Selective Oxidation of Aldehyde over Hydroxymethyl Group Catalyzed by Gold Nanoparticles in Aqueous Phase

Han-bao Chong\textsuperscript{a,b}, Gui-qi Gao\textsuperscript{b}, Guang Li\textsuperscript{a}\textsuperscript{*}

\textsuperscript{a}. School of Physics and Material Science, Anhui University, Hefei 230601, China
\textsuperscript{b}. Institute of Physical Science and Information Technology, Anhui University, Hefei 230601, China

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A protocol for selectively oxidizing aldehyde over hydroxymethyl group is developed, using biomass starch protected gold nanoparticles (NPs) as catalyst. The Au NPs show high selectivity that aldehyde is oxidized into carboxylic acid while alcoholic hydroxyl group stays intact in selective oxidation of 4-(hydroxymethyl)-benzaldehyde. The heterogeneous catalysis system is composed of soluble catalysts and insoluble substrate. The gold catalyst is prepared, preserved and applied for catalytic oxidation all in water. After reaction conditions are optimized, \( \text{H}_2\text{O}_2 \) is found to be the best oxidizing agent with complete conversion. Besides, the gold catalyst displays good versatility for aldehyde derivatives. After reaction completes, organic components are extracted by organic solvent and gold NPs in water are separated and recycled.

Key words: Au nanoparticle, Water-solubility, Selective oxidation, Starch

I. INTRODUCTION

Having been used as coinage, jewelry and arts for thousands of years, gold was considered inert in organic synthesis until it was discovered efficient for CO oxidation and chlorination of ethylene [1–4]. Afterwards, gold nanoparticles witnessed an increasing popularity as catalysts and they have been identified as the most active catalyst in a variety of reactions [5–8]. Usually the gold nanoparticles are anchored on metal oxide [9–13], carbon [14–16], graphene [17, 18], chitosan [19, 20], polymer [21–24], and silica [25–27], etc., to serve as heterogeneous catalysts. The insolubility of heterogeneous catalysts assists isolation and recovery of catalysts from the slurry, which makes them more popular [28, 29]. Utilization of these catalysts in aqueous phase leads to highly efficient and environmentally benign catalytic systems [30–33]. Usually the supported catalysts are heterogeneous with substrates that are soluble in organic solvents. In this work, we reverse the logic to prepare soluble catalyst while the substrate and product are dispersed in media.

Oxidation of aldehydes to corresponding carboxylic acids is of great significance for industrial manufacturing due to its great potential in organic synthesis [34]. Wang group developed a catalyst-free aerobic oxidation of aldehydes method in water, but with low aldehyde concentration [35]. Both aldehyde and alcohol groups can be oxidized into carboxylic acid, while some alcohol groups can be first oxidized into aldehyde and then to carboxylic acid. As a result, controllable oxidation of alcohol and aldehyde is a technical issue of synthesis. Herein, we develop a strategy to prepare an efficient catalytic system to selectively oxidize 4-(hydroxymethyl)-benzaldehyde in aqueous phase by \( \text{H}_2\text{O}_2 \). The gold NPs are generated in water under oxygen atmosphere at 363 K, no reducing agent like \( \text{NaBH}_4 \) or urea is used except the use of naturally abundant starch as both capping agent and reducing reagent. The oxidation process occurs in water as \( \text{H}_2\text{O}_2 \) is also stored in aqueous, and the product is isolated by extraction with organic solvents as well as the residual aldehydes after reaction completes. In the past decades, the growing awareness of the environment has evoked a demand for efficient oxidation process with environmentally friendly oxidants. Hence, the quest for more sustainable and selective oxidation systems is a current hot research field [36].

In this work, water, \( \text{H}_2\text{O}_2 \) and starch are cheap and facile in industry. No base, buffer or co-catalyst are required, which all consent with the idea of “sustainable development”. Starch is a qualifiedly reducing agent and protecting ligand [37] which is innoxious to operator. The facile synthesis and catalytic reaction protocol are presented in FIG. 1. Briefly, gold salt is mixed with starch in water under oxygen atmosphere at 363 K for 4 h. The colloid is preserved in fridge prior to use. After catalytic reaction completes, dichloromethane is used to extract organic components for several times while the aqueous layer containing catalys is separated. The gold NPs are characterized by transmission electron microscope (TEM), infrared radiation (IR), and X-ray

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\textsuperscript{*}Author to whom correspondence should be addressed.
E-mail: liguang1971@ahu.edu.cn

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photoelectron spectroscopy (XPS). And Au loading on supported NPs and in water is determined by ICP AES as 16 mg/g and 160 mg/L, respectively.

