

A comparison of SiO_2 -, Cu-, and Ni-supported Au nanoparticles for selective glycerol oxidation to acetic acid*

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Introduction

We tested for the first time the efficiency of SiO_2 -, Cu-, and Ni-supported Au in deep glycerol oxidation in a diluted and viscous $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ liquid phase. Acetic acid (AA), the C_2 oxidate, was preferentially formed in such a system. High conversion (100%) and AA yields (90%) were observed for the sol-gel SiO_2 -suppported Au in diluted solutions. Although with the increase of glycerol concentration in the viscous liquid phase these values decreased to ca. 40% (conversion) and 20% (AA yield), the addition of acetonitrile improved the AA yield to ca. 40%, while the surfactants were found to be capable of a many-fold enhancement of the catalyst activity at the room temperature highly-viscous liquid phase. High performances were also observed for the bimetallic Au/Cu and Au/Ni catalysts obtained by nano-Au transfer; however, these catalysts were destroyed during the reaction by the Cu or Ni leaching effect.

Experimental methods

Nano-Au catalyst (20 mg, 0.1–10.0 μmol Au) was suspended in a mixture of 1.0 mL of 30% hydrogen peroxide (10 mmol H_2O_2) and 0.5 mL (0.5–13.6 mol/L) glycerol (Fisher BioReagents® – Glycerol For Molecular Biology) by sonication at room temperature for 10 min (RK 52 H, Bandolin Electronics, 35 kHz). Reagents were stirred at 770 rpm in a sealed tube (septa system) placed in a thermostated oil bath at 80 °C for 24 h. The resulted reaction mixture was centrifuged and decanted. The supernatant was dissolved into deuterated water and analyzed using ^1H and ^{13}C NMR. For quantitative determination of the reaction products we used an external standard procedure with a (NMR Coaxial Small Volume NMR Insert tubes from ARMAR Chemicals) hydroquinone as the reference substance. Additionally, the 2D COSY and HMQC methods were used to identify and quantify products. The spectra were recorded on Bruker Avance 400 or 500 spectrometers with TMS as the internal standard (400 MHz, ^1H , 101 MHz ^{13}C or 500

MHz, ^1H , 126 MHz ^{13}C) at room temperature. The signal from water was suppressed using 90 water-selective pulses (zgppwg). Optionally this oxidation procedure was modified by the addition of 1.0 mL acetonitrile (19.10 mmol) or surfactants: Sulforkanol (sodium laureth sulfate – SLES), Triton X-100, PEG 400, ca. (0.05 wt. %).

The results had an error of $\pm 2\%$ throughout the experiments. The formation of acetic acid was confirmed using spectroscopic techniques. Eqs. [1] to [3] were used to calculate conversion, product selectivity and yield, respectively.

$$\text{conversion (mol\%)} = (\text{initial moles of glycerol} - \text{final moles of glycerol}) / \text{initial moles of glycerol} \times 100 \quad [1]$$

$$\text{selectivity of products (mol\%)} = \text{percentage amount of product formed} / \text{the total percentage of all product formed} \times 100 \quad [2]$$

$$\text{yield (\%)} = \text{conversion of glycerol} \times \text{selectivity of desired product} / 100 \quad [3]$$

Results and discussion

We assumed that treatment of the concentrated glycerol solutions under mild conditions would potentially be a major advantage for processing waste glycerol. Intuitively, the glycerol concentration that influences the viscosity of a system should strongly control the glycerol contact with the catalyst surface. In practice, the catalytic reactions of glycerol in water solutions have been performed previously in a relatively diluted solutions, e.g., in the liquid phase: 0.6 mol/L (mol of glycerol per litre of the reaction mixture, if recalculated using data from the literature; glycerol to H_2O_2 molar ratio amounted to 1 : 4)¹⁾ or in the vapor phase: Ar/glycerol/ H_2O = 5 : 1 : 21²⁾ or $\text{N}_2/\text{H}_2\text{O}/\text{Gly}$ = 46/48/6³⁾.

