XAFS study of catalytic nanosystems promising for environmental catalysis

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Methane Acid conversion of a synthesis gas

CH₄ + CO₂ → 2CO + 2H₂

Active component: TiO₂

Side of membrane: TIPS RAS

Membrane

\( d_{\text{pores}} = 2-1000 \text{ nm} \)

Industrial useful substratums:

Basicle principle of formation

Application area:

Catalytic conversion of hydrocarbons into hydrogen containing gas
Tasks:

Objects to analyzed with complex methods:
- Original catalitics systems
- Calcined with different conditions systems

Application systems
Pd-Co/TiO₂
Pd-Mn/TiO₂

To understand principle of formation bi-metall active centres of supports and there structural features
Tasks of XAFS method:

With XAFS-spectroscopy we can:
- Establish a symmetry of the immediate environment, charge state of atoms and local structure

Using another methods such as X-ray Photoelectron Spectroscopy and XRF spectroscopy we can know:
- Elements composition on a surface
- Size of particles
- Phase state
Systems with Pd-Co. Preparation:

Parents compounds: 
\(\text{н}-\text{butoxide Ti} \)  
\(\text{PdCo(\text{µ-OOCMe})_4(\text{NCMe})}\) 

Coprecipitation in toluene with the addition of an alcohol-water mixture for hydrolysis

Next steps:

1) Drying with 25°C (gel)

2) With Ar
   - 5 hours, 550°C

3) Microwave, then Ar
   - 2 hours, 550°C
Study:

XRF spectroscopy
Only for TiO₂
XANES (Pd-K) and FT of Pd for 1%Pd-2%Co/TiO₂ and comparison sample:

a) 1%Pd-2%Co - previous (gel, drying 25°C);

b) 1%Pd-2%Co/TiO₂ (550°C, microwave, calcination);

c) 1%Pd-2%Co/TiO₂ (550°C, air);

d) 1%Pd-2%Co/TiO₂ (550°C, Ar);

e) PdO – comparison oxide;

f) Pd – foil.
XANES (Pd-K) and FT of Co for 1%Pd-2%Co/TiO₂ and comparison sample:

a) 1%Pd-2%Co - previous (gel, drying 25°C);
b) 1%Pd-2%Co/TiO₂ (550°C, microwave, calcination);
c) 1%Pd-2%Co/TiO₂ (550°C, air);
d) 1%Pd-2%Co/TiO₂ (550°C, Ar);
e) Co₃O₄ – comparison oxide;
f) Co – foil.
System with Pd-Co:

The main parts of Pd stay in oxide phase. It's a result from comparing distances and coordination numbers with crystallographic data.

<table>
<thead>
<tr>
<th>model</th>
<th>Pd-O</th>
<th>Pd-Pd</th>
<th>Pd-Me</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1 Me=Pd</td>
<td>2.0 Å</td>
<td>3.04 Å</td>
<td>3.34-3.4 Å</td>
</tr>
<tr>
<td></td>
<td>3.6-3.8</td>
<td>0.9-1.0</td>
<td>4.8-5.1</td>
</tr>
<tr>
<td>#2 Me=Co</td>
<td>2.0 Å</td>
<td>3.04 Å</td>
<td>3.4-3.6 Å</td>
</tr>
<tr>
<td></td>
<td>3.6-3.8</td>
<td>0.9-1.0</td>
<td>4.8-5.1</td>
</tr>
</tbody>
</table>

Presumably we saw formation of non-stoichiometric compounds with structural properties similar mixed oxides Co-Ti и Pd-Co.

<table>
<thead>
<tr>
<th>sample</th>
<th>Co-O</th>
<th>Co-Co</th>
<th>Co-O-Me</th>
<th>Co-O-Me</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.96 Å</td>
<td>2.85 Å</td>
<td>3.32 Å</td>
<td>3.76 Å</td>
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<tr>
<td></td>
<td>3.9-4.1</td>
<td>0.2</td>
<td>0.6</td>
<td>0.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>model</th>
<th>Co-Co</th>
<th>Co-Me</th>
<th>Co-Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoTiO₃</td>
<td>2.99</td>
<td>3.39</td>
<td>3.74</td>
</tr>
<tr>
<td>PdCoO₂</td>
<td>2.83</td>
<td>3.38</td>
<td>-</td>
</tr>
</tbody>
</table>
System with Pd-Mn. Preparation:

- **Precursor**
- **Gel formation**
- **Drying (Ar) and calcinization (500 °C)**

XRF spectroscopy

*Only for TiO$_2$*
XANES (Pd-K) and FT of Co for Pd-Mn/TiO$_2$ and comparison sample
a) Pd-Mn/TiO$_2$ - gel
b) Pd-Mn/TiO$_2$ – oxide, T=500C
c) PdO comparison sample
d) Pd – foil

<table>
<thead>
<tr>
<th>№</th>
<th>#1 – Pd-Mn/TiO$_2$ (gel)</th>
<th>#2 – Pd-Mn/TiO$_2$ (metall)</th>
<th>PdO</th>
<th>Pd$^0$ metall</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R$_1$, Å</td>
<td>N</td>
<td>R$_2$, Å</td>
<td>N</td>
</tr>
<tr>
<td>Pd-O</td>
<td>1.9 8</td>
<td>4.1</td>
<td>2.0 0</td>
<td>3.8</td>
</tr>
<tr>
<td>Pd-Pd</td>
<td>2.9 9</td>
<td>2.0</td>
<td>3.0 3</td>
<td>2.5</td>
</tr>
<tr>
<td>Pd-Pd-</td>
<td>3.5 0-3.5 5</td>
<td>3.4 3</td>
<td>3.4 3</td>
<td>8.0</td>
</tr>
</tbody>
</table>
XANES (Pd-K) and FT of Co for Pd-Mn/TiO₂ and comparison samples:

a) Pd-Mn/TiO₂ - gel
b) Pd-Mn/TiO₂ – oxide, T=500°C
c) Mn₃O₄ (*0.5)
d) MnO (*0.5)
e) Mn₂O₃ (*0.5)
f) MnO₂ (*0.5)

System with Pd-Mn: Mn-k edge

\[ R_{\text{Mn-O}} = 2.11 \AA, \; N = 4.9 \]

**Pd-Mn/TiO₂ - gel**

\[ R_{\text{Mn-O}} = 2.03 \AA, \; N = 4.5 \]
\[ R_{\text{Mn-Me (Mn, Ti)}} = 2.96-3.02\AA, \; N = 2 \]
\[ R_{\text{Mn-Me (Mn, Ti)}} = 3.7-3.8\AA, \; N = 1 \]

**Pd-Mn/TiO₂ T=500°C**

\[ R_{\text{Ti-O}} = 1.94-1.98\AA, \; N = 6 \]
\[ R_{\text{Ti-Ti}} = 3.0-3.04\AA, \; N = 4 \]
\[ R_{\text{Ti-Ti}} = 3.74-3.78\AA, \; N = 4 \]
Results:

For Pd-Co:
- We supposed that systems has strong interaction between Pd and Co in a precipitation stage. In this situation Co take place in structure of supporte to locate atoms of Pd. They formatited a mixed oxide that are not non-stoichiometric.

For Pd-Mn:
- As a result we supposed that for gel state for Pd-Mn systems formed to a defect nanophase PdO, that consists of basic Pd-Mn complexes and PdO.
- We saw deffects of $\text{MnO}_x$ nanophase with stabilization of ions with local deffects.
Thanks for your attention