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Selective oxidation of monoethanolamine to glycine over supported gold catalysts: The influence of support and the promoting effect of polyvinyl alcohol

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ABSTRACT

Glycine is an important fine chemical used in many fields, and the traditional synthetic methods like Strecker synthesis and ammoniation of chloroacetic acid use highly toxic reagents or produce equal molar byproducts. Herein, selective aerobic oxidation of monoethanolamine (MEA) to glycine using Au catalysts supported on various supports, including Al₂O₃, SiO₂, TiO₂, ZnO, and ZrO₂, was investigated and the correlation between acid-base properties of the catalysts and catalytic performance was established. Catalysts with higher base content exhibited higher initial activity and that with lower acid content gave higher glycine selectivity. The influence of preparation methods was revealed using Au/ZrO₂ with the best catalytic performance and it was demonstrated that the presence of polyvinyl alcohol (PVA) has a significant promoting effect. *In-situ* FTIR and ¹H NMR analysis revealed that the hydrogen bonds between PVA and MEA can enhance adsorption of MEA on catalysts, resulting in doubled turnover frequency (TOF) and improved MEA conversion; and the preferential hydrogen bonds between the amino group of MEA and the hydroxyl of PVA can prevent the coordination of amino group with Au nanoparticles, favoring reaction of the hydroxyl group of MEA on the active sites, accounting for the enhanced glycine selectivity. The reaction conditions were optimized and the optimal yield of glycine was 95%.

Introduction

Amino acids and their derivatives play important roles in both biology and chemistry fields, and they are mainly obtained from protein enzymolysis or, as an alternative, by chemical synthesis [1]. Traditional chemical processes for amino acid synthesis involve amination of halo acids [2–4], Gabriel synthesis [5], Sorensen method [6], and Strecker synthesis [7], which are complicated and not environmental benign due to the use of toxic reagents, catalysts or the formed by-products. For example, Gabriel synthesis involves protection and deprotection steps since the unprotected amine groups can undergo side reactions, making the procedure more complicated with reduced atom efficiency. Strecker synthesis uses highly toxic cyanide or hydrocyanic acid as the reagent, limiting its wide application in modern sustainable society.

Glycine is the simplest amino acid and an important compound in chemical, food, pharmaceutical, and agricultural industries [8].

Ammoniation of chloroacetic acid to produce glycine is widely utilized in many countries including China, the world's main supplier for glycine with an annual output of 600,000 tons [9]. However, the hexamethylenetetramine (HMTA) catalyst used in chloroacetic acid ammoniation would decompose during the reaction and product purification processes, resulting in the formation of formaldehyde and increased production cost. Besides, equal molar amount of ammonium chloride would form as the byproduct, and lots of volatile methanol is needed in order to get purified glycine product. These drawbacks restrict the application of chloroacetic acid ammoniation to produce glycine in the upcoming future, especially in the context of green chemistry and the atom economy of modern society [10].

Although hydrolyzing the nitrile group of amino-nitrile under moderate conditions using microorganisms seems to be a green method to producing amino acids, this route has disadvantages of low activity per unit time and difficulty in recovery of the ammonia by-product

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[11,12]. Amination of biomass-derived α -hydroxyl acids is also a sustainable approach for the direct synthesis of amino acids, however, severe reaction conditions like temperature as high as 220 °C are required [13,14]. The oxidation of aminoalcohols is another promising synthetic pathway for amino acids under moderate conditions without the usage of fatal toxic reactants or the formation of chloric byproducts that would contaminate the product [15,16]. In 1943, Billman reported that glycine could be made from monoethanolamine (MEA) by first protecting the amino group with acyl radical, then oxidizing the hydroxyl group by acidified potassium dichromate, followed by removing the acyl radical after the formation of the carboxyl group [17]. This method was then modified by replacing the acyl radical with acid and converting the amino group into a substituted ammonium ion before oxidizing the hydroxyl group to the carboxyl group [18]. Among the tested oxidants, potassium permanganate showed the best performance in the acid medium [18]. However, both methods mentioned above involve protection and deprotection steps using stoichiometric strong and toxic oxidants, which generate a large amount of waste and pollution.

Recently, transition metals catalyzed oxidation of primary or secondary alcohols to aldehydes, carboxylic acids or ketones has been intensively investigated [19-22]. A copper-containing system was reported to catalyze the conversion of amino alcohol to amino acid salts with a large amount of catalyst at higher temperatures (e.g., 160 °C) [23]. Biella et al. studied the oxidation of various aminoalcohols in the presence of oxygen using supported Au, Pd and Pt nanoparticles as the catalysts, among which Au nanoparticles showed the highest activity, while amino groups could irreversibly adsorb on the surface of Pt and Pd metals, resulting in deactivation of the Pt and Pd catalysts [15,16]. A series of Au supported catalysts, including Au/Al₂O₃, Au/MgAl₂O₄, Au/ C, etc., were screened as the catalysts for liquid phase oxidation of aminoalcohols and it was concluded that the substituent groups on the nitrogen atoms and reaction conditions were of vital importance for the catalytic performance [24,25]. However, effects of the support nature and preparation methods on the catalytic performance still need to be systematically explored and the yields of amino acids should be improved.

In this study, gold nanoparticles supported on different kinds of metal oxides (*i.e.*, Al_2O_3 , SiO_2 , TiO_2 , ZnO, and ZrO_2) were prepared and their physicochemical properties were explored using XPS, TEM, TPD, ICP, *etc.* Catalytic performance of these catalysts in the selective oxidation of MEA to glycine (Scheme 1) was studied. The influence of preparation methods on the catalyst property was further revealed by using the support with the best performance. The role of the protective agent in improving the catalytic activity and glycine selectivity was explored with *in situ* FTIR, and NMR analysis. Optimization of reaction parameters, including reaction temperature, NaOH/MEA ratio, substrate/metal ratio, and concentration of MEA, was carried out to give the best conditions.

Experimental

Materials

All chemicals (AR grade) were purchased commercially and used as received unless otherwise noted. The powder supports, including γ -Al₂O₃, ZrO₂, and ZnO, were purchased from Shanghai Macklin Biochemical Co. Ltd. (Shanghai, China). TiO₂, with an average particle size of 25 nm, was from Degussa (Frankfurt am Main, Germany). SiO₂ was from Sigma-Aldrich (Shanghai, China). HAuCl₄·4H₂O (99.99%),



Scheme 1. Reaction scheme for the oxidation of MEA to glycine.

NaBH₄ (>96%), and AgNO₃ (\geq 99.8%) were supplied by Sinopharm Chemicals. Polyvinyl alcohol (PVA; with a molecular weight of 10,000, 80% hydrolyzed) from Sigma-Aldrich (Shanghai, China) was used. MEA (>99.0%) and NaOH (>99.0%) were from Xilong Scientific Co., Ltd. (Guangdong, China). O₂ (99.9%) was supplied by Beijing Beiwen Gas Factory. Maleic acid (internal standard for quantitative NMR analysis) and all other standard samples were purchased from Sigma-Aldrich Trading Co., Ltd. (Shanghai, China).

Catalyst preparation

Sol-immobilization (SI) method

Au catalysts supported on different supports were prepared using the SI method as described in literature [26,27]. In a typical preparation process, the required amount of the protecting agent PVA solution (1 wt%) was added to the aqueous solution of HAuCl₄ (0.24 mmol/L), with the PVA/Au weight ratio of 1.2:1 at room temperature under vigorous stirring. The obtained solution was then left under stirring for 5 min. A freshly prepared 0.1 M solution of NaBH₄ (NaBH₄/Au (mol/ mol) = 5) was added to the above solution to form a dark orangebrown gold sol. After sol generation for 30 min, the colloid gold solution was immobilized by adding the support under vigorous stirring, with the amount of supporting material being calculated to give a final metal loading of 1% by mass. For the loading of gold on SiO₂ support, the pH of colloid gold needed to be adjusted to 3.0 to achieve similar Au loading content [27]. After 2 h, the slurry was filtered and the obtained catalyst was thoroughly washed with deionized water to remove all the water-soluble species. Finally, the catalysts were dried in air at 80 °C overnight.

