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Specific Selectivity of Au-Catalyzed Oxidation of Glycerol and Other C_3-Polyols in Water without the Presence of a Base

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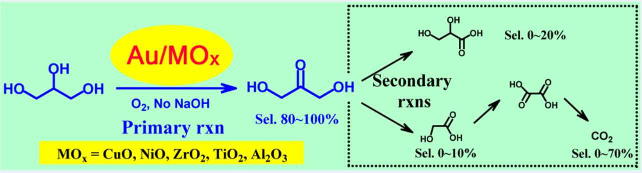
S *Supporting Information*



ABSTRACT: A big challenge in upgrading bio-oxygenate platform molecules is to develop catalysts for the selective oxidation of a nonterminal HO-bonded carbon atom in polyols. We report herein the first finding of a specific selectivity of oxide-supported nano-Au catalysts for dihydroxyacetone (DHA) production in glycerol oxidation in water without NaOH. Though the support nature (Al_2O_3, TiO_2, ZrO_2, NiO, and CuO) significantly affects the Au activity, a highly active Au/CuO catalyst offering DHA yields up to 80% at 40–50 °C has been identified. Rich data are provided to clarify that DHA is the only primary product of glycerol oxidation. This propensity of nano-Au for oxidizing the HO-bonded secondary (central) carbon is further verified by comparing the oxidation of propanediols and propanols. Molecular insight into the reactions is given on the basis of the kinetic isotopic effect study of deuterium on the oxidation of 2-propanol, uncovering an unanticipated chemistry of Au catalysis.

KEYWORDS: *heterogeneous catalysis, supported gold catalyst, selective oxidation, glycerol, propane polyols, dihydroxyacetone, reaction mechanism*

Recent interest in the use of renewable bioresourced oxygenate *platform molecules* for chemicals has been challenging the catalysis community to develop heterogeneous catalysts for selective conversion of polyols, among them, glycerol (GL) would be the most popular molecule.[1,2] GL is also a coproduct of biodiesel manufacturing from either vegetable or animal oils. Its highly functionalized molecular structure and annual production rate (ca. 250 million tons) will enable GL to be a viable feedstock for value-added chemicals and materials.[1−3] Among many possible catalytic reactions like oxidation, hydrogenolysis, dehydration, etherification, transesterification, and so forth,[4−13] the oxidation of GL could potentially produce a number of valuable products including glyceric acid (GLA), tartronic acid (TTA), dihydroxyacetone (DHA), or glyceraldehyde (GLD).[14−16] This richness in product candidates of catalytic GL oxidation would be discouraging if highly selective catalysts could not be developed, making it a greater challenge to develop efficient catalysts that can offer a high selectivity toward a clean oxidation reaction to produce a specific product.

The catalytic GL oxidation reaction has often been studied using an aqueous solution of GL and with the presence of NaOH or a base, employing supported Au nanoparticles (NPs) or immobilized Au colloids as active catalysts.[4−8,14−20] The added NaOH (OH^-, in essence) was believed to serve as an indispensable activator or initiator, activating GL by abstraction of a proton from one of the three hydroxyls.[4−8,14−16,19,20] Regardless of the supporting material, size and morphology of catalytic Au, the oxidation of GL usually produces fairly high selectivity toward the formation of GLA (50–70%), though coproduction of TTA, glycolic acid (GCA), oxalic acid (OA), and/or lactic acid (LA) was never avoided.[4−8,14−20] The formation of GLA was assumed to be preceded by a step forming GLD and/or DHA as the reactive intermediate(s).[14,15,18] However, a clear detection of GLD during the reaction has never been reported over any Au catalyst, although under electrochemical conditions in alkaline media, GL oxidation on gold seemed to proceed with GLD being an intermediate.[21] The formation of DHA was detected only when carbon[18,22,23] or CeO_2[24] was the support material of Au NPs. Considering that the measured selectivity for DHA was dependent on GL conversion and the reactor type,[18,22−24] it would be possible that the presence of NaOH could modify the overall reaction channel and make it difficult to detect the primary product and to offer a high selectivity toward one product.

