Bimetallic Pd-Cu Catalysts for CO₂ Hydrogenation to Methanol

X. Jiang1,2, N. Koizumi1, X. Guo1 and Chunshan Song1,2,3*

1Clean Fuels & Catalysis Program, PSU-DUT Joint Center for Energy Research, EMS Energy Institute
2John and Willie Leone Family Department of Energy and Mineral Engineering, The Pennsylvania State University, 209 Academic Projects Building, University Park, PA 16802, USA
3PSU-DUT Joint Center for Energy Research, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China
*csong@psu.edu

Introduction
Catalytic CO₂ hydrogenation for synthesis of alcohol and hydrocarbon has attracted significant attention recently as a way of recycling carbon resources [1]. In the past decades, most prior works focused on Cu-ZnO based catalysts and supported Pd catalysts to hydrogenate CO₂ to CH₃OH. Cu-Ni alloy was reported as active surface for catalytic CO/CO₂ hydrogenation to CH₃OH [2]. In addition, Nakamura et al. [3] demonstrated the importance of surface formed Cu-Zn alloy in active methanol synthesis from CO₂/H₂. The present work seeks to clarify if Pd and Cu combination could result in active catalysts as they form stable alloy after reduction [4]. A series of supported Pd-Cu catalysts with a wide range of Pd and Cu loadings were prepared using amorphous silica as support. CO₂ hydrogenation activity and selectivity were investigated under pressurized condition. In order to examine the structure-activity relationship for Pd-Cu catalysts, these catalysts were characterized by XRD, TEM, STEM/EDS, XPS, and H₂-TPD.

Materials and Methods
Amorphous silica (Davisil Grade 62, particle size = 75-250 × 10⁻⁵ m) was used as support. The bimetallic catalysts were prepared by coimpregnation method in acetone solution. For comparison, monometallic catalysts were prepared as well. CO₂ hydrogenation was performed in a fixed bed stainless-steel reactor. Prior to the reaction, the catalysts were reduced in a H₂ flow at 300 °C for 2 h. A premixed gas, 24 vol% CO₂/72 vol% H₂/4 vol% Ar (99.995 %), was fed into the reactor. Gaseous products were periodically sampled and analyzed by two online GCs equipped with TCD and FID detector, respectively. The catalysts are denoted as Pd(X)-Cu(Y)/SiO₂, where X and Y represent Pd and Cu loadings (support basis), respectively. Prior to the characterization, the catalysts were reduced in-situ and passivated by 1 vol% O₂ in He, and hereafter denoted as "reduced catalyst".

Results and Discussion
As compared in Table 1, CH₃OH formation rate over bimetallic catalyst is 2 times as much as the simple summation of those over monometallic catalysts. The effect of combining Pd and Cu was also investigated using catalysts with different Pd/(Pd+Cu) atomic ratios. As illustrated in Fig. 1 (right), CH₃OH formation rate exhibits volcano-like shape with the rise of Pd/(Pd+Cu) atomic ratio and maximizes within the range of 0.25-0.34 (Pd: 5.7-8.7 wt%), where Pd(5.7)-Cu(10)/SiO₂ yields 31 μmol g-cat⁻¹ h⁻¹. These observations indicate the combination of Pd and Cu leads to a significant bimetallic promotion on CH₃OH formation from CO₂ hydrogenation. The structural properties of reduced Pd(X)-Cu/SiO₂ catalysts were evaluated by X-ray diffraction measurements. As observed in Fig. 1 (left), the allowed Pd-Cu phase changes with different Pd/(Pd+Cu) atomic ratios. Less Pd (black) causes the formation of alloy PdCu along with Cu²⁺, while excessive Pd (blue) leads to PdCu and PdCu₃ together with Pd²⁺. Interestingly, pure alloy PdCu and PdCu₃ are found when Pd/Pd+Cu was at 0.34 (red). The alloy particle size of this sample is nano-sized and estimated to be ~5 nm.

Table 1. CO₂ hydrogenation activity over Pd-Cu/SiO₂ catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>CO₂ Conv. / %</th>
<th>Prod. Formation rate / μmol g⁻¹ h⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(5.7)/SiO₂</td>
<td>3.0</td>
<td>0.09</td>
</tr>
<tr>
<td>Cu(10)/SiO₂</td>
<td>2.8</td>
<td>0.05</td>
</tr>
<tr>
<td>Pd(5.7)-Cu(10)/SiO₂</td>
<td>6.7</td>
<td>0.28</td>
</tr>
</tbody>
</table>

* Reaction condition: 523 K, 4.1 MPa, and W/F=6.2 g-cat h⁻¹.

Correlating characterization results (XRD, TEM, STEM/EDS, XPS, and H₂-TPD) with CH₃OH promotion, Pd-Cu alloy formation is suggested to be a crucial factor for the observed bimetallic promotion.

Significance
The findings, alloy effect, would be of critical importance for developing new catalytic CO₂ hydrogenation process technology/catalysts and for fundamental understanding of chemistries involved in CO₂ hydrogenation to form methanol.

Figure 1. XRD patterns (Left) of reduced catalysts and change in CH₃OH formation rate (Right) as a function of Pd/(Pd+Cu) atomic ratio. Reaction condition: 523 K, 4.1 MPa, W/F=6.2 g-cat h⁻¹.

References