Selective Catalytic Conversion of Glycerol by Au nanoparticles loaded PTA-functionalized Mesoporous Silica Materials

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Abstract: We reported a strategy for catalytic conversion of glycerol using gold-loaded mesoporous silica materials in the presence of hydrogen peroxide. Two kinds of silica materials were employed as supports for Au NPs (gold nanoparticles), eg, mesoporous SBA-15(⊥) with perpendicular nanochannels and pore-expanded mesoporous silica nanoparticles (exMSN), respectively. Phosphotungstic acid (PTA) was introduced into the silica nanochannels via post-modification and applied as a solid acid for efficiently catalyze the oxidative cleavage of glycerol. Overall, our Au@PTA-exMSN catalyst shows excellent selective catalysis ability to convert glycerol to formic acid with a high yield of 85%.

Keywords: Glycerol oxidation, phosphotungstic acid, mesoporous silica materials

1. Introduction

Glycerol is one of the main byproducts of biodiesel production. In recent years, an increasing amount of glycerol is produced during the biodiesel production, due to the rising consumption of biodiesel as an alternative fuel source. For the purpose of rational utilizes the overproduced glycerol, selective catalytic approaches are developed to convert glycerol into the economic benefit chemicals. However, variety oxidation products were obtained during glycerol catalysis, such as dihydroxyacetone, glyceraldehyde, oxalic acid, acetic acid, formic acid and so on. Moreover, Hutchings et al. demonstrated that gold nanoparticles can also achieve comparable catalytic efficiency with that of platinum or palladium catalysts in oxidation catalysis glycerol. Meanwhile, R. Wölfel et al. reported that Keggin-type $H_5PV_2Mo_{10}O_{40}$ polyoxometalate can be used as the catalyst for carbohydrate-based biomass transformation. Thus, we designed the Keggin-type catalyst with confined Au nanoparticles in phosphotungstic acid (PTA) modified mesoporous silica for selectivity oxidize glycerol.

2. Experimental

Two kinds of mesoporous silica materials, mesoporous SBA-15(⊥) with perpendicular nanochannels and pore-expanded mesoporous silica nanoparticles (exMSN) were modified with (3-aminopropyl) trimethoxysilane (APTMS) as the highly amino group on the silica surface, respectively. Then, phosphotungstic acid (PTA) was introduced into the silica nanochannels via post-modification. Subsequently, the Au NPs were deposited onto the mesoporous silica by UV-assisted photoreduction method. Then, products were rinsed with ethanol and collected by centrifugation. The as-prepared samples were labeled as Au@PTA-SBA-15(⊥) and Au@PTA-exMSN, respectively.

Glycerol oxidation catalytic experiments: mesoporous silica materials (10 mg) were suspended in a mixture of hydrogen peroxide and 5 mL (0.6 mol/L) glycerol aqueous solution under 80℃ for 24 h.

3. Results and discussion

The TEM micrographs of bare exMSN, bare SBA-15(⊥), Au@PTA-exMSN, and Au@PTA-SBA-15(⊥) are shown in Figure 1, respectively. As shown in Figure 1, after PTA modification and loading Au NPs, the mesoporous structure of Au@PTA-exMSN and Au@PTA-SBA-15(⊥) become inconspicuous, indicated that the pores of Au@PTA-exMSN and Au@PTA-SBA-15(⊥) are filled with PTA and Au NPs. As shown in Table 1, Au@PTA-exMSN can achieve higher formic acid (FA) selectivity (85%) than that of

Au@PTA-SBA-15(⊥)(33%). This was attributed to the higher specific surface area of PTA-exMSN compared with PTA-SBA-15(⊥), which can confine uniform Au NPs in the mesoporous pores and provide more active sites for the glycerol oxidation. In addition, the loading amount of tungsten would also influence C-C cleavage efficiency. Therefore, we demonstrated that Au@PTA-exMSN own excellent selectivity catalysis performance in glycerol oxidation.

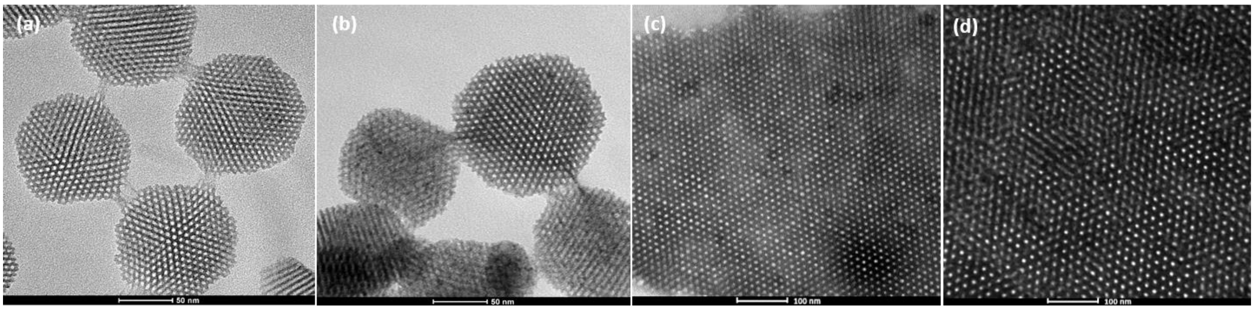

Figure 1. TEM images of (a)exMSN (b)Au@PTA-exMSN (c)SBA-15(⊥) (d)Au@PTA-SBA-15(⊥).

Table 1. Oxidation of glycerol using Au@PTA-exMSN and Au@PTA-SBA-15(⊥) catalysts.

	Catalyst	Glycerol : H_2O_2 molar ratio	FA selectivity	TON	Au%	W%
1	Au@PTA-exMSN	1:10	85%	2052	1.2%	52%
2	Au@PTA-SBA-15(⊥)	1:10	33%	2249	1.2%	49%
3	PTA-exMSN	1:10	-	-	-	87%
4	PTA-SBA-15(⊥)	1:10	-	-	-	74%

4. Conclusions

In summary, we have synthesized mesoporous Au@PTA-exMSN and Au@PTA-SBA-15(⊥) by photoreduction method. We investigate the catalysis ability of the samples by selectively oxidize glycerol. In our reaction system, we find that Au@PTA-exMSN achieve excellent catalysis activity for catalytic conversion glycerol to formic acid than that of Au@PTA-SBA-15(⊥), which benefit from the abundant active reaction sites. This work provides a novel strategy for efficient selective catalysis overproduced glycerol into economic benefit formic acid.

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