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Gold Nano-size Effect in Au/SiO_2 for Selective Ethanol Oxidation in Aqueous Solution

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Abstract Narrowly sized colloidal Au particles of varying average sizes (3–30 nm) were immobilized on an inert support (SiO_2) to study the Au size effect on the aerobic oxidation of ethanol in aqueous solution. Au particles with an average diameter of 5 nm showed an areal activity that was about three times that of the smaller (3 nm), and 15 times that of larger (10–30 nm) Au particles. Investigation on the dependence of product yields on ethanol conversion over these differently sized Au particles clearly uncovered that the yield of acetic acid increased always with the ethanol conversion, while that of acetaldehyde passed a maximum at an ethanol conversion of 20–30%, therefore well demonstrating that acetaldehyde is the intermediate product in the oxidation of ethanol to acetic acid.

Keywords Gold catalyst · Nano-size effect · Ethanol · Aerobic oxidation · Acetic acid

1 Introduction

Catalysis by gold is one of the fastest growing research topics in the field of catalysis [1, 2]. Nanosized gold particles in intimate contact with support materials was found to exhibit high activity/selectivity in a number of reactions, including low temperature CO oxidation [1–3], propylene epoxidation [1–3], selective hydrogenation of unsaturated hydrocarbons, and so on [4–6]. Recently, it was further found that Au nanoparticles, as compared with Pt-group catalysts, are more selective as well as stable for liquid-phase oxidation of various alcohols to their corresponding aldehydes/acids [7–21].

As in many other gold catalyzed reactions, smaller Au particles generally showed higher alcohol conversion, due to their increased number of exposed Au atoms. However, controversial results were reported with regard to the Au size effect based on per surface atom or per unit surface area of Au [17–20], which would be most probably due to the strong Au-support interaction. It has been well documented in literature that carbon supported Au particles generally exhibited higher activity for glycerol or glycol oxidation than oxides supported catalysts [7–10], and the catalytic activity was also significantly affected by nature of the supporting carbon materials [17, 18, 21]. A number of recent investigations further revealed that Au nanoparticles supported on some oxides (e.g., CeO_2, TiO_2) and Cu–Mg–Al mixed oxide could also show high activity for the oxidation of aliphatic and aromatic alcohols [11–16]. In the aerobic oxidation of aliphatic alcohols (e.g., 3-octanol), activity of Au/CeO_2 catalyst was even significantly enhanced with reducing the particle size of CeO_2 [11].

It is expected that any disturbance of supporting material on our understanding of size-dependent catalysis by Au would be minimized if an inert or non-interacting material like silica was used to support narrowly sized Au nanoparticles. We have practiced this strategy in the present study by synthesizing first narrowly sized Au colloids of different average sizes, followed by immobilization of these colloids on an aerosil SiO_2 to prepare "model" Au/SiO_2 catalysts for selective aerobic oxidation of aqueous ethanol, a very promising reaction for utilization of biomass-derived ethanol (i.e., bioethanol) [14, 15]. Our data clearly uncover that Au particles of ca. 5 nm are the most active for the reaction. We show also that acetaldehyde is

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the intermediate product in the oxidation of ethanol to acetic acid.

2 Experimental

Gold nanoparticles with diameters of 3.0 ± 0.6, 5.0 ± 0.8 and 10.0 ± 1.2 nm and designated as Au(3), Au(5) and Au(10), respectively, were synthesized by reduction of $HAuCl_4$ (Guiyang Institute of Precious Metals) in aqueous solution. The Au(3) nanoparticles were synthesized using polyvinyl alcohol (PVA, Beijing Chemical Reagent Company) as a protector and $NaBH_4$ (Beijing Chemical Reagent Company) as the reductant following the method of Porta et al. [22] with a few modifications to obtain a narrower size distribution [23]. Briefly, 1 mL PVA (10 mg mL^{-1}) solution was mixed with 200 mL $AuCl_4^-$ solution (0.25 mM) (PVA/Au (wt/wt) ratio = 1.0) for 1 h under vigorous stirring, then 5 mL fresh $NaBH_4$ solution (0.1 M) was dropwise added and the solution was stirring for 2 h to produce the Au colloid. The similar method was also used for the synthesis of the Au(5) nanoparticles except that the PVA/Au (wt/wt) ratio was reduced to 0.5. The Au(10) nanoparticles were synthesized by using tri-sodium citrate (Beijing Chemical Reagent Company) as the reductant following the method of Enustun and Turkvich [24]. Typically, 170 mL of 0.3 mM $AuCl_4^-$ solution was refluxed under vigorous stirring, 30 mL tri-sodium citrate solution (1 wt%) was then added and the solution was kept to reflux for 1 h to produce the Au particles.

