«SOFT» Chemistry Methods Appear as an Effective Way for Production of Superdispersive (Nano-Sized) Materials Based on Re and d-Elements of V-VIII Groups

Dmitry V. Drobot

Chemical design of precursor
1. Choice of metals
   Re, Mo, W, Nb, Ta, Ni
2. Choice of ligands
   MeOH, EtOH, i-PrOH, BuOH
3. Creation of methods of synthesis
   Electrochemical Synthesis

Precursors
$M_1^{1}M_2^{2}L_m^{1}L_n^{2}$

Investigation of structure in solid phase and in solution, stages of thermal decomposition, P-T diagrams of Metal-Oxygen, etc.

1. Preparation of metals, alloys and ligatures (Re-Mo, Re-W) at record-breaking low temperatures.
2. Regulation of grain size, preparation of nano-sized materials (20-50 nm).
3. Preparation of new phases in Nb(Ta)-O systems and complex oxide phases with high phase and chemical purity.
4. Usage in catalysis with obtaining of expressed synergetic effect.

M – metal, L – ligand
The main problems:

- Search for and development of methods of synthesis of rhenium alkoxides and oxoalkoxide derivatives, including cluster and heterometallic ones;
- Study of their physicochemical properties including the structure in the solid state and the thermal decomposition processes;
- Determination of the chemical and phase compositions of the products of the thermal decomposition of rhenium alkoxides and oxoalkoxide derivatives under various conditions and the search for rational applications of the materials produced in this way.

Synthetic approaches to rhenium-containing alkoxide derivatives

1. Electrochemical synthesis (anodic dissolution of metals in alcohols in the presence of LiCl)
   - One metal dissolution (Re)
   - Subsequent dissolution of several metals (Mo-Re, W-Re)

2. Interaction of Re₂O₇ with metal alkoxides
   - Mo₂O₂(OMe)₉ or W₂O₂(OMe)₉
   - Nb₂(OR)₁₀ or Ta₂(OR)₁₀
   - Nb₂(OR)₁₀ and Ta₂(OR)₁₀

Patent RU 2227788. 21.05.2002

Monometallic derivatives
- Re₆O₆(OMe)₁₂
- Re₄O₄(OMe)₈
- Re₄O₄(OEt)₁₂
- Re₄O₄(OPr-i)₁₀

Bimetallic derivatives
- Re₄MoxO₄(OMe)₁₂ (V), Re₄WxO₄(OMe)₁₂ (VII)

Trimetallic derivatives
- Nb₂Mo₂O₆(OMe)₁₂ (V), Nb₂W₂O₆(OMe)₁₂ (VII)
- Nb₂MoxO₆(OMe)₁₂ (V), Nb₂WxO₆(OMe)₁₂ (VII)

R = Me, Et or Pr′
Electrochemical synthesis – a convenient approach to rhenium alkoxides

Structure of Re₄O₆(OC₃H₇-i)₁₀ (Re-Re 2.52-2.55 Å)

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>LiCl</th>
<th>UV</th>
<th>I.A</th>
<th>Duration</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>j-PrOH</td>
<td>0.2</td>
<td>170</td>
<td>0.08-0.04</td>
<td>0.01</td>
<td>Re₄O₆(OEt)₁₂</td>
</tr>
<tr>
<td>250</td>
<td>0.025</td>
<td>110</td>
<td>0.05</td>
<td>8-38</td>
<td>Re₄O₆-y(OMe)₁₂+y</td>
</tr>
<tr>
<td>264</td>
<td>0.025</td>
<td>110</td>
<td>0.05</td>
<td>8-38</td>
<td>Re₄O₆-y(OMe)₁₂+y</td>
</tr>
<tr>
<td>2,52(2)</td>
<td>2.550(5)</td>
<td>3.45-3.65</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,550(5)</td>
<td>3.45-3.65</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Cluster compounds
Characteristics of metal-metal bonds in alkoxide compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>$r$(M–M), Å</th>
<th>M–M bond order</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Re}_3\text{O}<em>6\text{y}(\text{OMe})</em>{12+y}$</td>
<td>3.45; 3.65</td>
<td>no bond</td>
<td>*</td>
</tr>
<tr>
<td>$\text{Re}_3\text{O}<em>3(\text{OEt})</em>{12}$</td>
<td>2.54(2); 2.648(19); 2.65(2)</td>
<td>&gt;1, -1</td>
<td>*</td>
</tr>
<tr>
<td>$\text{Re}_4\text{O}<em>6(\text{OPr})</em>{10}$</td>
<td>2.5204(7) - 2.5501(5)</td>
<td>&gt;1</td>
<td>*</td>
</tr>
<tr>
<td>$\text{ReMoO}_2(\text{OMe})_2$</td>
<td>2.658(2)</td>
<td>1</td>
<td>*</td>
</tr>
<tr>
<td>$\text{Re}_2\text{O}<em>3(\text{OMe})</em>{6}$</td>
<td>2.559(1)</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$\text{Re}<em>2(\text{OMe})</em>{10}$</td>
<td>2.5319(7)</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>$\text{Re}_3(\text{OPr})_9$</td>
<td>2.36</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>$\text{Re}_3(\text{OCH}_2\text{Bu})_3$</td>
<td>2.365(1) - 2.372(1)</td>
<td>2</td>
<td>4</td>
</tr>
</tbody>
</table>