In Table 1, we specified the performance of catalytic Au/ SiO_2 systems in the oxidation of glycerol in the diluted liquid phase; 0.2 mol/L glycerol, whereas glycerol to H_2O_2 molar ratio amounted to 1 : 37. For the new catalysts, i.e., SiO_2 -supported Au, both the conversion and selectivity of the process reached as high as 100% and 90 to 99% (Table 1, entries 1 and 3), respectively, while in these conditions, the Au/C system (Table 1, entry 7) provided much lower conversion (ca. 35%). AA (Au/ SiO_2) or glycolic acid (GA) and aldehyde (Au/C) were the main products observed for the reactions, respectively. The performance of the Au/C system, typically used for catalytic glycerol oxidation⁴⁾, compares well to the published data for the

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Table 1. Catalytic performance of SiO_2 and C supported Au NPs in diluted glycerol solutions at 80 °C^a

Catalyst	TON ^b	TOF ^b (h ⁻¹)	Conv. (mol%)	Selectivity to products (mol%)						Yield to AA (%)	
				GLAD	GA	TA	AA	FA	OS		
1	0.1% Au/SiO ₂	2660	111	100.0	2.2	0	0	90.0	4.9	2.9	90.0
2	1.0% Au/SiO ₂	201	8	75.5	1.6	1.8	1.3	84.3	0	11.0	63.7
3	1.0% Au/f-SiO ₂	266	11	100	0	0	0	99.3	0	0.7	99.3
4	2.0% Au/SiO ₂	125	5	94.3	2.2	0.3	0.4	92.5	0	4.6	87.2
5	5.0% Au/SiO ₂	45	2	84.4	1.3	3.2	0	90.9	0	4.6	76.7
6	10.0% Au/SiO ₂	23	1	86.0	0	0.7	0	94.0	0	5.3	80.8
7	1.0% Au/C	93	4	35.1	66.7	25.9	0	0	0	7.4	0

^a0.2 mol/L of glycerol in the reaction mixture (glycerol/H₂O₂ molar ratio 1 : 37), 20 mg of catalyst (0.1–10.0 µmol Au), 80 °C, 24 h, 770 rpm^bturnover number (TON) or turnover frequency (TOF) based on the total gold content in the material

GLAD – glycolaldehyde, GA – glycolic acid, TA – tartronic acid, AA – acetic acid, FA – formic acid, OS – others

Table 2. Catalytic performance of SiO_2 supported Au NPs in undiluted glycerol solutions at 60 °C with (+) and without (–) acetonitrile

Catalyst	CH ₃ CN	Conv. (mol%)	Conv. (mol%)	Selectivity to products (mol%)						Yield to AA (%)	
				GLAD	GA	TA	AA	FA	OS		
1	1.0% Au/SiO ₂	+ ^a	40.2	0	0	0	0	99.5	0	0.5	40.0
2	1.25% Au/f-SiO ₂	+ ^a	23.6	0	1.6	0	0	88.2	4.8	5.4	20.9
3	1.0% Au/SiO ₂	– ^b	14.9	0	2.9	0	0	91.4	0	5.7	13.6
4	1.25% Au/f-SiO ₂	– ^b	33.7	7.9	0	21.6	14.8	0.7	41.3	13.7	0.3

^a2.7 mol/L of glycerol in the reaction mixture (glycerol/H₂O₂/acetonitrile molar ratio 1 : 1.5 : 2.8), 20 mg catalyst (1.0–1.25 µmol Au), 60 °C, 24 h, 770 rpm^bglycerol: 4.5 mol/L (glycerol/H₂O₂ molar ratio 1 : 1.5)

GLA – glyceric acid, GA – glycolic acid, GLAD – glycolaldehyde, HPA – hydroxypyruvic acid, AA – acetic acid, FA – formic acid, OS – others

