Design of Pt-Sn catalysts on mesoporous titania films for microreactor application

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Selective hydrogenation of \(\alpha,\beta\)-unsaturated aldehydes to unsaturated alcohols

Catalyst and Reactor design to achieve the higher selectivity of unsaturated alcohols formation

Unsaturated alcohols – products for pharmaceutical, food and perfume industry.
Selective hydrogenation of $\alpha,\beta$-unsaturated aldehydes to unsaturated alcohols

**CITRAL**

- E-isomer geranial
- Z-isomer neral

**3,7-dimethyl-2,6-octadienal**

**GERANIOL**

$\beta$-$(\text{trans}-3,7\text{-dimethyl}-2,6\text{-octadien}-1\text{-ol})$

**NEROL**

$\beta$-$(\text{cis}-3,7\text{-dimethyl}-2,6\text{-octadien}-1\text{-ol})$
Approach to solve the problem

- **Microchannel reactor** reactor, which contains channels with diameter less than 500 μm and high ratio surface/volume (105 m²/m³)
- **Increase of selectivity of desired product formation:**
  - 1. High coefficient of heat transmission provides isothermal conditions
  - 2. The contact time is controlled precisely.

- **Mesoporous TiO₂ support**

- **Pt-Sn active component**

- **Bimetallic cluster adsorption**

**Pt-Sn/TiO₂ catalyst**
Selection of reactor: microchannel reactor

Chemical microreactor – reactor, which contains channels with diameter less than 500 μm and high ratio surface/volume ($10^5 \text{ m}^2/\text{m}^3$)

Increase of selectivity of desired product formation:

1. High coefficient of heat transmission provides isothermal conditions
2. The contact time is controlled precisely.
Levels of catalyst development – from «nano-» to «micro-»:

Nanoclusters, nanopores of coating, mesoporous highly organized coating, channel structure of microreactor, microstructured plate

Development of Pt-Sn nanosized bimetallic catalysts on mesoporous TiO$_2$ coatings for the microreactors of the selective hydrogenation of $\alpha,\beta$-unsaturated aldehydes.
Materials and methods selection

Support:

- SiO$_2$
- TiO$_2$
- Al$_2$O$_3$
- C

TiO$_2$-supported catalysts show the higher selectivity to unsaturated alcohols in comparison with others. Mesoporous TiO$_2$ is appropriate support with uniform mesoporous structure, which is accessible for big molecules of organic compounds-reagents.

Active component:

- Au
- Pt
- Rh
- Pt-Sn
- Pt-Ru

Noble metals (Pt, Rh) are known to be active catalysts in this reaction. Increasing of selectivity of C=O bond hydrogenation occurs after modification of the noble metal catalysts with more electropositive metals (Sn, Ru).

Synthesis technique:

- successive impregnation
- combined impregnation
- bimetallic complexes adsorption

• Uniform distribution of bimetallic particles with a size 1-2 nm.
• Mild activation conditions.
Target:
Catalyst and Reactor design to achieve the higher selectivity of unsaturated alcohols formation

Tasks:

• Preparation of Pt and Pt-Sn complexes, study influence of synthesis conditions (solvent, concentrations) on their composition;

• preparation and choice of bulk TiO$_2$ and mesoporous film;

• Investigation of adsorption kinetics of Pt-Sn complexes on mesoporous TiO$_2$;

• Preparation of Pt-Sn/TiO$_2$ catalyst on b; influence of synthesis conditions on physicochemical properties and activity in citral hydrogenation reaction.
Synthesis and investigation of Pt-Sn carbonyl clusters – precursor of active component

• uniform composition of bimetallic particles
• particles size of 1-2 nm
• mild activation conditions (180-200°C, vacuum)

Composition of Pt carbonyl anion depends on the preparation conditions:
• solvent type
• water concentration
• composition of gas atmosphere.