SI-calcinated method

In this method, the obtained Au catalysts prepared by SI method were calcinated at 250 °C for 3 h in static air to get the calcinated samples. This method for catalyst preparation was named as SI-calcinated method.

Deposition-precipitation (DP) method

Catalysts prepared using the deposition-precipitation procedure was similar to the method described in literature [28,29]. Briefly, a solution of HAuCl₄·3H₂O (0.24 mmol/L) was adjusted to pH of 8.0 by adding NaOH solution (0.1 M). Subsequently, the support with a mass of 1.0 g was added to the solution under vigorous stirring and the obtained slurry was readjusted by NaOH solution to make sure the pH was 8.0. After stirring for 2 h, the sample was filtered and washed with an excess amount of deionized water until no chloride could be detected by titration with an aqueous AgNO₃ solution. The obtained catalyst was dried overnight at 80 °C and then calcined for 3 h at 250 °C in air.

Impregnation (IMP) method

The catalyst was also prepared by impregnation method following procedure described in literature [30,31]. A required amount of the support was mixed with 100 mL of aqueous solution of HAuCl₄·3H₂O (0.24 mmol/L), and all the water in the mixture was evaporated at 80 °C with vigorous stirring. The solid was dried in an oven at 80 °C for 12 h, which was then treated with 0.1 M of NaBH₄ aqueous solution (the molar ratio of NaBH₄ to metal was 5) at room temperature for 2 h. Then the catalyst was filtered, washed and dried overnight at 80 °C in air to give the Au catalysts.

Characterization

Powder X-ray diffraction (XRD) of the catalysts was performed on Rigaku RINT 2500 Diffractometer using monochromated Cu K α radiation with a scan speed of 15° min⁻¹ and a scan range of 5-90° at 30 kV and 15 mA. The X-ray photoelectron spectroscopy (XPS) studies were performed on a PHI-5400 spectrometer with an Al K α source. The

binding energy scale was calibrated relative to the C1s peak (285.0 eV) of contaminant carbon [27,32]. The images from transmission electron microscope (TEM) were collected using a JEOL JEM-2100 F operated at 200 kV. Samples were deposited on the TEM grids after dispersion in ethanol. At least 200 particles were randomly measured to determine the average diameter of Au nanoparticles for every sample. The catalyst surface area, pore volume, and average pore size were measured at -196 °C from the N₂ adsorption-desorption isotherm on a Micromeritics ASAP 2460 apparatus. Prior to the measurements, all samples were degassed overnight at 300 °C. The Au loading of the catalysts was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) using an IRIS Intrepid II XSP (Thermofisher, USA). ¹H NMR spectra were recorded on a Bruker AVANCE III HD NMR spectrometer operating at 600 MHz. High resolution mass spectra (HRMS (ESI-TOF)) were collected on a Brucker high resolution mass spectrometer (micrOTOF-QII).

Temperature-programmed desorption of ammonia and carbon dioxide (NH3- and CO2-TPD) experiments were carried out using Cat-Lab (BEL JAPAN, INC.) equipped with an online QIC-200 quadrupole mass spectrometer (Inprocess Instruments, GAM 200) as the detector. The NH₃ desorption profiles were measured by fixing the m/z signal at 15, and those for CO_2 desorption were measured by fixing the m/z signal for molecular CO₂ at 44. The loadings of all samples were around 50 mg and the calculations for the total acidity and basicity concentration of Au catalysts were based on the weight of the catalysts. In-situ FTIR spectra were recorded on a Thermo-Nicolet (Nicolet 6700) spectrometer equipped with the high temperature reaction chamber and transmission accessory. Spectra with 4 cm^{-1} resolution and 64 scans were recorded at room temperature using ZnSe windows in the range from 4000 cm^{-1} to 650 cm^{-1} . The powders (KBr and sample) were pressed at 10 MPa for 10 min and loaded into a home-made stainless steel reaction chamber. Then the catalyst was pretreated by heating to 120 °C with a heating rate of 8 °C min⁻¹ in vacuum for 2 h and cooled to room temperature. Adsorption behavior of MEA on the catalysts were started by flowing the He/MEA gas mixture at a flow rate of 5 mL min⁻¹ and FTIR spectra were recorded at 30, 60, 120, 180, 240, 300, 360 min for analysis.

Oxidation of MEA

The oxidation reaction of MEA was carried out in a 100 mL batch type Teflon-lined stainless-steel autoclave, which was connected to an 8 L reservoir of O_2 with constant pressure. In a typical procedure, 40 mL aqueous MEA solution (0.3 M), 0.96 g NaOH (molar ratio of NaOH/MEA was 2), and 0.236 g catalyst (molar ratio of MEA/Au was 1000) were loaded into the autoclave successively. The autoclave was purged 3 times with O_2 and then pressurized at desired oxygen pressure at room temperature. Once the system reached the desired temperature, the reaction was initiated by vigorous stirring with a magnetic stirrer and samples were taken at 15, 30, 60, 120, 180 min for analysis.

The products were identified by HRMS and comparing the ¹H NMR spectra of the reaction solutions with those for standard samples. Conversion of MEA and selectivity of glycine was quantitatively analyzed using ¹H NMR as described in the literature [24,25]. In the preparation of the samples for analysis, 34.8 mg of maleic acid (standard for quantitative NMR) was added to each sample solution (2 mL) as the internal standard to quantify the products. ¹H NMR spectra were recorded with suppressed water signal using a low power PRESAT pulse to minimize signal distortions [24,33]. The concentrations of the reactant and products were determined by comparing the integration of the products signals to standard ones.

Results and discussion

The surface area, pore volume, pore diameter and support particle size of the five catalysts are shown in Table S1, Electronic Supporting



Fig. 1. TEM micrographs and corresponding Au particle size distributions for Au catalysts: a -Au/Al₂O₃, b -Au/TiO₂, c -Au/ZnO, d -Au/ZrO₂, e -Au/SiO₂.

Information (ESI). Au/SiO₂ and Au/Al₂O₃ have higher surface area compared with other catalysts. All the supports are nanosized particles with diameters from 10 nm to 50 nm. XRD patterns of Au/TiO₂, Au/ZnO, and Au/ZrO₂ in Fig. S1, ESI show well-crystallized diffraction peaks of the supports, while the diffraction peaks of Au/SiO₂ and Au/Al₂O₃ are broad, indicating that these supports are not well crystallized. No diffraction peak of Au was found in any catalyst, indicating that Au particles are well dispersed.

Support effect

Nature of the support usually plays an important role in supported Au catalysts for the oxidation of alcohols, and an in-depth understanding of the support effect on the catalyst property and activity could help to rationally design efficient catalysts. Study of the support

Table 1

Selective oxidation of MEA over various Au catalysts.^{[a].}

Catalyst	Au loading (wt%)	Au particle	Initial MEA conversion ^[b] (%)		Selectivity (%) ^[c]		
		size (iiii)		GLY	ANHA	FA	Others
No ^[d]	_	_	4	0	_	_	_
Au/ZnO	0.86	2.7	49	46	41	2	11
Au/Al ₂ O ₃	0.71	2.6	39	47	34	2.5	16
Au/ZrO ₂	0.77	2.8	34	59	29	3.8	8
Au/TiO ₂	0.76	2.7	33	55	36	3	6
Au/SiO ₂	0.68	4.6	9	30	22	15	33

[a] Catalysts were prepared by SI method; reaction conditions: $C_{\text{MEA}} = 0.3 \text{ M}$, MEA/Au = 1000/1 (mol/mol), NaOH/Au = 2, T = 50 °C, $P(O_2) = 0.5 \text{ Mpa}$, t = 15 min. [b] Calculated after reaction for 15 min.

