Silica Supported Dilute Limit Alloy Nanoparticles by Strong Electrostatic Adsorption

Leandro De Castro, Anhua Dong, Abolfazl Shakouri, Christopher Williams, John R Regalbuto

Southeastern Catalysis Society
18th Annual Fall Symposium
Crowne Plaza, Knoxville, TN
Outline:

- Introduction
- Review of Literature
- Objective and Significance of the Study
- Methodology
- Results & Discussion
- Conclusions
Introduction

• Recent synthesis of supported metal catalyst aims to not only maximize noble metal utilization but also to exploit the unique intrinsic electronic differences and binding capacities of catalyst arising from various forms ranging from single atoms to clusters and to nanoparticles.

• The addition of another metal to form bimetallic catalyst have shown improvements in catalyst activity and selectivity towards a specific type of reactions.

• In trying to achieve the desired catalyst characteristics, as predicted by computational technique, various synthesis methods are being developed and applied.
Review of Literature — Synthesis

- Simultaneous strong electrostatic adsorption (co-SEA) have been applied to synthesized ultra-small (<1nm) homogeneously dispersed NPs with well mixed bimetallic alloy.

- Deposition of palladium on supported copper nanoparticles using galvanic replacement method to synthesize single atom alloy.

\[ \text{Cu} + \text{Pd}^{2+} \]

- Sequential reduction method (same as GR) was used to add trace amount (0.4%at) of palladium into pre-formed Au nanoparticles.

Fig. 3. Atomically resolved Z-contrast images showing NP speckling of alloys. (A and B) Pt-Co and Pt-Cu, separated by two rows in the table of elements. (C to E) Pd-Ni, Pd-Cu, and Pt-Pd, separated by one row. (F) Cu-Co, in the same row. Scale bars, 5 nm.
**Review of Literature — Characterization by CO-FTIR**

**CO Adsorption on 1%Pd/SiO₂**


<table>
<thead>
<tr>
<th>Species</th>
<th>Linear, Pd-CO</th>
<th>Two-Fold Pd₂-CO</th>
<th>Three-Fold Pd₃-CO</th>
<th>Three-fold with Dipole-dipole coupling</th>
<th>Three-Fold Pd₃-CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavenumber, cm⁻¹</td>
<td>2078</td>
<td>1948</td>
<td>1889</td>
<td>1830</td>
<td>1815</td>
</tr>
<tr>
<td>Conditions</td>
<td>50-1000 ppm CO, 90°C at Equilibrium</td>
<td>50 ppm CO, 90°C at Equilibrium</td>
<td>25 ppm CO, 90°C at Equilibrium</td>
<td>10 ppm CO (low) 90°C at equilibrium</td>
<td></td>
</tr>
<tr>
<td>Characteristic</td>
<td>On set of linear CO</td>
<td>1948 assigned to two-fold sites</td>
<td>1815 is also present</td>
<td>Shift in wavenumber to a higher value due to dipole-dipole coupling</td>
<td>Broad band</td>
</tr>
<tr>
<td>Current Study, monometallic</td>
<td>2080, 2056</td>
<td>1944</td>
<td>1901</td>
<td>1847</td>
<td></td>
</tr>
</tbody>
</table>

*Broad band coordinatively saturated Pd surface sites such as (111, 100)*
Review of Literature – Characterization by CO-FTIR

CO Adsorption on Cu/SiO2


<table>
<thead>
<tr>
<th>Species</th>
<th>Cu$^0$–CO, Cu$^+$–CO band</th>
<th>Cu-(CO)$_2$, dicarbonyl Species B</th>
<th>Cu-CO, monocarbonyls, Species A</th>
<th>Cu-(CO)$_2$ Dicarboxyls</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavenumber, cm$^{-1}$</td>
<td>2129</td>
<td>2045</td>
<td>2018</td>
<td>2003</td>
</tr>
<tr>
<td>Conditions</td>
<td>appears after Prolong CO exposure</td>
<td>sample reduced at 573 K,</td>
<td>samples reduced at 673 K</td>
<td></td>
</tr>
<tr>
<td>Characteristic</td>
<td>Decrease in intensity with decreasing CO</td>
<td>with a lower frequency shoulder, decrease in intensity of the principal Cu$^0$–CO , Blue Shifted</td>
<td>decrease in intensity of the principal Cu$^0$–CO band, Appears at the expense of Species B</td>
<td></td>
</tr>
<tr>
<td>Observed Peak</td>
<td>2125</td>
<td></td>
<td>2012</td>
<td></td>
</tr>
</tbody>
</table>
Review of Literature – Characterization by CO-FTIR

