Synthesis of supported active phases

20 October 2017

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Heterogeneous catalysts

From large scale production of platform chemicals to dedicated synthesis of pharmaceuticals and electrocatalytic applications: Heterogeneous catalysts are composed of a formulated active mass adapted to the applied technology.

Methanol synthesis plant
Length scales

Methanol synthesis catalyst
Length scales

Methanol synthesis catalyst
Length scales

Methanol synthesis catalyst
Length scales

Methanol synthesis catalyst
Length scales

Methanol synthesis catalyst
Length scales

Methanol synthesis catalyst
Length scales

Methanol synthesis catalyst
Time scales

- Activation and breaking a chemical bond: picoseconds
- Completion of an entire reaction cycle: microseconds – minutes
- Diffusion in and outside pores, and through shaped catalyst particles: seconds – minutes
- Residence time of molecules inside a reactor: seconds - infinity
Hierarchical systems

Figure 4.2.2 Hierarchical catalyst structure with the schematic representation of active sites.

Active site approximations

Langmuir

- The surface consists of sites which were energetically identical and non-interacting, and which would adsorb just one molecule from the gas phase in a localized mode.
- Real surfaces are approximated by “checkerboard structures”

\[
\theta = \frac{N}{N_m} = \frac{K p}{1 + K p}
\]

Taylor

"The activation of such catalysts as platinum and silver gauzes when used in catalytic oxidation would be attributable ... to a production, ..., of metal atoms to a large degree unsaturated and detached from the normal crystal lattice of the metal and capable of adsorbing several molecular reactants."

Active site approximations

Taylor

„The activation of such catalysts as platinum and silver gauzes when used in catalytic oxidation would be attributable ... to a production, ..., of metal atoms to a large degree unsaturated and detached from the normal crystal lattice of the metal and capable of adsorbing several molecular reactants. “


Steps at the surface of dehydroxylated MgO

Fig. 4. High resolution TEM images of MW-MgO viewed along [100]. The inset in (A) shows a power spectrum, which allows to identify the orientation of the MgO crystal. (B) represents a higher magnified micrograph of (A) taken at the marked region of interest. The mono-atomic steps at the surface are clearly visible and marked by arrows.

HRTEM by Thomas Lunkenbein, Marc Willinger
Major effects on “active sites”

The local chemical interactions are controlled for example by

- **Medium**
  - Ligand
  - Cavity (electrostatic effects)
  - Solvent (dielectric constant)

- **Matrix**
  - Particle size
  - Morphology
  - Exposed facets
  - Defects
  - Electronic bulk properties

---


Courtesy of M. Eichelbaum
Can we synthesize “active sites”?

“The amount of surface which is catalytically active is determined by the reaction catalyzed.”


\[
\text{Crystalline MoVTeNb “M1” oxide}
\]

Can we synthesize “active sites”? 

“The amount of surface which is catalytically active is determined by the reaction catalyzed.”


- We can only synthesize catalyst **precursors**
- The active surface is formed under reaction conditions
The surface of catalyst precursors

H.S. Taylor: A Theory of the Catalytic Surface

Steps at the surface of dehydroxylated MgO
Journal of Catalysis 2015, 326, 560-573.

Exposed MnOx species on MnWO₄

Defects on MoVOₓ “M1” oxide
Supported monolayer models

Mo$_{x}$O$_{y}$/SiO$_{2}$ (SBA-15)

$2 \text{C}_3\text{H}_8 \rightarrow \text{C}_4\text{H}_8 + \text{C}_2\text{H}_4$

$2 \text{C}_3\text{H}_8 + \text{O}_2 \rightarrow 2 \text{C}_3\text{H}_6 + 2 \text{H}_2\text{O}$

0.2 - 2.5 Mo nm$^{-2}$
Formation of Mo=CHR sites

$\Delta H_{\text{diff}} = 80 \text{ kJ mol}^{-1}$


$JACS, 2012, 134, 11462-11473;$

Formation of Mo=CHR sites

- Maximum number of active carbene species at high sub-monolayer coverage, but just about 1-2%* of Mo

- The active sites are formed by interaction of propylene with the precursor in an oxyhydration reaction (microcalorimetry, FTIR, TPD)

- Why is Mo reduced at such a low temperature?
- What is the origin of acidity?
- Why are only 1% of Mo species transformed into active carbene species?