II. METHODS

A. Experimental methods

All the chemicals and reagents were purchased from Aladdin corporation. All the organic products were analyzed by Bruker AM 400 MHz NMR to confirm the structure. The UV tests of NPs were operated with the help from Hewlett-Packard (HP) 8453 diode array spectrophotometer. TEM images were acquired by JEM 2100. TLC plates (Merck Silica Gel 60 F254) were used for analytical thin layer chromatography. Merck Kieselgel 200—300 was used for preparative column chromatography. The Au loading was determined by ICP AES (iCAP 7400 Duo) from Thermo Fisher. XPS data are collected by ESCALAB 250Xi from Thermo Fisher.

B. Sample preparation

1. Synthesis of gold NPs

100 µL HAuCl₄·4H₂O (0.05 mmol) solution was injected into 100 mL water containing 1 g starch under stirring. The mixture was heated to 363 K for 4 h under oxygen atmosphere. After reaction completed, the colloid was cooled down and then preserved in fridge at 277 K prior to use.

2. Typical procedure for the catalytic reaction

0.1 g 4-(hydroxymethyl)-benzaldehyde (0.735 mmol) was added into 5 mL catalyst storage solution (Au loading 0.004 mmol). Then the slurry was heated to 363 K for 6 h before adding 1215 µL H₂O₂ (30% V/V). After cooled down, the organic layer was extracted by dichloromethane (3 mL for 6 times). Finally, the purification process was carried out by column chromatography.

After reaction completed, the organic components were washed with 3 mL dichloromethane for 5 times, and the water phase was collected after skimming. The water containing gold NPs could be used for next round of catalysis.

III. RESULTS AND DISCUSSION

A. Material characterization

The size of polydisperse Au NPs is characterized by TEM ranging from 3 nm to 60 nm, and the results are illustrated in FIG. 2 (a) and (b). The gold NPs size mostly distributes between 3—20 nm based on 500 counted particles. UV-Vis spectrum further confirms with TEM result: a broad absorption band centered at 540 nm (FIG. 2(c)). The gold NPs are relatively stable after 5 runs of catalysis, which is verified by TEM (FIG. S1 (a) and (b) in supplementary materials) and UV-Vis (FIG. S1(c) in supplementary materials), probably due to identical reaction conditions of synthesis and catalysis. UV-Vis spectrum shows 3 nm bathochromic-shift and TEM image exhibits slight aggregation.

XPS spectrum of Au (FIG. 3) indicates binding energy of Ar 4f is 84.0 and 87.6 eV, implying the elemental state of metal. Lewis acid of Au (I and III) is available for various kinds of catalytic reactions, the absence of these species eradicates the possibilities of Lewis acid catalysis. Besides, it means starch is an excellent reducing agent to reduce gold salt and extra reducing agent is absolutely unnecessary. The binding energy of O 1s is found lower after stabilizing gold NPs interprets that starch serves as the capping agent (FIG. S2 in supplementary materials). Meanwhile, deflating of absorption band centered at 3400 and 1644 cm⁻¹ which are ascribed to OH stretch vibration in IR spectra is consistent with the XPS result (FIG. S3 in supplementary materials).

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B. Results of catalytic evaluation for selective oxidation

Starch stabilized Pt/Au NPs supported on hydro-}
talcite are characteristic for polyols oxidation with
good activity [38]. In this work, water-dispersed
gold NPs are employed to catalyze selective ox-
idation of 4-(hydroxymethyl)-benzaldehyde into 4-
hydroxythylbenzoic acid while terephthalaldehyde and
terephthalic acid are possible byproducts. Several ox-
idation agents are examined to test selectivity of starch
capped gold NPs. Oxygen is the weakest agent which
gives rise to nothing while the catalyst is absent (Entry
1 in Table I). When the NPs are present, negligible en-
hancement is observed and the catalyst prefers acid as
the product (Entry 2). Metal salts K$_2$Cr$_2$O$_7$ and NaClO
exhibit similar selectivity preference with or without
catalyst, while less K$_2$Cr$_2$O$_7$ is required to achieve anal-
ogous conversion as NaClO does (Entry 3–6). These
results indicate, in the presence of metal salt oxidiz-
ing agents, gold NPs don’t function as catalyst species.
H$_2$O$_2$ is readily degradable which decomposes into wa-
ter and oxygen making it environmentally benign ox-
idizing agent. TBHP (tert-butyl hydroperoxide) and
H$_2$O$_2$ are both peroxides, and they show much better
activity and selectivity, especially the latter with very
high selectivity (Entry 7–10). Meanwhile, in the ab-
ence of NPs, slight conversion of substrate is acquired
compared with excellent conversion when catalysts are
added. Sole starch added in the system doesn’t lay any
influence on the outcome (Entry 11), suggesting gold
NPs are true active species. No matter what kind of
oxidation agents are employed, no over-oxidized prod-
uct such as terephthalic acid is detected. In this work,
environment-friendly reagent H$_2$O$_2$ utilized as the ox-
idizing agent which gives complete conversion and ab-
solute selectivity is in line with “sustainable develop-
ment”.