* Own data

## Metal–Metal Bonds in clusters based on Ti₄(OMe)₁₆ core structure

<table>
<thead>
<tr>
<th>Compound</th>
<th>L₁, Å</th>
<th>L₂, Å</th>
<th>D, Å</th>
<th>Number of core cluster electrons</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba₁₄Mo₈O₁₆</td>
<td>2.616(1)</td>
<td>2.578(1)</td>
<td>2.578(1)</td>
<td>10</td>
<td>[1]</td>
</tr>
<tr>
<td>Ba₁₄Mo₁₆</td>
<td>2.847(1)</td>
<td>2.546(1)</td>
<td>2.560(1)</td>
<td>8,28 (average)</td>
<td>[1]</td>
</tr>
<tr>
<td>W₄(OEt)₁₆</td>
<td>2.936(2)</td>
<td>2.646(2)</td>
<td>2.763(1)</td>
<td>8</td>
<td>[2]</td>
</tr>
<tr>
<td>Re₄O₄(OPr-i)₁₂</td>
<td>2.54(2)</td>
<td>2.648(19)</td>
<td>2.65(2)</td>
<td>8</td>
<td>[*]</td>
</tr>
<tr>
<td>Re₄O₄(OPr-i)₁₀</td>
<td>2.5501(5)</td>
<td>2.5399(5)</td>
<td>2.5204(7)</td>
<td>6</td>
<td>[*]</td>
</tr>
<tr>
<td>Mo₄O₆(OPr-i)₄(Py)₄</td>
<td>3.472(1)</td>
<td>2.600(1)</td>
<td>3.218(1)</td>
<td>4</td>
<td>[2]</td>
</tr>
</tbody>
</table>

[*] Own data  

---

## Computer Aided Composition of Atomic Orbitals (C.A.C.A.O.)

A Package for Molecular Orbital Analysis  
[PC Beta-Version 5.0, 1998]

*Carlo Mealli u Davide M. Proserpio*  
*With major contribution of Andrea lenko.*
Method – Extended Method of Hukkel.

- Molecules geometry is approximate to the real.
- The radicals –CH₃ and –CF₃ are used as –C₂H₅ and –CH₂CF₃.

Cluster Re₄

<table>
<thead>
<tr>
<th></th>
<th>№1</th>
<th>№2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Re₄O₆(OEt)₁₂</td>
<td>Re₄O₆(OPr)₁₀</td>
</tr>
<tr>
<td></td>
<td>Re (V)</td>
<td>Re (V, VI)</td>
</tr>
<tr>
<td></td>
<td>[Re₄]²⁺</td>
<td>[Re₄]²²⁺</td>
</tr>
<tr>
<td></td>
<td>e=8</td>
<td>e=6</td>
</tr>
<tr>
<td></td>
<td>C₂h</td>
<td>D₂h</td>
</tr>
</tbody>
</table>

The main results of the calculations are:

- Anodic oxidation of Rhenium in EtOH-PrOH allows to obtain heteroligand derivatives with general composition $\text{Re}_4\text{O}_n\text{(OEt)}_4\text{(OPr)}_y$. Probability of the formation compounds containing Re4 cluster and based on the structure of $\text{Re}_4\text{O}_4\text{(OEt)}_{12}$ or $\text{Re}_4\text{O}_6\text{(OPr)}_{10}$ is equal.

