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Short communication

Deactivation behavior and aggregation mechanism of supported Au nanoparticles in the oxidation of monoethanolamine to glycine



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ABSTRACT

Deactivation behaviors of gold catalysts in the liquid-phase oxidation of monoethanolamine to glycine were revealed. Properties of the catalysts including Au loading, the valence distribution, and particle size of Au nanoparticles before and after batch reactions were investigated by BET, ICP, XRD, XPS, and TEM. It was found that the main reason for the catalytic deactivation was aggregation of Au nanoparticles. The Au aggregation mechanism of oxidative dissolution-reductive deposition in the reaction was proposed and this mechanism could help to understand the common aggregation of Au nanoparticles in the liquid-phase oxidation of alcohols.

1. Introduction

Oxidation of alcohols to aldehydes or carboxylic acids is a fundamental and important functional transformation in chemical industry. The selective oxidation of compounds with both amino and hydroxyl groups represents an alternative and sustainable approach to producing amino acids besides the amination of biomass-derived α -hydroxyl acids, without the use of fatal toxic reactants (e.g., cyanide or halo acids) or complex separation process (e.g. separation of the amino acid from chloric byproducts in amination of halo acids and from other different amino acids in hydrolysis and fermentation processes) [1-11]. Various non-catalytic (using acidified potassium dichromate or potassium permanganate as the oxidant) and catalytic (mainly copper and gold-based catalysts) systems have been developed for this process [2-8,12]. Among them, gold-based catalysts are superior to others in view of high product selectivity and mild reaction conditions. For instance, the direct conversion of chitosan to glucosaminic acid by tandem hydrolysis and oxidation was achieved over supported Au catalysts, and in the selective oxidation of monoethanolamine (MEA), the glycine yield could reach 95% at 323 K over Au/ZrO2 [5,6,11]. However, in these reaction systems, the gold-based catalysts are easy to deactivate as indicated by the gradually unchanged conversion when the reaction proceeded for certain time, even it was proved to have better resistance to deactivation compared with palladium or platinum nanoparticles [3-5].

Villa et al. [4] investigated the effect of amino groups on the

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catalytic behaviors of gold catalysts by comparing the liquid-phase oxidation of amino alcohols (serinol and MEA) and the corresponding polyols (glycerol and ethylene glycol). It was found that the catalyst deactivation was far more evident in the case of amino alcohols than that in the oxidation of glycerol or ethylene glycol. Gaiassi et al. [3] explored the effect of nitrogen substitution of MEA on the product selectivity and stability of the supported gold catalysts. They demonstrated that the deactivation was more influenced by the reactant structure than by experimental parameters and aliphatic amines which could form strong interactions with noble metals aggravated the catalytic deactivation. The aggregation of Au particles in MEA oxidation after being used for three cycles was also observed in our previous study, which should be an important reason for the decrease of catalytic activity [5].

Although the influences of amino groups and the growth of particle size on the stability of gold catalysts in the liquid-phase oxidation of amino alcohols were emphasized, rare report focuses on deactivation behaviors of the catalysts, and the possible relationship between the amino group and the aggregation of Au nanoparticles in the reaction remains unclear. In this study, the deactivation behaviors of gold catalysts in the liquid-phase oxidation of amino alcohols, *i.e.* MEA, was investigated using different catalysts. The Au loading, electronic and structural change of the catalysts before and after batch reactions were investigated by BET, ICP, XRD, XPS, and TEM. The aggregation mechanism of Au nanoparticles was proposed.



2. Experimental

2.1. Materials

All chemicals (AR grade) were purchased commercially and used as received unless otherwise noted. HAuCl₄:4H₂O (99.99%) and AgNO₃ (\geq 99.8%) were supplied by Sinopharm Chemicals (Beijing, China). The commercial ZrO₂ support was purchased from Shanghai Macklin Biochemical Co. Ltd. (Shanghai, China). Mesoporous carbon CMK-3 was homemade as described in our previous work [13]. MEA (> 99.0%), NaOH (> 99.0%), and acetaldehyde (99.5%) were from Xilong Scientific Co., Ltd. (Guangdong, China). O₂ (99.9%) was supplied by Beijing Beiwen Gas Factory (Beijing, China). Maleic acid (internal standard for quantitative NMR analysis) and all other standard samples were purchased from Sigma-Aldrich Trading Co., Ltd. (Shanghai, China).