The immobilization of Au particles on SiO_2 were accomplished by adding aerosil SiO_2 (Degussa, 90 m^2/g) in the colloidal solution of Au, followed by adjusting the solution acidity to pH = 0.5 with nitric acid under stirring. The solids were then separated, washed and dried at 110 °C to produce Au/SiO_2 catalysts. Three sets of Au catalysts were prepared and coded as Au(3)/SiO_2, Au(5)/SiO_2 and Au(10)/SiO_2, respectively, according to the average sizes of colloidal Au in solution. The loading of Au in each set of catalyst was controlled by varying the volume of Au colloidal solution of a given concentration, and was confirmed by AES-ICP analysis. Transmission electron microscopy (TEM) analysis was performed on a JEM-2010 system operating at 200 kV.

Catalytic oxidation of ethanol in aqueous solution was performed in a stainless autoclave (25 mL) with magnetic stirring. Typically, the autoclave was charged with 2 mL 5 wt% ethanol aqueous solution and 20 mg Au/SiO_2 catalyst, and then sealed and pressurized with O_2 to 0.6 MPa at room temperature. When the temperature of the autoclave reached 210 °C, the reaction was initiated by switching on the magnetic stirring. The reaction was stopped by cooling the autoclave in an ice-water bath. The liquid products were analyzed on a HP-6890 GC with a PEG-20M capillary column and a FID detector. The gas phase carbon-containing by-products were also analyzed on another GC with a TDX column and a TCD detector, showing that the selectivity of CO_x was below 2% by carbon calibration.

3 Results and Discussion

Figure 1 shows the representative TEM images of the colloid Au particles together with their size distribution. In all of the cases, approximately spherical shaped particles with a narrow size distribution in the range of 3.0 ± 0.6, 5.0 ± 1.5 and 10 ± 1.2 nm, respectively, were obtained. The average Au particle size on SiO_2 obtained by TEM measurement was 3.7 ± 0.6 nm on Au(3)/SiO_2 and 4.9 ± 0.6 nm on Au(5)/SiO_2 catalysts. Thus the morphologic characteristics of Au(3) and Au(5) colloidal particles were maintained after the immobilization. However, some large Au particles in the range of 10–30 nm could be observed on Au(10)/SiO_2, suggesting a slight agglomeration of Au(10) during the immobilization process. In each set of the Au/SiO_2 catalysts, increasing the Au loading from 1 to 5 wt% only increased the number or surface density of Au nanoparticles in the samples; the average size of Au particles and their size distribution were not altered.

The catalytic reaction results of aerobic oxidation of ethanol (EtOH) in aqueous solution are shown in Table 1. Over each set of the Au/SiO_2 catalysts, ethanol conversion increased with the Au loading due to the increased number of Au nanoparticles on SiO_2; whereas, at a fixed Au loading, the ethanol conversion changed remarkably according to the particle size of Au. At each of the Au loadings, the highest ethanol conversions were always obtained over the Au(5)/SiO_2 catalysts; the Au(10)/SiO_2 catalysts always produced the lowest ethanol conversions that were no higher than 3%.

Ethanol oxidation over the present Au/SiO_2 catalysts produced consistently acetic acid (AcOH) and acetaldehyde (AcH) as the main products. The only by-product identified was ethyl acetate (AcOEt), which was formed due to a minor reaction (esterification) between ethanol and AcOH [15]. Very interesting, we see clearly in Fig. 2 that the selectivity to AcOH was counter-related with that to AcH, and the level of ethanol conversion appeared to be the sole factor in determining the product selectivity, irrespective of the Au particle sizes. The selectivity to AcH was close to 100% when the ethanol conversion was less than 3%. On increasing the level of ethanol conversion, the selectivity to AcH gradually decreased with a concomitant increase in the selectivity to AcOH, and the overall reaction shifted gradually from an AcH-selective to AcOH-selective catalytic

