Synthesis and characterization of Pd and Ni nanoparticles confined in microporous structures for the LENR applications

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Overcoming the Coulomb Barrier

Driving of adjacent potential wells occupied by hydrogen ions

- large amplitude anharmonic lattice oscillations (discrete breathers)
- fast phase transformation of quasicrystals (phasons)

nuclear active sites

Result of molecular dynamic modelling
Reversible phason flips from CUBO to ICO symmetry is possible for Pd or Ni nanoclusters

Pd-13 and Ni-13 clusters

Cuboctahedral

Icosahedral
Pd and Ni nanoclusters

Cuboctahedral clusters

Icosahedral clusters

Template synthesis
Pd and Ni nanoclusters: templates

Zeolite (alumosilicate) structure
three-dimensional framework
with two types of cages:
1.3 nm and 0.74 nm.
Uniform pore size distribution

Porous carbon
three-dimensional framework
Pore size depends on the
carbonization and activation conditions
Pore size is controllable
SEM and TEM images, XRD pattern and pore-size distribution of C42 carbon sample used as a template for Pd-particle growth

Poro\c{s} carbon

$S_{\text{BET}}=1100 \text{ m}^2/\text{g}$

C42

Pore volume, cc/g

Pore size, nm

micropores
Syntesis protocol:

Pd nanoparticles were obtained using saturation of activated at 250°C microporous carbon with tetrachloropalladous acid - acetone (1:2) solution and reduction procedures in H₂/Ar flow at 200°C for 4 hours. The Pd content (EDX data) was about 11 wt.%.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic %</th>
<th>Wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>90.9</td>
<td>80.0</td>
</tr>
<tr>
<td>O</td>
<td>6.8</td>
<td>7.9</td>
</tr>
<tr>
<td>Al</td>
<td>0.4</td>
<td>0.8</td>
</tr>
<tr>
<td>Si</td>
<td>0.1</td>
<td>0.3</td>
</tr>
<tr>
<td>Cl</td>
<td>0.3</td>
<td>0.7</td>
</tr>
<tr>
<td>Pd</td>
<td>1.5</td>
<td>11.3</td>
</tr>
</tbody>
</table>

SEM images and EDX data of Pd-doped carbon
Pd-clusters in porous carbon matrix

**Synthesis protocol:**
Pd nanoparticles were obtained using saturation of previously activated at 250°C microporous carbon with tetrachloropalladous acid - acetone (1:2) and reduction procedures in H₂/Ar flow at 200°C for 4 hours. The Pd content (XRF data) was about 9-11 wt.%.

Average size of Pd clusters (XRD data) was about 1.5-1.7 nm.

**Fig. 1.** XRD pattern and pore-size distribution of carbon matrix and Pd-doped carbon
Pd-clusters in porous carbon matrix

Fig. 1. TEM images of Pd-doped carbon
Fig. 1. Adsorption-desorption isotherm and Raman spectra of Pd-doped carbon
**Synthesis protocol:**
Activated NaY zeolite was mixed with an nickelocene Ni(C₅H₅)₂ and heated at 130°C for 10 h to enable Ni(C₅H₅)₂ sublimation and adsorption in the zeolite pores. The Ni(C₅H₅)₂ adsorbing zeolite was exposed to ultraviolet light at room temperature for 3-5 days to organic ligand decomposion. The material was reduced under Ar/H₂ flow at 300°C.

**Syntesis protocol:**
Three ion exchange procedure using Nickel Chloride solution, reduction procedures in H₂/Ar flow at 200°C for 4 hours

Final Ni content is about 18.5 mass %

XRD data
No traces of X-ray crystal nickel-containing phases were observed.

**Syntesis protocol:**
Three ion exchange procedure using \((\text{NH}_3)_4\text{Cl}_2\text{Pd}\) aqueous solution, reduction procedures in H₂/Ar flow at 200°C for 4 hours

Final Pd content is about 14.0-14.5 mass %

Average particles size of Pd is about 11-12 nm
**PdNi-clusters in zeolite matrix**

**Synthesis protocol:**
S7a (Pd-Ni) NaY – two ion exchanges with tetraamin palladium dichloride and one exchanges with nickel acetate
S7b (Ni-Pd) NaY – two ion exchanges with nickel acetate and one exchanges with tetraamin palladium dichloride

**Graphs and data:**

- **S7A (PdNi:NaY)**
  - Ni content: 4.9 mass %
  - Pd content: 15 mass %
  - After reduction

- **S7B (NiPd:NaY)**
  - Ni content: 15 mass %
  - Pd content: 7.5 mass %
  - After reduction

**Observations:**
- Only Pd (15-19 nm), nickel particles too small
- The phase of metallic Pd (16-20 nm) and nickel-palladium intermetalide (6-10 nm) were observed

**Synthesis protocol details:**
- **S7a (Pd-Ni) NaY**: Two ion exchanges with tetraamin palladium dichloride and one exchange with nickel acetate.
- **S7b (Ni-Pd) NaY**: Two ion exchanges with nickel acetate and one exchange with tetraamin palladium dichloride.
The NaY zeolite was used as a template for adsorption and decomposition of a sublimated organometallic compound (tetraamine palladium chloride and nickelocene). Reduction procedures in Ar/H2 flow were performed at 200, 300 and 350°C. No traces of Pd or Ni-containing phases were observed.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pd, mass %</th>
<th>Ni, mass %</th>
<th>Cl, mass %</th>
</tr>
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<tbody>
<tr>
<td>S53</td>
<td>1.0</td>
<td>13.6</td>
<td>5.0</td>
</tr>
<tr>
<td>S53-200</td>
<td>0.3</td>
<td>7.0</td>
<td>4.1</td>
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<tr>
<td>S53-300</td>
<td>0.2</td>
<td>8.0</td>
<td>1.5</td>
</tr>
<tr>
<td>S53-350</td>
<td>0.2</td>
<td>12.0</td>
<td>1.8</td>
</tr>
</tbody>
</table>

**Synthesis protocol:**
The evolution of pore structure for PdNi-doped zeolite (S53 sample)
Synthesis protocol:
Two stages:
1. Activated carbon was used as a template for adsorption and decomposition of nickelocene with reduction procedures in Ar/H2 flow at 300°C.
2. Ni-doped carbon was saturated with tetraamine palladium chloride solution reduced in Ar/H2 flow at 200°C.
Pd-clusters in SBA-15 silica

Pore volume, cc/g

SBA-15

Pore size, nm

2 4 6

0.00
0.01
0.02
0.03
0.04
0.05
0.06
0.07

SBA-15+Pd

SBA-15+Pd+cytric acid

SBA-15

Intensity, arb. units

2θ, °

10 20 30 40 50 60

S40-1-200

Pore size, nm

Pore volume, cc/g

0.00
0.01
0.02
0.03
0.04
0.05
0.06
0.07

S40-2-200

Pd- 1.6 wt.%

12 nm

1.4 nm

12 nm

S40-1-200

Pd- 1.2 wt.%

10 nm

10 nm
Conclusions

• The methods of experimental obtaining of ultrasmall Pd and Ni, and also combined Pd-Ni clusters were successfully approbated.

• Porous carbon and zeolite matrixes were used for synthesis Pd and Ni nanoparticles with the average size about 1.5 nm.

• The analysis of hydrogen adsorption/desorption for synthesized Ni- Pd- doped carbons and zeolites was realized.

• The testing of obtained systems as a perspective LENR active materials with nuclear active sites due generation of discrete breathers or fast phase transformation of quasicrystals was started.
Thank you for attention

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