Reducing carbonilation of Pt (IV):

\[
\begin{align*}
[\text{PtCl}_6]^{2-} & \rightarrow [\text{Pt(CO)Cl}_3]^- \rightarrow [\text{Pt}_3(\text{CO})_6]_{10}^{2-} \rightarrow [\text{Pt}_3(\text{CO})_6]_{6}^{2-} \rightarrow [\text{Pt}_3(\text{CO})_6]_{5}^{2-} \rightarrow [\text{Pt}_3(\text{CO})_6]_{4}^{2-} \rightarrow [\text{Pt}_3(\text{CO})_6]_{3}^{2-} \rightarrow [\text{Pt}_3(\text{CO})_6]_{2}^{2-} \rightarrow [\text{Pt}_3(\text{CO})_6]^{2-}.
\end{align*}
\]
Synthesis of high-nuclearity cluster H2[Pt3(CO)6]10

\[ H_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O} \]

(1) + CO

\[ H_2\text{[Pt}_3\text{(CO)}_6]_{10} \]

(2) + solvent, H2O

\[ H_2\text{[Pt}_3\text{(CO)}_6]_n \]

(3) + SnCl2·2H2O

\[ \text{H}_2\text{n[Pt}_3\text{(CO)}_3\text{(SnCl}_3)_2\text{(SnCl}_2\text{H}_2\text{O})]_n} \]

- **t = 2-24 ч**
- **C_{Pt} = 0,5; 2; 10 mg/ml**

- Solvent nature: acetone, tetrahydrofuran, ethanol, isopropanol
- gas atmosphere (CO, Ar)

**Synthesis of Pt-Sn carbonyl clusters**
FTIR study of Pt carbonyl clusters composition

\[
\text{H}_2\text{PtCl}_6 \times 6\text{H}_2\text{O} \xrightarrow{\text{CO}} \text{H}_2[\text{Pt}_3(\text{CO})_6]_{10} \xrightarrow{\text{solvent, H}_2\text{O}} \text{H}_2[\text{Pt}_3(\text{CO})_6]_n, \ n = 5, 6
\]

Pt concentration:
- 0 mg/ml; (C\textsubscript{2}H\textsubscript{5}OH)
- 2 mg/ml;
- 10 mg/ml.

Position of terminal CO ligand absorbance band indicate quantity of platinum triangular units.

**Terminal CO**
1945-2065 cm\(^{-1}\)

**Bridging CO**
1740-1900 cm\(^{-1}\)
Synthesis of carbonyl clusters $H_2[Pt_3(CO)_6]_n$: effect of solvent

$H_2[Pt_3(CO)_6]_{10} \xrightarrow{\text{solvent, } H_2O} \text{presipitate}$

$2H^+ + 2[Pt_3(CO)_6]^{2-} \xrightarrow{\text{solution}} 2H_2O + 2[Pt_3(CO)_6]_n$

$CO + H_2O = CO_2 + 2H^+ + 2e$

$C_2H_5OH \xrightarrow{\text{solvent}} C_4H_8O$

Pt concentration:
- 0 mg/ml; (C$_2$H$_5$OH)
- 2 mg/ml;
- 10 mg/ml.

Wavenumber, cm$^{-1}$

$n=5$  
$n=6$

T, %

$1887 \text{ cm}^{-1}$  
$1880 \text{ cm}^{-1}$  
$2065 \text{ cm}^{-1}$  
$2056 \text{ cm}^{-1}$

$1886 \text{ cm}^{-1}$  
$2058 \text{ cm}^{-1}$  
$2057 \text{ cm}^{-1}$

$n=5$  
$n=6$
Synthesis of carbonyl clusters $\text{H}_2[\text{Pt}_3(\text{CO})_6]^n$: effect of solvent and Pt concentration

Synthesis conditions (solvent nature, Pt concentration) providing cluster $[\text{Pt}_3(\text{CO})_6]^n$ formation with number of triangular units equal to 5 and 6 have been determined.
Synthesis of Pt-Sn carbonyl clusters

\[
[\text{Pt}_3(\text{CO})_6]_{n}^{2-} + 2\text{SnCl}_3^{-} + \text{SnCl}_2\cdot\text{H}_2\text{O} \xrightarrow{\text{HCl}} [\text{Pt}_3(\text{CO})_3(\text{SnCl}_3^{-})_2\text{SnCl}_2\cdot\text{H}_2\text{O}]_{n}^{-2n}
\]

Absorbance band of bridging CO ligands disappears from spectra, that is evidence of substitution of bridging CO ligands by Sn-containing ligands.