We provide herein a clear observation on the formation of DHA in the Au-catalyzed oxidation of aqueous GL under base (NaOH)-free conditions. Even under weakly acidic conditions (pH = 4), Au NPs on different supporting oxides (Al_2O_3, TiO_2, ZrO_2, NiO, and CuO) are found to be very selective in catalyzing GL oxidation for DHA formation under mild conditions (30–100 °C). For the first time, DHA is identified as the only primary product of GL oxidation, and Au NPs supported on CuO are found to be the most active for this GL-to-DHA chemistry. Oxidation of 1,2- and 1,3-propanediols are

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Table 1. Catalytic GL Oxidation in Water over Supported Au Catalysts without the Presence of NaOH[a]

		product sel. (C%)[b]					
catalyst	GL conv. (%)	DHA	GLA	GCA	OA	CO_2	TOF (h^{-1})[f]
CuO	0						
$1Au/Al_2O_3$	4.9	96.1	3.5	0	0	0.4	6.6
$1Au/TiO_2$	3.0	76.4	16.9	5.6	0	1.1	4.7
$1Au/ZrO_2$	2.9	68.5	13.7	14.5	0	3.3	4.1
1Au/NiO	10.5	83.7	5.2	1.5	3.7	6.0	19.9
1Au/CuO	19.4	83.3	1.3	1.6	2.6	11.2	39.2
2Au/CuO	20.6	82.5	1.6	1.2	2.4	12.3	40.6
2Au/CuO[c]	34.6	74.9	0.7	1.3	1.4	21.8	
2Au/CuO[d]	20.0	82.3	2.2	1.6	2.7	11.3	
2Au/CuO[e]	19.5	81.7	2.7	1.7	2.1	11.9	

[a] Rxn conditions: 20 mL 0.1 M GL, GL/Au = 1000 mol/mol, pH = 6.7, 80 °C, P_{O2} = 10 bar, stirring speed = 900 rpm, time = 2 h. [b] DHA = dihydroxyacetone, GLA = glyceric acid, GCA = glycolic acid, OA = oxalic acid. [c] This reaction was conducted with GL/Au = 500 mol/mol. [d] pH = 6.0. [e] pH = 4.0. [f] TOF = GL consumption rate (mol/h)/(total number of exposed Au atoms (mol)). The dispersion (D) of Au was estimated according to $D = 1/d$, where d refers to the average Au particle size in nanometer measured by TEM.

Table 2. Catalytic GL Oxidation in Water over Supported Au Catalysts with the Presence of NaOH[a]

		product sel. (C%)[b]							
catalyst	GL conv. (%)	GLA	GCA	LA	TTA	OA	AC	FA	CO_2[c]
$1Au/Al_2O_3$	48.2	60.0	14.5	7.5	4.5	1.2	0	12.3	0
$1Au/TiO_2$	34.2	58.0	10.7	6.4	11.5	1.6	0	10.7	1.2
$1Au/ZrO_2$	34.4	60.3	11.1	6.7	5.4	0.4	2.8	10.6	2.7
1Au/NiO	19.6	33.1	5.1	0	30.6	5.0	0.7	25.4	0
1Au/CuO	27.9	43.4	23.7	0	7.6	0.4	0	24.6	0.2
2Au/CuO	24.8	44.8	24.4	0	1.2	0.8	0	27.6	1.1

[a] Rxn conditions: 20 mL 0.3 M GL, GL/Au = 8000 mol/mol, NaOH/GL = 2 mol/mol (pH = 13.8), 60 °C, P_{O2} = 10 bar, stirring speed = 900 rpm, time = 30 min. [b] LA = lactic acid, TTA = tartronic acid, AC = acetic acid, FA = formic acid; for others see the footnote of Table 1. [c] Detected as carbonate anions (CO_3^{2-}) by analysis with ion chromatography of the product solution.

also studied, and the results demonstrate a specific selectivity toward the oxidative dehydrogenation of the secondary alcohols for acetone production. These findings point to a direct activation of GL over the Au catalyst without the help of a base activator, which sheds light on a new dimension in chemistry of catalysis by gold for selective oxidation of nonterminal HO-bonded secondary (central) carbon atoms in polyols and perhaps other bio-oxygenates containing multiple functional groups.

