

# Article

# Catalytic oxidation of glycerol to tartronic acid over Au/HY catalyst under mild conditions



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### 1. Introduction

# As a major byproduct in biodiesel production, glycerol has received great attention with the rapid global development of biodiesel [1–5]. Glycerol has been recognized as an important biomass-based building block for valuable C3 molecules. The surplus of glycerol has inspired researchers to develop efficient methods to use glycerol [6–9]. Because glycerol is a highly functionalized molecule containing three hydroxyl groups, it is feasible to convert glycerol into valuable oxygenated derivatives via catalytic oxidation, such as tartronic acid (TARAC), glyceric acid (GLYA), and dihydroxyacetone (DIHA) [6,10,11]. Among these compounds, TARAC is a high value-added chemical that is widely used as a pharmaceutical and anti-corrosive protective agent, as well as for the monomer of biopolymers [12–15]. It is challenging and important to develop cost-efficient and environmentally friendly methods to oxidize

#### ABSTRACT

Gold nanoclusters or nanoparticles on various supports (CeO<sub>2</sub>, activated carbon, HY, REY, and NaY) were investigated for glycerol oxidation in the aqueous phase under mild conditions. Compared with other catalysts, Au/HY showed remarkable catalytic performance in forming dicarboxylic acid (tartronic acid) over the monocarboxylic acid (glyceric acid) or the C–C cleavage product (oxalic acid). Au/HY achieved 98% conversion of glycerol and 80% yield of tartronic acid at 60 °C under 0.3 MPa O<sub>2</sub>. Further characterization showed that the small size of Au clusters is the key factor for the high oxidation performance. In situ Fourier transform infrared spectroscopy revealed that glycerol was first transformed to glyceric acid, and then glyceric acid was directly oxidized to tartronic acid.

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glycerol into TARAC using oxygen as oxidant and water as solvent under mild conditions. However, little research has been reported on this topic.

Currently, supported precious metal catalysts are used in glycerol oxidation. Au/C, Pd/C, and Pt/C are effective for producing GLYA but inefficient for producing TARAC [16–22]. Recently, Zope et al. [17] employed an Au/TiO<sub>2</sub> catalyst for the oxidation of glycerol and achieved 100% conversion with 20% selectivity of sodium tartronate. Kimura et al. [14] reported that glycerol oxidation over Pd/Pt-based catalyst yielded 58% disodium tartronate. These studies indicate that the unsatisfactory yield of TARAC results from the difficulty in further oxidation of GLYA and the occurrence of C–C cleavage or decarboxylation. To achieve a high yield of TARAC, it is imperative to develop new efficient heterogeneous catalysts avoiding C–C cleavage or decarboxylation. It is also important to investigate the reaction pathway of dicarboxylic acid formation.

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In our previous study, we found that gold-based catalysts are effective for alcohol oxidation [23]. Moreover, we have successfully encapsulated 1-nm Au nanoclusters in the supercage of HY zeolite. Au/HY showed high efficiency in 5-hydroxymethyl-2-furfural oxidation, achieving 99% yield of 2,5furandicarboxylic acid [24]. In this study, inspired by its excellent performance in converting hydroxyl groups to carboxyl groups, we investigated supported Au catalysts for the oxidation of glycerol. We compared the catalytic performance of Au on different supports, investigated the oxidation pathway, and explored the conversion process of GLYA to TARAC.

# 2. Experimental

# 2.1. Catalyst preparation and characterization

The catalysts were prepared based on the methods in our previous work [24]. A certain amount of support was added to HAuCl<sub>4</sub> aqueous solution (50 mL, 0.1 mol/L). After stirring at 60 °C for 2 h, sodium citrate solution was added. The obtained mixture was stirred for another 2 h. After centrifugation and washing with distilled water, the sample was treated at 100 °C in H<sub>2</sub> atmosphere (0.1 MPa) for 6 h. The Au loading for these catalysts was 1.5 wt%.

Transmission electron microscopy (TEM) studies were performed in a FEI Tecnai G2 F30 S-Twin electron microscope. The real-time in situ Fourier transform infrared spectroscopy (FT-IR) measurements were carried out with a Mettler Toledo ReactIR 45m spectrometer. An Infrared Associates liquid nitrogen-cooled AgX fiber conduit diamond-attenuated total reflection probe was used.

#### 2.2. Glycerol oxidation and product analysis

A typical reaction procedure was as follows. Glycerol (2.5 mmol),  $H_2O$  (4.6 g), NaOH (0.4 g), and catalyst (0.3 g, 0.023 mmol) were added into the autoclave. The autoclave was charged with dioxygen (0.3 MPa), maintained at 60 °C for 9 h, and then cooled. The reaction mixture was acidified and analyzed by high-performance liquid chromatography (HPLC) on a Waters 2695 system.

