Non-hydrolytic sol-gel route to mesoporous Mo-Si-Al and Re-Si-Al mixed oxide metathesis catalysts


1 Institut Charles Gerhardt (Montpellier, France)
2 Leibniz-Institut für Katalyse e. V. (Rostock, Germany)
3 Institute of Condensed Matter and Nanoscience (Louvain-La-Neuve, Belgium)
Nobel Prize in Chemistry 2005 (Chauvin, Grubbs and Schrock)

Heterogeneous catalysts: Supported Mo, W and Re oxides on silica-alumina (silica, alumina) by impregnation
Non-hydrolytic Sol-Gel (NHSG):

▲ Organic oxygen-donors instead of H$_2$O

“ether route” = in situ formation of alkoxide groups

MCI + ROR → MOR + RCl  "Etherolysis"

MCI + MOR → MOM + RCl  Condensation

▲ Advantages:

- Cheap MCI$_n$ precursors
- High degree of condensation
- Homogeneous mixed oxide gels
- Mesoporous oxides

One-step synthesis of mesoporous mixed oxides:

no reactivity modifiers,
no templating agents,
no supercritical drying

**Synthesis:** precursors + stoichiometric amount of O donor + solvent

\[ \text{SiCl}_4 + x\text{AlCl}_3 + y\text{MCl}_5 \rightarrow \text{SiO}_x\cdot x\text{Al}_2\text{O}_3\cdot y\text{MO}_x \]

\[ ^{i}\text{Pr}_2\text{O}, \text{CH}_2\text{Cl}_2 \quad 110 \, ^{\circ}\text{C}, 4 \, \text{d} \]

\[ \rightarrow \quad \text{Drying} \quad \text{Calcination} \quad 500 \, ^{\circ}\text{C} \]

\[ M= \text{Re or Mo} \]

**Nomenclature** MaSAb

- a = wt% MO\(_x\) (MoO\(_3\) or Re\(_2\)O\(_7\))
- b = wt% Al\(_2\)O\(_3\)

1) a **fixed** (10 wt % MO\(_x\)) and b ranging from 0 to 90 wt% Al\(_2\)O\(_3\)

2) a ranging from 5 to 20 wt % MO\(_x\) and b **fixed** (5 wt% and 60 wt% Al\(_2\)O\(_3\))

**Influence of a and b on:**
- texture
- structure
- acidity
- catalytic activity
Characterizations:
ICP-AES, EDX, N$_2$-physisorption, TEM, XRD, NMR $^{29}$Si and $^{27}$Al, H$_2$-TPR, Raman, NH$_3$-TPD, XPS, ToF-SIMS, TGA-MS

Catalytic tests: 40°C

Comparison: NHSG vs Impregnation (WI)
vs Thermal Spreading (TS)
vs Flame Spray Pyrolisis (FSP)
ICP-AES:

Good control of the composition

<table>
<thead>
<tr>
<th>Sample</th>
<th>wt% MoO$_3$</th>
<th>wt % Al$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo10SA5</td>
<td>10.7 (10.0)</td>
<td>5.4 (5.0)</td>
</tr>
<tr>
<td>Mo10SA10</td>
<td>10.1 (9.7)</td>
<td>10.0 (9.6)</td>
</tr>
<tr>
<td>Mo20SA5</td>
<td>18.8 (19.8)</td>
<td>4.2 (4.4)</td>
</tr>
</tbody>
</table>

XRD:

Well dispersed MoO$_x$ species

crystalline MoO$_3$
**TEM: Mo10SA5**

Non-ordered and large opened pores


**N\textsubscript{2}-physisorption:** Mo10SA5

S = 520 m\textsuperscript{2} g\textsuperscript{-1}  
V\textsubscript{p} = 1.5 cm\textsuperscript{3} g\textsuperscript{-1}
**Acidity**

**NH$_3$-TPD:**

![Graph showing NH$_3$ desorption over temperature for Mo10SA0 and Mo10SA15.]

