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Preparation and application of highly efficient Au/SnO₂ catalyst in the oxidative lactonization of 1,4-butanediol to γ -butyrolactone

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ABSTRACT

A series of gold catalysts supported on commercial SnO₂ were synthesized by deposition-precipitation while accurately controlling pH and precipitant species. The supported catalysts were characterized by X-ray diffraction, inductively coupled plasma atomic emission spectrometry, transmission electron microscopy, and X-ray photoelectron spectroscopy. Gold loading and calcination temperature both affected the dispersion and nature of gold species on SnO₂. The performance of the catalysts in the oxidative lactonization of 1,4-butanediol to γ -butyrolactone was investigated. The catalyst with 3% gold that was calcined at 573 K exhibited the highest activity, which was 15 times higher than that of Au/TiO₂. The excellent catalytic performance was attributed to the high dispersion of gold particles and adequate Au⁰ and Au^{δ-} species formed because of the strong interaction between Au and SnO₂ and the intrinsic properties of SnO₂.

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1. Introduction

Over the past decades, gold catalysts have been widely considered as outstanding catalysts for oxidation of CO [1,2] and other compounds [3–5]. Gold nanoparticles (AuNPs) dispersed on solid carriers are attractive as catalysts because of their increased stability, high activity under mild conditions, and easy recovery compared with bulk Au or free AuNPs [6,7].

Tin dioxide (SnO₂) is an n-type semiconductor with a wide band gap. In recent years, SnO₂ has been extensively studied for various applications in catalysis [8], gas sensing [9], and rechargeable Li batteries [10]. Bulk and supported SnO₂ are also effective catalysts for selective reduction of NO_x by hydrocarbons [11,12]. There are many reports of gold catalysts dis-

persed on semiconductor metal oxides [13] such as TiO₂ [14], α -Fe₂O₃ [15], and Co₃O₄ [16]. However, the studies on Au supported on SnO₂ have mainly focused on sensors [17], electrodes with indium tin oxide [18], and catalytic oxidation of CO [19,20]. In addition, these materials were limited to core-shell structures [19,21] or gold particles dispersed on SnO₂ by co-precipitation (CP) [20,22]. Au/SnO₂ catalysts prepared by deposition-precipitation (DP) and their application in the oxidation of alcohols have not been reported.

Compared with CP, DP possesses a significant advantage that all of the active components remain on the surface of the support and none is buried within its bulk [23]. DP is readily scalable and works for any type of support. Usually, it allows complete precipitation of a gold precursor from solution

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(<0.1% Au is left in the liquid phase), whereas more than 50% of gold remains in solution after CP [23,24]. Au/Fe₂O₃ prepared by DP exhibits higher catalytic activity in CO oxidation than that fabricated by CP [23]. Therefore, we prepared a series of Au/SnO₂ catalysts by DP under a range of controlled conditions and used them to catalyze the oxidation of alcohols.

Lactones and their derivatives are widely distributed in nature and industry where they are used as solvents, extraction agents and intermediates in agriculture, the petroleum industry, pharmaceuticals, resins, and fibers [25–28]. The aerobic oxidation of 1,4-butanediol is promising as an industrially acceptable process [5]. Some supported gold catalysts induce conversion of 1,4-butanediol to γ -butyrolactone with high performance [29–31], including that we previously reported n-type semiconductor TiO₂ as the carrier [32]. Herein, oxidative dehydrogenation of 1,4-butanediol to γ -butyrolactone is used as a test reaction to determine the activities of the series of Au/SnO₂ catalysts.

2. Experimental

2.1. Catalyst preparation

Au/SnO₂ catalysts were synthesized by homogeneous DP as follows. An aqueous solution of HAuCl₄ (6.4 ml, 2.43 mmol/L) was mixed with deionized water (32 ml) at room temperature. Alkali was added as a precipitation agent to adjust the pH to the required value along with commercial SnO₂ (1.0 g). The mixture was stirred at 333 K for 2 h. The resulting precipitate was collected by filtration, washed five times with deionized water, and then dried in air overnight at 373 K. Finally, catalysts were calcined in air for 4 h at a desired temperature.

For recycling tests, each used catalyst was washed with ethanol to remove contaminants and then calcined at 573 K in a muffle oven for 4 h.