→ Investigation of catalyst synthesis

Synthesis of the support SBA-15 (SiO$_2$)

Template: non-ionic amphiphilic triblock copolymer
Poly(ethylene oxide)-block-poly(propylene oxide)-block poly(ethylene oxide)x
(EO)$_{20}$-(PO)$_{70}$-(EO)$_{20}$
(EO ethylene oxide; PO = propylene oxide)

Aging
T=358 K, 24 h
Filtration, washing, drying

Calcination in air
T=823 K, 2 h

Aging at (A) 60 °C, (B) 100 °C, and (C) 130 °C: different pore diameters, wall thicknesses, microporosities, and interconnections between main channels

Mesostructured silica SBA-15
Synthesis of the support SBA-15 (SiO$_2$)

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$T_{\text{aging}}$ (°C)</th>
<th>$T_{\text{calc}}$ (°C)</th>
<th>S (m$^2$/g)</th>
<th>$V_p$ (cm$^3$/g)</th>
<th>$V_M$ (cm$^3$/g)</th>
<th>Micro$_{\text{Vol}}$ %</th>
<th>$S_M$ (m$^2$/g)</th>
<th>Micro$_{\text{Area}}$ %</th>
<th>d (nm)</th>
<th>a (nm)</th>
<th>b* (nm)</th>
<th>$\delta_{\text{silanol}}$ (OH/nm$^2$)</th>
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<tr>
<td>SBA-85</td>
<td>85</td>
<td>550</td>
<td>1017</td>
<td>1.190</td>
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<td>40</td>
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<tr>
<td>SBA110</td>
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<td>550</td>
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<td>1.129</td>
<td>0.029</td>
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<td>72</td>
<td>17</td>
<td>10.9</td>
<td>11.70</td>
<td>0.82</td>
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<td>140</td>
<td>550</td>
<td>585</td>
<td>1.217</td>
<td>0.036</td>
<td>3</td>
<td>88</td>
<td>15</td>
<td>9.4</td>
<td>11.68</td>
<td>2.26</td>
<td>6.79</td>
</tr>
</tbody>
</table>

* $b = a - d$
Precursor synthesis

Functionalization with (3-aminopropyl)trimethoxysilane

1. $\text{H}_2\text{N}(\text{CH}_2)_3\text{Si(OCH}_3)_3$ + $\text{HCl}$

2. $\text{NH}_4^+_{\text{ads}}$

$\text{Mo=CHR}$

Ion exchange

$+ [\text{(NH}_4]_6\text{Mo}_7\text{O}_{24}]_{\text{aq}}$

Calcination at 823 K

Predominant configuration of Mo in the precursor (UV-vis, Mo K-edge XANES, EXAFS)
Speciation of Mo in aqueous solution

Molybdate ions in aqueous solution

\[
\begin{align*}
7 \text{MoO}_4^{2-} + 8 \text{H}^+ &\rightarrow \text{Mo}_7\text{O}_{24}^{6-} + 4 \text{H}_2\text{O} \\
3 \text{Mo}_7\text{O}_{24}^{6-} + 4 \text{H}^+ &\rightarrow \text{Mo}_3\text{O}_{10}^{2-} + 2 \text{H}_2\text{O} \\
8 \text{Mo}_3\text{O}_{10}^{2-} + 4 \text{H}^+ &\rightarrow \text{Mo}_8\text{O}_{26}^{4-} + 2 \text{H}_2\text{O} \\
8 \text{Mo}_7\text{O}_{24}^{6-} + 20 \text{H}^+ &\rightarrow \text{Mo}_3\text{O}_{10}^{2-} + 10 \text{H}_2\text{O} \\
4.5 \text{Mo}_8\text{O}_{26}^{4-} + 10 \text{H}^+ &\rightarrow \text{Mo}_{36}\text{O}_{112}^{8-} + 10 \text{H}_2\text{O} \rightarrow \text{Mo}_3
\end{align*}
\]

