Metalized aerogels for applications in catalysis

Background:
- The majority of heterogeneous catalysts are linked to inorganic carrier matrices.
- Relatively few aerogel matrices are being used; examples are predominantly restricted to gas-phase reactions.

Advantages of organic aerogel matrices:
- Tailored (hierarchical) porosity allows for an optimization of reagent flow.
- Different solvent systems are feasible when compared to inorganic carrier systems.
- Sustainable Feedstocks may be used.
- Redox-active aerogels backbones may facilitate electroless metal deposition.

Electroless plating:
- Compared to nanoparticle loading, a more film-like metal coating is possible.
- Catalyst bleeding should be less likely compared to nanoparticle loading because of chemical matrix-metal interaction.

Results

Preparation of wet gels:
- Resorcinol-formaldehyde (RF) Aerogels were prepared by sequential sol-gel process followed by aging in an oven.
- Cellulose-based gels (CA) were obtained by reversible dissolution with salt melt hydrates.

Advantages of (electroless) plating methods:
- Use of aerogels as matrix for electroless plating of metals.
- Implementation of (bio)organic aerogels as matrices in heterogeneous catalysis.
- Further applications of metalized aerogels (thermal management (e.g. heat pipes/heat pumps) and sensors).

Electroless plating:
- Plating was achieved in two steps: a) seeding with metal nanoparticles/sensitizing with Sn(II) and b) plating with metal salt/chemical reductant (e.g. tartrate).
- Final drying (RF: ambient conditions; cellulose: supercritical CO2) afforded metalized aerogels.

Table 1: Properties of aerogel metal composites

<table>
<thead>
<tr>
<th>Properties</th>
<th>Envelope density [g/cm³]</th>
<th>Skeletal density [g/cm³]</th>
<th>Porosity [%]</th>
<th>Specific surface area [m²/g]</th>
<th>Gas permeability [μm]</th>
<th>Thermal conductivity (Hot Disk) [mW/m*K]</th>
<th>Compressive modulus E' (DMA, 1Hz) [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF</td>
<td>0.2910</td>
<td>1.5012</td>
<td>80.1</td>
<td>&lt; 1</td>
<td>8.08</td>
<td>70</td>
<td>4.28</td>
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<tr>
<td>RF-Ag</td>
<td>0.6072</td>
<td>3.1283</td>
<td>78.4</td>
<td>1.19</td>
<td>1.88</td>
<td>205</td>
<td>15.51</td>
</tr>
<tr>
<td>RF-Au</td>
<td>0.6202</td>
<td>2.7871</td>
<td>77.9</td>
<td>&lt; 1</td>
<td>3.34</td>
<td>124</td>
<td>15.07</td>
</tr>
<tr>
<td>RF-Pt</td>
<td>0.6386</td>
<td>3.3025</td>
<td>77.2</td>
<td>0.53</td>
<td>3.07</td>
<td>83</td>
<td>14.68</td>
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<tr>
<td>RF-NB</td>
<td>0.6990</td>
<td>3.1298</td>
<td>75.1</td>
<td>1.15</td>
<td>2.87</td>
<td>87</td>
<td>19.48</td>
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<tr>
<td>CA (3 wt.%)</td>
<td>0.0571</td>
<td>1.4547</td>
<td>96.2</td>
<td>192.13</td>
<td>0.465</td>
<td>32</td>
<td>4.30</td>
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<tr>
<td>CA-Ag</td>
<td>0.0930</td>
<td>2.2494</td>
<td>95.9</td>
<td>98.46</td>
<td>0.410</td>
<td>-</td>
<td>12.41</td>
</tr>
</tbody>
</table>

Preliminary catalytic test:
- Reduction of nitrophenol with CA-Ag composite:
  - Apparent rate kapp of ca. 1.10⁻⁵ s⁻¹ (high concentrations of NaBH₄; pseudo-1st order kinetics).
  - Comparable to colloidal Ag nanoparticles (kapp of ca. 2.10⁻⁵ s⁻¹).

Summary:
- Several metal aerogel composites were prepared using wet gels and electroless plating approach.
- Ag-plated cellulose gels show competitive performance in the reduction of nitrophenol.

Conclusions:
- Other late transition metals will be plated to both cellulose and resorcinol-formaldehyde gels.
- Based on the initial results in catalysis, further studies on synthetically useful reactions (e.g. hydrogenations, cross-coupling reactions) are planned.

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References

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Outlook:
- Other late transition metals will be plated to both cellulose and resorcinol-formaldehyde gels.