2.2. Catalyst characterization

The specific surface areas of samples were determined by nitrogen adsorption at 77 K (Micromeritics Tristar ASAP 3000) using the Brunauer-Emmett-Teller (BET) method. Gold loadings were determined by inductively coupled plasma (ICP) mass spectrometry (Thermo E. IRIS). X-ray diffraction (XRD) patterns were recorded on a diffractometer (Bruker D8 Ad-

vance) with Cu K α radiation ($\lambda = 0.154$ nm) operating at 40 mA and 40 kV. Transmission electron microscope (TEM) micrographs were obtained on a TEM (JOEL JEM 2010). The average size and relative distributions of gold particles were estimated from the sizes of more than 100 Au particles. X-ray photoelectron spectra (XPS) were acquired under ultrahigh vacuum (<10⁻⁶ Pa) at a pass energy of 93.90 eV on an XPS (Perkin-Elmer PHI 5000C ESCA) equipped with a dual X-ray source using an Mg K α anode (1253.6 eV) and a hemispherical energy analyzer. Binding energies were calibrated using adventitious carbon (C 1s = 284.6 eV) as a reference.

2.3. Catalytic tests

Catalytic tests were performed using a stainless steel autoclave equipped with a magnetic stirrer at 413 K. 1,4-Butanediol (1.645 g) was dissolved in tributyl phosphate (TBP, 20 ml). A specified amount of Au/SnO₂ catalyst was added to give a molar ratio of gold to 1,4-butanediol of 1:200. The autoclave was sealed and filled with air to a pressure of 1.2 MPa. The solution was stirred at a rate of 750 r/min. The reaction mixture was sampled at regular time intervals and analyzed by a gas chromatography (GC9560, Shanghai Huaai GC Co. Ltd) fitted with a flame ionization detector and PEG-20M capillary column to determine the conversion and selectivity. Gas chromatography-mass spectrometry (GC 8000 TOF-MS voyager) was used to detect the distribution of products.

Recycling experiments using the Au/SnO₂ catalysts were performed under identical reaction conditions to those above using recycled catalyst.

3. Results and discussion

3.1. Characterization of catalysts

The XRD patterns (not shown) indicated the carrier was standard SnO₂ (JCPDS 41-1445). Although the BET area of plate-like SnO₂ (TEM image shown in Fig. 1(d)) was not large at just 11.3 m²/g, the vast majority of gold was successfully loaded on the surface of the support, which was confirmed by XPS and TEM measurements, as shown in Table 1 and Figs. 2 and 3. The good utilization of Au could be attributed to the use of DP to prepare the catalysts. The morphology, phase, and BET area of SnO₂ showed little variation after Au NPs were deposited on

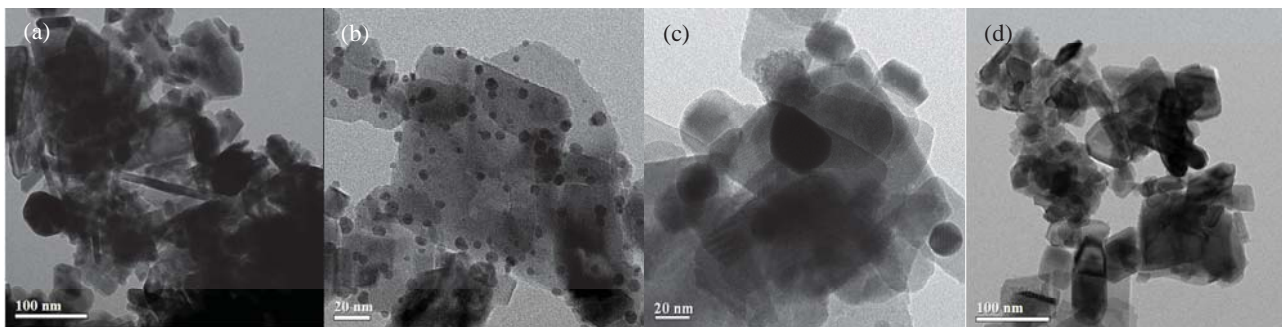


Fig. 1. TEM images of Au/SnO₂ with different pH. (a) pH = 6; (b) pH = 8; (c) pH = 9, (d) SnO₂.

Table 1
 Physicochemical properties and catalytic activities of Au/SnO₂.