The GL oxidation reaction was conducted in a Parr autoclave reactor (50 mL) using a catalyst suspension in 20 mL aqueous GL (0.1 M) without addition of any base (NaOH) or at pH ≤ 6.7. Unless otherwise specified, the reaction was conducted at 80 °C for 2 h with an initial molar GL/Au ratio of 1000, an O_2 pressure (P_{O2}) of 10 bar, and an acidity of pH = 6.7. The products and unreacted GL were determined quantitatively by HPLC and GC analyses. The catalysts used were $1Au/Al_2O_3$, $1Au/TiO_2$, $1Au/ZrO_2$, 1Au/NiO, 1Au/CuO, and 2Au/CuO, and the preceding numbers in these sample codes denote the Au loadings in weight percent (Table S1). Au/Al_2O_3 and Au/TiO_2 were AuTEK products from the World Gold Council; Au/ZrO_2, Au/NiO, and Au/CuO catalysts were prepared by deposition−precipitation with urea as the precipitant.[25] The Au particle sizes in these catalysts, as measured by transmission electron microscopy (TEM, Figure S1), were in the range of 2−4 nm by diameters. Detailed information on the catalyst preparation and characterizations, procedures of the catalytic reaction, and product analysis is given in Supporting Information.

Table 1 shows the catalytic data of GL oxidation over the oxide-supported Au catalysts. Irrespective of the supporting oxides, every catalyst produced a high selectivity (69−96%) for the formation of DHA. However, the conversion of GL varied widely over different catalysts; for instance, the GL conversion over the two Au/CuO catalysts (ca. 20%) were 4−7 times those of the other catalysts. In separate experiments, the supporting oxides (Al_2O_3, TiO_2, ZrO_2, NiO, CuO) with no Au were found totally inactive for the reaction; CuO is shown in Table 1 as a representative of the supporting oxides. Obviously, Au NPs functioned as the catalyst for GL oxidation. The numbers in the last column of Table 1 give the catalytic GL consumption rates normalized to the surface Au sites, TOF_{GL} (h^{-1}), which reveal that Au NPs in Au/CuO were ca. 2−9 times more active than those in the other catalysts (Au/Al_2O_3, Au/TiO_2, Au/NiO, and Au/ZrO_2). Further, both the activity and selectivity of 2Au/CuO were found to be essentially unaffected by lowering with dilute nitric acid the initial pH of the reaction solution to pH = 6.0 and 4.0, as shown in the last two rows of Table 1.

The catalysts listed in Table 1 were also used to catalyze GL oxidation in the presence of NaOH, under conditions well-adopted in earlier studies (60 °C, 10 bar O_2, GL/Au = 8000 mol/mol, NaOH/GL = 2 mol/mol).[14−17] The results from these experiments (Table 2) confirmed no formation of DHA but a fairly high selectivity (58−60%) for GLA production of the Au/Al_2O_3, Au/TiO_2, and Au/ZrO_2 catalysts; other products detected were LA (ca. 6%) and TTA (5−10%), GCA (10−15%), OA (ca. 1%), and formic acid (FA, 11−12%). These results are similar to those documented frequently in earlier literature.[4−8] Similar catalytic performance was also observed over the two Au/CuO catalysts, though they produced considerably lower selectivity for GLA (ca. 44%) and higher selectivity for GCA (23.7% and 24.4%) and FA (24.6% and 27.6%) (Table 2). The Au/NiO catalyst showed a preference for TTA formation, though its selectivity for GLA was the lowest (33%). The reaction under the presence of NaOH also produced small amounts of carbonate (CO_3^{2-}) according to IC analysis of the reacted solutions, though the formation of carbonate was seldom considered earlier.[14−16,19,20] A comparison of the data in Tables 1 and 2 therefore demonstrates that the high selectivity for DHA formation is distinctive of Au catalysis for GL oxidation under the base (NaOH)-free conditions, at least within the window of $4.0 \leq pH \leq 6.7$.