2.2. Catalyst preparation

The Au/ZrO₂ catalysts were prepared by deposition-precipitation method as described before [6], and the obtained catalysts calcined at 623 K and 823 K were labelled as Au/ZrO₂–623 and Au/ZrO₂–823, respectively. The Au/CMK-3 catalyst was prepared using a deposition-reduction method as described in our previous study [13].

2.3. Evaluation of the catalyst and the reusability

Oxidation of MEA was used to evaluate the catalytic activity of the catalysts, and the reaction was conducted according to the described procedures reported in literature [5,6]. After reaction, the solid catalyst was separated from the liquid by filtration, washed with deionized water and dried at 323 K. Then the catalytic activity of the recycled catalyst was evaluated following the same procedure as that for the fresh one.

3. Results and discussion

It is widely accepted that preparation method, support, and the particle size play key roles on the properties of Au catalysts, which determine the catalytic performance including stability of the catalyst. Therefore, Au catalysts with different Au particle sizes or supports, i.e., Au/ZrO2-623, Au/ZrO2-823 and Au/CMK-3, were prepared for the aqueous oxidation of MEA, and their properties were characterized. As shown in Table S1, ESI, the Au loadings of both the Au/ZrO2-623 and Au/ZrO₂–823 catalysts were 0.8 wt%. The calcination temperature has negligible influence on the specific surface area (SBET) of the catalysts despite the significant difference of the Au particle sizes (4.7 nm for Au/ ZrO₂-623 vs. 8.1 nm for Au/ZrO₂-823). Mesoporous carbon CMK-3 supported Au catalyst has a little bit higher Au loading of 0.9 wt% with smaller Au particle size of 3.7 nm and much larger S_{BET} of 1164 m²/g. The large difference in properties of the catalysts, including the Au particle size, type and structure of the supports, made it possible to reveal the catalytic stability of different Au catalysts in the liquid-phase oxidation of alcohols.

The liquid-phase oxidation of MEA was selected as a model reaction to test the stability of Au catalysts with different preparation methods, Au particle sizes, and supports. The reusability of the catalysts is shown in Fig. 1. In the oxidation of MEA, all the three catalysts showed obvious loss of activity during the reaction process. MEA conversion over Au/ZrO₂–623 obviously decreased from 99% (fresh catalyst) to 17% in the third run, and that over Au/ZrO₂–823 decreased from 68% to 17%. Mesoporous carbon CMK-3 supported gold catalyst showed slower decrease in MEA conversion from 60% to 27% due to the porous structure of CMK-3 and partial particles inside the pores [13,14]. The evident catalytic deactivation for all the tested gold catalysts indicated that deactivation was common for catalysts with various Au particle sizes and supports.



Fig. 1. Reusability of Au/ZrO₂-623 (MEA/Au = 300/1 (mol/mol)), Au/ZrO₂-823 (MEA/Au = 300/1 (mol/mol)), and Au/CMK-3 (MEA/Au = 500/1 (mol/mol)) in MEA oxidation. Reaction conditions: $C_{MEA} = 0.3$ M, NaOH/MEA = 4, T = 323 K, $P(O_2) = 0.5$ MPa, stirring speed = 1000 r/min, average catalyst diameter = 106 µm, and t = 2 h.

The active component loading is of vital importance for a catalytic reaction and metal leaching cannot be excluded in the solvent medium [5,6]. Au loadings of the fresh and recycled catalysts were investigated through chemical analysis by ICP. The result showed that the Au content of the as-prepared Au/ZrO₂-623 was 0.8 wt%, and that of the catalyst after three runs was the same. That is, no obvious metal leaching was observed during the reaction, and thus Au leaching was not the reason for deactivation.