Calcination temperature (K)	Au loading (%)		$A_{\text{BET}}/(\text{m}^2/\text{g})$	$d_{\text{Au}}^{\text{a}}/\text{nm}$	Au content (%)			Conversion ^d (%)	Selectivity ^d (%)	$R^{\text{e}}/(\text{mol}/(\text{mol}\cdot\text{h}))$
	Nominal	Actual			$\text{Au}_{\text{surf}}^{\text{b}}$	Au^0^{c}	$\text{Au}^{\delta-}\text{c}$			
473	3	2.9	11.8	5.2	13	55	45	40	60	31.3
573	3	2.9	12.7	3.9	12	54	46	94	59	33.3
673	3	2.9	10.3	10.1	10	84	16	39	41	20.3
773	3	2.9	8.2	21.3	7	85	15	18	11	14.2
573	1	1.7	10.3	4.3	5	25	75	20	9	36.3
573	5	5.0	11.9	4.5	30	65	35	53	83	21.5
573	8	8.1	10.7	6.3	26	67	33	45	22	8.0

^aGold particle size was the average of more than 100 particles observed in TEM images. ^bThe surface gold loading was calculated from the atomic ratio of surface Au to Sn obtained from XPS. ^cThe metallic and anion gold contents were obtained from the peak areas of Au⁰ and Au^{δ-} species from XPS data. ^dThe conversion and selectivity were determined after 8 h. ^e R = the amount of 1,4-butanediol reacted per mol of gold per hour for the first 2 h. Reaction conditions: 1,4-butanediol 1.645 g, Au:1,4-butanediol = 1:200, TBP 20 ml, 1.2 MPa air, 413 K.

it according to Table 1 and Figs. 2 and 3. Au diffraction peaks were not detected in the XRD patterns because the signals from Au and SnO₂ overlapped.

3.2. Effect of preparation conditions on Au/SnO₂ catalysts

3.2.1. Effect of pH

It is usually considered that a suitable pH at different stages of catalyst preparation is favorable for nucleation, growth, and redispersion of Au NPs [33–35]. Under acidic or neutral conditions, Au particles are difficult to disperse on the surface of SnO₂, leading to low gold loading. When pH < 6, the average gold particle size was 50 nm (Fig. 1(a)) and the color of the catalyst was light purple. In strong basic solution (pH = 9.0), the structure of SnO₂ was destroyed, the Au particle size increased to 25 nm (Fig. 1(c)) and the surface color turned to purple-red. When pH = 8.0, the resulting Au/SnO₂ catalyst contained the smallest gold particles (3.9 nm, Fig. 1(b)) and the color was dark purple.

3.2.2. Effect of precipitant

The precipitating agent clearly influences catalytic activity, so we prepared catalysts using three kinds of precipitants: urea, ammonia (NH₃·H₂O), and NaOH. The conversion of 1,4-butanediol (94%, 8 h) was the highest using NaOH as a precipitant (Table 2), because this catalyst contained the smallest Au particles. Meanwhile, the catalyst obtained using urea showed the highest selectivity (68%, 8 h). This is because the thermal decomposition of urea allowed the pH of the solution to be maintained throughout the whole deposition process, which could facilitate homogeneous precipitation of gold [36]. Because formation of [Au(NH₃)₄]³⁺ would induce the loss of Au, the catalyst produced using NH₃·H₂O exhibited poor conversion of 1,4-butanediol and selectivity for γ -butyrolactone of 23% and 0.1%, respectively. It has been reported that not all gold is used in DP with NaOH [37], but using urea can avoid this problem. Therefore, we chose urea as the precipitant in this study. The desired Au/SnO₂ catalysts were obtained by accurately controlling the concentration of urea during DP.