CO adsorption on Ru/SiO₂


<table>
<thead>
<tr>
<th>Adsorption Band</th>
<th>HF1 (High Frequency 1)</th>
<th>HF2 (High Frequency 2)</th>
<th>LF (Low Frequency)</th>
<th>Bridge-Bonded CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavenumber range (cm⁻¹)</td>
<td>2120-2156</td>
<td>2060-2110</td>
<td>2000-2060</td>
<td>1866,1988</td>
</tr>
<tr>
<td>Adsorbed CO Species</td>
<td>Type II Carbonyls</td>
<td>Type III Carbonyls</td>
<td>Type I carbonyls</td>
<td>Bridge</td>
</tr>
<tr>
<td></td>
<td>Ruⁿ⁺-(CO)ₓ</td>
<td>Ruⁿ⁺-(CO)₂</td>
<td>Ru⁰-CO</td>
<td>Ru₂-(CO)</td>
</tr>
</tbody>
</table>
Review of Literature — Applications


- Ni$_{0.01}$Cu NPs lowers the barrier of C-H bond activation to improve catalytic activity of Cu for ethanol dehydrogenation. (Shan, J., Liu, J., Li, M., Lustig, S., Lee, S., & Flytzani-Stephanopoulos, M. (2018). Applied Catalysis B: Environmental, 226, 534–543)

- Selective partial hydrogenation of 1,3-butadiene using Pt$_{0.2}$Cu$_{12}$/Al$_2$O$_3$ to butene to increase the purity of alkenes feedstock used in polymerization. (Lucci, F. R., Liu, J., Marcinkowski, M. D., Yang, M., Allard, L. F., Flytzani-Stephanopoulos, M., & Sykes, E. C. H. (2015). Nature Communications, 6, 1–8.)
Why use Strong Electrostatic Adsorption?

Advantages of SEA:
• Deposition thru adsorption of metal complex with strong attraction to the support prevents the formation of larger particle size during the reduction process.
• Simple method which could be extended to Charged Enhanced Dry Impregnation

Challenges in using co-SEA
• Stability of metal complex on surface during co-adsorption (Ammonia Environment for ammine complex stability)
• Predictability of bimetallic ratio of final supported metal catalyst. (Metal Complex concentration within one monolayer of maximum surface density)

XRD Plot of Silica-Supported Bimetallic Pd and Cu with varying molar ratios using co-Dry Impregnation and co-SEA Synthesis method
Objective & Significance of the work:

• **Objective:**
  
  To synthesize and characterize supported bimetallic alloy at dilute limit using the method of strong electrostatic adsorption.

  To evaluate catalyst activity and selectivity on promising catalytic reactions involving Dilute Limit Alloy.

• **Significance:**
  
  A generalizable method of preparing dilute limit alloy of one metal (precious) in another metal that is simpler without the limitation of reduction potential compatibility.

  Question: Can we make a dilute limit alloy via co-SEA method?

• **Limitations**

  Metal loading is dependent on the available surface density of the support for strong electrostatic adsorption.

  Requires an oppositely charge and stable metal complex precursors from that of the support
Methodology:

• Extending the method of co-SEA to dilution limit of one or two atoms in a crystallite of 30 or 40 atoms. The synthesis of various combinations of representative metals (Ru, Pd, Pt, Au, Ni, Co, and Cu) on high surface area amorphous silica were prepared.