[c] GLY: glycine, others include glycolic acid, glycylglycinate, 2-iminoethanol, etc.

[d] Selectivities of some by-products can not be determined accurately due to their very low concentrations.

effects requires that the catalysts are in uniform Au particle size. The supported Au catalysts were prepared by deposition of Au colloids with PVA as a protective agent using SI method as this method could produce Au particles with similar size on different supports [32]. Fig. 1 displays the representative TEM micrographs and corresponding Au particle size distributions of the prepared catalysts. An average Au particle size of 2.7 nm with similar particle size distributions (ranging from 1 nm to 5 nm) were obtained on the Al₂O₃, TiO₂, ZnO, and ZrO₂ supports, while the average diameter of gold on SiO₂ was 4.6 nm with particle size distribution from 1 nm to 8 nm. XRD patterns of the catalysts in Fig. S1, ESI showed no characteristic peaks of metallic gold at 20 around 44.4°, indicating that the size of Au particles was less than 5 nm [34], in good agreement with the TEM observation.

Oxidation of MEA in the presence of these catalysts was carried out in an autoclave as described in the Experimental section. Products from the MEA oxidation were qualified by NMR and HRMS (Figs. S2 and S3, ESI), which were proved to be glycine, 2-amino-N-(2-hydroxyethyl) acetamide (ANHA), formic acid (FA), *etc.* The performance of these catalysts in the selective oxidation of MEA is shown in Table 1. Control trial was conducted with the absence of the catalyst and the result showed that under these specific conditions, MEA conversion was only 4% and no glycine was detected. With the addition of Au catalysts, both MEA conversion and glycine selectivity were improved. Among the tested catalysts, Au/SiO₂ gave much lower activity with only 9% MEA conversion and 30% selectivity for glycine in 15 min. Au/ZnO showed the best catalytic activity with 49% MEA conversion, while Au/ZrO₂ gave the highest selectivity towards glycine (59%), followed by Au/ TiO₂, Au/Al₂O₃, and Au/ZnO.

The electronic state of the catalysts and the gold content on the surface were analyzed by XPS, and the results were shown in Fig. 2 and Table 2. All spectra of the catalysts showed two distinct XPS signals with binding energies around 83.9 eV and 87.7 eV, corresponding to the characteristic electrons of $4f_{7/2}$ and $4f_{5/2}$ in the metallic Au of the catalysts [35]. The binding energies of Au $4f_{7/2}$ were 83.5, 83.4, 83.5 and 83.5 eV for Au/ZrO2, Au/Al2O3, Au/ZnO, and Au/TiO2, respectively. Compared to the binding energy of bulk Au metal at 83.9 eV, these lower binding energies of Au $4f_{7/2}$ in these catalysts indicate modification of the electronic states of Au due to the interaction between the gold nanoparticles and nanosized supports [36-40]. For Au/ SiO_2 , the binding energy of Au $4f_{7/2}$ was 83.8 eV, quite close to that of bulk Au, indicating that the interaction between Au and SiO₂ was weak. The valence state of Au for freshly prepared gold catalysts was also dependent on the identity of the support even the gold colloid was prepared by subjecting Au³⁺ to excessive strong reductive NaBH₄ before deposition. The gold nanoparticles tended to keep in the metallic state on SiO₂, Al₂O₃, and ZnO, while 17.0% and 5.5% of the gold species were in the oxidized state for those on supports like TiO₂ and ZrO₂, respectively (Table 2).

Acid-base property of the supporting materials usually relates to the

catalytic activity of alcohol oxidation over supported gold catalysts [41,42]. Temperature programmed desorption (TPD) of NH₃ and CO₂ over these Au catalysts was conducted to examine the acid and base properties of the catalysts and the results are shown in Figs. 3 and 4, respectively. All the catalysts exhibited abundant acid and base sites except Au/SiO₂, which showed negligible content of acidity or basicity [32]. From the temperatures and intensities of the NH₃ desorption peaks in Fig. 3, we can see that Au/Al₂O₃ possessed various sites of weak, medium and strong acidity, and that both Au/ZnO and Au/ZrO₂ had only medium acid sites, with the concentration of acid sites on Au/ ZrO₂ being relatively lower as indicated by the intensity. Au/TiO₂ possessed some weak acid sites. CO2-TPD profiles in Fig. 4 suggest that Au/ZnO and Au/Al₂O₃ possessed a high concentration of basic sites, while Au/ZrO₂ has a similar concentration of basic sites to Au/TiO₂. There was no obvious desorption of CO2 detected on Au/SiO2, indicating that this catalyst had no obvious basicity.

The relationship between the initial MEA conversion and the total basicity concentration of the catalysts was shown in Fig. 5 (Au/SiO₂) was not included in the plots because of the obvious difference in Au particle size and the solution pH value during preparation). It indicates that the initial MEA conversion increased almost linearly with the catalyst basicity except Au/TiO2. For Au/TiO2, it had similar concentration of basicity to that of Au/Al₂O₃ (0.105 vs. 0.109 mmol/g), but it exhibited relatively lower initial MEA conversion (33% vs. 39%), due to the less proportion of Au^0 on the surface of Au/TiO_2 (83% for Au/ TiO_2 vs.100% for Au/Al₂O₃) as reduced gold was the active component for the reactant activation [19,43]. As shown in Fig. 5, the selectivity of glycine seems to be negatively correlated with the acidity concentration of the catalysts. Possessing the highest acidity concentration (0.159 mmol/g), Au/ZnO showed the lowest selectivity for glycine (46%) and the highest selectivity for ANHA (41%), which was formed by the oxidative coupling of hydroxyl group of MEA with amino group of another MEA molecule (discussed in Section 3.5) as gold nanoparticles can also catalyze amide synthesis from alcohols and amines [44,45]. Au/ZrO₂, with an acidity concentration of 0.125 mmol/g, exhibited the highest selectivity for glycine (59%) and the low selectivity for ANHA (29%), attributed to the relatively low adsorption and activation amount of the amino group [46].

To test the durability of Au/Al₂O₃, Au/TiO₂, Au/ZnO, and Au/ZrO₂, which gave good MEA conversion or glycine selectivity in 15 min' reaction (Table 1), the oxidation of MEA was carried out for 3 h over these catalysts and the changes of MEA conversion and selectivities of products during the reaction were shown in Figs. 6 and S4. MEA conversion first increased with reaction time and then reached maximum values for all the tested catalysts. The same phenomena were also observed by Prati et al. and Lu et al., the invariable conversions of MEA or benzyl alcohol were attributed to deactivation of the catalysts [24,25,47]. As shown in Fig. 6, both Au/TiO₂ and Au/ZrO₂ showed relatively higher stability, and MEA conversion reached maximum



Fig. 2. Au 4f XPS spectra of the supported Au catalysts.

 Table 2

 Surface content and relative surface distribution of gold species in the catalysts.