3.2.3. Effect of calcination temperature

Calcination of the catalyst plays an essential role in trans-

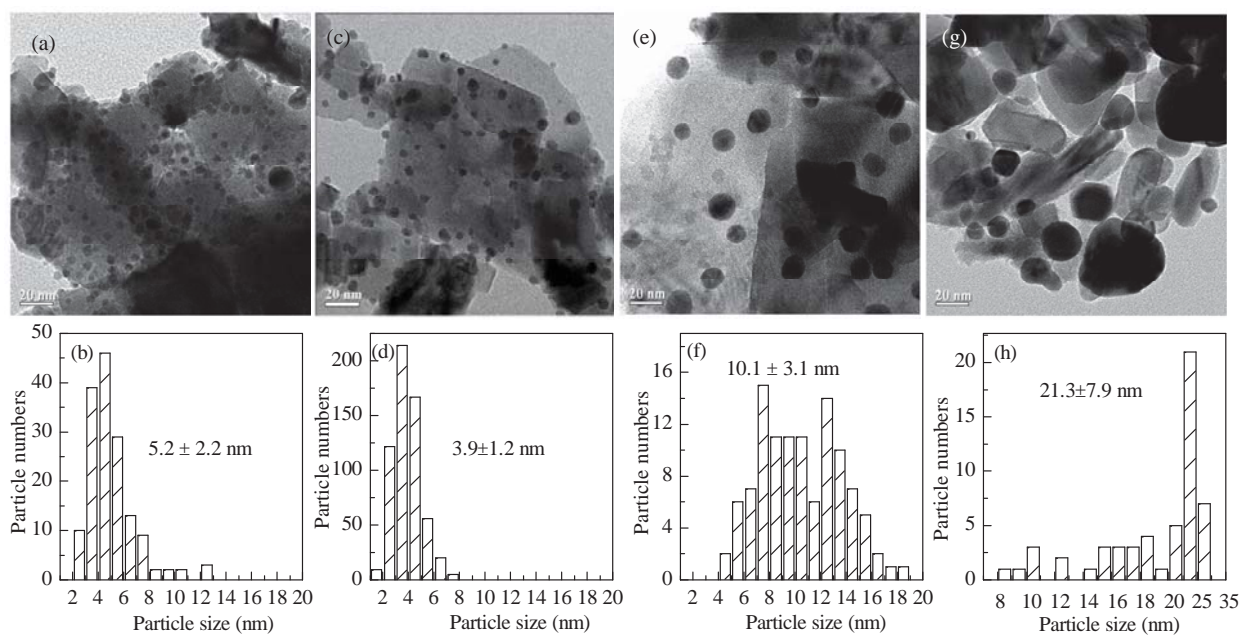


Fig. 2. TEM images and Au particle size distributions of 3% Au/SnO₂ calcined at different temperatures. (a, b) 473 K; (c, d) 573 K; (e, f) 673 K; (g, h) 773 K.

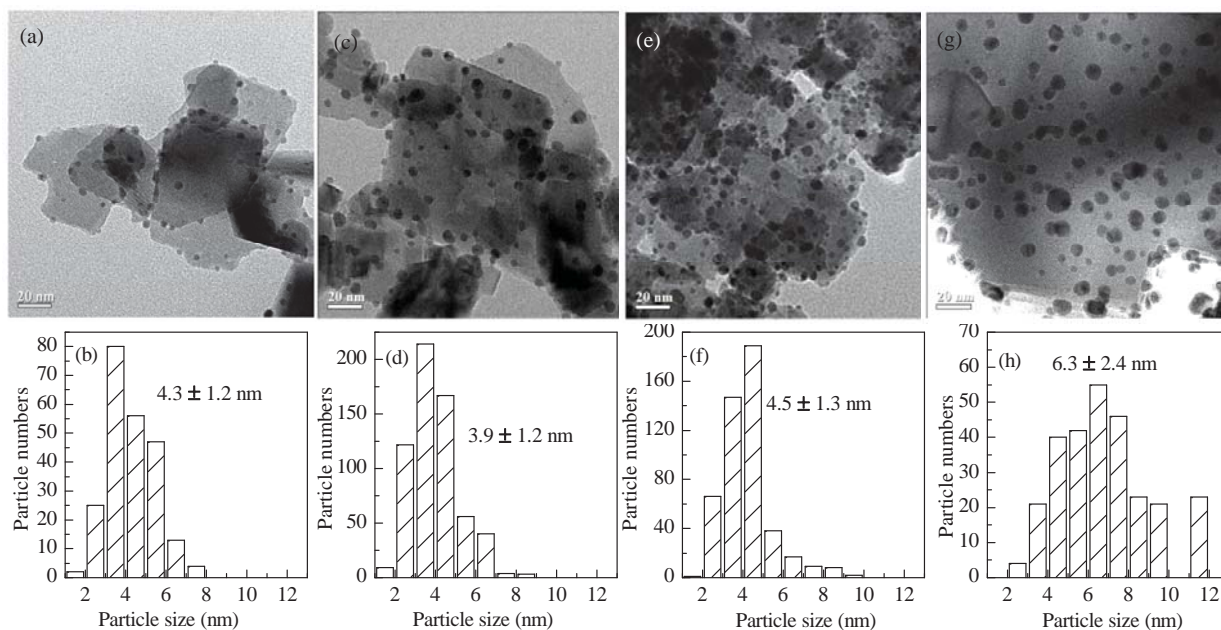


Fig. 3. TEM images and Au particle size distributions of Au/SnO₂ with different Au loadings calcined at 573 K. (a, b) 1%; (c, d) 3%; (e, f) 5%; (g, h) 8%.