\[Z^+ = \frac{v_{H^+}}{v_{\text{MoO}_4^{2-}}}\]

\[Z = \left(\frac{C_{H^+} - c_{H^+} + K_w}{c_{H^+}}\right) / c_{\text{MoO}_4^{2-}}\]

Removal of the solvent:

Mateusz Marianski, Sabrina Jung, et al.

Ion exchange of amphootheric oxides

Oxide-solution interphase

\[ [\text{M-O}]^- + \text{H}_3\text{O}^+ \rightleftharpoons \text{M-OH} + \text{H}_2\text{O} \rightleftharpoons [\text{M-OH}_2]^+ + \text{HO}^- \]

\( M = \text{Si, Al, Ti, etc.} \)

- Hydroxyl groups are formed on the oxide surface (M-OH) in contact with water
- M-OH may behave as Brønstedt acids or bases
- Surface charge depends on solution pH
- Zeta (\( \zeta \)) potential is an estimation of surface charge Z
Measurement of the electrophoretic mobility in an electric field by optical (laser Doppler velocimetry and phase analysis light scattering (PALS)) or acoustic methods

The isoelectric point (IEP) is the pH at which the surface charge density is zero, i.e., $\sigma_0 = 0$. At pH greater than the IEP ($\text{pH} > \text{pH}_{\text{IEP}}$), the surface is negative, and cations will be adsorbed. At pH less than the IEP ($\text{pH} < \text{pH}_{\text{IEP}}$), the surface is positive, and anions will be adsorbed.

Point of zero charge (PCZ) is characterized by pH$_{\text{pzc}}$.

At low ionic strength, and also in the case of equal affinities of counterions (cations and anions) towards association with oppositely charged surface groups, IEP and PCZ coincide.

Zeta potential

Figure S4. Zeta potential of NCNT and OCNT support materials.

Zailai Xie, Benjamin Frank, Xing Huang, Robert Schlägl, and Annette Trunschke
Commercial Co- and Mn-containing N-doped CNTs as a support for Rh catalysts in higher alcohol synthesis

PZC of classical supports

Gamma-alumina adsorbs cations as well as anions

Silica basically adsorb cations

Complex speciation in solution

pH<3: Ligand substitution (in HCl)

\[ [\text{Rh}]_{\text{tot}} = [\text{RhCl}_6]^{3-} + [\text{RhCl}_5]^{2-} + [\text{RhCl}_4]^- \]

pH>3: (in water)

\[ [\text{Rh}]_{\text{tot}} = [\text{Rh}_{\text{aq}}^{3+}] + K_1[\text{Rh}_{\text{aq}}^{3+}][\text{Cl}^-] + \beta_2[\text{Rh}_{\text{aq}}^{3+}][\text{Cl}^-]^2 + \text{RhCl}_{3-n}(\text{H}_2\text{O})_{2+n-m}(\text{OH})_m]^{(n-1-m)+} \]

\[ [\text{RhCl}_{3-n}(\text{H}_2\text{O})_{3+n}]^{n+} + \text{H}_2\text{O} \]

Fig. 3. Rhodium chloride speciation diagram (after [14]) at 25°C.