Bridging CO

1740-1900 cm\(^{-1}\)
Structure of Pt carbonyl cluster is not damaged under interaction with SnCl$_2$ at 0.5-2 mgPt/ml. At higher concentration 10 mgPt/ml complex formation with $n=3-6$ occurs.
Support: mesoporous TiO₂

- uniform porous structure (2-6 nm)
- specific surface area (∼ 200 m²/g)
- thermal stability (∼ 600°C)
- acid properties of surface (∼3-7 LAS/nm²)

Sol-gel synthesis TiO₂ with using surfactant:

\[
\left(EO\right)_{100}\left(PO\right)_{65}\left(EO\right)_{100} \quad \text{Pluronic F127}
\]

\[
2 \text{Ti}[OiPr]_{4-x}(OH)_{x} \rightarrow [OiPr]_{4x}(OH)_{x-1} \text{Ti-O-Ti}[OiPr]_{4x}(OH)_{x-1} + H₂O
\]
Synthesis of mesoporous TiO$_2$

- **Precursor solution**: Ti(OiPr)$_4$
- **Surfactant solution**: Pluronic F127 (EO)$_{100}$(PO)$_{65}$(EO)$_{100}$

- **Initial sol**
- **Aging**
- **Spin-coating**
  - speed
  - time

**Drying**
- 100°C/1h

**Surfactant removing**
- 550°C/4h

**Substrat** – glass, silicic or titanic plates 1x1x0.05 cm

**Mesoporous bulk TiO$_2$**

**Mesoporous TiO$_2$-film**

- **pH** 1.5-2.0
- **Ti(OiPr)$_4$ : F127 : C$_2$H$_5$OH**
  - 1 : 0.005-0.009 : 40
Influence of surfactant content

Mesoporous films have a hexagonal pore structure. Parameter of unit cell decrease with increasing of surfactant content.

S/P = 0.009, \( a_0 = 7.0 \text{ nm} \)
S/P = 0.007, \( a_0 = 8.5 \text{ nm} \)
S/P = 0.006, \( a_0 = 9.3 \text{ nm} \)

Hexagonal pore structure
Synthesis of Pt-Sn/TiO$_2$ catalysts

\[ \begin{align*} &H_2PtCl_6 \cdot 6H_2O \quad \text{+ CO} \quad C_{Pt} = 0.5; 2; 10 \text{ mg/ml} \\ &H_2[Pt_3(CO)_6]_{10} \quad + \text{solvent} \quad \text{Solvent nature: acetone, ethanol, tetrahydrofuran (THF), isopropanol} \\ &H_2[Pt_3(CO)_6]_n \quad + \text{SnCl}_2 \cdot 2\text{H}_2\text{O} \quad C_{Sn} = 0.3; 1.2; 6.0 \text{ mg/ml (Pt:Sn molar=1:1)} \\ &H_{2n}[Pt_3(CO)_3(SnCl)_3]_2(SnCl_2\text{H}_2\text{O})_n \quad + \text{TiO}_2 \quad \text{method of Pt-Sn cluster loading (adsorption, impregnation)} \\ &\quad \text{drying} \quad \text{duration of adsorption (0.3-24 h)} \\ &\quad \text{activation} \quad \text{condition of activation (vacuum/190°C-220°C, H}_2/400°C) \\ &\text{TiO}_2 \text{ powder} \quad \text{Pt-Sn/TiO}_2 
\end{align*} \]
### Synthesis conditions of Pt-Sn/TiO₂ catalysts