forming ionic gold species into Au NPs, affecting both Au particle size and reaction activity [38]. The performance of catalysts exposed to various calcination temperatures was examined. TEM images in Fig. 2 show that different calcination temperatures gave rise to different Au particle sizes. The catalyst calcined at 573 K contained the smallest average Au particles of 3.9 nm with the narrowest size distribution. With increased temperature (773 K), the size of the gold particles increased to 21.3 nm because of the aggregation of Au NPs. The sample calcined at 473 K showed an average particle size of 5.2 nm, which was larger than that calcined at 573 K, possibly because of a large proportion of gold remaining as ionic species, as demonstrated by the subsequent XPS characterization.

The XPS results in Table 1 reveal the surface gold (Au_{surf}) content exceeded that of the bulk, indicating that Au was mainly loaded on the surface of the support by DP with urea. As the calcination temperature increased, the amount of Au_{surf} decreased because more Au_{surf} entered the bulk of SnO₂. The Au 4f XPS peaks were quite asymmetric, demonstrating that there were both metallic (binding energy (BE) = 83.0 eV) and ionic (BE = 82.2 eV) gold species present. The BE of metallic gold (Au^0) was lower than that of the bulk gold at 84.0 eV, suggesting a strong metal-support interaction formed [30,32]. According to the deconvolution of Au 4f peaks, more than half of Au_{surf} was metallic and the rest was in the δ^- state. The anionic gold ($Au^{\delta-}$) formed by electrons from SnO₂ shifting into Au NPs fur-

ther indicates the strong interaction between Au and the SnO₂ support. The catalysts calcined at 473 and 573 K contained the most $Au^{\delta-}$ species (45% and 46% for 473 and 573 K) of the samples, indicating they possessed the strongest interactions between Au and SnO₂. As the calcination temperature increased, the amount of $Au^{\delta-}$ reduced as more $Au^{\delta-}$ species was transformed into Au^0 . The content of Au^0 was further confirmed by observing the colors of the samples. The fresh catalyst before drying and calcination was light yellow, indicating the presence of a large proportion of $Au^{\delta-}$. After being dried at 373 K, the surface of catalyst began to turn to purple, and the color deepened as the calcination temperature was increased.

3.2.4. Effect of gold loading

Adjusting Au loading directly influences catalytic properties, so the dependence of activity on Au loading was also studied. The results of ICP-AES analysis presented in Table 1 show that the actual gold loadings of various catalysts were all near the nominal amount. TEM images in Fig. 3 reveal the average Au particle size in the catalyst with 3% loading was the smallest at 3.9 nm. When the gold loading was increased, the size of the Au NPs increased because of readily aggregated on the surface of the support whose BET surface area is low. The average Au particle size of 4.3 nm in the catalyst with 1% loading was larger than that with 3% loading, maybe because a large proportion of gold was present as ionic species as detected by XPS, similar to the catalyst calcined at 473 K. For the catalyst with 8% loading of Au, the average Au particle size was 6.3 nm, which was much larger than those of the other catalysts. This is because the low BET surface area of SnO₂ could not accommodate all of the Au NPs, causing them to agglomerate.

XPS results also revealed that the Au_{surf} content increased with Au loading (Table 1). However, Au_{surf} in the catalyst with 8% loading was less than that with 5% loading, indicating that more surface gold entered the bulk SnO₂ in the catalyst with

Table 2

Effect of precipitant on the catalytic activity of Au/SnO₂.

Precipitation agent	Conversion (%)	Selectivity (%)
NaOH	94	32
Urea	56	68
NH ₃ ·H ₂ O	23	0.1

Reaction conditions: 1,4-butanediol 1.645 g, Au:1,4-butanediol = 1:200, TBP 20 ml, 1.2 MPa air, 413 K. Deposition temperature 333 K; deposition time 2 h.