E. Benguerel et al., Hydrometallurgy 40 (1996) 135-152.
**Ion exchange of amphotheric oxides**

<table>
<thead>
<tr>
<th>oxide</th>
<th>PZC</th>
</tr>
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<tbody>
<tr>
<td>MgO</td>
<td>~12.5</td>
</tr>
<tr>
<td>ZnO</td>
<td>9-10</td>
</tr>
<tr>
<td>α-Fe₂O₃</td>
<td>5.5-9</td>
</tr>
<tr>
<td>α-Al₂O₃</td>
<td>6.5-10</td>
</tr>
<tr>
<td>TiO₂</td>
<td>3.5-6.5</td>
</tr>
<tr>
<td>SiO₂</td>
<td>2-4</td>
</tr>
<tr>
<td>WO₃</td>
<td>~0.4</td>
</tr>
</tbody>
</table>

Point of zero charge (PZC) of a surface depends on:

- Chemical nature (polarization of the surface groups by the cation)
- Crystal structure and particle morphology
- Heat treatment and physicochemical history of the oxide
Support modification in water

Graph showing the concentration of SiO$_2$ (mg/l) over time (h) for different samples, including mother SBA, 2Ti/SBA, 8Ti/SBA, SBA MP, V/SBA MP, SBA110, and V/SBA110.

Bar charts comparing the surface area (m$^2$/g) and micropore area (m$^2$/g) before and after loading for pure Si, Ti loaded, and V loaded samples.
Grafting in organic media

Silica supported molybdenum oxide

\[
\text{SiOH} + \text{MoCl}_5 (g) \xrightarrow{473 \text{ K}} \text{OMoCl}_4 \xrightarrow{773 \text{ K}} \text{grafted species}
\]

Silica supported titanium oxide

\[
2 \text{SiOH} + [\text{Ti(O-i-Pr)}_4]_{\text{toluene}} \rightarrow \text{grafted species} + 2 \text{i-C}_3\text{H}_7\text{OH}
\]
Atomic layer deposition (ALD)

1. Reaction: Precursor \((\text{CH}_3)_3\text{Al}\) with surface OH sites

\[
\text{Si} - \text{Si} - \text{Si} \quad \text{OH} + \text{Al} + \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{Si} - \text{Si} - \text{Si} \quad \text{OH} - \text{CH}_4
\]

2. Reaction: Reactant \(\text{H}_2\text{O}\) with chemisorbed precursor on surface

\[
\text{Si} - \text{Si} - \text{Si} \quad \text{CH}_3 - \text{Al} - \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{Si} - \text{Si} - \text{Si} \quad \text{CH}_3 - \text{Al} - \text{CH}_3 \quad \text{H}_2\text{O} \quad \text{Si} - \text{Si} - \text{Si} \quad \text{OH} - \text{CH}_4
\]

- vapor phase precursors, self-limiting process, precise thickness control
- established for flat substrates

n-Butane oxidation – $PO_x$ ALD on $V_2O_5$

**V$_2$O$_5$ Reference**

Selectivity MAN in %

Conv. $C_4H_{10}$ in %

- $V_2O_5$ Reference catalyst served as starting material for the Phosphorus modification

- $V^{+5}$ 3.87 m$^2$ g$^{-1}$

- 9.76 Atom$_V$/nm$^2$ [6]

**P/V$_2$O$_5$ D1 ALD [5]**

- P/V$_2$O$_5$ D1 catalyst synthesized in a flow-type diffusion based commercial ALD tool with one cycle (hexamethyl phosphoramide and $O_3/O_2$)

- Surface ratio P/V 0.06 : 1

**P/V$_2$O$_5$ FT1 ALD**

- P/V$_2$O$_5$ FT1 catalyst synthesized in fixed bed with a forced flow through with one cycle (hexamethyl phosphor amide and $O_3/O_2$)

- Surface ratio P/V 0.98 : 1

Testing parameters: GHSV 2000 h$^{-1}$, 1 atm, Feed: 2 % $C_4H_{10}$, 3 % $H_2O$, 20 % $O_2$