Catalyst	Au _{surf} (%)	Au 4f _{7/2} (eV)	Au 4f _{5/2} (eV)	Au species (%)	
				Au ⁰	Au ⁺
Au/ZrO ₂	0.5	83.5	87.2	94.5	5.5
Au/ZnO	0.5	83.5	87.2	100	0
Au/Al ₂ O ₃	0.5	83.4	87.0	100	0
Au/TiO ₂	0.4	83.5	87.2	83.0	17.0
Au/SiO_2	0.1	83.8	87.5	100	0

values of 89% and 81% after 2 h, respectively. However, it seems that Au/Al_2O_3 and Au/ZnO deactivated in 1 h, when the maximum MEA conversion reached 63% and 62%, respectively. In fact, the amino groups can strongly interact with the supported Pt and Pd metals and decrease the durability of the gold catalysts, as demonstrated by the contrastive study of the oxidations of ethylene glycol and ethanolamine [15,25]. Au/Al_2O_3 and Au/ZnO catalysts with higher acidity concentrations (0.21 and 0.29 mmol/g, respectively) compared with Au/TiO₂ and Au/ZrO₂ (0.15 and 0.13 mmol/g, respectively) can adsorb more amino groups on the surface, which could decrease the durability of the catalysts. As shown in Fig. S4, the selectivity of glycine enhanced with time going on, while the selectivity of ANHA decreased, which could be attributed to the hydrolysis of ANHA to glycine in the presence



Fig. 3. NH₃-TPD profiles for the supported Au catalysts.



Fig. 4. CO₂-TPD profiles for the supported Au catalysts.



Fig. 5. Correlation between initial MEA conversion and the total basicity concentration of Au catalysts (**■**) as well as the correlation between the selectivity of glycine and the total acidity concentration of Au catalysts (**●**) (Reaction conditions: $C_{\text{MEA}} = 0.3 \text{ M}$, MEA/Au = 1000/1 (mol/mol), NaOH/Au = 2, T = 50 °C, $P(O_2) = 0.5 \text{ Mpa}$, t = 15 min).

of NaOH at 50 °C as verified in Section 3.4.1. The selectivity of formic acid increased with the reaction time slowly, indicating that cleavage of the C–C bond was a continuous process. Taking both conversion of MEA and the selectivity of glycine into consideration, Au/ZrO₂ was



Fig. 6. Conversion of MEA using supported gold catalysts as a function of reaction time (Reaction conditions: $C_{\text{MEA}} = 0.3 \text{ M}$, MEA/Au = 1000/1 (mol/mol), NaOH/Au = 2, T = 50 °C, $P(O_2) = 0.5 \text{ Mpa}$).

viewed as the best catalyst and chosen as a model catalyst in the following study.

Comparison of catalyst preparation methods

Catalysts prepared using different methods usually have different properties and thus catalytic activities. Au/ZrO₂ prepared using four different methods including SI, SI-calcinated, DP, and IMP methods were tested for the selective oxidation of MEA. The results are shown in Fig. 7. It is obvious that the preparation methods have a significant influence on the catalytic performance with the catalyst prepared by SI method showing the best performance, with MEA conversion and glycine selectivity reaching 81% and 67%, respectively in 2 h.

To determine the possible reasons for the difference in the catalytic performance, the most important properties of electronic state and particle size that would affect the activity of Au/ZrO₂ were characterized using XPS and TEM. The Au 4f spectra of all the investigated Au/ZrO₂ samples are shown in Fig. 8. Lower binding energies of Au 4f around 83.5 eV in all samples were detected due to the modification of the electronic states of Au by the nanosized support as mentioned before. In order to determine the possible gold states in Au/ZrO₂ prepared by different methods, the curve fitting of the Au 4f core-level spectra was performed by using two spin-orbit split Au 4f_{7/2} and Au 4f_{5/2} components, separated by 3.7 eV, in a fixed intensity ratio of 1.33 and reasonable half-maximum values [48]. All the samples showed two Au 4f_{7/2} components around 83.5 eV and 85.2 eV, which could be attributed to Au⁰ and Au⁺ species, respectively [35,49,50]. It should be



Fig. 7. Effect of preparation methods for Au/ZrO_2 on the oxidation of MEA (Reaction conditions: $C_{MEA} = 0.3$ M, MEA/Au = 1000/1 (mol/mol), NaOH/Au = 2, T = 50 °C, $P(O_2) = 0.5$ Mpa, t = 2 h).



Fig. 8. Au 4f XPS spectra of Au/ZrO2 catalysts prepared by a) SI, b) SI-calcinated, c) DP, d) IMP methods.

noted that the relative contents of different gold species for all the investigated Au/ZrO₂ samples were quite similar, for example, the proportions of Au⁰ were 94.5%, 95.2%, 90.0%, and 95.4% for Au/ZrO₂ catalysts prepared by SI, SI-calcinated, DP and IMP, respectively, indicating that the preparation methods didn't affect the electronic state too much and that the variation in catalytic performance of the Au/ZrO₂ catalysts was not directly related to the electronic state in this case.

Fig. 9 shows the representative images and corresponding particle size distributions for Au/ZrO₂ catalysts prepared by SI, SI-calcinated, DP, and IMP methods. MEA conversion was inversely correlated to the average particle sizes as shown in Fig. 7. Au/ZrO₂ prepared by IMP method had the largest particle size of 5.3 nm and the lowest activity, while the catalyst prepared by DP method showed smaller particle and relatively high MEA conversion. There is no obvious correlation between glycine selectivity and the average particle size. Interestingly, Au/ZrO2 prepared by SI method showed similar average particle size to that prepared by DP method (2.8 vs. 3.1 nm), but much higher conversion of MEA (81% vs. 55%) and selectivity of glycine (67% vs. 51%) were observed when using $\mathrm{Au}/\mathrm{ZrO}_2$ prepared by SI method as the catalyst. Considering that there was no significant difference of the surface electronic state of gold as shown in Fig. 8, we attributed the improvement in both activity and selectivity to the presence of PVA in Au/ZrO2 obtained by SI method.

The role of PVA

PVA is a commonly used effective steric stabilizer, which can be easily adsorbed on the surfaces of the particles to form a capping layer to protect metal nanoparticles from aggregating through steric hindrance of bulky molecules that induce a repulsive force against the van der Waals attraction between two metal nanoparticles [51–53]. The ratio of PVA to Au could influence the thickness of the protective layer, and therefore the stability of the colloidal metal particles and accessibility of the reactant to the active site [53]. Thick capping layer usually leads to shielding effect on the surface of Au active sites for catalytic reactions, while the reactant would pass through thin layer and reach the active site [52,54].

To investigate the effect of PVA of the catalyst on the oxidation of MEA, we used various PVA/Au weight ratios of 0.2, 0.4, 0.8, 1.2, 2.0 and 3.0 to prepare 1% Au/ZrO₂ by SI method. The representative TEM images and Au particle size distributions for Au/ZrO2 prepared with different PVA amounts are shown in Fig. 10. It can be seen that the average gold particle size decreased from 3.4 nm to 2.8 nm with the increase of the PVA/Au ratio from 0.2 to 0.8. With the PVA/Au ratio further increasing, the average gold particle size remained around 2.8 nm, indicating that excessive amount of PVA cannot reduce the particle size further as particle growth could be well prevented and the velocity of nucleation became the main factor to determine the particle size when the PVA amount reached a certain point [55]. In addition, the decreasing trend of statistical standard deviation (given in the top right corner of every graph for Au particle size distributions) of the particle size with the increase of PVA/Au ratio indicated that aggregation of the nanoparticles was inhibited at higher PVA/Au ratios.

XPS studies of Au/ZrO_2 prepared by SI method using various PVA/ Au ratios were performed to check the possible change of the electronic state, and the results were shown in Table 3 and Figs. S5 and S6, ESI. As the ratio of PVA to Au varied, there was no obvious difference in the binding energy of Au4f, Zr3d, C1s, or O1s signals and the relative surface distribution of the gold species, which was consistent with the results that PVA could not lead to the change of binding energy of Au 4f [54,56]. It should be noted that the atomic ratios of carbon on the surface increased with the PVA/Au ratio, confirming the increase of PVA capping layer.