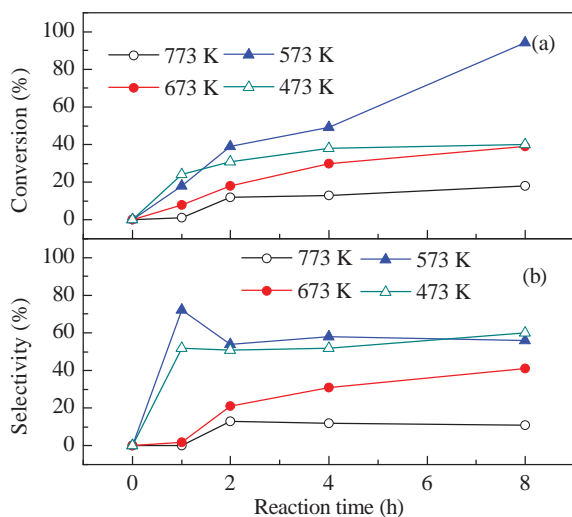


Fig. 4. Conversion (a) and selectivity (b) of the oxidation of 1,4-butanediol catalyzed by 3% Au/SnO₂ calcined at different temperatures. Reaction conditions: 1,4-butanediol 1.645 g, Au:1,4-butanediol = 1:200, TBP 20 ml, 1.2 MPa air, 413 K.

8% Au. This was a result of the low BET surface area of SnO₂, which led to saturation of Au_{surf} when the Au loading reached 5%. Moreover, the BE of Sn 3d_{5/2} in Au/SnO₂ was 488.0 eV, which was higher than that of pristine SnO₂ (486.4 eV). This finding implies that electrons were transferred from the SnO₂ support to surface gold particles, further indicating the formation of strong interactions between Au and SnO₂ [39].

3.3. Catalytic oxidative lactonization of 1,4-butanediol

3.3.1. Effect of calcination temperature

The performance of the catalysts in the oxidative lactonization of 1,4-butanediol was examined at 413 K, and the results are shown in Table 1 and Fig. 4. The Au/SnO₂ catalyst calcined at 573 K showed the highest activity with a conversion of 94% of 8 h because it contained the most dispersed gold particles. The reaction rates of catalysts calcined at 473 and 573 K were 31.3 and 33.3 mol/(mol·h), respectively, which were faster than those calcined at higher temperatures because they contained smaller gold particles. In addition, the rate of conversion decreased after 1 h for the sample calcined at 473 K, and the final conversion was relatively low (40% after 8 h). Meanwhile, the catalyst calcined at 773 K was inferior to the others because of the intrinsic agglomeration of Au, which led to it containing the largest gold particles. The catalysts containing more Au^{δ-} exhibited higher catalytic performance, so we propose that Au^{δ-} species contribute to the high activity. As a result, the decreased conversion of the catalyst calcined at 473 K could be ascribed to the transformation of Au^{δ-} to Au⁰ during the catalytic reaction.

3.3.2. Effect of gold loading

The catalytic activities of Au/SnO₂ catalysts with various gold loadings are shown in Table 1 and Fig. 5. The catalyst with 3% loading exhibited the highest conversion of 94%, while that with 5% loading had the highest selectivity of 83%. Catalysts

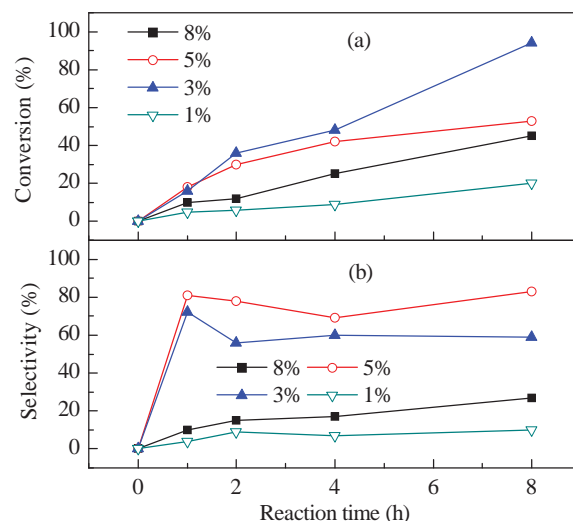


Fig. 5. Conversion (a) and selectivity (b) of the oxidation of 1,4-butanediol catalyzed by Au/SnO₂ calcined at 573 K with different gold loading. Reaction conditions: 1,4-butanediol 1.645 g, Au:1,4-butanediol = 1:200, TBP 20 ml, 1.2 MPa air, 413 K.