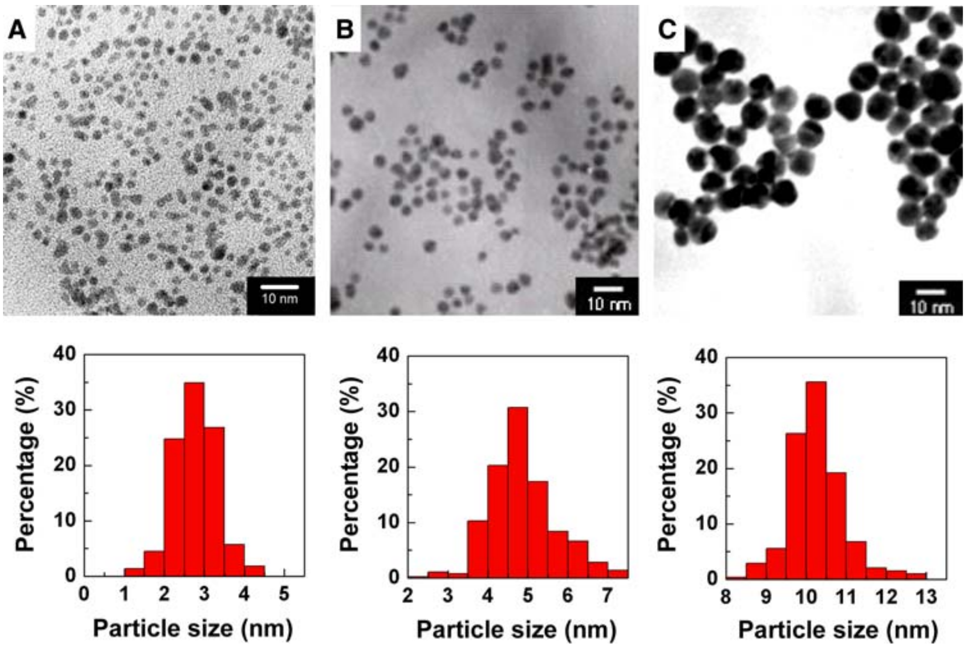

Fig. 1 Representative TEM images of Au colloids and their size distribution. (**a**) Au(3); (**b**) Au(5); (**c**) Au(10)

Table 1 Aerobic oxidation of ethanol in aqueous solution over Au/SiO_2 catalysts prepared by immobilization of pre-formed colloidal Au particles on aerosil SiO_2[a]

Catalyst	EtOH conv. (%)	Product select. (C %)		
		AcH	AcOH	AcOEt
1% Au(3)/SiO_2	6.4	75.5	24.5	0
3% Au(3)/SiO_2	17.5	40.4	58.1	1.6
5% Au(3)/SiO_2	36.6	24.9	72.2	2.9
1% Au(5)/SiO_2	11.5	60.9	36.4	2.7
3% Au(5)/SiO_2	47.4	16.0	79.3	4.7
5% Au(5)/SiO_2	58.0	12.6	83.9	3.6
1% Au(10)/SiO_2	0.2	100	0	0
3% Au(10)/SiO_2	1.1	100	0	0
5% Au(10)/SiO_2	2.2	100	0	0

[a] Reaction conditions: 20 mg catalyst, 2 mL 5 wt% ethanol aqueous solution, 210 °C, 6 atm O_2, 4 h

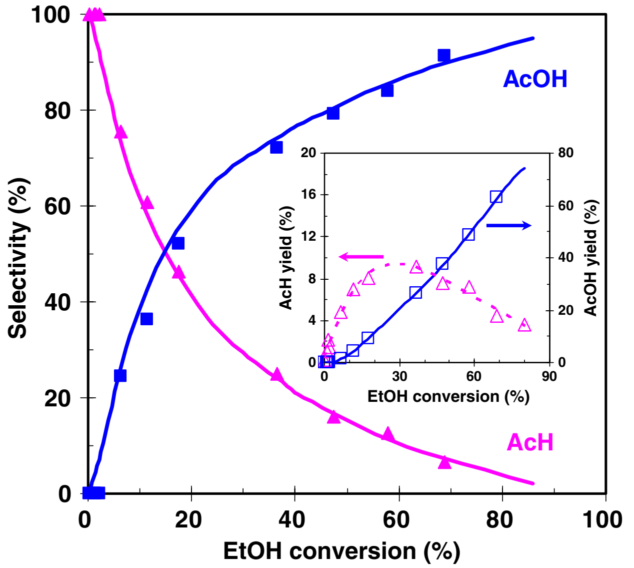

Fig. 2 Dependence of product selectivity on ethanol conversion. Insert: relationship between product yields and ethanol conversion