The surface elements and their corresponding contents of the fresh and recycled Au/ZrO₂-623 were then analyzed, as shown in Table 1. N species were present in the recycled catalyst after three runs because of the possible adhesion of the reactant or products on the catalyst surface, consistent with the reported strong interactions between the amino group and noble metals [1,3]. Comparing the element contents of the recycled catalyst with those of the fresh one, no obvious change was found for the surface contents of Zr and Cl, while the surface content of the active Au element decreased remarkably from 0.37% to 0.09%. Considering that no metal leaching occurred during the reaction as proved before, the low surface content of Au may result from the decrease of Au dispersion [6]. EDS mapping was also performed to study element compositions and distributions of Au/ZrO2-623 catalyst before reaction and after being used for three runs. As shown in Figs. S1 and S2, ESI, Au and Zr were the dominant metallic elements for both fresh and recycled catalysts. For Au/ZrO2-623 after being used for three runs, the line analysis of the elements shown in Fig. S2b confirmed the presence of larger Au particles. The Au 4f XPS spectra of fresh and recycled Au/ZrO₂-623 were collected, as shown in Fig. S3, ESI. The valence distribution of Au species was determined by subjecting the Au 4f peaks to deconvolution, and no obvious difference of the proportion of metallic gold species was found before and after reaction (89% vs. 91%), indicating that catalytic deactivation was not caused by variation

Table 1

Surface elements and their contents of fresh and recycled $\mathrm{Au}/\mathrm{ZrO_2}\text{-}623$ after three runs.

Au∕ ZrO₂–623	Au _{surf} (%)	Zr _{surf} (%)	O _{surf} (%)	C _{surf} (%)	N _{surf} (%)	Cl _{surf} (%)
Fresh Recycled after three runs	0.37 0.09	20.8 19.6	50.0 56.76	16.3 11.0	0 0.66	12.4 11.9



Fig. 2. Change of the Au particle size distributions of fresh and recycled Au/ZrO₂-623 (a) and Au/ZrO₂-823 (b).

of the Au electronic state.

The Au particle size of fresh and recycled Au/ZrO₂ was further investigated by XRD and TEM. As shown in Fig. S4, ESI, compared with the fresh catalysts, both recycled Au/ZrO₂–623 and Au/ZrO₂–823 showed increased intensity of the characteristic peak of Au (111) at 20 of 38.2° (JCPDS-PDF: 89–3697), indicating increase of crystal size of Au and decrease of dispersion. The average Au particle size was examined by TEM, and the representative micrographs in Fig. 2 and Fig. S5 showed the change of Au particle size before and after reuse. With the increase of recycling times, Au particle size gradually increased for both Au/ZrO₂–623 and Au/ZrO₂–823. For Au/ZrO₂–623, the Au particle size increased from 4.7 (\pm 0.9) nm before reaction to 18.7 (\pm 5.0) nm after three runs, and that for Au/ZrO₂–823 increased from 8.1 (\pm 1.9) nm to 18.6 (\pm 5.9) nm. The Au sintering and decrease of Au dispersion were the main reasons for the continuous decrease of catalytic activity.

The sintering processes of gold nanoparticles can be mainly classified into two categories: particle migration and coalescence (PMC) as well as atomic ripening (AR) [15]. PMC is usually related to temperature-induced increased mobility and the lower melting point of small particles [16], while AR includes the migration of species containing metallic atoms and usually occurs for compounds that can form complexes containing the metallic atom [17]. In the liquid-phase oxidation at low temperature (e.g., 323 K), the AR process was considered to be the main pathway for the growth of Au nanoparticles. To test this hypothesis, different solutions, containing one or more compounds existing in the solution of MEA oxidation, were used to treat the Au/ ZrO₂-623 catalyst under reaction conditions unless otherwise noted. The typical TEM images and the corresponding Au particle size distributions of the catalysts after various treatment processes as well as those of the catalyst after the 1st run are shown in Fig. 3 and Fig. S6. Compared with the control group (fresh Au/ZrO2-623 treated with 1.2 M aqueous solution of NaOH under 0.5 MPa of O_2), the addition of MEA (O2 was replaced by N2 to avoid the occurrence of reaction) or acetaldehyde (representing the possible 2-aminoacetaldehyde intermediate, which was commercially unavailable) in the solution didn't obviously change the distribution of Au particle size. However, the glycine solution with the presence of O₂ and 1.2 M of NaOH slightly increased the Au particle size distribution from 4.7 (\pm 0.9) nm to 5.0 (± 1.3) nm. Obvious increase of Au particle size was observed for the sample treated with the solution of mixed acetaldehyde and glycine in the presence of O₂ and 1.2 M of NaOH, and the average Au particle size increased to 6.3 (\pm 1.6) nm, approaching that of Au/ZrO₂-623 after the 1st run (7.6 (\pm 2.9) nm). These phenomena illustrated that glycine in the reaction solution under O₂ can change the distribution of Au particle size, and there existed synergistic effect between glycine and acetaldehyde to promote the growth of the supported Au nanoparticles.