The effect of the ratio of PVA to Au on the oxidation of MEA is presented in Table 4. MEA conversion first increased with the increase of PVA/Au ratio, and it reached the maximum value when the ratio was 1.2. With the ratio of PVA to Au further increasing to 3.0, the MEA



Fig. 9. Representative TEM micrographs and corresponding Au particle size distributions for Au/ZrO₂ catalysts prepared by a -SI, b -SI-calcinated, c -DP, d -IMP methods.

conversion decreased. It is worth to mention that when the ratio of PVA to Au was higher than 0.8, the average gold particle size was 2.8 nm, implying that the change of the catalytic activity was irrelevant to the particle size when the PVA/Au ratio varied from 0.8 to 3.0. Interestingly, the MEA turnover frequency (TOF, calculated with conversions ranging from 11%⁻³⁶% at 15 min) was doubled over Au/ZrO₂ by SI method when the PVA/Au ratio changed from 0.4 to 1.2, compared with that over Au/ZrO₂ by DP method (Entry 1, Table 4). Further increase of PVA/Au ratio led to decrease of the TOF to 0.6 s⁻¹. In addition, the selectivity of glycine continuously increased with the increase of the PVA/Au ratios), and the selectivity of FA was inversely proportional to the PVA/Au ratio. These phenomena observed above indicated the promoting effect of suitable amount of PVA in the catalytic oxidation of MEA over gold catalysts.

In-situ FTIR spectra of MEA adsorbed on ZrO_2 , Au/ZrO_2 prepared by DP method (no PVA) and Au/ZrO_2 prepared by SI method (prepared using the PVA/Au ratio of 1.2) were collected to reveal the role of PVA. As shown in Fig. 11, before introduction of MEA into the system (time = 0), the spectrum of Au/ZrO_2 prepared by SI method shows the characteristic bands at 1731.4 cm^{-1} (C==O, stretching vibration) and 1384.2 cm⁻¹ (O–H, deformation vibration), which confirmed the presence of PVA. All samples including ZrO_2 , Au/ZrO_2 prepared by DP method and Au/ZrO_2 prepared by SI method could adsorb MEA and the



Fig. 10. Representative TEM micrographs and corresponding Au particle size distributions for Au/ZrO_2 catalysts prepared by SI method with different PVA/Au ratios: a -0.2, b -0.4, c -0.8, d -1.2, e -2.0, f -3.0.

amounts of adsorbed MEA increased with time, as indicated by the intensity increase of the band for MEA C–N stretching vibration at 1076 cm⁻¹ with increasing adsorption time. Particularly, the intensity of the band at 1076 cm⁻¹ increased significantly in 180 min for MEA adsorbed on Au/ZrO₂ prepared by SI method, while the intensity of the

Table 3

Content of carbon on the surface, the binding energy of Au 4f, and the relative surface distribution of gold species of Au/ZrO₂ with different PVA/Au ratios.

PVA/Au	C1s(%)	Au 4f _{7/2} (eV)	Au 4f _{5/2} (eV)	Au species (%)	
				Au ⁰	Au ⁺
0.2	15.4	83.6	87.3	93.5	6.5
0.4	14.7	83.5	87.2	95.1	4.9
0.8	15.1	83.5	87.2	93.3	6.7
1.2	16.3	83.5	87.2	94.5	5.5
2.0	16.9	83.5	87.2	95.9	4.1
3.0	19.0	83.5	87.2	91.3	8.7

Table 4

MEA oxidation with Au/ZrO_2 prepared by DP method and SI method using different PVA/Au ratios.

PVA/Au	Au particle size (nm)	Conversion (%) ^[a]	Selectivity of GLY (%) ^[a]	Selectivity of FA (%) ^[a]	TOF at 15 min (s ⁻¹) ^[b]
_[c]	3.1	55	51	5.8	0.7
$0.2^{[d]}$	3.4	48	58	6.5	0.5
0.4 ^[d]	3.3	55	62	6	1.5
0.8 ^[d]	2.8	70	67	4.8	1.5
$1.2^{[d]}$	2.8	81	67	4.2	1.4
$2.0^{[d]}$	2.8	71	68	3.6	1.3
3.0 ^[d]	2.7	60	70	3.2	0.6

[a] Reaction conditions: $C_{MEA} = 0.3$ M, MEA/Au = 1000/1 (mol/mol), NaOH/Au = 2, T = 50 °C, $P(O_2) = 0.5$ Mpa. Conversion and selectivities were calculated at reaction time of 2 h.

[b]TOF (s⁻¹) = Number of MEA molecules consumed per second/Number of exposed Au atoms, calculated after reaction for 15 min.

[c] Au/ZrO₂ prepared by DP method.

[d] Au/ZrO₂ prepared by SI method using different PVA/Au ratios.



Fig. 11. FTIR spectra of MEA adsorbed on ZrO_2 , Au/ZrO_2 prepared by DP method (no PVA) and Au/ZrO_2 prepared by SI method (prepared using the PVA/Au ratio of 1.2) with time (curves from top to bottom: 0, 60, 120, 180, 240, 300, 360 min for MEA adsorbed on ZrO_2 , Au/ZrO_2 prepared by DP method, and 0, 30, 60, 120, 180 min for MEA adsorbed on Au/ZrO_2 prepared by SI method).

same band slightly increased in 360 min for MEA adsorbed on ZrO_2 and Au/ZrO_2 prepared by DP method, indicating the increased amount and rate of MEA adsorption on Au/ZrO_2 prepared by SI method due to the presence of PVA compared with the other two. For the FTIR spectra of MEA adsorbed on the ZrO_2 support, the intensity of the band at 1595 cm⁻¹ (N–H of MEA, deformation vibration) increased with the increasing amounts of MEA, while for the FTIR spectra of MEA adsorbed on Au/ZrO_2 prepared by DP method, no obvious change of peak

intensity around 1595 cm⁻¹ was observed as the adsorption amount of MEA increased, indicating the coordination between the amino group of adsorbed MEA and the surface of Au nanoparticles [34,57,58]. For the FTIR spectra of MEA adsorbed on Au/ZrO2 with PVA capping layer around Au particles, the intensity of the characteristic band for MEA at 1595 cm⁻¹ (N–H, deformation vibration) obviously increased with the adsorption amounts of MEA, indicating that in this case, the N-H bond was more "free" and coordination of the MEA amino group with Au nanoparticles was effectively prevented by PVA capping layer. In short, the presence of PVA can enhance the adsorption of MEA on the catalysts and prevent the coordination of the amino group with Au nanoparticles. Therefore, the doubled TOF (from 0.7 s^{-1} for DP catalyst to 1.4 s^{-1} for SI catalyst with the PVA/Au ratio of 1.2), improved MEA conversion (from 55% for DP catalyst to 81% for SI catalyst with the PVA/Au ratio of 1.2) and selectivity of glycine (from 51% for DP catalyst to 70% for SI catalyst with the PVA/Au ratio of 3.0) for Au/ZrO2 prepared by SI method could be attributed to the ability of PVA to enhance the adsorption of substrate and mediate the interaction between MEA and the Au nanoparticles, making the hydroxyl group of MEA preferentially react on the active sites.

In order to study the reason for the enhanced MEA adsorption on the catalysts and the prevented coordination of the MEA amino group with Au nanoparticles by PVA capping layer, the interactions between MEA and PVA were explored with spectroscopic analysis and simulation. ¹H NMR spectra of aqueous MEA/PVA solutions, with the same concentrations of MEA but different PVA/MEA ratios of 0, 1, 3, were collected as shown in Fig. S7, ESI, and the chemical shifts of H-1 (NH₂CH₂CH₂OH) and H-2 (NH₂CH₂CH₂OH) were summarized in Table 5. It was revealed that with the increase of the ratio of PVA to MEA, both H-1 and H-2 shifted downfield. These trends indicated that hydrogen bonds were formed between PVA and MEA, as the oxygen atom in the hydroxyl group or nitrogen atom in the amino group in MEA could provide lone pair electrons to form hydrogen bonds with the hydroxyl hydrogen of PVA, leading to deshielding effect and downfield shifts of H-1 and H-2 in the neighboring methylene groups. However, the greater downfield shift of H-1 compared with H-2 (0.5 vs. 0.3 ppm) indicated a preferential trend for the amino nitrogen atoms to interact with the hydrogen of -OH in PVA.