The remarkably different activity data in Table 1 demonstrate that the activation of GL on supported Au NPs under the base-free conditions is sensitive to the nature of the supporting materials, Au/CuO ≫ Au/NiO > Au/Al_2O_3 > Au/TiO_2 ≈ Au/ZrO_2. Obviously, CuO was a highly demanded supporting material for the GL-to-DHA chemistry. The same activity data by TOF_{GL} of Au NPs in 1Au/CuO and 2Au/CuO (Table 1) are not a surprising because the Au NPs in these two samples showed basically the same sizes, and these catalytic Au NPs actually “occupied” only a few percent (<5%) of the support (CuO) surface.

The 2Au/CuO sample was then used as the priority catalyst to investigate effects of reaction conditions (temperature, P_{O2}, and duration of reaction) on the catalytic oxidation of GL, DHA, propanediols, and propanols, because the higher Au loading entitled us to use larger amounts of the alcohol substrates for the reaction tests at constant molar GL/Au ratios. Shown in Table 3 are the catalytic results of GL oxidation over the 2Au/CuO catalyst under diversified conditions. Very high selectivity for DHA (>94%) was always obtained when the reaction temperature was no higher than 60 °C and when the GL conversion was lower than 10%. An important observation of Table 3 is that the DHA selectivity increased with a decrease in the GL conversion, and DHA became the only product at 30 °C when the GL conversion was less than ca. 1%. This strongly suggests that DHA was the primary product of GL oxidation under the base-free conditions.

Table 3. Effects of Reaction Temperature and Oxygen Pressure on Catalytic GL Oxidation over 2Au/CuO Catalyst under Base-Free Conditions[a]

			product sel. (C%)[c]				
P_{O2} (bar)	rxn temp (°C)	GL conv. (%)	DHA	GLA	GCA	OA	CO_2
variation of reaction temperature							
10	30[b]	1.0	100	0	0	0	0
10	40	2.1	99.0	0	0	0.7	0.3
10	50	3.6	97.1	0	0	2.2	0.6
10	60	8.7	94.4	0.8	0.5	1.3	3.0
10	70	16.4	85.3	1.2	1.2	4.6	7.7
10	80	20.6	82.5	1.6	1.2	2.4	12.3
10	100	22.9	60.4	3.2	2.2	1.6	32.5
variation of oxygen pressure							
5	80	17.1	82.8	0	0	3.3	13.9
10	80	20.6	82.5	1.6	1.2	2.4	12.3
15	80	23.2	79.2	2.0	0.8	2.3	15.7
20	80	25.3	78.4	1.6	0.8	1.8	17.4

[a] Other conditions for the reaction: 20 mL 0.1 M GL, GL/Au = 1000 mol/mol, stirring speed = 900 rpm, time = 2 h. [b] Time = 1 h. [c] See the footnote of Table 1.

It was proposed previously[22] that GL oxidation over Au catalysts would occur according to an oxidative dehydrogenation mechanism, hinting that the possible primary product(s) could be either GLD or DHA, or both.[14] We also attempted to detect a possible formation of GLD, but the result was always negative under the various reaction conditions in Tables 1 and 3. No formation of GLD was also confirmed by analyses with HPLC-MS, which were detailed in Figures S2 and S3 (Supporting Information).