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Synthesis conditions (molar ratio Pt : Sn = 1)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Metal concentration in solution, mg/ml</td>
</tr>
<tr>
<td></td>
<td>Pt</td>
</tr>
<tr>
<td>Adsorption from solution of carbonyl Pt-Sn cluster</td>
<td></td>
</tr>
<tr>
<td>AA-OR-2</td>
<td>2</td>
</tr>
<tr>
<td>AE-OR-2</td>
<td>2</td>
</tr>
<tr>
<td>AT-OR-2</td>
<td>2</td>
</tr>
<tr>
<td>AE-OR-10</td>
<td>10</td>
</tr>
<tr>
<td>AE-V-2</td>
<td>2</td>
</tr>
<tr>
<td>Impregnation by solution of carbonyl Pt-Sn cluster</td>
<td></td>
</tr>
<tr>
<td>IE-OR-2</td>
<td>2</td>
</tr>
<tr>
<td>Impregnation by solution of inorganic metal salts precursor (H₂PtCl₆+SnCl₂)</td>
<td></td>
</tr>
<tr>
<td>IA-OR-33</td>
<td>33</td>
</tr>
<tr>
<td>IE-OR-33</td>
<td>33</td>
</tr>
</tbody>
</table>

- **Method of deposition**: Adsorption (A), Impregnation (I)
- **Solvent**: Acetone (A), Ethanol (E), THF (T)
- **Thermal treatment**: Ox-Red (OR), Vacuum (V)
- **Pt concentration in solution**: 2, 10, 33 mg/ml
Adsorption kinetics and isotherm of Pt-Sn carbonyl cluster on TiO₂

Adsorbed cluster quantity increases with an increase of adsorption duration from 0.3 to 24 hours and then remains practically constant.

Adsorbed cluster quantity increases from 0.035 to 0.22 mgPt/m² at an increase of Pt equilibrium concentration from 0.5 to 4.6 mgPt/ml.
Influence of solution concentration on particle size distribution

Adsorption of Pt-Sn carbonyl cluster from ethanol solution

2 mg/ml

Adsorption of Pt-Sn carbonyl cluster from ethanol solution

10 mg/ml

Pt$_3$Sn
d$_{111}$ = 2.37 Å

average particle size 1.5 nm
max 2.9 nm

Pt$_3$Sn
d$_{200}$ = 2.03 Å

average particle size 3.2 nm
max 11.3 nm

The increase of solution concentration leads to the increase of metals content, average particle size and boarding of particle size distribution.
Influence of solvent nature on particle size distribution

Adsorption of Pt-Sn carbonyl cluster from solution of ethanol

\[ \text{Pt}_3\text{Sn} \]
\[ d_{111} = 2.37 \, \text{Å} \]

Average particle size 1.5 nm
Max 2.9 nm

Adsorption of Pt-Sn carbonyl cluster from solution of tetrahydrofurane

\[ \text{Pt}_3\text{Sn} \]
\[ d_{111} = 2.34 \, \text{Å} \]

Average particle size 2.2 nm
Max 11.4 nm

Using of tetrahydrofurane as a solvent instead ethanol during adsorption lead to the increase of metals content, average particle size and boarding of particle size distribution.
Influence of acid site concentration of TiO$_2$ support

The concentration of acid sites of TiO$_2$ support does not influence on adsorption of Pt-Sn anion carbonyl cluster and, consequently, on metals content in the Pt-Sn/TiO$_2$ catalysts.

<table>
<thead>
<tr>
<th>Synthesis conditions of TiO$_2$</th>
<th>Acid site concentration of TiO$_2$ support</th>
<th>Pt and Sn content in Pt-Sn/TiO$_2^*$</th>
<th>Pt :Sn molar ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surfactant/Ti</td>
<td>pH</td>
<td>C(BAS)$^{**}$, μmol/g</td>
<td>C(LAS)$^{***}$, μmol/g</td>
</tr>
<tr>
<td>0.008</td>
<td>1.5</td>
<td>37</td>
<td>110</td>
</tr>
<tr>
<td>0.008</td>
<td>1.8</td>
<td>110</td>
<td>170</td>
</tr>
</tbody>
</table>

*adsorption from ethanol solution of Pt-Sn cluster (C$_{Pt} = 2$ mg/ml, C$_{Sn}=1.2$ mg/ml) during 24 hrs

$^{**}$BAS - Broensted acid sites

$^{***}$LAS - Lewis acid sites
Comparison of catalysts activated in vacuum and H\textsubscript{2}

Adsorption of Pt-Sn carbonyl cluster from ethanol solution  
**Activation:** vacuum 190°C/2h

Activation of dried Pt-Sn/TiO\textsubscript{2} samples in vacuum at 190°C/2h gives smaller particle size and narrow distribution.