Fig. 3. Au particle size distributions for Au/ZrO₂–623 catalysts after treatments with different solutions: a) control, 0.5 MPa of O_2 , 1.2 M aqueous solution of NaOH, b) 0.5 MPa of N_2 , aqueous solution containing 0.3 M of MEA and 1.2 M of NaOH, c) 0.5 MPa of O_2 , aqueous solution containing 0.3 M of acetaldehyde and 1.2 M of NaOH, d) 0.5 MPa of O_2 , aqueous solution containing 0.3 M of acetaldehyde and 1.2 M of NaOH, d) 0.5 MPa of O_2 , aqueous solution containing 0.3 M of acetaldehyde, 0.3 M of glycine, and 1.2 M of NaOH, f) after the 1st run.

It was reported that amino acids can be used as alternative leaching agents for cyanide in gold extraction from minerals due to strong complex formation between gold and amino acids by coordinating through the carbonyl oxygen and nitrogen [18]. The stability constant of the complex between gold and glycine could reach 18 [19]. In alkaline solution with the presence of glycine and O_2 , gold dissolution can be expressed as the following reaction equation [19]:

$$4Au + 8NH_2CH_2COOH + 4NaOH + O_2 = 4Na[Au(NH_2CH_2COO)_2] + 6H_2O$$
(1)

The formation of gold (I)-amino acid complex can not only increase the solubility of metal but also decrease the redox potentials, thus promoting the oxidative dissolution [20,21]. In order to confirm the oxidative dissolution of Au, the concentrations of dissolved Au after Au/ZrO₂–623 was treated with different solutions were detected by ICP. As shown in Table S2, ESI, in aqueous solutions without glycine (containing 1.2 M of NaOH (control), 0.3 M of MEA and 1.2 M of NaOH, or 0.3 M of acetaldehyde and 1.2 M of NaOH, respectively), ultratrace of Au (concentration < 0.2 ppm) was detected, corresponding to negligible change of the average Au particle size and size distributions (Fig. 3, A-C). While in solutions containing glycine (*i.e.*, 0.3 M of glycine and 1.2 M of NaOH; 0.3 M of glycine, 0.3 M of aldehyde and 1.2 M of NaOH; or the reaction solution), the concentration of Au was higher than 3 ppm, and both the average Au particle size and size distributions increased (Fig. 3, D-F), indicating that gold dissolution and Au sintering were closely related to the presence of glycine. These phenomena demonstrated the oxidative dissolution process.

The gold (I)-amino acid complex obtained in the oxidative dissolution process contained oxidized gold, which was instable and easy to be reduced to Au⁰, especially in the presence of the reductive aldehyde intermediate (*i.e.* 2-aminoacetaldehyde) in MEA oxidation. The reduction of oxidized gold by 2-aminoacetaldehyde is shown as follows:

$$2Na[Au(NH_2CH_2COO)_2] + NH_2CH_2CHO + 3NaOH$$
$$= 2Au + 5NH_2CH_2COONa + 2H_2O$$
(2)

For Au/ZrO₂-623 treated with solutions containing glycine (Fig. 3, D-F), the presence of aldehyde in the solution increased the average Au particle size and size distributions, indicating that reductive aldehyde played a role in aggregation of Au nanoparticles. Even the concentration of Au was the highest in the mixed solution of glycine and NaOH (conditions "d", Table S2), the aggregation was not obvious until the addition of Au particle size close to that after the 1st run.