The role that temperature plays in the catalysis per-
formance is evaluated (FIG. S4 in supplementary mate-
rials). The temperature is set from 303 K to the water
boiling point with 10 K increment and reaction time is
overnight. It is obvious that high temperature is help-
ful for high conversion, however, it needs more energy.
The target molecule with too low content is generated at
room temperature. The substrate is completely trans-
formed at 363 K, so 373 K is unnecessary for more yield.

The transformation process of 4-(hydroxymethyl)-
benzaldehyde is monitored by GC-MS (FIG. 4). From
the very beginning, only trace byproduct terephtha-
aldehyde is detected and the pattern is kept till the end
of reaction. In the first 3 h, 84% substrate is consumed.
To totally convert the starting material, another 3 h is
requested. After 6 h stirring, almost all the substrate is
switched into target product with exclusive selectivity.

The water-dispersed gold catalysts are capable of re-
cycling use (FIG. 5). Unreacted aldehyde and car-
boxylic acid are washed by organic solvent, hence, the
aqueous phase could be used directly for next run of
catalysis. However, some activity loss is observed in
first use which drops to 82%. It’s possibly ascribed
to catalyst aggregation. In the subsequent 4 tests, the
yields are stable between 63% and 69%. The lower ac-
tivity may be due to slight catalyst aggregation. The
results demonstrate starch-capped gold NPs are highly
active and recyclable up to the 5th run with little loss
TABLE I Gold NPs catalyzed oxidation of 4-(hydroxymethyl)-benzaldehyde in water with different oxidizing agent.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Oxidizing agent (equiv.)</th>
<th>Conversion (%</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Oxygen b Balloon</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>Oxygen c Balloon</td>
<td>79</td>
<td>21</td>
</tr>
<tr>
<td>3</td>
<td>K₂Cr₂O₇b</td>
<td>38</td>
<td>9</td>
</tr>
<tr>
<td>4</td>
<td>K₂Cr₂O₇c</td>
<td>41</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>NaClO b</td>
<td>34</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>NaClO c</td>
<td>35</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>TBHP b</td>
<td>5</td>
<td>68</td>
</tr>
<tr>
<td>8</td>
<td>TBHP c</td>
<td>66</td>
<td>63</td>
</tr>
<tr>
<td>9</td>
<td>H₂O₂ b</td>
<td>9</td>
<td>&gt;99</td>
</tr>
<tr>
<td>10</td>
<td>H₂O₂ c</td>
<td>100</td>
<td>&gt;99</td>
</tr>
<tr>
<td>11</td>
<td>H₂O₂ d</td>
<td>9</td>
<td>&gt;99</td>
</tr>
</tbody>
</table>

* Reaction conditions: 5 mL catalyst storage solution (water, 0.004 mmol), 0.1 g substrate (0.735 mmol), 6 h, 363 K. N.D.=not detected.
* No Au NPs added.
* Au NPs are present.
* No Au NPs added, only starch.

![FIG. 4 Conversion-time plot of 4-(hydroxymethyl)benzaldehyde selective oxidation. Reaction condition: 5 mL catalyst storage solution (water, 0.004 mmol), 0.1 g substrate (0.735 mmol), 363 K.](image)

Oxidation mechanism of aldehyde group and hydroxyl group are different, aldehyde oxidation adopts racial path while hydroxyl oxidation can’t. As shown in FIG. 6, the possible mechanism is speculated to elucidate the transforming process. The aldehyde group could be oxidized into peracid by H₂O₂ in the presence of Au NPs. Afterwards, 4-(hydroxymethyl)benzaldehyde collides with peracid into two molecules of carboxylic acids. The hydroxyl group is relatively stable when blended with H₂O₂ and Au NPs, besides, it doesn’t react with peracid. As a result, 4-(hydroxymethyl)-benzaldehyde is selectively oxidized into 4-hydroxythylbenzoic acid.