process. When the level of ethanol conversion exceeded 58%, the selectivity to AcOH increased to above 83%, while that to AcH decreased to below 15%. The insert of Fig. 2 further shows the relationships between the product yields and ethanol conversion. The yield of AcOH increased with ethanol conversion, while that of AcH passed a maximum at an ethanol conversions of 20–30%. A recent study of the effect of reaction duration on product yields of ethanol oxidation by Christensen et al. also revealed that the AcH yield passed a maximum at the initial stage of the reaction (less than 1 h) over both Au/TiO_2 and Au/$MgAl_2O_4$ catalyst, while that of AcOH increased continuously with the reaction time [15], although no formation of AcH was reported in their first work on the same reaction over the same Au/$MgAl_2O_4$ catalyst [14]. The present observation on a clear correlation between the product yield and ethanol conversion in fact provides a further proof in confirming that the oxidation of ethanol in aqueous solution without the presence of a base to form AcOH over supported Au nanoparticles is a complex consecutive reaction with AcH being the intermediate product [15]. Furthermore, the present data also showed that the dependence of product yield on the ethanol conversion (Fig. 2) remained valid for all Au/SiO_2 catalysts containing differently sized Au

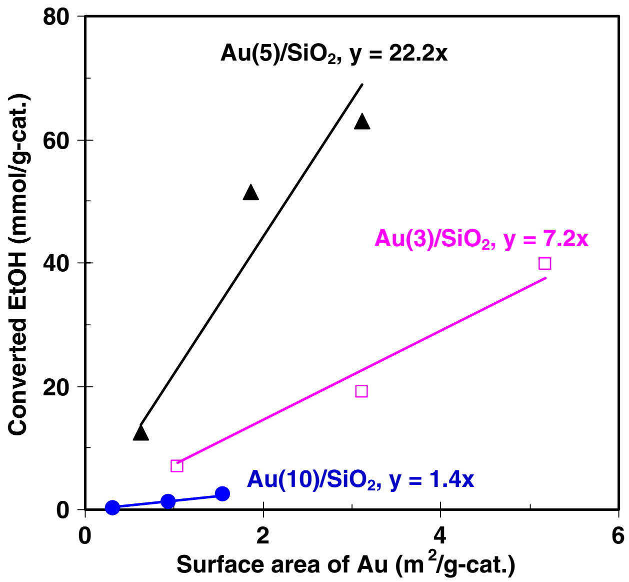

Fig. 3 Dependence of the mole of converted ethanol on the Au surface area in each set of Au/SiO_2 catalysts

nanoparticles and it could be possible to obtain a 100% AcH selectivity at up to a few percent ethanol conversions (Table 1).

To gain insight into the Au nano-size effect on its catalytic activity for ethanol oxidation, the surface area of metallic Au per gram Au/SiO_2 catalyst was calculated based on the loading and average particle size of Au, assuming closed-shell Au particle of nearly spherical shapes [25]. The catalyst activity by the number of converted ethanol molecules was then correlated with the Au surface area in the same catalyst (Fig. 3). No general relationship could be found for all of the catalysts containing differently sized Au nanoparticles. Surprising, however, the catalyst activity obtained with each individual set of the Au/SiO_2 catalysts appeared to increase linearly with increasing the Au surface area in the same set of catalysts. The curve slope correlating each set of Au/SiO_2 catalysts in Fig. 3 would therefore measure the areal activity of Au particles in that very set of Au/SiO_2 catalysts. The Au areal activity data obtained as such were 7.2, 22.2 and 1.4 mmol-EtOH/m^2-Au, respectively, for the Au(3)/SiO_2, Au(5)/SiO_2 and Au(10)/SiO_2 catalysts. Thus, it is apparent that the surface of Au particles narrowly sized at around 5 nm was 3 and 15 times more active that of the smaller (ca. 3 nm) and larger (10–30 nm) Au particles, respectively. These data clearly demonstrate that the selective oxidation of ethanol over Au catalyst is sensitive to the surface structure of Au and the most favorable particle size for the Au catalyst would be at around 5 nm, the smaller (ca. 3 nm) and larger (10–30 nm) Au particles are not that efficient for the reaction.

