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Catalytic Oxidation of Glucose to High Value Products Using Heterogeneous Catalysts

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1. INTRODUCTION

- ***Gluconic acid*** is a key renewable platform chemical due to its wide range of applications in biochemistry, biomedicine, food and polymer industries.
- ***Industrially*,** bio-based gluconic acid can be synthesized enzymatically via glucose conversion having however multiple disadvantages (enzymes deactivation, slow reaction rates, etc).
- ***Alternatively***, heterogeneous chemo-catalytic processes ***can overcome these drawbacks*.** The most promising catalysts studied are primarily noble metals (Au, Pd, Pt) supported on metal oxides, modified carbon materials and mesoporous silicas, using oxygen as oxidant.

2. AIM

- Study the ***catalytic performance of Au catalysts supported on silicas with variable porosity and structural characteristics*** for the selective ***oxidation of glucose to gluconic acid***.
- ***Optimization study (t***ime, temperature, pH) using the most effective catalyst.

2. METHOD

- **Commercial Supports**: SiO_2 provided from Sigma-Aldrich for comparison reasons
- **Synthesized mesoporous silicas**: MCM-41, HMS, SBA-15 with **self-assembly process** and the **sol-gel method** combined in some cases with the **hydrothermal method**
- **Au catalysts**: Au modification via polyvinyl alcohol (PVA)-protected method with in-situ parallel reduction by using $NaBH_4$ as a reducing agent (**Figure 1**)
- **Characterization:** All catalysts were characterized concerning their crystallinity (XRD) and porosity properties (N_2 porosimetry)

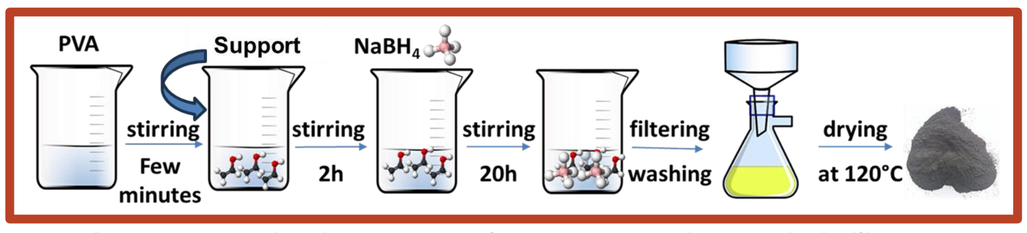


Figure 1: Synthesis of Au catalysts supported on varied silicas

- **Chemocatalytic conversion of glucose to gluconic acid**

Batch, stirred, autoclave reactor of 450mL

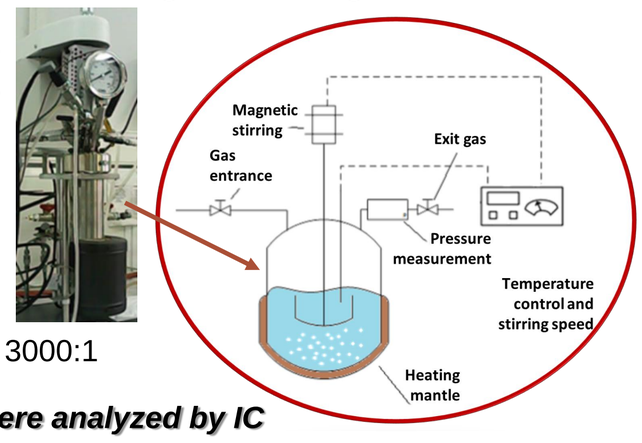
Oxidant: H_2O_2

Temperature: 80 °C

Time: 30 min

pH = 12

Glucose/ Au molar ratio = 3000:1



- The ***reaction products were analyzed by IC***
- **Leaching tests** on the liquid phase were applied with ICP-AES