# 3. Results and discussion

#### 3.1. Catalytic performance

Initially, we employed Au catalysts with different supports (CeO<sub>2</sub>, activated carbon (AC), HY, REY, and NaY) on glycerol oxidation reaction at 60 °C under 0.3 MPa O<sub>2</sub> in water. As the reactions were conducted in alkaline solution, the final products were in the form of glycerate, tartronate, and oxalate. Thus, acidification to the carboxylic acid form was required for analysis. The catalysts had remarkably different performance for glycerol oxidation (Table 1). When gold was supported on CeO<sub>2</sub>, it gave 98% conversion. However, the main product was oxalic acid (OXALA, 55% yield), and the yield of TARAC was only 24%, suggesting that the oxidation process was accompa-

#### Table 1

Catalytic oxida	tion of glycerol over	Au catalysts with	different supports

Catalyst	$D_{\mathrm{Au}}$	Conversion	Product yield (%)				
	(nm)	(%)	GLYA	TARAC	OXALA	Others	
Au/AC	15	90	80	6	2	2	
Au/CeO2	10	98	2	24	55	17	
Au/NaY	6	98	26	43	4	25	
Au/REY	2	99	5	69	6	19	
Au/HY	1	98	3	80	12	3	
HY	_	4	4	0	0	0	

Reaction conditions: 0.23 g glycerol in 4.6 g H<sub>2</sub>O, 0.4 g NaOH, 0.3 g catalyst (1.5 wt% Au), 60 °C,  $p(O_2)$ = 0.3 MPa, 9 h, the Au/glycerol molar ratio 1/150.

GLYA: Glyceric acid; TARAC: Tartronic acid; OXALA: Oxalic acid.

nied by C–C cleavage with formic acid and OXALA as the degradation products. In the case of Au/AC, glycerol was efficiently oxidized to GLYA with 80% yield, but the yield of TARAC was low (6%), which is consistent with previous studies that GLYA was the main product over Au/AC [16]. For the Au/HY, Au/REY, and Au/NaY catalysts, there was a higher yield of TARAC than for the Au/AC and Au/CeO<sub>2</sub> catalysts. Gold nanoclusters on HY zeolite had extremely high activity, achieving 98% conversion with 80% yield of TARAC. However, the HY support alone only had very low activity. Over the Au/REY catalyst, 90% conversion with 69% yield of TARAC was achieved, and Au/NaY only gave 43% yield of TARAC.

As shown in Fig. 1, the Au particle size varies immensely on different supports. For AC and  $CeO_2$  supports, Au particles had average sizes of 15 and 10 nm, respectively. Their different catalytic performance may be attributed to the differences in C–C cleavage active sites on the supports and the metal support interaction. For Au/HY, the Au nanoclusters had a size around 1 nm, which has been demonstrated by detailed characterizations in our previous study [24]. It seems that the yield of TARAC increased from 43% to 80% when the Au nanoparticle size decreased from 6 to 1 nm. These results suggest that the formation of TARAC can be significantly increased by decreasing the Au particle size. Therefore, the small size of the Au nanoclusters is the main reason for the formation of TARAC when choosing Y type zeolite as support.

#### 3.2. Reaction course and proposed catalytic route

In the reaction, TARAC may be produced either by the consecutive reaction in which glycerol is first converted to GLYA and then to TARAC, or by parallel reactions where two hydroxyl groups are simultaneously oxidized and glycerol is directly transformed to TARAC in one step. For the Au/AC catalyst, glycerol was efficiently oxidized to GLYA with production of a small amount of TARAC (Table 1). Moreover, glycerol oxidation over Au/HY showed 10% yield of GLYA. It is proposed that GLYA may be the intermediate substance. To study the process, the influence of reaction time on the catalytic performance of Au/HY was investigated. As shown in Fig. 2(a), the conversion of glycerol increased with time and reached 98% after 3 h. The yield of GLYA increased in the initial 2 h and reached a maximum value of 38%. Then the amount of GLYA gradually de-



Fig. 1. Representative TEM images and size distributions of (a) Au/AC, (b) Au/CeO<sub>2</sub>, (c) Au/REY, and (d) Au/NaY.

creased, and the yield was low (2%) after 9 h. The trend of GLYA concentration went through a volcano curve, which is consistent with the character of consecutive reaction, suggesting that glycerol may first convert to GLYA and then GLYA is oxidized to TARAC [22].

