zeolites, SiO$_2$, Al$_2$O$_3$, TiO$_2$, ZrO$_2$, CeO$_2$, ZnO
- Carbon materials

Dispersed phase
- Increased surface area
- Stabilized

Goal: disperse an *active phase* on an inexpensive and inert (?) *support*
Active Species Sources

- Liquid Phase - Solid Reactions: Soluble metal complexes, e.g. [Pt(NH₃)₄]²⁺

- Solid-Solid-Reactions: Oxides

- Gas Phase - Solid Reactions: Volatile metal compounds, e.g. Ni(CO)₄, SiCl₄
Termination of Oxides

Brønsted sites
proton or OH donor

Lewis acid sites
electron pair acceptor

H
O
M\textsuperscript{x+}

H
O
M\textsuperscript{x+} M\textsuperscript{x+}

type I
type II
type III
Solid Surface in Solution

- surfaces can be charged in solution
- changes with pH
- *Point of zero charge (pzc)*: surface charge $\sigma_0$ is zero
Solid Surface in Solution

- **Isoelectric point**: no mobility of particle in electric field (ζ-potential zero)
- any ion present in solution can interact with surface
Influence of pH: Example for Change in Zeta-Potential

- Silica does easily not adsorb cations
- Alumina amphoteric

Precursor Complex and Support

**pH Effects**
- Surface charge
- Solvation of complexes
- Degree of condensation of precursor species (e.g., from $\text{MoO}_4^{2-}$ at high pH to $\text{Mo}_8\text{O}_{26}^{4-}$ at low pH)
- Solubility of Support

**Foreign ions**
- Can compete for adsorption sites
Interaction of Precursor Complex and Support
Interaction of Precursor Complex and Support
Main Categories of Distribution

- **homogeneous**: MC and A same affinity
- **egg shell**: MC high affinity, no competitor
- **egg white**: High affinity of A, low affinity of MC, low A/MC ratio
- **egg yolk**: High affinity of A, low affinity of MC, high A/MC ratio

MC: Metal complex, A: Competitor
Capillary vs. Diffusional Impregnation

- Pore space filled with same solvent
- Concentration gradient driving force

- Predried support
- Capillary forces driving force
- Exothermic
- Pressure in pores
Solvent Removal

- Filtration: only ion exchanged / strongly adsorbed complexes on support
- Evaporation: species in solution will settle on support
Gas Phase Reactions

- Metal halides, e.g. MoCl$_5$, TiCl$_4$,
- Metal alkoxides, e.g. Ti(OC$_2$H$_5$)$_4$
- Metal carboxylics, e.g. Ni(CO)$_4$
Preparation of SCR Catalyst by Solid-Solid-Wetting

- MoO$_3$/TiO$_2$: typical catalyst for selective catalytic reduction (reaction of NO$_x$ with NH$_3$ to give N$_2$ and H$_2$O)

720 K heating in O$_2$, saturated with H$_2$O

- start out with physical mixture: small particles, intimate mixture
- evoke spreading through thermal treatment
Interaction Between Active Phase and Support

Figure 1. The solid–solid-gas interphase.
Effect of Different Preparation Methods

Figure 4. Logarithmic reaction rate of CO oxidation over Au/Al₂O₃, Au/SiO₂, and Au/TiO₂ as a function of reciprocal temperature. The temperature for calcination is the same as that in figure 1. (▲) 5.3 wt% Au/Al₂O₃ by CVD, (△) 0.96 wt% Au/Al₂O₃ by DP, (▼) 4.2 wt% Au/Al₂O₃ by CP, (●) 6.6 wt% Au/SiO₂ by CVD, (●) 4.7 wt% Au/TiO₂ by CVD, (○) 2.0 wt% Au/TiO₂ by DP.

Rates in Heterogeneous Catalysis

- Rate with respect to mass or surface area

\[
\begin{align*}
\text{Rate} &= \frac{\text{mol}}{\text{min} \ g_{\text{catalyst}}} \\
\text{Rate} &= \frac{\text{mol}}{\text{min} \ m^2_{\text{catalyst surface}}}
\end{align*}
\]
Turn Over Frequency (1966)

- Rate with respect to number of active sites

- Turnover frequency (TOF) is the number of molecules formed per active site per second (in a stage of saturation with reactant, i.e. a zero order reaction with respect to the reactant)

\[
\frac{\text{molecules}}{\text{site s}} = [s^{-1}]
\]