In short, the presence of PVA capping layer on the catalyst was confirmed by FTIR and XPS analysis. It can not only stabilize Au nanoparticles but also influence the catalytic performance by the hydrogen bonds between PVA and the substrate. As shown in the proposed collision models of MEA on different catalysts in Fig. 12, the enhanced adsorption of the substrate on the catalyst significantly promoted the catalytic activity, and the preferential interactions between the MEA amino group and PVA favored the reaction of hydroxyl group of MEA on the active sites. However, when the ratio of PVA to Au was higher than 1.2, the thicker PVA capping layer could hinder diffusion of the reactant and decrease the catalytic activity, which was consistent with the previous report for PVA stabilized Au nanoparticles supported on activated carbon and TiO₂ [26,56].

Influence of the reaction parameters

The effects of reaction parameters, including temperature, NaOH/

Table 5

Chemical shifts of H-1 (NH $_2$ CH $_2$ CH $_2$ OH) and H-2 (NH $_2$ CH $_2$ CH $_2$ OH) in the solutions of MEA with different PVA/MEA ratios.

PVA/MEA (wt/wt)	δ _{-CH2OH} (ppm)	δ _{-CH2NH2} (ppm)	Δ _{-CH2OH} (ppm)	Δ _{-CH2NH2} (ppm)
0	3.60	2.73	0	0
1	3.62	2.76	0.2	0.3
3	3.63	2.78	0.3	0.5



Fig. 12. Proposed collision models of MEA on (a) naked gold nanoparticles and (b) PVA capped gold nanoparticles (N -blue; H -white; C -gray; O -red) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

MEA ratio, substrate/metal ratio, and MEA concentration, on the conversion of MEA and selectivities of the products were investigated over 1% Au/ZrO₂ prepared by SI method using PVA/Au ratio of 1.2.

Effect of reaction temperature

Reaction temperature is an important parameter to influence a chemical process. The temperature effect on MEA oxidation was studied in the range from 10 °C to 90 °C and the results are shown in Fig. 13. As expected, the conversion of MEA increased with the temperature increasing from 10 °C to 50 °C, and reached the maximum value at 50 °C. With the reaction temperature further increasing to 90 °C, the MEA conversion decreased apparently from 81% at 50 °C to 59% at 90 °C, which could be attributed to the quick removal of PVA capping layer in water at higher temperatures, similar to the fact that Au/ZrO2 prepared by DP method with no PVA exhibited lower MEA conversion of 55% [26]. However, the selectivity of glycine increased with temperature in the tested range, and the selectivity of ANHA decreased to nearly zero at 90 °C. The reaction solutions obtained at 50 °C were further treated at 90 °C or at 50 °C with 4 more eqv. NaOH in the absence of the catalyst for 2 h, respectively, and the results are shown in Table S2, ESI. The content of ANHA decreased to zero and the concentrations of glycine and MEA improved accordingly (corresponding to increased glycine selectivity and decreased MEA conversion), indicating that ANHA could be easily hydrolyzed under higher temperature or with the presence of



Fig. 13. Effect of reaction temperature on the oxidation of MEA (Catalyst: Au/ ZrO₂ prepared by SI method using PVA/Au ratio of 1.2; reaction conditions: $C_{\text{MEA}} = 0.3 \text{ M}$, MEA/Au = 1000/1 (mol/mol), NaOH/Au = 2, *P* (O₂) = 0.5 Mpa, *t* = 2 h).

more base to yield both glycine and MEA. The selectivity of formic acid increased with the increase of temperature, suggesting cleavage of the C–C bond was boosted, which was consistent with the phenomena observed in gold catalyzed glycerol oxidation that the amount of products from the C–C cleavage increased by increasing the reaction temperature [59]. Considering the activity and stability of the catalyst, 50 °C was chosen as the reaction temperature in the following study.

Effect of the molar ratio of NaOH to MEA

The presence of strong base has important effects on both conversion and product distribution in the oxidation of alcohols [60-62]. In this study, oxidation of MEA was carried out over Au/ZrO₂ catalysts keeping all parameters constant except the initial molar ratio of NaOH to MEA, and the results were shown in Fig. 14. As expected, the conversion of MEA per pass increased with increasing ratio of NaOH to MEA. Despite the amino group can provide a basic environment, the conversion of MEA and the selectivity of glycine were very low in the absence of NaOH (11% and 23%, respectively). When the ratio of NaOH to MEA increased to 1.0, the conversion of MEA dramatically increased to a maximum value of 80% in 2 h. The need for the addition of strong base is consistent with the situations of the glycerol oxidation, where strong base helped the initial deprotonation of a primary alcohol group, followed by being rapidly dehydrogenated to glyceraldehyde [60,61,63]. For the product distribution, the selectivity of glycine



Fig. 14. Effect of NaOH/MEA ratio on the oxidation of MEA (Catalyst: Au/ZrO₂ prepared by SI method using PVA/Au ratio of 1.2; reaction conditions: $C_{\text{MEA}} = 0.3 \text{ M}$, MEA/Au = 1000/1 (mol/mol), T = 50 °C, $P(O_2) = 0.5 \text{ Mpa}$, t = 2 h).



Fig. 15. Effect of substrate/metal molar ratio on the oxidation of MEA (Catalyst: Au/ZrO₂ prepared by SI method using PVA/Au ratio of 1.2; reaction conditions: $C_{\text{MEA}} = 0.3 \text{ M}$, NaOH/Au = 4, T = 50 °C, $P(O_2) = 0.5 \text{ Mpa}$, t = 2 h).

enhanced while the selectivity of ANHA decreased with the NaOH/MEA molar ratio, which could be attributed to the hydrolysis of ANHA to glycine in the presence of NaOH. Taking the MEA conversion and the glycine selectivity into consideration, the NaOH/MEA ratio of 4.0 was chosen for further experiments.

Effect of substrate/metal molar ratio

Catalyst loading is another parameter that could influence the processing of a chemical reaction. The MEA/Au molar ratio was varied in the range from 300 to 1500 while the other reaction parameters were kept constant to study the effect of substrate/metal ratio on MEA conversion and product distribution. Fig. 15 shows that the conversion of MEA and selectivities of the products were dependent on the catalyst amount. The decrease of MEA/Au ratio (i.e., increase catalyst amount) helped to improve MEA conversion from 65% to 100% when the ratio varied from 1500 to 500 because of the increase of the concentration of active sites. Glycine selectivity increase from 80% to 85% was observed. Meanwhile, the selectivities of FA and ANHA decreased from 4.5% and 9% to 1.3% and 0.4%, respectively, when the MEA/Au ratio decreased from 1500 to 300. Lower MEA/Au ratio meant increased catalyst amount and number of active sites, which would lead to increased initial reaction rate and MEA conversion in a short time before removal of PVA (PVA could be removed from the gold surfaces by water reflux [26] and this phenomenon had been confirmed by FTIR as shown in Fig. S8, ESI). Therefore, the total selectivity of glycine increased and the selectivity of formic acid was reduced at lower MEA/Au ratios.

Effect of the concentration of MEA

Various concentrations of MEA aqueous solutions show different base strengths, which would influence the proceeding of the reaction. The effects of initial MEA concentration on its selective oxidation were illustrated in Fig. 16. Strong dependence of catalytic activity and product selectivity on the substrate concentration was observed. At lower substrate concentrations (e.g., 0.1-0.5 M), conversions higher than 96% could be achieved. Further increasing the concentration led to decreased MEA conversion. For instance, when the MEA concentration was 1.0 M, the conversion decreased to 79%, indicating that too high MEA concentration accelerated deactivation of Au/ZrO₂ catalyst. The selectivity of glycine enhanced with the concentration of MEA until 0.5 M. At MEA concentrations higher than 0.5 M, apparent decrease in selectivity of glycine and increase in formic acid selectivity were observed, indicating that the side reactions were boosted under higher MEA concentrations. The selectivity of ANHA decreased with the increasing concentration of MEA due to hydrolysis of ANHA at higher base concentration.