- In the structure of the $\text{Re}_4\text{O}_4\text{(OEt)}_{12}$ part of Et-groups can be substitute by (OCH$_2$CF$_3$) groups. Replacement of hydrogen atoms by fluorine atoms at $\mu_2$ position increases the heteroligand complex stability.

- It is possible to prepare compound containing Re4 cluster and $\mu_3$-S ligands.
Application of the metal alkoxide derivatives for the preparation of rhenium-containing materials

Particle-size distribution of the products of thermal decomposing of Re₄O₄n(OEt)ₓ(OPrᵢ)ᵧ, Tᵢ=const

XRDA data of ReO₃cub obtained at thermal decomposition of Re₄O₄n(OEt)ₓ(OPrᵢ)ᵧ, Tₘₐₓ = 470 °C.

ReO₃cub a=3,745 Å (a = 3,748Å, ICDD–JCPDS, No.33-1096)

Photography of nano-sized particles
(a) ReO₃cub, obtained at polythermal decomposing of Re₄O₄n(OEt)ₓ(OPrᵢ)ᵧ, Tₘₐₓ = 470 °C.
(b) ReO₃cub, obtained at iso-thermal annealing of Re₄O₄n(OEt)ₓ(OPrᵢ)ᵧ, T=245 °C; M:100 nm.
The aim

Our aim is to obtain fine (nanosized) powders of alloys Re-Ni, Re-Co, Re-Ni-Co; simple and complex oxides.

Alloys for aerospace application

<table>
<thead>
<tr>
<th></th>
<th>Co</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>T_m</td>
<td>1495 C</td>
<td>1455 C</td>
</tr>
<tr>
<td>Re</td>
<td>3168 C</td>
<td></td>
</tr>
</tbody>
</table>

Main questions:
1. Whether Re-Ni alloys can be obtained at low (< 500 °C) temperatures?
2. What particles size thus obtained powders have?

XRD and structure of Ni(OCH₃)₂

1. Experimental
   - a = 3.0739 Å (0.03)
   - c = 7.9774 Å (0.55)

   **APS.** Average particles size (from Sherrer equation) ~ 9 nm

2. Ni(OCH₃)₂ [1]
   - a = 3.1±0.2 Å; c = 7.9±0.5 Å

Mg(OH)₂ – type hexagonal structure.

XRD of Ni(OCH₃)₂ hydrolysis product

1. Experimental
   \[ a = 3.0811 \text{ Å} \quad (0,000) \]
   \[ c = 23.4128 \text{ Å} \quad (0.035) \]

**APS**, Average particles size (from Sherrer equation) \(~14 \text{ nm}\)

2. Ni(OH)₂·0.75H₂O
   ICDD 38-715
   \[ a = 3.080 \text{ Å} \]
   \[ c = 23.410 \text{ Å} \]

3. Ni(OH)₂·0.67H₂O
   ICDD 22-444
   \[ a = 5.340 \text{ Å} \]
   \[ c = 7.500 \text{ Å} \]

XRD of NiₓReᵧCo₂(OCH₃)ₙ thermal decomposition (in hydrogen medium) product

1. Experimental
   (Tdecomp = 400°C)

2. Ni (cub.)
   ICDD 65-0380

3. Re (hex.)
   ICDD 88-1735

4. Co
   ICDD 70-2633

% mass

% atomic

Temperature °C
Re, Ni, Co methoxocomplexes decomposition products

<table>
<thead>
<tr>
<th>Compound</th>
<th>Hydrolysis product</th>
<th>Thermal decomposition products</th>
</tr>
</thead>
<tbody>
<tr>
<td>In air medium</td>
<td>In argon medium</td>
<td>In hydrogen medium</td>
</tr>
<tr>
<td>Re₂Ni₃(Ο(CH₃))₉</td>
<td>-</td>
<td>NiReO₄</td>
</tr>
<tr>
<td>Ni₂Co₃(Ο(CH₃))₄</td>
<td>Ni(OH)₂</td>
<td>NiCo₂O₄ Co(OH)₂ NiO NiO-CoO</td>
</tr>
<tr>
<td>Ni(OCH₃)₂</td>
<td>Ni(OH)₂</td>
<td>NiO NiO Ni NiO NiO NiO-CoO Ni</td>
</tr>
<tr>
<td>Co(OCH₃)₂</td>
<td>Co(OH)₂</td>
<td>Co₃O₄ CoO Co</td>
</tr>
<tr>
<td>Re₄O₆(Ο(CH₃))₁₂</td>
<td>-</td>
<td>ReO₃ - ReO₃ ReO₃</td>
</tr>
<tr>
<td>Ni₆Re₇Co₄(OCH₃)₁₄</td>
<td>-</td>
<td>NiReO₄ NiO NiReO₄ NiO NiO-CoO Ni-Re-Co alloy</td>
</tr>
</tbody>
</table>