Activation in H\textsubscript{2}/400°C/2h -- increase maximum particle size and wider distribution
Influence of temperature activation in vacuum

Adsorption of Pt-Sn carbonyl cluster from ethanol solution
Activation: vacuum 190°C/2h

average particle size 2.3 nm
max 5.4 nm

Adsorption of Pt-Sn carbonyl cluster from ethanol solution
Activation: vacuum 220°C/2h

average particle size 2.6 nm
max 5.6 nm

The increase of activation temperature in vacuum of dried Pt-Sn/TiO₂ catalysts from 190°C to 220°C does not lead to change of average and maximum Pt-Sn particle size.
Deposition of Pt-Sn carbonyl cluster onto TiO$_2$

Adsorption of Pt-Sn carbonyl cluster

Impregnation by solution, contained Pt-Sn carbonyl cluster

- solvent nature
- concentration of cluster in the solution
- ratio solution/support
- duration of adsorption
- solvent nature

acetone  ethanol  THF  2 mgPt/ml  10 mgPt/ml  20  100  2 h  24 h  acetone  ethanol  THF

- increase of metals content
- increase of average particle size
- broadening of particle size distribution
### Particle size distribution and composition of Pt-Sn active component supported on TiO$_2$ film

<table>
<thead>
<tr>
<th>$C_{\text{Pt}}$ in solution (mol L$^{-1}$)</th>
<th>$t$ adsorption (h)</th>
<th>average particle size, nm</th>
<th>Min and Max particle size, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>24</td>
<td>3.3</td>
<td>1.1-7.4</td>
</tr>
<tr>
<td>2</td>
<td>0.3</td>
<td>1.8</td>
<td>0.7-5.7</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>2.3</td>
<td>0.8-3.9</td>
</tr>
<tr>
<td>2</td>
<td>24</td>
<td>2.3</td>
<td>1.2-3.6</td>
</tr>
<tr>
<td>3</td>
<td>24</td>
<td>2.5</td>
<td>1.3-4.5</td>
</tr>
</tbody>
</table>

**Solvent:** ethanol

**Duration of adsorption:** 24 h.

Adsorption of Pt-Sn complex on mesoporous TiO$_2$-film provides narrow particle size distribution of bimetallic particles on titania surface.
Solvent: ethanol
Duration of adsorption: 24 h.

XRD bands for Pt-Sn system

<table>
<thead>
<tr>
<th>Composition</th>
<th>Interplanar spacing, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>$d_{111} = 2.2650$</td>
</tr>
<tr>
<td>Sn</td>
<td>$d_{101} = 2.5710$</td>
</tr>
<tr>
<td>PtSn</td>
<td>$d_{102} = 2.1570$</td>
</tr>
<tr>
<td>Pt$_3$Sn</td>
<td>$d_{111} = 2.3107$</td>
</tr>
<tr>
<td>Pt$_2$Sn$_3$</td>
<td>$d_{110} = 2.1680$</td>
</tr>
</tbody>
</table>
XPS Pt4f region: effect of metal loading on chemical state

Spectra show presence of both Pt metal and PtOₓ. Pt metal prevailing for the Pt-Sn/TiO₂ catalysts prepared via Pt-Sn carbonyl cluster precursor, PtOₓ – for catalysts prepared via inorganic metal salts precursors.
Spectra show presence of both Sn metal and SnOₓ. Sn metal prevailing for the Pt-Sn/TiO₂ catalysts prepared via Pt-Sn carbonyl cluster precursor, SnOₓ – for catalysts prepared via inorganic metal salts precursors.
Activity of Pt-Sn/TiO$_2$ catalysts in the reaction of citral hydrogenation

Main products of citral hydrogenation are geraniol and nerol.