Table 3. Catalytic performance of 0.1% Au/SiO₂ at room temperature, if enhanced by surfactant addition

Surfactant	Conv. (mol%)	TON ^b	TOF ^b (h ⁻¹)	Selectivity (mol%)		Yield to AA (%)
				AA	OS	
Sulforokanol	8.8	5876.1	244.8	68.8	31.2	6.0
Triton X-100	7.9	5312.6	221.4	88.4	11.6	7.0
PEG 400	9.4	6278.5	261.6	80.6	19.4	7.6
None	4.7	3192.9	133.0	30.2	69.8	1.4

^a4.5 mol/L of glycerol in the reaction mixture (glycerol/H₂O₂ molar ratio 1 : 1.5) surfactant (0.05 wt.%), 25 °C, 24 h, 770 rpm^bturnover number (TON) or turnover frequency (TOF) based on the total gold content in the material

AA – acetic acid, OS – others

1% Au/C (0.6 mol/L glycerol to H₂O₂ molar ratio 1 : 4), which provides only slightly higher conversions of ca. 40%¹⁾.

In non-diluted glycerol solutions, the selectivity to AA can be increased (up to 99.5% selectivity at 40% conversion, 1.0% Au/SiO₂) under the addition of acetonitrile (Table 2). It is worth mentioning that the addition of acetonitrile allowed us to decrease the reaction temperature to 60 °C vs. 80 °C in acetonitrile-free conditions; however, a nominal glycerol concentration after the addition of acetonitrile was the lower 2.7 mol/L vs. ca. 4.5 mol/L in the acetonitrile-free conditions. Moreover, the addition of acetonitrile (Table 2, entries 2 (+) and 4 (–)) also increases the selectivity of the AA formation for the f-SiO₂-supported Au system (AA selectivity ca. 88% and AA yield ca. 21% with acetonitrile, vs. AA selectivity 0.7% and AA yield 0.3% without acetonitrile). Thus, we observed a decrease in conversion but an increase in AA selectivity for the reaction in the

acetonitrile/water solution. We proved that no changes occurred for the blind experiment with the catalysts heated in acetonitrile without glycerol (results not shown).

Thus far, the results of the exhaustive oxidation of glycerol indicated that catalyst availability is of major importance for the observed performance of the system. Below, we report the results of the experiments in which we tested possible applications of the surfactants to improve this feature (Table 3). We observed that a conversion and the yield of AA can be almost doubled at room temperature when Sulforokanol, PEG 400, or Triton X-100 was used as surfactants.

Conclusions

We observed that, within the complex network of possible reactions, a process of deep glycerol oxidation proceeded on Au/SiO₂ catalysts preferentially to acetic acid. The selectivity of glycerol oxidation to C₃ products

was investigated thoroughly. It is not a coincidence, because only C_3 oxygenates can form the single carbonous products of glycerol processing, while any oxidation to C_2 must also yield the C_1 oxygenate ($C_3 \rightarrow C_2 + C_1$). This means that, although the process can be fully selective, we obtain at least two products.

Thus, the reactivity to C_3 products has been well described, in contrast to the C_1 and C_2 products. Herein, we described the systems providing high selectivity to acetic acid, the C_2 glycerol oxygenate. High conversions (100%) and acetic acid yields (90–99%) were observed for the best catalysts in the diluted aqueous glycerol solutions. Although in a relatively viscous liquid phase these values decreased to ca. 40% and 20%, the addition of acetonitrile could improve the acetic acid yield to ca. 40%, while surfactants were found to be capable of a many-fold enhancement of the catalyst activity. However, this was relatively low at the room temperature highly-viscous liquid phase.

In summary, SiO_2 -supported Au NPs can form an interesting catalytic system for deep selective glycerol oxidation to acetic acid in undiluted viscous liquid solutions. This seems especially interesting for the processing of glycerol wastes.

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Conflicts of interest: none.

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