Increasing the reaction temperature from 30 to 100 °C with invariant initial P_{O2} and fixed reaction duration (e.g., P_{O2} = 10 bar, 2 h) resulted in continued lowering of DHA selectivity from 100% to 60.4%, though the GL conversion was improved from ca. 1.0% to 23%. The data in the lower part of Table 3 demonstrate a fairly mild effect of P_{O2} on the product selectivity of GL oxidation at 80 °C; a 4-fold increase in P_{O2} lowered the DHA selectivity only by 5%. Interestingly, the significant lowering in DHA selectivity at the higher temperatures was compensated mainly by formation of gaseous CO_2; GLA, GCA, or/and OA, which were typical products in Au-catalyzed GL oxidation with the presence of NaOH (Table 2),[4−8] were produced only in very small amounts (<ca. 3%). Consistently, the other possible minor products of GL oxidation under the basic conditions, TTA, LA, and acetic acid (AC),[14] were not at all produced under the present base (NaOH)-free conditions (Table 3). These different product distribution data further suggest that under the base-free conditions, the Au-catalyzed oxidation of GL would take place with a different mechanism from that operating with the presence of a base (NaOH).

With the presence of NaOH, DHA was previously considered as an active intermediate of GL oxidation over the Au catalyst, and the formation of GLA, LA, TTA, and GCA was proposed to be produced from subsequent secondary DHA oxidations.[14,17] We then investigated the oxidation reaction of DHA over 2Au/CuO under the base-free conditions by replacing GL with DHA for the reaction, using the same reactor and reaction procedure as for GL oxidation study (Table 4). Without presence of the catalyst (2Au/CuO), DHA itself was stable in the solution under the reaction conditions (40−80 °C, 10 bar O_2). Addition of 2Au/CuO mainly led to nonselective or complete oxidation of DHA toward CO_2 formation, though the conversion of DHA was not high; the selective oxidation products (GLA, GCA, OA, and AC) were formed only in small amounts. These results clearly

Table 4. Catalytic Results of DHA Oxidation with the Absence and Presence of Au/CuO Catalyst under Base-Free Conditions[a]

			product sel. (C%)[b]				
rxn temp (°C)	catalyst	DHA conv. (%)	GLA	GCA	OA	AC	CO_2
40−80		0					
40	2Au/CuO	0.2	13.9	9.9	0	0	76.2
60	2Au/CuO	4.4	14.0	6.0	6.0	0	73.9
80	2Au/CuO	13.1	18.5	3.7	4.7	10.3	62.9

[a] Other conditions for the reaction: 20 mL 0.1 M DHA in water (pH = 6.0), DHA/Au = 1000 mol/mol, P_{O2} = 10 bar, stirring speed = 900 rpm, time = 2 h. [b] See the footnote of Table 1.

demonstrate that the oxidation of DHA over the Au/CuO catalyst was nonselective, favoring a complete oxidation to form CO_2 instead of selective oxidations to form the organic acids (GLA, GCA, OA), which would indicate that the GLA, GCA, OA, and CO_2 products in Tables 1 and 3 were indeed formed by secondary oxidation of DHA.

To gain insights into the stability and reactivity of the individual GLA, GCA, and OA over the Au/CuO catalyst under the base-free condition, each of these individuals was also used to replace GL for the reaction. The results (Table S2) disclose that GLA was stable under the reaction conditions but OA was the most reactive molecule, whose oxidation produced CO_2 as the only product. GCA could be easily oxidized to CO_2, probably with OA as the reaction intermediate. These results entitle us to propose the reaction channels for GL oxidation under the base-free conditions (Figure 1).

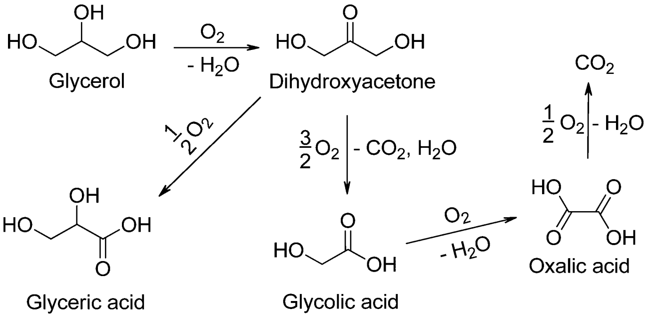

Figure 1. Glycerol oxidation over Au/CuO without the presence of NaOH.