Recycle and reuse of Au/ZrO2 prepared by SI method was studied in



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Fig. 16. Effect of initial substrate concentration on the oxidation of MEA (Catalyst: Au/ZrO₂ prepared by SI method using PVA/Au ratio of 1.2; reaction conditions: MEA/Au = 500/1 (mol/mol), NaOH/Au = 4, T = 50 °C, *P* (O₂) = 0.5 Mpa, t = 2 h).

this work. Results (Fig. S9, ESI) indicate that the recycled catalyst exhibited much lower activity than the fresh one. In addition, it was found that the Au nanoparticles seriously aggregated after being used for 3 cycles (Fig. S10, ESI). Based on the above discussion, Au particle aggregation, PVA leaching from the catalyst into the solution, and possible adsorption of the reactant on the catalyst surface led to the decreased activity of the recycled catalyst. Work to solve the problem of catalyst deactivation is currently undergoing in our laboratory.

Reaction pathway for MEA oxidation

Possible reaction pathways of MEA oxidation on Au catalysts were proposed based on the detected intermediates and products, as well as the widely accepted mechanisms of gold-catalyzed alcohol oxidation and oxidative dehydrogenation of primary and secondary amines [15,19,44,64-67]. As shown in Scheme 2, there exist at least two pathways as both the hydroxyl and amino groups of the MEA molecule are active on Au catalysts. In pathway A, the oxidation of the hydroxyl group of MEA follows a similar process to the common alcohol oxidation on Au to produce 2-aminoacetaldehyde, which could be subsequently oxidized to the target product glycine (pathway A1) or could couple with the primary amine to produce amide or imine by-products [15,19,44,45]. Amide (mainly ANHA, *m*/*z* 117.07, Fig. S2 and Table S3, ESI) was the Au catalyzed oxidative coupling products of the aldehyde intermediate with MEA. Imine (mainly $H_2N - CH_2 - C =$ N-CH₂-CH₂-OH, m/z 101.07, Fig. S2 and Table S3, ESI), was the coupling products of the aldehyde intermediate with MEA [44,45]. In pathway B, the MEA molecules proceeded through the oxidative dehydrogenation of the amine to the imine intermediate RCH = NH (m/z58.03), as detected by MS (Fig. S2, ESI), which subsequently reacted with water to form glycolaldehyde [64-68]. According to the literature, glycolaldehyde could be subsequently oxidized into formic acid and glycolic acid, which were detected by NMR and HRMS (Fig. S2 and S3, ESI) [69,70].

Conclusions

In this study, a series of Au catalysts supported on different metal oxides were synthesized and characterized by TEM, XRD, ICP, XPS, and TPD. These catalysts were used to catalyze MEA oxidation to produce glycine. It was shown that the catalytic activity, product selectivity, and stability of the catalysts were strongly dependent on the acid-base properties of the supporting metal oxides. The catalytic activity was positively correlated with the total basicity concentration of catalysts,



Scheme 2. Proposed reaction pathways for the gold-catalyzed aerobic oxidation of MEA.

and the selectivity of glycine and the stability were negatively correlated with the acidity concentration. The highest catalytic performance in the oxidation of MEA among the tested catalysts was observed on Au/ZrO_2 .

Preparation methods have a significant influence on the catalytic activity of the Au nanoparticles. Au/ZrO2 catalyst prepared by SI method exhibited good activity and glycine selectivity because of the presence of PVA capping layer and the appropriate Au particle size. Insitu FTIR and ¹H NMR analysis demonstrated that the PVA capping layer can enhance MEA adsorption on the catalysts and MEA molecules were preferentially hydrogen bonded with PVA through interactions between amino group of MEA and hydroxyl group of PVA, favoring the reaction of the hydroxyl group of MEA on the active sites, which led to doubled TOF, improved MEA conversion and selectivity of glycine when the catalyst was capped with PVA layer. The reaction conditions for the oxidation of MEA were also optimized and under these optimal conditions, the MEA conversion and the selectivity of glycine could reach 97% and 98%, respectively. This study provides a systematic study on an alternative route for glycine synthesis and a deeper understanding of the role of the PVA layer, which is helpful for designing more efficient catalysts to improve the catalytic performance.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2019.03.011.

References

- [1] R.J. Block, Chem. Rev. 38 (1946) 501-571.
- [2] J.M. Orten, R.M. Hill, J. Am. Chem. Soc. 53 (1931) 2797-2799.
- [3] W.C. Tobie, G.B. Ayres, J. Am. Chem. Soc. 64 (1942) 725.
- [4] Y. Ogata, A. Kawasaki, T. Goto, J. Org. Chem. 33 (1968) 1107-1111.
- [5] M. Gibson, R. Bradshaw, Angew. Chem. Int. Ed. 7 (1968) 919–930.
- [6] E.J. Corey, D.E. Cane, J. Org. Chem. 35 (1970) 3405–3409.
- [7] R. Williams, Oxford, (1989).
- [8] A. Huges, Amino Acids, Peptides and proteins in organic chemistry, Origins and Synthesis of Amino Acids Vol. 1 Wiley-VCH Verlag GmbH & Co., KGaA, Weinheim, 2009, p. 610.
- [9] Y. Zeng, Z. Li, G.P. Demopoulos, Ind. Eng. Chem. Res. 53 (2014) 16864–16872.
- [10] Y. Zeng, Z. Li, G.P. Demopoulos, Ind. Eng. Chem. Res. 55 (2016) 2426–2437.
- [11] H. Shimizu, C. Fujita, T. Endo, I. Watanabe, Google Patents, (1993).