Anchorage of Mo oxide species


2D Silica surface by STM
Strain due to limited anchoring groups

Low Mo coverage

High Mo coverage

Silica network

corners represent \equiv \text{SiOH}

Di-oxo \text{MoO}_4

anchored by 6, 8, 10-membered ring

stable

frustrated
"Relaxed" di-oxo models reproduce spectra at low Mo density.
- Strained configurations may explain the spectra at higher Mo density.
- Strain may favor the reducibility of MoO\textsubscript{x} and the formation of active sites.
OH groups on MoO$_x$/SiO$_2$

**IR**

$v(Mo-O-Si)$

- $E / \text{cm}^{-1}$
  - 3400
  - 3500
  - 3600
  - 3700
  - 3800

$v_s(Mo=O)$

- $E / \text{cm}^{-1}$
  - 1050
  - 1000
  - 950
  - 900
  - 850

**1H-NMR**

- $\delta / \text{ppm}$
  - 0
  - 1
  - 2
  - 3
  - 4
  - 5
  - 6
  - 7

*SBA-15* MoO$_x$/SBA-15 x5

isolated Si-OH

H-bonded Si-OH

excluded

high Mo coverage

MoO$_x$/Silica lattice

low Mo coverage
Several fortunate circumstances must coincide to generate carbene species on silica-supported Mo oxide:

- Reducibility at low temperature is explained by strain in Mo dioxo species
- Acidity is generated by a close contact of silanol groups and Mo oxide species in strained configuration

→ Strain really needed?
Concept of self-supported surface layer

Nanostructuring MnWO$_4$

\[2 \text{C}_3\text{H}_8 + \text{O}_2 \rightarrow \text{C}_3\text{H}_6 + 2 \text{H}_2\text{O}\]

Surface termination of the b plane viewed along the growth direction [001] by FFT-filtered atomic-resolution STEM images.

a) HAADF, and b) inverted HAADF image. Mn green, W violet.

Synthesis of nanostructured MnWO$_4$

Analytical autoclave for hydrothermal synthesis

\[ \text{Mn(NO}_3\text{)}_2 + \text{Na}_2\text{WO}_4 \]

V=400ml
\[ T_{\text{max}}=250°C \]
\[ p_{\text{max}}=(60)200\text{bar} \]
Hastelloy C22
Sampling possible

Faraday Discussions, 2016, 188, 99-113
Dissolution - recrystallization

Figure S6. HAADF-STEM images of MnWO₄ nanoparticles viewed along <001> with different aspect ratios: a) AR 1.5, b) AR 5.1 and c) perspective model for a typical faceted nanoparticle.

Figure S8. Schematic representation of the formation of W-OH groups at {001} planes during dissolution-recrystallization under hydrothermal conditions at 180°C.

Fig. 2  Electron microscopy images of the as-synthesized (top row) and thermally treated (bottom row) nanostructured MnWO₄ materials AR 1.5 (a) and (f), AR 1.7 (b) and (g), AR 3.2 (c) and (h), AR 3.9 (d) and (i), and AR 5.1 (e) and (j); uncoloured TEM images are presented in the ESI (Fig. S4†).
Surface layer generated under reaction conditions

54 % (V)

Single crystal analysis at MX 14.2 beamline at BESSY

ACS Catalysis, 2017, 7, 1403.
Conclusions

- A solid catalyst is a hierarchical system, in which the active sites are embedded and subjected to dynamic interactions with the matrix and the environment.

- Active sites cannot be synthesized, but are formed under reaction conditions; Catalyst synthesis results in a catalyst precursor.

- Successful synthesis requires that the operation parameters of the catalytic reaction and the requirements of the reactor are taken into consideration from the very beginning; Therefore, catalyst synthesis is generally accompanied by kinetic studies and process development.

- Reliable and reproducible synthesis of homogeneous catalysts requires a certain batch size and well defined reaction conditions documented by process control.

- Rational catalyst design implies fundamental understanding of the elemental processes that can be elucidated by model experiments and the application of in-situ/operando techniques.