• Catalyst characterization includes using high sensitivity powder x-ray diffraction, aberration-corrected electron microscopy, temperature programmed reduction, X-ray photoelectron spectroscopy and FTIR spectroscopy. Catalyst activity will be tested on reactions requiring enhanced selectivity.
Methodology:

Charged metal precursors are strongly adsorbed onto oppositely charged oxide or carbon surfaces by controlling the pH relative to the surface point of zero charge (PZC)

\[ \text{pH} < \text{PZC} \quad \text{protonates} \]

\[ \text{pH} > \text{PZC} \quad \text{deprotonates} \]

Fumed Silica

\[ \text{PZC} = 3.6 \]

\[ \text{pH} = 12 \]

\[ \begin{align*}
\text{M}_1 \quad [\text{Pd(NH}_3)_4\text{]}^{2+} \\
[\text{Ni(NH}_3)_6\text{]}^{2+} \\
[\text{Cu(NH}_3)_6\text{]}^{2+} \\
[\text{Co(NH}_3)_6\text{]}^{2+} \\
[\text{Au(en)}_2\text{]}^{3+}
\end{align*} \]
## Methodology: co-SEA Synthesis Condition

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Surface Area Support</td>
<td>Amorphous Silica (Aerosil® 300)</td>
</tr>
<tr>
<td>Support Surface Area</td>
<td>~315 m²/g</td>
</tr>
<tr>
<td>Surface Loading for SEA</td>
<td>1000 m²/L</td>
</tr>
<tr>
<td>Initial pH</td>
<td>12</td>
</tr>
<tr>
<td>Adsorption time</td>
<td>15 mins</td>
</tr>
<tr>
<td>Shaking speed</td>
<td>120 rpm</td>
</tr>
<tr>
<td>Metal Precursors</td>
<td>Metal Ammine Complexes</td>
</tr>
<tr>
<td>Metal Complex Total Concentration</td>
<td>~ 1 μmole/m²</td>
</tr>
<tr>
<td>Desired Metal Molar Ratios</td>
<td>1:30 (typical)</td>
</tr>
<tr>
<td>Drying Conditions</td>
<td>Overnight RT drying + 4 hrs @120°C in muffle furnace</td>
</tr>
<tr>
<td>Reduction condition</td>
<td>1 hr at 400°C, 5C/min Ramp Rate under 20%H₂/80%N₂ Gas</td>
</tr>
</tbody>
</table>
# Results:

As Synthesized Dilute Limit Alloy Catalyst

<table>
<thead>
<tr>
<th>Metal 1</th>
<th>Metal 2</th>
<th>As Synthesized Catalyst (wt%)</th>
<th>Molar Ratio (M2/M1)</th>
<th>Total Surface Density (µmole/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Palladium</strong></td>
<td><strong>Gold</strong></td>
<td>0.05%Pd2.4%Au/SiO₂</td>
<td>28</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td><strong>Copper</strong></td>
<td>0.09%Pd2.02%Cu/SiO₂</td>
<td>38</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td><strong>Cobalt</strong></td>
<td>0.08%Pd1.59%Co/SiO₂</td>
<td>38</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td><strong>Nickel</strong></td>
<td>0.09%Pd1.52%Ni/SiO₂</td>
<td>29</td>
<td>0.9</td>
</tr>
<tr>
<td><strong>Platinum</strong></td>
<td><strong>Copper</strong></td>
<td>0.16%Pt2.14%Cu/SiO₂</td>
<td>40</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td><strong>Cobalt</strong></td>
<td>0.11%Pt1.76%Co/SiO₂</td>
<td>54</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td><strong>Nickel</strong></td>
<td>0.18%Pt1.60%Ni/SiO₂</td>
<td>29</td>
<td>0.9</td>
</tr>
<tr>
<td><strong>Ruthenium</strong></td>
<td><strong>Copper</strong></td>
<td>0.07%Ru2.11%Cu/SiO₂</td>
<td>50</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td><strong>Cobalt</strong></td>
<td>0.08%Ru1.75%Co/SiO₂</td>
<td>36</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td><strong>Nickel</strong></td>
<td>0.10%Ru1.64%Ni/SiO₂</td>
<td>29</td>
<td>0.9</td>
</tr>
</tbody>
</table>
Results:

XRD Pattern for Dilute Limit Alloy Bimetallic Catalyst

No visible sharp peak for large nanoparticles.
Results:

TPR Profile of Dried SEA samples of Pt, Cu, and PtCu on Amorphous Silica Support

- Significant decrease of Cu reduction T even with very dilute amount of Pt (1/81)
TPR profile of Pd-X Bimetallic up to Dilute Limit

- Lowering of copper reduction peak with dilute amount Palladium
- Lowering of cobalt reduction peak with dilute amount Palladium
- Lowering of nickel reduction peak with dilute amount Palladium
Results: TPR Profile of Monometallic and Bimetallic at Dilute Limit

Palladium | Platinum | Ruthenium

Copper | Cobalt | Nickel

• Generally, the addition of dilute amount of palladium, platinum or ruthenium lowers the reduction T of the abundant metal
CO-FTIR Spectra Analysis for Silica-Supported Dilute Limit Alloy of Palladium on Gold

- 0.09%Pd/\text{SiO}_2
- 0.09%Pd2.4%Au (1/14)

- Linear CO appears to exist on a variety of sites
- Linear /bridged ratio increases with dilution
- Linear CO peak shifted to a lower wavenumber sites
Results: CO-FTIR Spectra Analysis for Silica-Supported Dilute Limit Alloy of Palladium on Gold

- Positions of linear CO becomes stable
- Linear/bridged ratio continues to increases with dilution
Results: Area Ratio of Linear to Bridge CO adsorption vs Pd/Au Ratio

Increasing Linear/Bridge Ratio
**Results:**

A significant decrease in intensity of the bridged CO region was observed with the dilute limit alloy of Pd on Cu.

The same shift in linear Pd-CO peak to a lower wavenumber.

No Shift of Copper CO adsorption peak.

**L:** Linear Pd-CO: 2078 cm\(^{-1}\)

**B:** di-coordinated, bridging CO, Pd\(_2\)-CO:1948,1970 cm\(^{-1}\)

**H:** triply bridging CO, Pd\(_3\)-CO : 1815,1830,1889 cm\(^{-1}\)
Pd, Cu and PdCu CO-FTIR SPECTRA (N2 Purged)

- 0.09\%Pd/SiO\textsubscript{2}
- 0.11\%Pd\textsubscript{2.35}\%Cu/SiO\textsubscript{2} (1/36)
- 2.38\%Cu/SiO\textsubscript{2}

Absorbance a.u.

Wavenumber, cm \textsuperscript{-1}
**Results:**

CO-FTIR Spectra of Silica Supported Dilute Limit Alloy of Palladium on Cobalt

CO-FTIR Spectra of Silica Supported Dilute Limit Alloy of Palladium on Nickel

- Green line: 0.09%Pd, 1.52%Ni (1/29)
- Blue line: 0.09%Pd
- Yellow line: 1.43%Ni
Results:

CO-FTIR Spectra of Silica Supported Dilute Limit Alloy of Platinum on Copper

CO-FTIR Spectra of Silica Supported Dilute Limit Alloy of Platinum on Cobalt

CO-FTIR Spectra of Silica Supported Dilute Limit Alloy of Platinum on Nickel

- 0.18%Pt 1.60%Ni (1/29)
- 0.21%Pt/SiO2
- 1.43%Ni
**Results:**

CO-FTIR Spectra of Silica Supported Dilute Limit Alloy of Ruthenium on Copper

CO-FTIR Spectra of Silica Supported Dilute Limit Alloy of Ruthenium on Cobalt

CO-FTIR Spectra of Silica Supported Dilute Limit Alloy of Ruthenium on Nickel

- Green line: 0.10%Ru1.64%Ni (1/29)
- Blue line: 0.10%Ru/SiO2
- Orange line: 1.43%Ni

Wavenumber (cm$^{-1}$) vs. Absorbance
Results:

Fitted Cu/SiO₂ Spectra

<table>
<thead>
<tr>
<th>Center</th>
<th>Height</th>
<th>Area</th>
<th>FWHM</th>
</tr>
</thead>
<tbody>
<tr>
<td>1893</td>
<td>0.014</td>
<td>2.363</td>
<td>156</td>
</tr>
<tr>
<td>1991</td>
<td>0.045</td>
<td>4.165</td>
<td>86</td>
</tr>
<tr>
<td>2012</td>
<td>0.046</td>
<td>1.705</td>
<td>34</td>
</tr>
<tr>
<td>2115</td>
<td>0.014</td>
<td>0.716</td>
<td>47</td>
</tr>
<tr>
<td>2125</td>
<td>0.040</td>
<td>0.933</td>
<td>21</td>
</tr>
<tr>
<td>2157</td>
<td>0.002</td>
<td>0.076</td>
<td>30</td>
</tr>
</tbody>
</table>

2.38%Cu/SiO₂ Fitted Cu Spectra
Results:

Fitted Ru/SiO2 Spectra

<table>
<thead>
<tr>
<th>Center</th>
<th>Height</th>
<th>Area</th>
<th>FWHM</th>
</tr>
</thead>
<tbody>
<tr>
<td>1841</td>
<td>0.006</td>
<td>1.398</td>
<td>202</td>
</tr>
<tr>
<td>1970</td>
<td>0.041</td>
<td>3.749</td>
<td>86</td>
</tr>
<tr>
<td>2007</td>
<td>0.078</td>
<td>3.450</td>
<td>41</td>
</tr>
<tr>
<td>2038</td>
<td>0.150</td>
<td>5.243</td>
<td>33</td>
</tr>
<tr>
<td>2062</td>
<td>0.124</td>
<td>2.071</td>
<td>16</td>
</tr>
<tr>
<td>2078</td>
<td>0.077</td>
<td>1.660</td>
<td>20</td>
</tr>
<tr>
<td>2100</td>
<td>0.026</td>
<td>1.020</td>
<td>37</td>
</tr>
<tr>
<td>2126</td>
<td>0.004</td>
<td>0.074</td>
<td>18</td>
</tr>
<tr>
<td>2140</td>
<td>0.011</td>
<td>0.206</td>
<td>17</td>
</tr>
</tbody>
</table>
Results: What CO adsorption peaks would fit the Dilute Limit Alloy of RuCu/SiO₂?

Our Approach:
1. Properly identify monometallic CO adsorption peaks at three stages:
   - At the onset of CO Flow
   - At the saturated CO
   - After inert gas purging of CO
2. Use the identified peaks from monometallic and fit the dilute limit alloy spectra using the same center and FWHM of the monometallic
3. Peaks for linear-CO may imply single atom sites.
Conclusions and Future Work:

- The method of simultaneous strong electrostatic adsorption (co-SEA) can be utilized to synthesize bimetallic alloy catalyst to the dilute limit.
- XRD profile of dilute limit alloy catalyst shows ultrasmall nanoparticles comparable to the bimetallic alloy prepared in a 1:1 ratio.
- Generally, a decrease in reduction peak temperature of the abundant metal occur upon addition of dilute amount of palladium, platinum or ruthenium. This strongly suggest the proximity of the two metals.
- CO-FTIR spectra measurement of dilute limit alloy shows linear CO adsorption peak which for a dilute amount of Palladium, Platinum or Ruthenium on another metal provides evidence of possible isolated single atom.
- The shift in linear CO adsorption peak for the dilute bimetallic as compared with a monometallic implies the promotion of different sites for linear CO adsorption which may imply the presence of single atom.
- Deconvolution of CO-FTIR spectra of the corresponding monometallic will be utilized in analyzing CO-FTIR spectra of dilute limit alloy bimetallic.
- Corresponding STEM analysis of catalyst is needed to further characterize the samples.
- Catalyst activity using a model catalytic reaction will also be made.
Reference:

THANK YOU!

Leandro T. De Castro  
PhD Candidate, Department of Chemical Engineering  
University of South Carolina  
Assistant Professor (Study-Leave),  
Department of Chemical Engineering  
University of the Philippines Los Banos  
Philippines  
E-mail: Leandrod@email.sc.edu
QUESTIONS?