with 1% and 3% loading exhibited similar reaction rates (36.3 and 33.3 mol/(mol·h) for 1% and 3%, respectively), which were higher than those of 21.5 and 8.0 mol/(mol·h) for catalysts with a loading of 5% and 8%, respectively, because they contained smaller gold particles. The catalyst with 1% loading exhibited the worst performance, with a conversion of 55% after 14 h. Such low Au loading did not afford enough active sites, demonstrating that the gold particle size was not the decisive factor influencing catalytic activity. The conversion by catalysts with 3% and 5% loading were alike at the beginning of the reaction, but after 2 h, the conversion decreased for the catalyst with 5% loading because of agglomeration of Au NPs.

3.3.3. Durability of Au/SnO2 catalyst

The recyclability of the Au/SnO₂ catalyst with 3% gold loading that was calcined at 573 K was examined. As shown in Table 3, the activity of catalyst decreased with conversion decreasing from 100% to 80% and selectivity falling from 68% to 30% after 3 uses. The used catalyst was characterized to determine the reason for deactivation. We performed a leaching test using ICP-AES, but no leaching of Au or Sn was detected in the reaction mixture. However, gold particle size increased from 3.9 to 8.6 nm after being used according to TEM images (Fig. 6), which explains the deactivation of the catalyst. Composite supports have been reported to improve the durability and stability of gold against sintering [40], and the relatively large BET surface area of such supports may prevent Au NPs from agglomerating. This may be a feasible way to improve the cata-

Table 3
Effect of precipitant on the catalytic activity of Au/SnO₂.

Run	Conversion (%)	Selectivity (%)	Yield (%)
Fresh	100	68	68
1	82	54	44
2	80	30	24

Reaction conditions: 1,4-butanediol 1.645 g, 3% Au/SnO₂ catalyst 0.6 g calcined at 573 K, TBP 20 ml, 1.2 MPa air, 10 h.

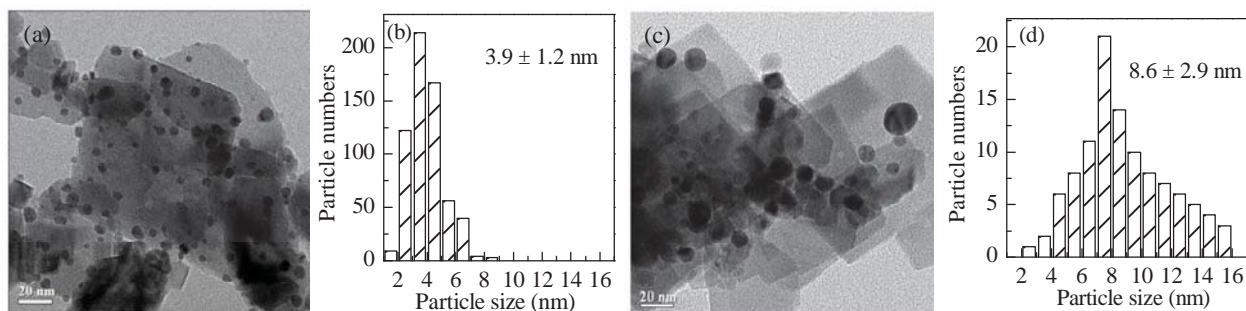


Fig. 6. TEM images (a, c) and Au particle size distributions (b, d) of 3% Au/SnO₂ calcined at 573 K. (a, b) Before reaction; (c, d) After 3 uses.

lytic performance and stability of Au/SnO₂, so we are currently investigating it.