Catalyst production by incorporation of alkoxides into zeolites matrix allows to max out synergetic effect

Methanol oxidation using catalysts produced by incorporation methoxo-derivativs into zeolites NaY:
Mo – [MoO(OMe)₄]; Re – Re₂O₃(OMe)₆; ReMo – ReMo₂O₃(OMe)₇;
A – conversion temperature dependence;
b – conversion and formaldehyde yield of 125°C.
Sources of motor fuel

Non-Renewable
- Oil
- Natural gas

Renewable
- Biomass
- Ethanol

Oil refining
- Fisher–Tropsch process (1)
- Mobil-process (2)
- Fermentation

Motor fuel
- Reductive dehydration (3)
- Alternative motor fuel

\[ vXO + (2v+1)H_2 \rightarrow X_nH_{2v+2} + vH_2O \]  

\[ XH_2OH \xrightarrow{\text{H}^+} [H_2O + (XH_3)_2O] \xrightarrow{\text{2TM, 500-400\degree C}, 2-15 \text{h}} X_nH_{2v+2} + \text{ApH} + X_nH_{2v} + H_2O \]  

\[ v/2X_nH_2OH + H_2 = X_nH_{2v+2} + v/2H_2O \]

Scheme of catalyst preparation

Mono- and polymetal alkoxide derivatives

INCORPORATION ON INERT MATRICES
- (zeolites, aluminium oxide)

HEAT TREATMENT
- in reducing atmosphere, \( H_2 \)
- in inert atmosphere
- in air

Catalysts
- \( \text{Re}_xW_0(OCH_3)_{12} \)
- \( \text{Ta}_xO_2(OCH_3)_{14}(\text{ReO}_4)_{12} \)

Created catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Precursor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Re/( \gamma )-Al(_2)O(_3)</td>
<td>( \text{Re}<em>2O_2(\text{OMe})</em>{12} ) – solution in ethanol</td>
</tr>
<tr>
<td>W/( \gamma )-Al(_2)O(_3)</td>
<td>( \text{WO}(\text{OCH}_3)_2 ) – solution in methanol</td>
</tr>
<tr>
<td>Ta/( \gamma )-Al(_2)O(_3)</td>
<td>( \text{Ta}<em>2(\text{OMe})</em>{12} ) – solution in methanol</td>
</tr>
<tr>
<td>Re - W/( \gamma )-Al(_2)O(_3)</td>
<td>( \text{Re}<em>xW_0(OCH_3)</em>{12} ) – solution in methanol</td>
</tr>
<tr>
<td>Re - Ta/( \gamma )-Al(_2)O(_3)</td>
<td>( \text{Ta}<em>2O_2(OCH_3)</em>{14}(\text{ReO}_4)_2 ) – solution in toluene</td>
</tr>
<tr>
<td>Re- Ta/( \gamma )-Al(_2)O(_3)</td>
<td>Mixture solutions ( \text{Re}<em>xO_2(\text{OMe})</em>{12} ) and ( \text{Ta}<em>2(\text{OMe})</em>{18} ) in methanol</td>
</tr>
</tbody>
</table>
The relationship between alkane-olefins fraction C5 – C9 yield and composition of active components in cross-coupling reaction of ethanol and glycerin.

Socatalitic effect of rhenium and tungsten obtained by using bimetallic precursor $W_xRe_{4-x}O_6(CH_3O)_{12}$

The dependence of catalytic activity and selectivity on the precursor chemistry

Fabrication of fine powders of metallic and oxide materials based on rhenium using alkoxide derivatives as precursors

**BASIC CONCEPT**
Synthesis of alkoxide derivatives containing one or several metals
Thermal treatment provides oxide (oxides, solid solutions, complex oxides) and metallic (fine metals and alloys) materials

**ADVANTAGES**
1. An approach to single-phase products with required stoichiometry: the control of the composition and the degree of homogeneity that preserves through the technological process
2. The decrease of the temperature and duration of synthesis
3. The preparation is feasible of both fine (several nanometers grain size) products and coarse-crystalline products (with micrometers scale grain sizes)

I am sorry, that have extended my time