Real-time in situ FT-IR spectroscopy further confirms the conversion of the monocarboxylic acid to the dicarboxylic acid during the glycerol oxidation process over Au/HY (Fig. 2). Be-

fore the reaction, the IR spectra of glycerol, TARAC, GLYA, and the Au/HY catalyst were recorded under reaction conditions (Fig. 2(b)) [25]. In the beginning, only the characteristic peaks of glycerol and the catalyst are observed at 1045 and 1640 cm<sup>-1</sup>, respectively. After 1 h reaction time, IR bands at 1340 and 1600 cm<sup>-1</sup> appeared (Fig. 2(b) and (c)), indicating the production of TARAC. In addition, the intensity of the glycerol peak at 1045 cm<sup>-1</sup> decreased with time (Fig. 2(d)). It should be noted



Fig. 2. Reaction course (a) and a segment of the in situ FT-IR spectra (b-d) for glycerol oxidation on the Au/HY catalyst.

that although the peak of GLYA at 1420 cm<sup>-1</sup> maintained a low intensity, it initially increased and then decreased during the reaction.

Through calculation, the glycerol oxidation rate was calculated to be 44  $mol_{glycerol}$  /( $mol_{Au}$ ·h) for the initial 2 h. The generation rates of TARAC and GLYA were 20 and 19  $mol_{product}$ /( $mol_{Au}$ ·h), respectively. The similar rate values for TARAC and GLYA can be explained by the fact that they were obtained via resemble oxidation processes and the reaction was composed of consecutive processes [26]. Each step of the consecutive process involves the oxidation of one hydroxyl group.

Oxidation of GLYA accompanying with real-time in situ FT-IR experiments was performed to determine whether it could be further oxidized to TARAC (Fig. 3). During the first 6 h, GLYA was gradually oxidized to TARAC. The reaction achieved 95% conversion with 75% yield of TARAC (Fig. 3(a)) after 9 h, which is consistent with the peak at 1115 cm<sup>-1</sup> (GLYA) decreasing and peak at 1340 cm<sup>-1</sup> (TARAC) increasing in the real-time in situ FT-IR spectrum (Fig. 3(b)) within 5 h oxidation reaction time. This experiment suggests that GLYA is the intermediate in glycerol oxidation. In addition, there is no detection of aldehayde production such as glyceraldehyde. The proposed reaction pathway for glycerol oxidation is shown in Scheme 1. Glycerol was first directly oxidized to GLYA, and then GLYA was further oxidized to TARAC.



**Fig. 3.** Reaction course (a) and a segment of the in situ FT-IR spectra (b) for GLYA oxidation over the Au/HY catalyst.



**Scheme 1.** Proposed reaction pathway for the formation of TARAC over Au/HY catalyst.

# 3.3. Effects of pressure and temperature on glycerol oxidation

The effect of oxygen pressure on glycerol oxidation was investigated, and the results are shown in Fig. 4. The conversion of glycerol gradually increased with increasing pressure from 0.1 to 0.5 MPa. In addition, the yield of TARAC increased from 30% to 80% when the  $O_2$  pressure was increased from 0.1 to 0.3 MPa. However, further increasing the pressure to 0.5 MPa did not further increase the yield of TARAC. In fact, the yield of TARAC decreased to 58% at 0.5 MPa, which may be caused by over-oxidation. Hence, the optimum  $O_2$  pressure was 0.3 MPa.

Figure 5 shows the effect of reaction temperature on glycerol oxidation over Au/HY. At 20 and 40 °C, the yield of TARAC was less than 60%. Increasing the temperature tended to increase the yield of TARAC. However, at 80 °C the yield of



Fig. 4. Effect of pressure on glycerol conversion and TARAC production



**Fig. 5.** Effect of reaction temperature on glycerol conversion and TARAC production.

TARAC decreased to 60%. Thus, the optimal oxidation temperature was 60 °C.

# 4. Conclusions

We have successfully fabricated an Au/HY catalyst for the oxidation of glycerol to tartronic acid (TARAC) with 98% conversion and 80% yield of TARAC under mild conditions. The high efficiency of Au/HY in the production of TARAC was attributed to the small size of the Au nanoclusters on the HY support. Real-time in situ FT-IR experiments combining with reaction course revealed that glycerol was initially oxidized to glyceric acid and then further oxidized to TARAC. These results have important implications for the oxidation of biomass-de-

rived hydroxyl compounds. Further application of the Au/HY catalyst to the oxidation of other biomass-derived hydroxyl compounds is in progress.

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