3.3.4. Effect of multiple parameters

To eliminate the influence from the surrounding environment on the catalyst before the catalytic experiment, we tested the performance of catalysts that were preprocessed by drying under vacuum or in oxygen. No difference was observed in the performance of catalysts that were pretreated or not. Combined the above results, the high activity of Au/SnO₂ was caused by the small mean gold particle size and appropriate Au loading, along with the suitable ratio of Au⁰ and Au^{δ-} species. The highest activity was obtained for the catalyst with 3% gold loading that was calcined at 573 K, which was a result of the low BET surface area of the support and the appropriate ratio of gold species coming from the moderate interaction between Au and the support. We calculated the turnover frequency (TOF) value of the reaction from the first 1 h. To our surprise, the TOF value is 974 h⁻¹, much larger than that of an Au/TiO₂ catalyst (64 h⁻¹, 3% Au loading, calcined at 573 K) under identical reaction conditions [32]. SnO₂ and TiO₂ both are n-type semiconductors, and possess similar physicochemical properties and applications [22,41], but Au/SnO₂ exhibited higher activity than Au/TiO₂ in this reaction. This difference is probably because gold generates an important surface state band on the valence band edge of SnO₂ and crystallographic distortion localized at the grain surface, which can enhance the catalytic performance at the active sites [42–46]. This finding has not been reported for Au/TiO₂. In addition, the gold is predominantly present in the form of Au^{δ-} in our samples, but it is mainly Au^{δ+} in Au/TiO₂ [32]. We believe that Au^{δ-} facilitates the oxidative reaction of diols, so Au^{δ-} also increases activity. Moreover, some reports indicated that Au^{δ+} could be photoreduced by natural light [33–35,47], so our catalysts avoid this shortcoming. Unlike TiO₂, SnO₂ has rarely been applied in gold catalysts, but according to the present study, SnO₂ is a promising candidate as a support for gold catalysts. We hope Au/SnO₂ will receive more attention as a catalyst.

4. Conclusions

Highly efficient Au/SnO₂ catalysts were prepared by DP and used for the oxidation of 1,4-butanediol to γ -butyrolactone. The highest catalytic activity was obtained on the catalyst with 3%

gold loading that was calcined at 573 K, and was prepared at pH = 8.0 using urea as the precipitant. This catalyst exhibited a TOF value 15 times higher than that of Au/TiO₂. The higher activity can be ascribed to the small gold particles and the strong metal-support interaction that induced a suitable ratio of Au⁰ and Au^{δ-} species by adjusting calcination temperature and gold loading. Our results show that urea-DP is an effective method to prepare Au/SnO₂ catalysts that could be used in a wide range of oxidation reactions. However, the stability and selectivity of this catalyst for oxidizing diols are still not very good, and the selectivity fluctuates during the reaction. We intend to improve the performance of these catalysts in the future.

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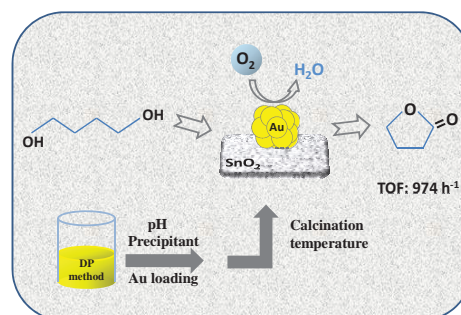
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Graphical Abstract

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Preparation and application of highly efficient Au/SnO₂ catalyst in the oxidative lactonization of 1,4-butanediol to γ -butyrolactoneLI Xian, ZHENG Jiamin, YANG Xinli, DAI Weilin*, FAN Kangnian
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Gold catalysts supported on tin dioxide prepared by deposition-precipitation exhibit high catalytic activity in the oxidative lactonization of 1,4-butanediol.



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高活性Au/SnO₂催化剂的制备及其在1,4-丁二醇氧化制 γ -丁内酯反应中的催化应用

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摘要: 采用沉积沉淀法制备了一系列商业SnO₂负载的纳米Au催化剂, 通过电感耦合等离子体发射光谱、X射线粉末衍射、透射电镜和X射线光电子能谱等方法研究了溶液酸碱性、沉淀剂种类、Au负载量和焙烧温度等对催化剂性质的影响。结果表明, Au的负载量以及催化剂的焙烧温度对Au颗粒状态有较大影响。其中, 于573 K焙烧的3%Au/SnO₂催化剂在1,4-丁二醇氧化制备 γ -丁内酯反应中的催化活性最好, TOF值是Au/TiO₂催化剂的15倍。这主要是由于SnO₂载体独特的性质对所负载的Au颗粒的影响。

关键词: 金催化; 二氧化锡; 沉积沉淀法; 1,4-丁二醇; 氧化内酯化; 焙烧温度; 金负载量

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