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Magnetically recoverable catalysts for cellulose conversion into ethylene- and propylene glycols

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PURPOSE OF THE ABSTRACT

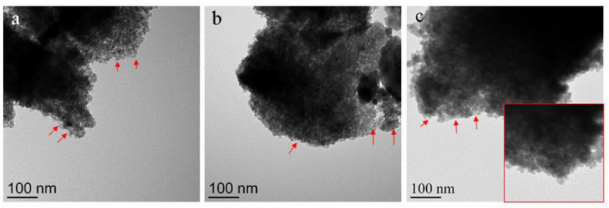
Biomass-derived polyols are emerging as promising building blocks for value-added chemicals [1]. In particular, ethylene glycol (EG) and propylene glycol (PG), are important precursors for pharmaceuticals, liquid fuels, emulsifiers, and surfactants [2, 3].

We developed magnetically recoverable catalysts containing 2 nm Ru nanoparticles (NPs) in mesoporous Fe3O4-SiO2 with the Ru nominal loading of 1, 3, and 5 wt.% (Figure 1). XPS showed that the surface of Ru NPs contains an equimolar ratio of Ru0 and Ru4+ species. All three catalysts exhibited excellent activities in cellulose hydrogenolysis to EG and PG, independent of the Ru loading, revealing that for all three compositions the Ru NP surface is accessible to reagents.

The EG and PG selectivities were shown to depend on temperature, reaction time, and Ru and Ca(OH)2 loadings. The highest selectivities to EG (19%) and PG (20%) were obtained for 50 min at 255 °?, 60 bar hydrogen pressure, 0.1167 mmol of Ru per 1 g of cellulose and 0.195 mole of Ca(OH)2 per 1 mole of cellulose. In these conditions the cellulose conversion was 100%. It is worth noting that the activities and selectivities of the Ru-Fe3O4-SiO2 catalysts described in this work significantly exceed those for the commercial Ru/C catalyst and Ru/MN-270 reported by some of us previously (table 1).

These factors and the excellent stability of the 5 % Ru-Fe3O4-SiO2 catalyst in the repeated use after magnetic recovery make this catalyst promising for industrial applications in biomass processing to value-added chemicals and biofuels.

FIGURES



Catalyst	Catalytic activity calculated as a gram of EG or PG per gram of the catalyst per hour, h^{-1}		Specific catalytic activity calculated as a gram of EG or PG per gram of Ru per hour, h^{-1}	
	EG	PG	EG	PG
1 % Ru-Fe_3O_4-SiO_2	0.12	0.23	13.39	25.66
3 % Ru-Fe_3O_4-SiO_2	0.36	0.68	13.72	25.69
5 % Ru-Fe_3O_4-SiO_2	0.62	1.18	13.84	27.02
5 % Ru-Fe_3O_4-SiO_2[b]	0.99	1.08	25.29	27.72
5 wt % Ru/C	0.30	0.48	6.05	9.66
3 wt % Ru/MN 270	0.22	0.38	7.51	12.71

[a] 0.1167 mmol Ru per 1 g of cellulose; 0.3 g of cellulose; 30 mL of H_2O; 255 °C; $P(H_2)$ 60 bar, 50 min;
[b] Addition of 0.195 mol of $Ca(OH)_2$ per 1 mol of cellulose.

FIGURE 1

Figure 1.

TEM images of the Ru-Fe3O4-SiO2 samples prepared with 1 wt.% (a), 3 wt.% (b), and 5 wt.% (c) of Ru. Inset in (c) shows a higher magnification image. Red arrows point to Ru NPs, whose electron contrast is higher than that of Fe3O4 NPs or SiO2.

FIGURE 2

Table 1.

Catalytic activities for EG and PG with the catalysts tested.a)

KEYWORDS

cellulose | glycoles | magnetic catalysts

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