**Reaction conditions:** 150 ml of 0.01 M solution of citral in 2-propanol (+ 0.01 M decahydronaphthalene (DHN) as an internal standard), temperature 343 K, $H_2$ pressure 12 bar, mixing rate 1500 rpm, catalyst mass ~ 0.1 g.
Activity of Pt-Sn/TiO$_2$ catalysts in citral hydrogenation

<table>
<thead>
<tr>
<th>N</th>
<th>Metal content, wt. %</th>
<th>Average particle size, nm</th>
<th>Initial TOF, s$^{-1}$</th>
<th>Selectivity, % (at 96-98% citral conversion)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pt</td>
<td>Sn</td>
<td></td>
<td>Geraniol +nerol</td>
</tr>
<tr>
<td>1</td>
<td>1.98</td>
<td>-</td>
<td>-</td>
<td>5.6</td>
</tr>
<tr>
<td>Adsorption of Pt carbonyl complex</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.61</td>
<td>0.25</td>
<td>1.5</td>
<td>0.18</td>
</tr>
<tr>
<td>3</td>
<td>4.04</td>
<td>1.75</td>
<td>2.2</td>
<td>0.20</td>
</tr>
<tr>
<td>4</td>
<td>3.55</td>
<td>2.8</td>
<td>3.2</td>
<td>0.54</td>
</tr>
<tr>
<td>Adsorption of Pt-Sn carbonyl complex</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Selectivity of geraniol+nerol formation increases from 3 to 40-90% after modification of Pt/TiO$_2$ catalyst with Sn.

Selectivity of Pt-Sn/TiO$_2$ catalysts in citral hydrogenation increases from 40 to 90% with an increase of metal particle size from 1.5 to 3.2 nm.
Pt-Sn catalyst for selective hydrogenation of citral
Conclusions:

1. Adsorption kinetics of Pt-Sn carbonyl complex on mesoporous bulk TiO$_2$ has been investigated. Adsorbed complex quantity increases with an increase of adsorption duration from 0.3 to 24 hours and then remains constant.

2. The metal content, average particle size, and particle size distribution can be regulated by variation of solvent nature and metal concentration. The average particle size increases from ~1.5 to ~3.5 nm at an increase of Pt and Sn content from 0.6 to ~3 wt. %.

3. Pt and Sn contents in Pt-Sn/TiO$_2$ catalysts, prepared by adsorption, depend on solvent nature and increase in the row: acetone < ethanol < tetrahydrofuran.

4. Activation of dried Pt-Sn/TiO$_2$ samples in vacuum at 190oC/2h gives smaller particle size and narrow distribution. Activation in H$_2$/400oC/2h -- increase maximum particle size and wider distribution

5. The selectivity of geraniol+nerol formation increases from 3 to 40-90% after modification of Pt/TiO$_2$ catalyst with Sn. The selectivity of Pt-Sn/TiO$_2$ catalysts in citral hydrogenation increases from 40 to 90% with an increase of metal particle size from 1.5 to 3.2 nm.
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Efimenko Tatyana

F.Garin
P.Bernhardt

NWO-RFBR 047.015.012.
THANK YOU FOR YOUR ATTENTION

First Snow in Novosibirsk. 17 September 2008


Bernard M. Mitzner, Vito J. Mancini, and Seymour Lemberg

Neither α-nerol nor α-geraniol has been reported or occurring in nature. The two isomeric materials have not previously been prepared in a pure form synthetically, and their spectra have not been characterized. In this note we report the preparation of pure α-nerol (I) (cis-2,6-dimethyl-1,6-octadiene-8-ol) and pure α-geraniol (II) (trans-2,6-dimethyl-1,6-octadiene-8-ol). (Their purity was ascertained by gas chromatography, with a nonpolar and a polar column.)