A volcano-type relationship between particle size of Au and its activity towards glycol oxidation was reported earlier by Bianchi et al., who observed that, among those of 3–21 nm Au particles supported by carbon, the medium-sized (7–8 nm) Au particles were always producing the highest glycol conversion [17]. However, even in the same paper they showed also that glycol conversion increased with decreasing Au particle size when Al_2O_3 was the support for Au catalysts. In the oxidation of hydroxylbenzyl alcohol, the smallest colloidal Au particles in the size range of 1.3–9.5 nm was found to show the highest areal activity [18]. In the case of glucose oxidation, the glucose conversion based on the mass of Au decreased with increasing the Au particle size in the range of 3–7 nm [19, 20]. However, when the same glucose conversion data were used to measure the areal activity of Au, one would see that the surface catalysis by Au was basically not affected by its particle size in Refs. [19, 20]. While it is impossible at this stage to make a general conclusion on the nano-size effect of Au in the different oxidation reactions, our present observation using non-interacting SiO_2 for the support of narrowly sized particles would help to better understand the intrinsic effect of Au particle size in the selective aerobic oxidation of ethanol (or primary alcohols). In our recent work on selective hydrogenation of cinnamaldehyde, these Au/SiO_2 catalysts were found peculiar to the C=C hydrogenation while competitive hydrogenation at both C=C and C=O bonds of cinnamaldehyde prevailed when the same Au particles were immobilized on ZrO_2 [6].

The Au particles in the present work were generally larger than 3 nm, which would imply that their electronic properties could be more close to those of massive Au [26–29]. Thus, it is unlikely that variation in the overall electronic properties of the Au particles can be responsible for the Au nano-size effect observed in our present study. Furthermore, the relationships shown in Fig. 2 would suggest that the aerobic oxidation of ethanol over all of the Au/SiO_2 catalysts occurred by the same reaction mechanism, in other words the nature of catalytically active sites on those differently sized Au particles would be the same. It is reasonable to assume that the population or number of active sites at the Au surface was dependent of the Au particle size. Thus, the volcano relationship between Au particle size and its areal activity (or intrinsic activity) would instead mean that the population of the active sites at the surface of Au(5) particles was higher than Au(3) and much higher than Au(10) particles in the Au/SiO_2 catalysts. The low-coordinated sites (surface atoms at edges and corners) on Au nanoparticles were proposed as the active sites for O_2 activation [27]. These sites were also considered responsible for the adsorption of aldehyde on Au catalysts [28]. It is likely that these low-coordinated sites served as the active sites for the selective oxidation of ethanol over the present Au/SiO$_2$ catalysts. However, it remains unclear why the population of active sites on Au(3) particles was lower than that on Au(5) ones. Recall that a variety of structures for Au nanoparticles smaller than 10 nm have been revealed either experimentally or theoretically [30], it would be not impossible that special multi-coordinated sites like the C-7 sites on iron [31] or B-5 sites on Ru surfaces [32] may also exist. Further investigations on the in-depth structure of the catalysts are needed to clarify the nature of active sites, and in particular in-situ characterization combined with theoretical calculation could be fruitful.

4 Conclusions

Remarkable Au nano-size effect on selective aerobic oxidation of aqueous ethanol was observed in Au/SiO$_2$ catalysts prepared by immobilization of pre-formed colloidal Au particles on aerosil SiO$_2$. The areal activity of the immobilized Au particles of ca. 5 nm was found higher than either smaller (3 nm) or larger (10–30 nm) Au particles. Further investigation on the dependence of product yields on ethanol conversion demonstrated that the oxidation reaction of ethanol proceeded by the same reaction mechanism over these differently sized Au particles, in which acetaldehyde was formed as the intermediate reaction product to acetic acid.

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