The high selectivity of Au/CuO for the oxidation of the central carbon in GL would uncover a new propensity of supported Au catalyst for a specific catalysis toward the oxidation of secondary alcohols under the base-free conditions. To confirm this possibility, other C_3-alcohols including 1,2-propanediol (1,2-PDO), 1,3-propanediol (1,3-PDO), 1-propanol (1-PO), and 2-propanol (2-PO) were then used, respectively, to replace GL for the reaction over 2Au/CuO. As shown in Table S3, the reaction of 1,2-PDO produced 1-hydroxylacetone (HA) as the only product. However, 1,3-PDO with no secondary OH showed little reactivity, its reaction was not detectable in 2 h but offered a conversion as low as 3.2% when the reaction time was extended for as long as 12 h. Similarly, the reactions of 2-PO and 1-PO gave, respectively, acetone and propionic acid (PA) as their only products. Note that the PA yield was only half of the acetone yield, which demonstrates a much lower reactivity of 1-PO than 2-PO.

Thus, all of our catalytic data point to the fact that under the base-free conditions, supported Au catalysts (like Au/CuO) have a special propensity to selectively oxidize the secondary alcohols to form their corresponding ketones. The fact that no aldehyde (and its drivatives) but only HA was produced in the catalytic oxidation of 1,2-PDO (Table S3) would indicate that under the base-free conditions, the terminal OH group could remain essentially “unreactive”. We therefore have reason to propose that the present observed oxidative dehydrogenation reactions of GL and 1,2-PDO is a strong indication that the catalytic activation of the secondary C−H bond dominated the chemistry involved in their oxidation reactions because a selected activation of the secondary OH without affecting the terminal OH in both reactants would be difficult to imagine.

The importance of the catalytic activation of the secondary C−H bond in the oxidation reactions of GL and 1,2-PDO was further supported by studying the kinetic isotope effect (KIE) on the oxidation of 2-PO over the 2Au/CuO catalyst, using unlabeled ($CH_3CH(OH)CH_3$) and deuterium-labeled (2-*d*-2-PO, $CH_3CD(OH)CH_3$) molecules for the reaction under the base-free conditions. The conversion of both 2-PO and 2-*d*-2-PO increased linearly with the reaction time unless the conversion was higher than ca. 35−40%, which clearly demonstrates a first order reaction kinetics in 2-PO (Figure S4A). The first-order reaction rate constant measured with 2-PO and 2-*d*-2-PO were $\boldsymbol{k}_H = 0.176\ h^{-1}$ and $\boldsymbol{k}_D = 0.054\ h^{-1}$, respectively, which give a KIE of $\boldsymbol{k}_H/\boldsymbol{k}_D = 3.5$ (Figure S4B). This very prominent KIE ascertains that the breakage of the secondary C−H bond is the kinetically significant or rate-determining step in the selective oxidation of 2-PO. These results would thus confirm that the catalytic activation of the secondary C−H bond is the key to the selective oxidation of both GL and 1,2-PDO for the formation of acetones (DHA and HA).

The high selectivity for DHA formation of the Au/CuO catalyst in GL oxidation under base-free conditions would be of potential for application, because the market price of DHA was ca. 250 times higher than that of GL.[26] Specifically, DHA is an important chemical in organic synthesis and a skin coloring