\[
\begin{align*}
\text{III} + \text{HCl} & \rightarrow \text{IV} + \text{V} \\
\text{V} & \rightarrow \text{VI} + \text{VII} \\
\text{VI} + \text{VII} & \rightarrow \text{I} + \text{II}
\end{align*}
\]

α-Myrcene (III) was hydrochlorinated to give α-neryl chloride (IV) and α-geranyl chloride (V) which, when treated with sodium acetate, gave the α-acetates VI and VII; hydrolysis with potassium hydroxide gave the alcohols I and II.
Selective hydrogenation of $\alpha,\beta$-unsaturated aldehydes to unsaturated alcohols

CITRAL

E-isomer geranial

Z-isomer neral

3,7-dimethyl-2,6-octadienal

GERANIOL

$\alpha$-($trans$-3,7-dimethyl-2,7-octadien-1-ol)

$\beta$-($trans$-3,7-dimethyl-2,6-octadien-1-ol)

NEROL

$\alpha$-($cis$-3,7-dimethyl-2,7-octadien-1-ol)

, $\beta$-($\mu$c-3,7-dimethyl-2,6-octadien-1-ol)
Synthesis of high-nuclearity cluster $\text{H}_2\text{[Pt}_3\text{(CO)}_6\text{]}_{10}$

$30\text{H}_2\text{PtCl}_6\times\text{6H}_2\text{O} + 121\text{CO} + 6\text{H}_2\text{O} = \text{H}_2\text{[Pt}_3\text{(CO)}_6\text{]}_{10} \downarrow + 61\text{CO}_2 + 180\text{HCl}$

Optimal duration of the reaction of reducing carbonilation is $t > 6$ h.
### FTIR: literature data for [Pt$_3$(CO)$_6$]$^{2-}$$_n$ (n = 1-6) clusters

<table>
<thead>
<tr>
<th>Composition of solution</th>
<th>Position of maximum of absorbance band, $\nu_{CO}$, cm$^{-1}$</th>
<th>Quantity of triangular units, n</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1995, 1818, 1795</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2030, 1855, 1840, 1830, 1810</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2040, 2030, 1880, 1860, 1825</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2055, 1890, 1870, 1840, 1830</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2065, 1900, 1875, 1855, 1840</td>
<td>6</td>
<td></td>
</tr>
</tbody>
</table>
Synthesis of carbonyl clusters $H_2[Pt_3(CO)_6]_n$: effect of solvent and Pt concentration

$$H_2PtCl_6\cdot 6H_2O \xrightarrow{CO} H_2[Pt_3(CO)_6]_{10} \xrightarrow{solvent, H_2O} H_2[Pt_3(CO)_6]_n, \ n = 5, 6$$

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Pt concentration, mg/ml</th>
<th>$\nu_{CO}, \text{cm}^{-1}$</th>
<th>Quantity of triangular units, n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>0.5</td>
<td>2067</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2065, 1887</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>2056, 1880</td>
<td>5</td>
</tr>
<tr>
<td>Acetone</td>
<td>0.5</td>
<td>2058</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2057, 1872</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>2057, 1882</td>
<td>5</td>
</tr>
<tr>
<td>Tetrahydrofurane</td>
<td>0.5</td>
<td>2062</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2058, 1886</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>2057, 1882</td>
<td>5</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>2</td>
<td>2065, 1890</td>
<td>6</td>
</tr>
</tbody>
</table>
Solvent nature influence on Pt content in Pt-Sn/TiO₂ catalyst

*Pt content in catalyst, mass. %*

Pt and Sn contents in Pt-Sn/TiO₂ catalysts, prepared by adsorption, depend on solvent nature and increase in the row:

acetone < ethanol < tetrahydrofuran.
Synthesis conditions influence on Pt content in Pt-Sn/TiO$_2$ catalyst

Pt content in catalyst, wt. %

Pt concentration in ethanol solution, mg/ml

Pt and Sn content in Pt-Sn/TiO$_2$ catalysts, prepared by adsorption of Pt-Sn carbonyl cluster, increase with solution concentration.
Influence of precursor nature on particle size distribution