- [12] T. Aoki, K. Kawakami, K. Otsubo, Google Patents, (2005).
- [13] W. Deng, Y. Wang, S. Zhang, K.M. Gupta, M.J. Hülsey, H. Asakura, L. Liu, Y. Han, E.M. Karp, G.T. Beckham, Proc. Natl. Acad. Sci. 115 (2018) 5093–5098.
- [14] G. Liang, A. Wang, L. Li, G. Xu, N. Yan, T. Zhang, Angew. Chem. Int. Ed. 129 (2017) 3096–3100.
- [15] C. Della Pina, E. Falletta, L. Prati, M. Rossi, Chem. Soc. Rev. 37 (2008) 2077–2095.
 [16] S. Biella, G. Castiglioni, C. Fumagalli, L. Prati, M. Rossi, Catal. Today 72 (2002)
- 43–49.
- [17] J.H. Billman, E.E. Parker, J. Am. Chem. Soc. 65 (1943) 761–762.
- [18] J.H. Billman, E.E. Parker, W.T. Smith, J. Biol. Chem. 180 (1949) 29-31.
- [19] T. Mallat, A. Baiker, Chem. Rev. 104 (2004) 3037–3058.
- [20] A. Villa, N. Dimitratos, C.E. Chan-Thaw, C. Hammond, L. Prati, G.J. Hutchings, Acc. Chem. Res. 48 (2015) 1403–1412.
- [21] D.I. Enache, J.K. Edwards, P. Landon, B. Solsona-Espriu, A.F. Carley, A.A. Herzing, M. Watanabe, C.J. Kiely, D.W. Knight, G.J. Hutchings, Science 311 (2006) 362–365.
- [22] K. Yamaguchi, N. Mizuno, Angew. Chem. Int. Ed. 41 (2002) 4538-4542.
- [23] S.F.I. Thaddeus, W.L. Moench Jr, Google Patents, (2003).
- [24] A. Gaiassi, L. Prati, Catal. Today 141 (2009) 378-384.
- [25] A. Villa, S. Campisi, M. Schiavoni, L. Prati, Materials 6 (2013) 2777–2788.
- [26] J.A. Lopez-Sanchez, N. Dimitratos, C. Hammond, G.L. Brett, L. Kesavan, S. White, P. Miedziak, R. Tiruvalam, R.L. Jenkins, A.F. Carley, Nat. Chem. 3 (2011) 551.
- [27] Y. Li, Y. Zheng, L. Wang, Z. Fu, ChemCatChem 9 (2017) 1960-1968.
- [28] Y. Kotolevich, E. Kolobova, E. Khramov, M.H. Farías, Y. Zubavichus, H. Tiznado, S. Martínez-González, V. Cortés Corberán, J.D. Mota-Morales, A. Pestryakov, N. Bogdanchikova, Mol. Catal. 427 (2017) 1–10.
- [29] C.C. Torres, V.A. Jiménez, C.H. Campos, J.B. Alderete, R. Dinamarca, T.M. Bustamente, B. Pawelec, Mol. Catal. 447 (2018) 21–27.
- [30] C. Xu, Z. Wang, X. Huangfu, H. Wang, RSC Adv. 4 (2014) 27337-27345.
- [31] S. Li, D. Gong, H. Tang, Z. Ma, Z.-T. Liu, Y. Liu, Chem. Eng. J. 334 (2018) 2167–2178.
- [32] Y.-H. Ke, X.-X. Qin, C.-L. Liu, R.-Z. Yang, W.-S. Dong, Catal. Sci. Technol. 4 (2014) 3141–3150.
- [33] T. Rundlöf, M. Mathiasson, S. Bekiroglu, B. Hakkarainen, T. Bowden, T. Arvidsson, J. Pharm. Biomed. Anal. 52 (2010) 645–651.
- [34] Y. Yang, J. Li, J. Mu, H. Rong, L. Jiang, Nanotechnology 17 (2005) 461.
- [35] E.D. Park, J.S. Lee, J. Catal. 186 (1999) 1-11.
- [36] X. Zhang, H. Wang, B.-Q. Xu, J. Phys. Chem. B 109 (2005) 9678–9683.
- [37] M. Comotti, C. Weidenthaler, W.-C. Li, F. Schüth, Top. Catal. 44 (2007) 275-284.
- [38] K. Yang, J. Liu, R. Si, X. Chen, W. Dai, X. Fu, J. Catal. 317 (2014) 229-239.
- [39] Y.-W. Chen, D.-S. Lee, H.-J. Chen, Int. J. Hydrogen Energy 37 (2012) 15140-15155.
- [40] W. Wang, Y. Xie, S. Zhang, X. Liu, M. Haruta, J. Huang, Catalysts 8 (2018) 60.
- [41] Z. Yuan, Z. Gao, B.-Q. Xu, Chin. J. Catal. 36 (2015) 1543-1551.
- [42] A. Villa, S. Campisi, K.M. Mohammed, N. Dimitratos, F. Vindigni, M. Manzoli, W. Jones, M. Bowker, G.J. Hutchings, L. Prati, Catal. Sci. Technol. 5 (2015) 1126–1132.
- [43] N. Weiher, A.M. Beesley, N. Tsapatsaris, L. Delannoy, C. Louis, J.A. van Bokhoven, S.L. Schroeder, J. Am. Chem. Soc. 129 (2007) 2240–2241.
- [44] J.-Fo. Soulé, H. Miyamura, S. Kobayashi, J. Am. Chem. Soc. 133 (2011) 18550–18553.
- [45] L. Zhang, W. Wang, A. Wang, Y. Cui, X. Yang, Y. Huang, X. Liu, W. Liu, J.-Y. Son, H. Oji, Green Chem. 15 (2013) 2680–2684.
- [46] T. Ishida, R. Takamura, T. Takei, T. Akita, M. Haruta, Appl. Catal. A Gen. 413 (2012) 261–266.
- [47] X. Huang, X. Wang, X. Wang, M. Tan, W. Ding, X. Lu, J. Catal. 301 (2013) 217–226.
- [48] M. Casaletto, A. Longo, A. Martorana, A. Prestianni, A. Venezia, Surf. Interface Anal. 38 (2006) 215–218.
- [49] A.M. Venezia, G. Pantaleo, A. Longo, G. Di Carlo, M.P. Casaletto, F.L. Liotta, G. Deganello, J. Phys. Chem. B 109 (2005) 2821–2827.
- [50] J. Chastain, R.C. King, J. Moulder, Handbook of X-ray Photoelectron Spectroscopy: a Reference Book of Standard Spectra for Identification and Interpretation of XPS Data, Physical Electronics Division, Perkin-elmer Corporation Eden Prairie, Minnesota. (1992).
- [51] D.F. Evans, H. Wennerström, (1999).

- [52] A. Villa, D. Wang, D. Su, G.M. Veith, L. Prati, Phys. Chem. Chem. Phys. 12 (2010) 2183–2189.
- [53] A. Roucoux, J. Schulz, H. Patin, Chem. Rev. 102 (2002) 3757–3778.
- [54] Y. Cao, X. Liu, S. Iqbal, P.J. Miedziak, J.K. Edwards, R.D. Armstrong, D.J. Morgan, J. Wang, G.J. Hutchings, Catal. Sci. Technol. 6 (2016) 107–117.
- [55] J. Polte, CrystEngComm 17 (2015) 6809-6830.
- [56] A. Villa, D. Wang, G.M. Veith, F. Vindigni, L. Prati, Catal. Sci. Technol. 3 (2013) 3036–3041.
- [57] D.V. Leff, L. Brandt, J.R. Heath, Langmuir 12 (1996) 4723-4730.
- [58] A. Kumar, S. Mandal, P. Selvakannan, R. Pasricha, A. Mandale, M. Sastry, Langmuir 19 (2003) 6277–6282.
- [59] L. Prati, P. Spontoni, A. Gaiassi, Top. Catal. 52 (2009) 288.
- [60] S. Carrettin, P. McMorn, P. Johnston, K. Griffin, G.J. Hutchings, Chem. Commun. (Camb.) (2002) 696–697.

- [61] F. Porta, L. Prati, J. Catal. 224 (2004) 397–403.
- [62] W.C. Ketchie, M. Murayama, R.J. Davis, Top. Catal. 44 (2007) 307–317.
 [63] S. Carrettin, P. McMorn, P. Johnston, K. Griffin, C.J. Kiely, G.A. Attard,
- G.J. Hutchings, Top. Catal. 27 (2004) 131–136.
- [64] S. Chi, G.T. Rochelle, Ind. Eng. Chem. Res. 41 (2002) 4178–4186.
 [65] A.J. Sexton, G.T. Rochelle, Ind. Eng. Chem. Res. 50 (2010) 667–673.
- [65] A.J. Sexion, G.I. Rochene, Ind. Eng. Chem. Res. 50 (2010) [66] M. Largeron, Eur. J. Org. Chem. 2013 (2013) 5225–5235.
- [67] B. Zhu, M. Lazar, B.G. Trewyn, R.J. Angelici, J. Catal. 260 (2008) 1–6.
- [66] K. Matsuoka, Z. Iriyama, T. Abe, M. Matsuoka, Z. Ogumi, Electrochim. Acta 51 (2005) 1085–1090.
- [69] Z. Wang, C. Xu, H. Wang, Catal. Lett. 144 (2014) 1919–1929.
- [70] F. Wang, Y. Wang, F. Jin, G. Yao, Z. Huo, X. Zeng, Z. Jing, Ind. Eng. Chem. Res. 53 (2014) 7939–7946.