The versatility of the oxidation catalytic system has been demonstrated by the oxidation of various aldehydes. The product selectivity is exclusive regardless of substrate structure that was used. The conversion varies from goodness to excellence with different substituted groups. Catalytic oxidation of aldehydes into acid is performed under identical conditions operated in catalytic synthesis process. Substrate is dispersed in 5 mL catalyst storage solution to generate acid product under vigorous stirring. After 1 h heating, 100% benzaldehyde is transformed into benzoic acid, the TON (turnover numbers) value is 183.8 mol(aldehyde)/mol(Au) while TOF (turnover frequency) value reaches the top as 183.8 h⁻¹. The derived substrates with electron-donating groups give rise to more product while the others with electron-donating groups show worse results. Interestingly, the o-positioned substrate (Entry 6, Table II) does not present as expected probably due to the hindrance from the adjacent position. In a word, the gold NPs are qualified catalysts for synthesis of carboxylic acid.

IV. CONCLUSION

A new heterogeneous catalysis system is established, water-dispersed gold NPs are prepared and evaluated for their excellent catalytic ability for selective oxidation of 4-(hydroxymethyl)-benzaldehyde and versatility for aldehyde derivatives. The catalyst displays complete conversion and excellent selectivity in the presence of H₂O₂. After reaction completes, slurry is washed by dichloromethane and aqueous layer containing gold NPs is separated, which doesn’t contaminate the product.
TABLE II Gold NPs catalyzed oxidation of 4-(hydroxymethyl)-benzaldehyde in water with different oxidizing agent*. 

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Time/h</th>
<th>Conversion/%</th>
<th>Selectivity/%</th>
<th>TON</th>
<th>TOF/h⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CHO</td>
<td>COOH</td>
<td>0.8</td>
<td>93</td>
<td>&gt;99</td>
<td>170.9</td>
<td>213.6</td>
</tr>
<tr>
<td>2</td>
<td>CHO</td>
<td>COOH</td>
<td>2.5</td>
<td>95</td>
<td>&gt;99</td>
<td>174.6</td>
<td>69.8</td>
</tr>
<tr>
<td>3</td>
<td>Br-CHO</td>
<td>Br-COOH</td>
<td>6</td>
<td>98</td>
<td>&gt;99</td>
<td>180.1</td>
<td>30.0</td>
</tr>
<tr>
<td>4</td>
<td>HO-CHO</td>
<td>HO-COOH</td>
<td>6</td>
<td>94</td>
<td>&gt;99</td>
<td>172.7</td>
<td>28.8</td>
</tr>
<tr>
<td>5</td>
<td>O₂N-CHO</td>
<td>O₂N-COOH</td>
<td>5</td>
<td>92</td>
<td>&gt;99</td>
<td>169.0</td>
<td>33.8</td>
</tr>
<tr>
<td>6</td>
<td>NO₂-CHO</td>
<td>NO₂-COOH</td>
<td>6</td>
<td>89</td>
<td>&gt;99</td>
<td>163.5</td>
<td>27.3</td>
</tr>
<tr>
<td>7</td>
<td>MeO-CHO</td>
<td>MeO-COOH</td>
<td>6</td>
<td>92</td>
<td>&gt;99</td>
<td>169.0</td>
<td>28.2</td>
</tr>
<tr>
<td>8</td>
<td>Br-CHO</td>
<td>Br-COOH</td>
<td>5</td>
<td>96</td>
<td>&gt;99</td>
<td>176.4</td>
<td>35.3</td>
</tr>
</tbody>
</table>

*a Reaction conditions: 5 mL catalyst storage solution (water, 0.004 mmol), 0.735 mmol substrate, 363 K. TON means turnover number and TOF means turnover frequency.

FIG. 6 Schematic illustrating of possible mechanism.

Biomass starch is used as protecting ligand and reducing agent, water is employed in synthesis and catalysis of protocol, both make the gold catalysts good candidates for “sustainable development”.

Supplementary materials: TEM images and UV-Vis spectrum of gold nanocatalyst after 5th round catalysis, IR and XPS characterization of NPs, temperature tests along with spectroscopic data and NMR spectra of catalytic products can be found in the supplementary materials.

V. ACKNOWLEDGMENTS

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