3. RESULTS & DISCUSSION

3A. Catalyst Characterization

Table 1: Composition, porosity and crystallinity of catalysts

Substrates/ Catalysts	XRD	N_2 Porosimetry				ICP
	Au Crystal* (nm)	Surface Area (m^2/g)	Textural (mL/g)	Total Pore Volume (mL/g)	Pore Size (nm)	Au (% wt.)
SiO_2	-	310	0.01	0.74	9.0	-
$1Au/SiO_2$	41.2/ 43.4	310	0.19	0.79	9.0	0.90
MCM-41	-	927	0.04	0.62	2.0	-
1Au/MCM-41	39.1/ 31.5	776	0.05	0.62	2.0	0.95
SBA-15	-	619	0.03	0.66	5.7	-
1Au/SBA-15	29.9/ 33.6	597	0.03	0.69	5.7	0.85
HMS-T	-	801	0.76	1.55	2.5	-
1Au/HMS-T	23.3/ 17.3	704	0.61	1.36	2.5	0.68
HMS-N	-	956	0.45	0.79	2.2	-
1Au/HMS-N	25.4/ 23.0	895	0.29	1.04	2.2	0.72

* Crystallite size was calculated before/ after reaction by Scherrer equation

- The highest crystal size was noticed on the surface of commercial silica having also the lowest surface area.
- All mesoporous silicas exhibited ***high surface areas and well-organized pores***, confirming their successful synthesis.
- Among synthesized silicas***, Au deposition on the surface of HMS favors the formation of smaller crystal sizes*** compared to the mesoporous silicas with hexagonal pore structure (MCM-41 and SBA-15).

3B. Catalyst Screening

- ***All catalysts were active***, converting 50 – 60 % glucose to gluconic acid with sufficient selectivity and yield (**Figure 2**).
- ***All catalysts exhibited high stability, with no leaching during the process.***
- The ***best catalytic results were achieved with Au supported on HMS-T*** having the lower crystal size of 23 nm (**Table 1**), which mostly favored selectivity towards the desired product.

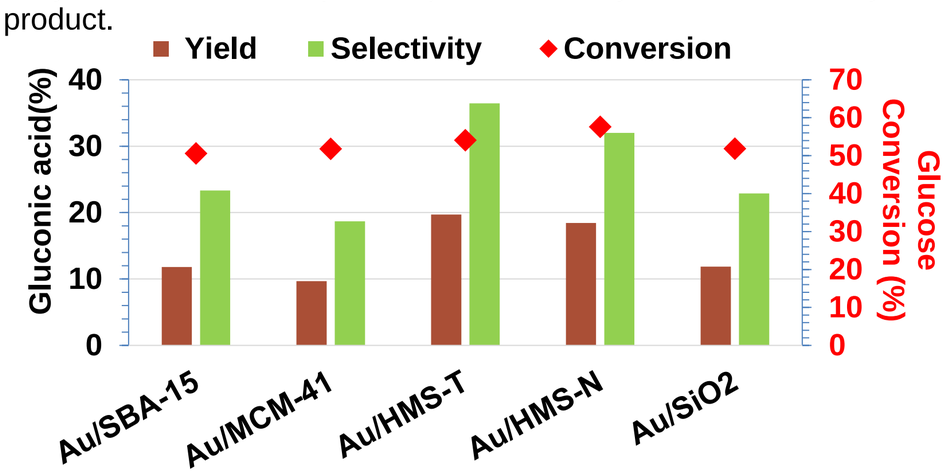


Figure 2: Screening of Au supported catalysts for glucose conversion to gluconic acid (Glucose 2 %w.t., H_2O_2 2.5 %w.t., Glucose/Au molar ratio: 3000/1, T=80°C, t=30min, pH=12)

3C. Optimization study over Au/HMS-T catalyst

- ***Increase in pH value*** favored both catalyst activity and selectivity (**Figure 3**).
- However, due to possible risk of catalyst degradation at high pH values, ***the optimal pH selected was 12.5.***