Adsorption of \textit{Pt-Sn carbonyl cluster} from ethanol solution
Activation: vacuum 190\degree C/2h

Pt$_3$Sn $d_{111}=2.33$ Å

average particle size 2.2 nm
max 5.4 nm

Co-impregnation of $H_2PtCl_6\cdot6H_2O + SnCl_2\cdot2H_2O$ from ethanol solution
Activation: $H_2$ 400\degree C/2h

Pt$_3$Sn $d_{111}=2.36$ Å

average particle size 1.8 nm
max 20.8 nm

Under using of Pt-Sn carbonyl cluster as a active component precursor instead inorganic metal salts during Pt-Sn/TiO$_2$ preparation the mild activation condition provides the formation of Pt$_3$Sn particles $\sim$ 2 nm in size.
Spectra show strong effect of differential electrical charging of catalyst surface depending on synthesis condition. This mean different schemes of Pt-Sn active component interaction with TiO$_2$ support, which important for catalysis.
XPS O1s region: effect of Pt-Sn active component interaction with TiO₂ support

Spectra include main contribution from TiO₂, as well as from PtOₓ, SnOₓ, and O-containing carbon groups. Spectra show correlation with effect of differential electrical charging in Ti2p region.
XPS: effect of Pt-Sn particle growth

Increase of 3D character in growth of Sn-containing particles with higher Sn contents (obtained from salt compared to carbonyl precursors): possibly from Frank van der Merwe (2D, island mode) to Volmer-Weber (3D, cluster mode) or to Stranski-Krastanov (2D/3D mode)

Pt-Sn carbonyl precursor

Pt4f spectral region, and so overall trend in Pt-Sn particle morphology, complementary to results of qualitative and quantitative analysis, can be obtained.

The three thin film growing modes. In the two-dimensional Frank van der Merwe mode, layers of material grow on top of each other, atoms or molecules grow layer-by-layer in a sequential fashion. In the Volmer-Weber mode, separate three-dimensional islands form on the substrate. And in the Stranski-Krastanov mode, the critical mechanism for forming quantum dots, one or two monolayers form first, followed by individual islands.
Selective hydrogenation of citral

 Particle diameter, nm

 TOF, s⁻¹

 Selectivity to unsaturated alcohols, %

 Citral conversion, %

 Pt content, % | Particle size, nm | Selectivity, %
---|---|---
0.77 | 1.1 | 70
1.44 | 2.8 | 70
2.65 | 5.1 | 74
6.65 | 16 | 57
3.59 | 28 | 48

Levels of catalyst development – from «nano-» to «micro-»:

Nanoclusters, nanopores of coating, mesoporous highly organized coating, channel structure of microreactor, microstructured plate

Target: development of Pt-Sn nanosized bimetallic catalysts on mesoporous TiO₂ coatings for the microreactors of the selective hydrogenation of α,β-unsaturated aldehydes.
Conclusions on Pt-Sn carbonyl clusters synthesis:

1. For $\text{H}_2[\text{Pt}_3(\text{CO})_6]_n$ ($n = 5, 6$) cluster formation following synthesis conditions are necessary: absence of precipitate $\text{H}_2[\text{Pt}_3(\text{CO})_6]_{10}$ washing stage; CO gas atmosphere during of dissolution of $\text{H}_2[\text{Pt}_3\text{CO}_6]_{10}$. The variation of water content in range $0.5-4\text{ vol.}\%$ in the solvent does not influences on Pt carbonyl cluster composition.

2. It have been established, that solvent type and Pt concentration influence on Pt carbonyl cluster composition. Synthesis conditions (solvent nature, Pt concentration) providing cluster $[\text{Pt}_3(\text{CO})_6]_n^{2-}$ formation with number of triangular units $n$ equal to 5 and 6 have been determined.

3. Structure of Pt carbonyl cluster does not damaged under interaction with $\text{SnCl}_2$ at $0.5-2\text{ mgPt/ml}$. At higher concentration $10\text{ mgPt/ml}$ complex formation with $n = 3-6$ occurs.