Table 5. Synthesis of DHA by Catalytic Oxidation of GL in Water under Base-Free Conditions[a]

					product sel. (C%)[b]					
rxn temp (°C)	Gl/Au (mol/mol)	P_{O2} (bar)	rxn time (h)	GL conv. (%)	DHA	GLA	GCA	OA	CO_2	DHA yield (%)
40	100	10	10.0	56.4	91.4	0	0.9	0.4	7.3	51.5
40	100	30	8.0	81.3	86.5	0	1.9	0.2	11.4	70.3
40	50	30	10.0	90.7	82.5	0	1.3	0.5	15.7	74.8
50	100	5	8.0	100	63.9	0	1.1	0.2	34.8	63.9
50	100	10	5.0	100	70.6	0	1.4	0.2	27.8	70.6
50	50	20	3.0	90.6	82.5	0	3.3	1.1	13.1	74.7
50	50	20	4.0	97.8	81.8	0	0.9	1.0	16.2	80.0
50	20	20	3.0	100	79.8	0	3.9	2.6	13.7	79.9
50	10	20	2.5	100	68.4	0	0.2	6.3	25.1	68.4
60	100	10	4.5	100	60.1	0	1.2	0.1	38.6	60.1
60	100	20	3.5	93.3	66.7	0	1.4	0.2	31.7	62.2
80	100	10	2.0	100	54.6	0.8	0.9	0.1	43.6	54.6

[a] Other conditions for the reaction: 20 mL 0.1 M GL, 2Au/CuO, stirring speed = 900 rpm. [b] See the footnote of Table 1.

agent in cosmetic industry.[27] Under the conditions employed in Table 3, prolongation of the reaction duration had only a limited effect on improving the DHA yield, due to the occurrence of secondary reactions of DHA (Table 4). Attempts were then made to enhance the DHA yield by using more catalyst (2Au/CuO) to reach a complete GL conversion in the possible shortest reaction duration. On increasing the catalyst loading up to GL/Au = 50 and 20 (mol/mol), we obtained high DHA yields of 75−80% at nearly complete GL conversion by adjusting the other reaction parameters (temperature, P_{O2}, and duration), as listed in Table 5.

Only two research groups detected earlier a formation of DHA in Au-catalyzed GL oxidation studies with the presence of NaOH at 60 °C; the supporting materials for the catalytic Au nanoparticles were carbons[18,22,23] and CeO_2.[24] One group worked with a batch (autoclave) reactor, and the obtained DHA selectivity was in the range of 20−27% at GL conversion levels of 30−50%.[18,22,24] The other group conducted the reaction in a continuous down-flow slurry bubble column reactor and reported a DHA selectivity of 53% at 30% GL conversion.[23] Obviously, the DHA yields obtained in Table 5 under the base-free conditions are far higher than those obtained over the earlier Au/C and Au/CeO_2 catalysts (<16%). In the literature, Bi- and Au-modified Pt, and bimetallic Pd−Ag on various carbon supports were registered as the selective catalysts for DHA synthesis from GL oxidation in water.[28] Though the selectivity to DHA could be up to 80−85%, their offered DHA yields were in the range of 20−52%,[28] which are also much lower than the high yields shown in Table 5.

Therefore, this study uncovers for the first time that DHA was the only primary product of catalytic GL oxidation over supported Au NPs under the base-free conditions in water. The Au NPs also catalyzed further oxidations of DHA, which produced CO_2 as the main and final product with GCA and OA being the intermediate products. On adjusting the catalyst loading and other parameters for GL oxidation, however, DHA yields up to 80% could be still obtained. Further studies on the reactions of 1,2- and 1,3-PDO, unlabeled and deuterium-labeled 2-PO, and 1-PO also confirmed the high activity and specific selectivity of Au NPs toward the oxidation of secondary alcohols under the base-free conditions, which strongly demonstrate that a selective activation of the secondary C−H bond is the key to the specific selectivity in the oxidation of both GL and 1,2-PDO. These findings reveal an unprecedented mode of Au catalyst for the selectivity control in polyol activation and oxidation catalysis and point to a new dimension in chemistry of Au-based oxidation catalysis. In particular, it sheds a light on innovating Au catalysts for fine-tuning oxidation catalysis toward special chemicals syntheses from bioresourced polyols.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and supporting tables and figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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