Study of Au-based heterogeneous catalysts on glucose oxidation to gluconic acid

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With numerous applications in the pharmaceutical and polymer industries, global demand for gluconic and glucaric acid is predicted to increase the next decade while both are included in the list of the top 12 'hot' biobased chemicals [1]. They are produced by the cascade oxidation of glucose, currently performed biotechnologically, accounting for their small-scale production and increased price. Therefore, intensive research has been focused towards the development of a chemo catalytic system for their production. Particular efforts are directed towards the synthesis of a heterogeneous catalyst as the current methods involve either electrochemical or stoichiometric oxidation using undesirable reagents such as NaBr, NaOCl, mineral acids and also HNO₃ or KMnO₄ [2]. However, these technologies, suffer from the inherent drawbacks of homogeneous catalysts and generation of toxic co-products. In the aspect of heterogeneous catalysis, the main difficulty is the accomplishment of catalyst stability under the oxidation reaction parameters combined with high productivity of the desired product. The most studied heterogeneous catalysts include Au, Pt or Pd on different supports with O₂ as oxidant [3].

In the present work, with the aim of developing an efficient heterogeneously catalyzed glucose oxidation process, we studied both catalytic performance and stability of Au-based catalysts where Au was either supported on silica materials or added as a chemical component in a mixed oxide. More specifically, Au supported on a commercial SiO₂ and mesoporous MCM-41, obtained via sol-gel synthesis with surfactant under mild conditions, (Au/SiO₂ and Au/MCM-41 respectively) were synthesized following the urea method by using NaBH₄ as a reducing agent. For enhancing reaction activity and minimizing the use of Au, a mixed oxide comprising of low-cost oxidation metals, Ni₃Mn₂Au_{0.1}FeO, was also synthesized. The mixed oxide was derived from the respective layered double hydroxide (Ni₃Mn₂Au_{0.1}FeOH) synthesized with co-precipitation method by using nitric salts as metal precursors, sodium carbonate as an anion and NaOH as pH regulator. The final mixed oxide was obtained after calcination at 400°C.

Physicochemical characteristics of the catalysts were fully measured by ICP-OES, XRD, SEM, N_2 adsorption/desorption measurements, TPD experiments and in-situ pyFTIR. Depending on the nature of the support and whether Au was inserted in the mixed oxide, varied textural, porosity and surface characteristics were achieved (Table 1).

The synthesized catalysts were applied in glucose oxidation, using H_2O_2 and/or O_2 as oxidants, while the effect of the temperature and time were also studied. Under the studied conditions, all the catalysts tested showed increased selectivity towards gluconic acid reaching up to 50%. However, according to the results obtained, Au supported catalysts demonstrated superior stability compared to the mixed oxide comprising of Au.

	ICP-OES (%w.t.)				BET measurements			
Catalyst	Au	Ni	Fe	Mn	Total Surface Area	Total Pore volume	Textural Volume	Average Pore size
	(%wt.)				(m²/g)	(ml/g)		(nm)
Au/SiO ₂	1.2	-	-	-	311	0.746	0.024	9.0
Au/MCM-41	0.4	-	-	-	651	0.499	0.067	2.7
Ni3Mn2Au0.1FeO	4.1	38.1	12.0	23.5	74	0.543	0.337	50

Table 1. Chemical and porosity characteristics of Au catalysts

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References

- 1. T. Mehtio, M. Toivari, M. G. Wiebe, A. Harlin, M. Penttila, A. Koivula, Crit Rev Biotechnol 36 904 (2016).
- Z. Zhang, G. W. Huber, *Chem Soc Rev* 47 1351 (2018).
 J. Lee, B. Saha, D. G. Vlachos, *Green Chemistry* 18 3815 (2016).





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