<table>
<thead>
<tr>
<th>Sample</th>
<th>NH$_3$ desorbed (mmol g$^{-1}$)</th>
<th>Density of acid sites (nm$^{-2}$)</th>
<th>Density of weak sites (nm$^{-2}$)</th>
<th>Density of medium + strong sites (nm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo10SA0</td>
<td>0.5</td>
<td>0.4</td>
<td>0.4 (100 %)</td>
<td>0 (0 %)</td>
</tr>
<tr>
<td>Mo10SA15</td>
<td>0.9</td>
<td>2.7</td>
<td>1.4 (51 %)</td>
<td>1.3 (49 %)</td>
</tr>
</tbody>
</table>

Addition of Al increases the acidity.
MoOx species migrate toward the surface during calcination
NHSG \(\rightarrow\) only monomeric \(\text{MoO}_x\) species at the surface

Comparison with catalysts prepared by ≠ methods (D. Debecker)

**Same test:** self-metathesis of propene (M. Stoyanova)

NHSG → up to twice higher specific activity
Re-based catalysts

Synthesis:

\[
\text{SiCl}_4 + x\text{AlCl}_3 + y\text{ReCl}_5 \xrightarrow{110 \degree C, 4 \text{ d}} \text{iPr}_2\text{O, CH}_2\text{Cl}_2 \xrightarrow{\text{Drying}} \text{Calcination} 500 \degree C \rightarrow \text{SiO}_2-x\text{Al}_2\text{O}_3-y\text{ReO}_x
\]

Composition: ICP-AES

<table>
<thead>
<tr>
<th>Sample</th>
<th>wt% Re$_2$O$_7$</th>
<th>wt% Al$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re5SA0</td>
<td>4.6 (10.6)</td>
<td>-</td>
</tr>
<tr>
<td>Re6SA53</td>
<td>6.4 (9.8)</td>
<td>53.3 (53.3)</td>
</tr>
<tr>
<td>Re15SA64</td>
<td>14.7 (15.6)</td>
<td>64.3 (64.7)</td>
</tr>
</tbody>
</table>

Re$_2$O$_7$ volatile (sublimation ≈ 260 °C)

Avoiding the loss of Re:

- increase the Al content

**N₂-physisorption:** Re10SA5

S = 730 m² g⁻¹  Vp = 1 cm³ g⁻¹

**NH₃-TPD:**

<table>
<thead>
<tr>
<th>Sample</th>
<th>NH₃ desorbed (mmol g⁻¹)</th>
<th>Density of acid sites (nm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re11SA0</td>
<td>0.8</td>
<td>0.6</td>
</tr>
<tr>
<td>Re10SA5</td>
<td>2.2</td>
<td>1.8</td>
</tr>
</tbody>
</table>
Re-based & Mo-based catalysts

Catalytic tests: Cross-metathesis of ethene and \textit{trans}-2-butene

![Graph showing catalytic activity over time for Re-based and Mo-based catalysts.]

- **Re20SA60**
  - 3 mol\% Re$_2$O$_7$

- **Re10SA5**
  - 1.5 mol\% Re$_2$O$_7$

- **Mo20SA5**
  - 9 mol\% MoO$_3$

Specific activity in mmol\_\text{conv.} \text{g}\_\text{cat}^{-1} \cdot \text{h}^{-1}

Time (min)
First **Mo-Si-Al** and **Re-Si-Al** ternary mixed oxides prepared by a one-step process:

→ composition of silica-alumina matrix easily adjusted:
  impacts texture, structure, acidity, activity

Migration of Mo and Re species toward the surface:

→ well dispersed **MoOx** and **ReOx** species

Simple one-step route to highly active metathesis catalysts
Acknowledgments

Thank you for your attention

Mariana Stoyanova, Uwe Rodemerck

Hubert Mutin

Damien Debecker, Eric Gaigneaux,
Pierre Eloy, Claude Poleunis

Mariana Stoyanova, Uwe Rodemerck