M. Boudart et al., J. Catal. 6 (1966) 92
TOF, TON, Catalysis

- **TON**
  Total number of product formed molecules per active site
  
  \[ \text{TON} = \text{TOF} \times \text{catalyst life time} \]

- **TON**
  - \( TON = 1 \) stoichiometric reaction
  - \( TON \geq 10^2 \) catalytic reaction
  - \( TON = 10^6-10^7 \) industrial application

- **TON** origins from enzyme kinetics, definitions vary
Examples for TOFs

Table 3
Turnover frequencies (TOF) of various reactions$^a$

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Feed</th>
<th>TOF molecule/site·sec</th>
<th>Relative TOF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cracking</td>
<td>Hexane</td>
<td>0.0469</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Nonane</td>
<td>0.150</td>
<td>3.2</td>
</tr>
<tr>
<td></td>
<td>Dodecane</td>
<td>1.07</td>
<td>23</td>
</tr>
<tr>
<td>Isomerization</td>
<td>$m$-Xylene</td>
<td>10.6</td>
<td>226</td>
</tr>
<tr>
<td>Polymerization</td>
<td>Propylene</td>
<td>40.7</td>
<td>868</td>
</tr>
<tr>
<td>Cracking</td>
<td>1-Hexene</td>
<td>36.7</td>
<td>782</td>
</tr>
<tr>
<td></td>
<td>1-Heptene</td>
<td>56.7</td>
<td>1209</td>
</tr>
<tr>
<td>Skeletal isom.</td>
<td>1-Hexene</td>
<td>$&gt;5 \times 10^3$</td>
<td>$&gt;1 \times 10^5$</td>
</tr>
<tr>
<td>Double-bond shift</td>
<td>1-Hexene</td>
<td>$4.7 \times 10^4$</td>
<td>$1 \times 10^6$</td>
</tr>
</tbody>
</table>

$^a$With ZSM-5 catalyst, 1 atm pressure, 450°C.

Because the reactions have different activation energies, the relative TOFs will be different at other temperatures.
Methods to Characterize Supported Catalysts

**Diffraction**
- XRD (shows ill-dispersed particles)

**Microscopy**
- SEM, TEM

**Chemisorption**

**Spectroscopy**
- IR and Raman spectroscopy
- X-ray absorption
- X-ray photoelectron spectroscopy
- Ion scattering spectroscopy
- UV-vis spectroscopy
Powder X-ray Diffraction

- 1 wt% Pt / H-Mordenite

- Pt/HM. calcined at 500°C
- Pt, PDF 4-802
Transmission Electron Microscopy
Dispersion of Metal Particles

- Dispersion: fraction of metal atoms exposed
- Total amount of metal known from synthesis
- Exposed metal surface area can be determined from chemisorption, provided the ratio of \textit{probe molecules : metal atoms} is known and there is no spill-over CO, H\textsubscript{2}, N\textsubscript{2}O, O\textsubscript{2}
- Further information from TEM and EXAFS
specific adsorption of probe on only one type of site (e.g. on metal and not on support): depends on strength of interaction of probe with metal/support sites, conditions (T, p) can be optimized
if adsorption is specific, number of sites can be derived from isotherm (no site heterogeneity, no spill-over)
The Ratio of H to M

- For very small particles, the stoichiometry H:M may change (verified by independent EXAFS measurement)
Although the probe molecule itself may not adsorb on the pure support, molecules or atoms can spillover from metal particles.
Cu Surface Area

$2 \mathrm{Cu}_S + \mathrm{N}_2\mathrm{O} \rightarrow (\mathrm{Cu}_S\mathrm{O}\mathrm{Cu}_S) + \mathrm{N}_2$

Ag Surface Area

Fig. 2. Effect of temperature on oxygen adsorption. Catalyst loading: 14.3 wt% Ag.

Fig. 6. Effect of loading on catalyst dispersion.

- **O:Ag = 1:1**

Fig. 8. Transmission-absorption infrared spectrum of carbonyl species a Rh/SiO₂ catalyst.