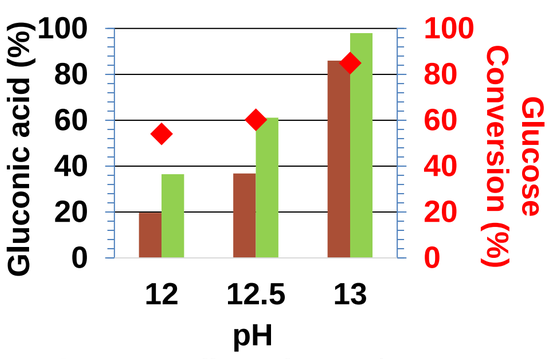


Figure 3: Effect of pH value (Glucose 2 %w.t., H_2O_2 2.5% w.t., Glucose/Au molar ratio: 3000/1, T=80 °C, t=30min)

- An increase in reaction temperature enhanced activity but ***reduced gluconic acid selectivity*** (**Figure 4**).
- ***The highest*** gluconic acid yield (45 %) and selectivity (94 %) were achieved ***at the lowest reaction temperature tested*** (60°C)

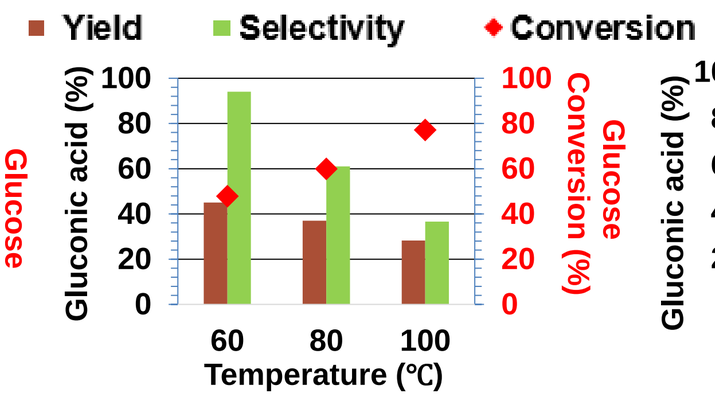


Figure 4: Effect of reaction temperature (Glucose 2% w.t., H_2O_2 2.5 % w.t., Glucose/Au molar ratio: 3000/1, t=30 min, pH=12.5)

- Reaction times up to 30 minutes presented similar results, also achieving ***the highest gluconic acid yield and selectivity.***

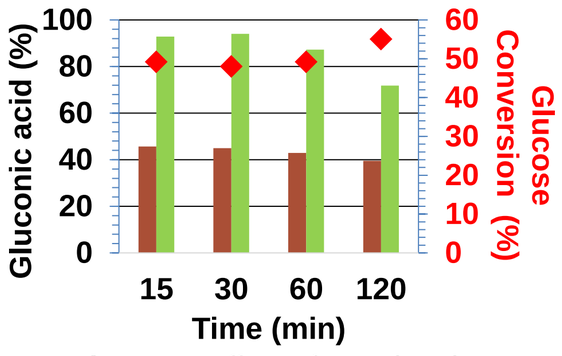


Figure 5: Effect of reaction time (Glucose 2% w.t., H2O2 2.5% w.t., Glucose/Au molar ratio: 3000/1, pH=12.5, T=60 °C)

4. CONCLUSIONS

- Deposition of Au on HMS structures favored the formation of smaller crystal size, which enhanced gluconic acid selectivity
- All synthesized catalysts exhibited ***excellent stability***, with no detectable leaching of Au during the reaction under hydrothermal conditions
- ***1Au/HMS-T*** proved the best performing stable catalyst with high gluconic acid selectivity and yield
- Under selected optimized conditions (pH 12.5, 60 °C, 30 min), glucose can be catalytically converted at 46 % to gluconic acid with 94 % selectivity over 1Au/HMS-T catalyst.