Hydrogenolysis of glycerol to 1,2-propanediol on copper core - porous silica shell - nanoparticles

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Introduction
Glycerol has become one of the top 12 building blocks of biorefinery. The hydrogenolysis of glycerol to 1,2-propanediol (shown in eq. 1) is one of the possibilities of glycerol utilization [1].

\[ C_3H_5(OH)_3 + H_2 \rightarrow \text{CH}_3\text{CH(OH)}\text{CH}_2\text{(OH)} + H_2O \]  

Copper-based catalysts are mostly often used for glycerol hydrogenolysis to produce 1,2-propanediol in the presence of high pressure hydrogen. In the literature, Cu/SiO\textsubscript{2} catalysts for glycerol hydrogenolysis were prepared by several different methods, including precipitation-gel, homogeneous-precipitation, heterogeneous deposition-precipitation, incipient wetness and ion-exchange.

For supported metal catalysts, applicable metal atom mobility appears at about T_m/3 (called Hutting temperature). The melting point of copper is 1357.77 K, therefore, copper atom mobility appears at 453K. Core-shell structure can be used to prevent the metal sintering of catalysts. Recently, we prepared palladium core - porous silica shell particles (Pd@SiO\textsubscript{2}) for catalyzing the hydrogenation of 4-carboxybenzaldehyde [2]. The palladium nanoparticles encapsulated in porous silica shell have been proved to be highly stable for CO oxidation [3].

In this work, hydrogenolysis of glycerol to 1,2-propanediol was studied over copper core - porous silica shell - nanoparticles (denoted as Cu@SiO\textsubscript{2}) for catalyzing the hydrogenolysis of 4-carboxybenzaldehyde [2]. The palladium nanoparticles encapsulated in porous silica shell have been proved to be highly stable for CO oxidation [3].

Materials and Methods
Cu@SiO\textsubscript{2} core-shell - particles with seven Cu/Si atomic ratios were prepared by coating silica onto the surface of Cu-PVP colloids, according to the well-known Stober method [2]. The Cu-PVP colloids were synthesized by chemical reduction of Cu\textsuperscript{2+} in an alkaline environment using formaldehyde as reducing agent and polyvinylpyrrolidone (PVP) as protecting agent. Catalysts were characterized with TEM, nitrogen adsorption, XRD, and temperature-programmed reduction.

Hydrogenolysis of glycerol to 1,2-propanediol was carried out with a 600 ml stirred reactor made of stainless steel with and without externally added hydrogen. In a typical run, a specific amount of glycerol, 1 g of Cu@SiO\textsubscript{2} core - shell particles prepared above, and methanol (total reaction solution= 50 g) were charged into the reactor, and the reaction mixture was then heated to the desired temperature. At the end of the reaction, the component compositions were determined with a high performance liquid chromatography.

Results and Discussion
Figures 1 and 2 show glycerol conversions and 1,2-propanediol (PDO) yields without and with externally added hydrogen (1000 psig), respectively. In Fig.1, the Cu@SiO\textsubscript{2} catalyst with a Cu/Si atomic ratio of 0.5 had the best 1,2-propanediol yield (79%) In Fig.2, the catalyst with a Cu/Si atomic ratio of 2 had the highest 1,2-propanediol yield (the yields were 86.8% and 96.6% at glycerol concentrations of 10 wt.% and 5 wt.%, respectively). Figure 3 shows the transmission electron micrographs of the reduced Cu@SiO\textsubscript{2} sample with Cu/Si atomic ratio of 0.5 (left) and 2 (right), indicating that copper particles were encapsulated in the silica shell.

![Figure 1](image1.png)
**Figure 1.** Effect of catalyst composition on conversion and yield at 5 wt.% glycerol (without externally added hydrogen).

![Figure 2](image2.png)
**Figure 2.** Effect of catalyst composition on conversion and yield at 10 wt.% glycerol (with 1000psig hydrogen).

![Figure 3](image3.png)
**Figure 3.** Transmission electron micrographs of Cu@SiO\textsubscript{2} core-shell-particles with Cu/Si atomic ratios of 0.5 (left) and 2 (right).

Significance
The hydrogenolysis of glycerol to 1,2-propanediol (PDO) was studied over a series of Cu@SiO\textsubscript{2} core - shell – catalysts. The structure can effectively reduce the copper sintering of catalysts. The highest 1,2-propanediol yield obtained was 96.5%, which occurred at a Cu/Si atomic ratio of 2.

References