Adsorption of CO on Pd/Al$_2$O$_3$ at 77 K: adsorption of 1 mbar CO at 77 K (a), evacuation at LT (b-f), evac. at 106 K (g), 110 K (h), 124 K (i)
## Metal Particle Size and TOF

<table>
<thead>
<tr>
<th>Catalyst*</th>
<th>Support</th>
<th>Catalytic reaction†</th>
<th>(H_2) treatment temperature of catalyst K</th>
<th>(\text{TOF} \dagger) (10(^{-3}) s(^{-1}))</th>
<th>(E_{\text{act}} \ddagger) (kJ mol(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Hr}<em>4(\text{CO})</em>{11}]^+)</td>
<td>MgO</td>
<td>Toluene hydrogenation</td>
<td>No treatment</td>
<td>0.00</td>
<td></td>
<td>This work</td>
</tr>
<tr>
<td>Ir(_4)</td>
<td>(\gamma)-Al(_2)O(_3)</td>
<td>Toluene hydrogenation</td>
<td>No (H_2) treatment</td>
<td>0.94</td>
<td>48</td>
<td>This work</td>
</tr>
<tr>
<td>Ir(_6)</td>
<td>MgO</td>
<td>Toluene hydrogenation</td>
<td>No (H_2) treatment</td>
<td>0.63</td>
<td>58</td>
<td>This work</td>
</tr>
<tr>
<td>Ir(_{10})</td>
<td>Na(_Y) zeolite</td>
<td>Toluene hydrogenation</td>
<td>No (H_2) treatment</td>
<td>0.25</td>
<td>47</td>
<td>This work</td>
</tr>
<tr>
<td>Ir(_{12})</td>
<td>MgO</td>
<td>Toluene hydrogenation</td>
<td>No (H_2) treatment</td>
<td>0.23</td>
<td>56</td>
<td>This work</td>
</tr>
<tr>
<td>Aggregates of (~20) atoms each, on average, formed from Ir(_4)</td>
<td>MgO</td>
<td>Toluene hydrogenation</td>
<td>573</td>
<td>0.17</td>
<td>53</td>
<td>This work</td>
</tr>
<tr>
<td>Ir(_6)</td>
<td>MgO</td>
<td>Toluene hydrogenation</td>
<td>573</td>
<td>0.03</td>
<td>53</td>
<td>This work</td>
</tr>
<tr>
<td>Ir(_6)</td>
<td>(\gamma)-Al(_2)O(_3)</td>
<td>Toluene hydrogenation</td>
<td>573</td>
<td>9.9(\dagger)</td>
<td>42</td>
<td>This work</td>
</tr>
<tr>
<td>Ir(_4)</td>
<td>Na(_Y) zeolite</td>
<td>Toluene hydrogenation</td>
<td>573</td>
<td>0.52</td>
<td>41</td>
<td>This work</td>
</tr>
<tr>
<td>Ir(_4)</td>
<td>MgO</td>
<td>Cyclohexene hydrogenation</td>
<td>573</td>
<td>18</td>
<td>—</td>
<td>This work</td>
</tr>
<tr>
<td>Ir(_{30})</td>
<td>MgO</td>
<td>Toluene hydrogenation</td>
<td>723</td>
<td>2.0</td>
<td>55</td>
<td>This work</td>
</tr>
<tr>
<td>Pt(_{228})</td>
<td>(\gamma)-Al(_2)O(_3)</td>
<td>Toluene hydrogenation</td>
<td>723</td>
<td>25</td>
<td>49</td>
<td>This work</td>
</tr>
<tr>
<td>Pt(_{228})</td>
<td>(\gamma)-Al(_2)O(_3)</td>
<td>Toluene hydrogenation</td>
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<td>27</td>
<td>51</td>
<td>16</td>
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<tr>
<td>Pt(_{228})</td>
<td>(\gamma)-Al(_2)O(_3)</td>
<td>Cyclohexene hydrogenation</td>
<td>673</td>
<td>440</td>
<td>—</td>
<td>This work</td>
</tr>
<tr>
<td>Pt(_{228})</td>
<td>(\gamma)-Al(_2)O(_3)</td>
<td>Cyclohexene hydrogenation(\ddagger)</td>
<td>673</td>
<td>861</td>
<td>—</td>
<td>17</td>
</tr>
</tbody>
</table>
Figure 3. Schematic representation of metal–support interactions (adopted from Ref. 16).
Ion Scattering Spectroscopy

- topmost layer of surface is probed with ion beam (He⁺)

- also: LEIS = low energy ion scattering
- kinetic energy after interaction depends on mass of scattering atom
- highly surface sensitive, destructive
Depth Profiling of Supported Noble Metal Catalyst

- Rh/TiO$_2$: a system with strong metal support interaction (SMSI)

**Figure 5.** Low energy ion scattering on Rh/TiO$_2$ model catalysts: (A) structure models; (B) expected intensity profiles; (C) experimental intensity profiles (adopted from Ref. 62).
Literature

- Gabor A. Somorjai, Introduction to Surface Chemistry and Catalysis, John Wiley, New York, 1994