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Influence of synthesis method of ZrO2-supported Au-Pt catalysts in aerobic base-free oxidation of glucose towards glucaric acid

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PURPOSE OF THE ABSTRACT

Glucaric acid is a top value-added chemical from biomass. Its potential applications are numerous such as detergents, food ingredients, corrosion inhibitors and medication.1 In place of the conventional production route by oxidation of glucose using nitric acid, glucaric acid could be produced using air and supported (bi)metallic catalysts.1-3 The aerobic oxidation of glucose to gluconic acid has been well investigated. On the other hand, the much slower consecutive oxidation of the primary alcohol to yield glucaric acid gives rise to a variety of overoxidation products resulting in poor yield of glucaric acid (Figure 1).

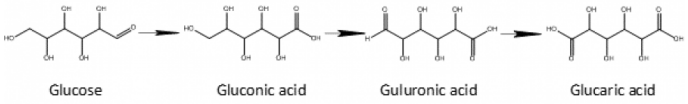
Figure 1

In this work, different methods of preparation of ZrO2 supported Au-Pt catalysts were studied: wet impregnation (WI) and reduction by NaBH4, 3 colloidal method (Colloid) with PVA as AuNPs stabilizer,4 and deposition precipitation (D-P) with urea.5 The Colloid and D-P methods were studied in 1 and 2 steps. The actual loading of both metals was determined by ICP-OES, the formation or not of a Au-Pt alloy was verified by XRD and TEM-EDX analysis. The catalysts were tested in batch reactor (glucose/metal molar ratio 80) or in trickle-bed reactor (100°C, 40 bar air, 0.25 M glucose). Substrate and products were analyzed by ion-chromatography

Table 1

Addition of a sonication step in an ultrasonic bath at 37 kHz during impregnation (WI-US) improved yield of glucaric acid up to 84%. Different times of sonication were investigated (Figure 2) and 1 h of treatment was sufficient.
Recycling of powder catalysts and tests in continuous reactor over pelleted catalysts demonstrated the stability of these catalysts.

FIGURES



Entry	Catalyst	method	Au/Pt mol ratio	alloy size (XRD) [nm]	max yield glucaric acid	reduction mode
1	2.7%Au-2.7%Pt	D-P 2 steps	1.02	7	4%	H_2
2	2.3%Au-2.2%Pt	D-P 1 step	1.04	9	25%	H_2
3	0.4%Au-2.8%Pt	Colloid 2 steps	0.14	-	15%	1st step $NaBH_4$ 2nd step H_2
4	0.7%Au-0.8%Pt	Colloid 1 step	0.81	10	50%	$NaBH_4$
5	3.1%Au-2.8%Pt	WI	1.10	8	63%	$NaBH_4$
6	3.8%Au-3.4%Pt	WI-US	1.11	9	**84%**	$NaBH_4$

Table 1 summarizes some characterization data and the maximum yield of glucaric acid obtained in batch experiments. The metal deposition efficiency was dependent on the method of preparation. XRD patterns of most of the bimetallic catalysts exhibited a main (111) diffraction peak between $2\theta = 38.2°$ (Au^0) and 39.7° (Pt^0) due to the formation of an alloy. The absence of alloy (entry 3) gave poor yield of glucaric acid, whereas the catalysts containing Au-Pt alloy exhibited different performances. The catalysts prepared by WI gave the most promising results therefore different Au/Pt ratio were investigated.

Figure 2 shows the maximum yield of glucaric acid as a function of Au/Pt ratio for catalysts prepared by WI method. The Au/Pt molar ratio was essential. A 63% yield of glucaric acid at optimum Au/Pt molar ratio of 1.1 was achieved.

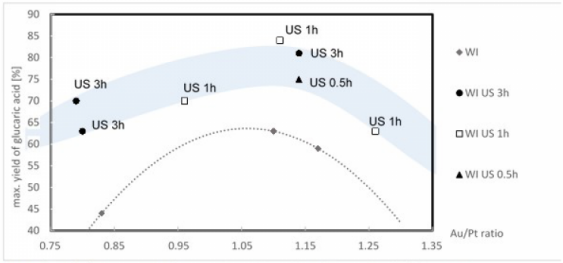


Figure 1 Effect of Au/Pt ratio and time of sonication during the catalyst synthesis on the yield of glucaric acid

FIGURE 1

Figure 1

Reaction pathway associated with the base-free oxidation of glucose to glucaric acid over Au-Pt/ZrO2 catalysts.

FIGURE 2

Table 1.

Characterization of Au-Pt/ZrO2 catalysts prepared by different methods and maximum yield of glucaric acid.

KEYWORDS

glucaric acid | bimetallic catalysts | base-free oxidation

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