Based on the above experiments and analysis, the aggregation mechanism of oxidative dissolution-reductive deposition of Au nanoparticles was proposed, as shown in Fig. 4. In the process of oxidative dissolution, a particle with a smaller radius and higher surface energy was preferentially dissolved in the aqueous solution containing glycine and NaOH with the presence of O_2 , forming gold (I)-amino acid complex. Then the produced gold (I) complex was reduced by the aldehyde intermediate and deposited on the surface of larger Au nanoparticles. Thus, the larger particles grew at the expense of smaller ones, in a way similar to Ostwald ripening [22].

In the liquid-phase oxidation of MEA, the faster deactivation of ZrO_2 -623 than that of ZrO_2 -823 can be attributed to the difference in Au particle sizes. On the one hand, smaller Au nanoparticles have larger proportion of reactive low-coordinated atoms exposed and higher surface energy, facilitating the oxidative dissolution step. On the other hand, according to the well-accepted size effect of gold catalyst [23], the disappearance of highly active particles less than 5 nm caused the rapid decrease of catalytic activity for Au/ZrO₂-623. Therefore, Au/



Fig. 4. Proposed aggregation mechanism of oxidative dissolution-reductive deposition of Au nanoparticles in MEA oxidation.

ZrO₂-623 with smaller Au particles showed faster deactivation behavior than Au/ZrO₂-823. Similar phenomenon was also observed in the liquid-phase oxidation of alcohols including glucose, glycerol, ethanol and 5-hydroxymethyl furfural [24,25]. For example, in the oxidation of glucose to gluconic acid, the conversion over Au/CeO2 was reduced from 70% in the 1st run to 4% in the 4th run as the average Au particle size increased from 2 nm to 7.1 nm [24]. In the aqueous ethanol oxidation over Au/CuFe₂O₄, the conversion was reduced slowly from 63% in the 1st run to 52% in the 5th run as the average Au particle size increased from 3.7 nm to 4.5 nm [25]. The formed carboxyl acids, including acetic acid and gluconic acid, can also work as ligands to form gold (I)-carboxylate complexes by Au–O bonds [26,27], promoting the oxidative dissolution as glycine does in Eq. (1). However, the stability constant of gold (I)-amino acid and dissolving capacity of gold nanoparticles were higher [21], resulting in higher aggregation rate of Au nanoparticles in MEA oxidation.

The above controlled experiments and proposed aggregation mechanism of Au nanoparticles revealed that the co-existence of ligand (amino acids), oxidant (oxygen), and reductant (aldehyde intermediate) in the reaction system was the main reason for the aggregation of Au nanoparticles. Considering that the aldehyde intermediate and amino acids products were inevitable in the oxidation of amino alcohol to amino acid and that the dehydrogenation of alcohols, including glycerol and benzyl alcohol, can occur using supported metal catalysts in the absence of oxygen [28,29], the oxygen-free dehydrogenation of amino alcohols to amino acids was considered to be an alternative method to reduce Au sintering, and corresponding progress has been made in our laboratory.

4. Conclusions

The deactivation behaviors of gold catalysts in the liquid-phase oxidation of MEA to glycine were revealed over gold catalysts including Au/ZrO₂-623, Au/ZrO₂-823, and Au/CMK-3, by measuring possible leaching of Au, compositions of surface elements, change of the valence distribution, and particle size of Au nanoparticles. No detectable leaching of Au and change of valence distribution were detected after Au/ZrO₂-623 was recycled for three cycles through chemical analysis by ICP and XPS. The obvious sintering of Au nanoparticles, confirmed by XRD, XPS, and TEM, accounted for the severe catalytic deactivation. By treating the Au/ZrO₂-623 catalyst with different solutions, the main factor inducing Au sintering was revealed and the aggregation mechanism of oxidative dissolution-reductive deposition in MEA oxidation was proposed. This study reveals the main reason for the common aggregation of Au nanoparticles in the liquid-phase oxidation of alcohols, which could provide valuable information for possible strategies to reduce Au sintering in such kind of reactions.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://

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