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Superior catalytic properties in aerobic oxidation of alcohols over Au nanoparticles supported on layered double hydroxide

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ABSTRACT

Extremely small-size Au nanoparticles mainly distributed at 1–5 nm were successfully prepared on layered double hydroxide by ion-exchange and reduction procedures (Au/LDH). This catalyst showed superior catalytic properties in aerobic oxidation of a wide range of secondary and primary alcohols under very mild conditions (e.g. 1 atm pressure of oxygen and even at room temperature). In addition, this catalyst is stable and recyclable during oxidations. These advantages are reasonably attributed to the interaction between Au sites and basic LDH.

1. Introduction

The oxidation of alcohols to the corresponding aldehydes or ketones is greatly important for the production of fine chemicals [1–3]. Conventionally, these oxidations are carried out using metallic salts as oxidants including permanganate, chromate and bromate. These processes are typically environmentally unfriendly because of the production of undesirable wastes and consequently high costs [3b,4,5]. In recent years, environmentally benign oxidants such as molecular oxygen with high atom efficiency have been used [6]. However, heterogeneous oxidations with molecular oxygen under very mild conditions (1 atm O_2 and even at room temperature) without additives is still a great challenge [7].

It is well known that a lot of metal ions and metal nanoparticles are catalytically active for alcohol oxidations using molecular oxygen as oxidants. For example, ruthenium, copper, cobalt, and palladium have been proved to be active for this kind of reactions [6d,8–11]. Recently, gold catalysts have been paid much attention because of their unprecedented catalytic properties, since the works of Hutchings and Haruta [12–15]. One of the most important findings is that Au nanoparticles are able to catalyze the oxidation of alcohols [7,16–19]. Compared with Pd and Pt catalysts, Au nanoparticles on supports show superior catalytic properties under mild conditions. In these cases, the activities are strongly dependent on Au nanosizes and support types [16,17]. For example, compared with silica, CeO_2 supported Au nanoparticles have improved activity and selectivity for the desired products in the aerobic oxidation of alcohols due to the synergetic electronic interactions between Au sites and CeO_2 [16a]. The use of Au/$Ga_3Al_3O_9$ could effectively promote the conversion of alcohol oxidations, since the $Ga_3Al_3O_9$ support might substantially facilitate the crucial alcohol-dehydrogenation step [16b].

More recently, we reported a communication that layered double hydroxide supported Au nanoparticles (Au/LDH) were active for aerobic oxidation of a few alcohols at 80 °C [17b]. Herein, we showed a systematical study on catalytic oxidations of a wide range of primary and secondary alcohols over Au/LDH catalyst under very mild conditions such as room temperature.

2. Experimental

2.1. Catalyst preparation

2.1.1. Preparation of LDH

As a typical run, 30.76 g of $Mg(NO_3)_2·6H_2O$ (AR, Beijing Chem Co.) and 15 g of $Al(NO_3)_3·9H_2O$ (AR, Beijing Chem Co.) were dissolved in 400 ml of water, followed by the addition of 72 g of urea (AR, Beijing Chem Co.) under stirring at room temperature. After heating to boiling point, a white precipitate was formed. After boiling for 8 h and precipitating at room temperature for 12 h, the solid LDH was collected by filtration and washing with water.

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2.1.2. *Preparation of Au/LDH*

Au/LDH was prepared by ion-exchange and $NaBH_4$ reduction. For a typical run, 0.22 g of hydrochloroauric acid ($HAuCl_4 \cdot 4H_2O$, AR, Shanghai Chem Co.) was dissolved in 80 ml of water, followed by the addition of 6 g of LDH and stirring for overnight. After filtrating, washing and drying, the sample was transferred to 50 ml of toluene (AR, Beijing Chem Co., dried by P_2O_5), followed by the addition of $NaBH_4$ (AR, Beijing Chem Co.). After stirring for 10 min, 15 ml of ethanol was added and the mixture was stirred for 6 h. Au/LDH with Au loading at 1.8% was collected by filtration and washing with ethanol and water. The Au loading was analyzed by inductively coupled plasma (ICP) technique.

2.1.3. *Preparation of Pd/LDH*

For a typical run, 0.38 g $PdCl_2$ (AR, Shanghai Chem Co.) and NaCl (molar ratio of $PdCl_2$/NaCl is 1:2.3) were dissolved in 80 ml of water, followed by the addition of 6 g of LDH and stirring for overnight. The following ion-exchange and reduction procedures were the same as the preparation of Au/LDH. The Pd loading analyzed by ICP was 1.8%.

2.1.4. *Preparation of Au/TiO_2, Au/MgO, Au/Fe_2O_3 and Au/SiO_2*

As typical run, solid supports such as TiO_2 was added to the solution of hydrochloroauric acid. After stirring at 80 °C for overnight (pH = 9.0), filtrating and washing at room temperature, drying at 100 °C for 12 h, and calcination at 400 °C for 4 h, the sample was obtained. The Au loading analyzed by ICP was 1.8%.

2.2. *Sample characterization*

Powder X-ray diffraction patterns (XRD) were obtained with a Rigaku D/MAX 2550 diffractometer with CuKα radiation ($\lambda = 0.1542$ nm). Transmission electron microscopy (TEM) experiments were performed on a JEM-3010 electron microscope (JEOL, Japan) with an acceleration voltage of 300 kV. The contents of Au and Pd were determined by ICP with a Perkin-Elmer plasma 40 emission spectrometer. XPS spectra were performed a Thermo ESCALAB 250 with Al Kα radiation at $\theta = 90°$ for the X-ray source, the binding energies were calibrated using the C1s peak at 284.9 eV. Temperature programmed surface reaction (TPSR) of adsorbed 2-propanol was carried out as follows: the catalysts were treated at 300 °C for 3 h and cooled down to room temperature, then 2-propanol vapor was introduced into the reaction system for 30 min. After sweeping with Ar for 1 h, the temperature was increased (10 °C/min) from room temperature to 500 °C, and the signals of H_2 ($M/e = 2$) were recorded by mass spectrometer with a thermal conductivity detector (TCD).

2.3. *Catalytic tests*

The oxidation of alcohols was carried out in a 50-ml glass reactor and stirred with a magnetic stirrer. The substrate, solvent and catalyst were mixed in the reactor and heated to the reaction temperature. Then molecular oxygen was introduced at air pressure. After reaction, the product was taken out from the reaction system and analyzed by gas chromatography (GC-14C, Shimadzu, using a flame ionization detector) with a flexible quartz capillary column coated with OV-17 and OV-1. The recyclability of Au/LDH catalyst was carried out by separating the catalyst from the reaction system by centrifugation, washing with a large amount of methanol and drying at 100 °C overnight, then the catalyst was reused in the next reaction.

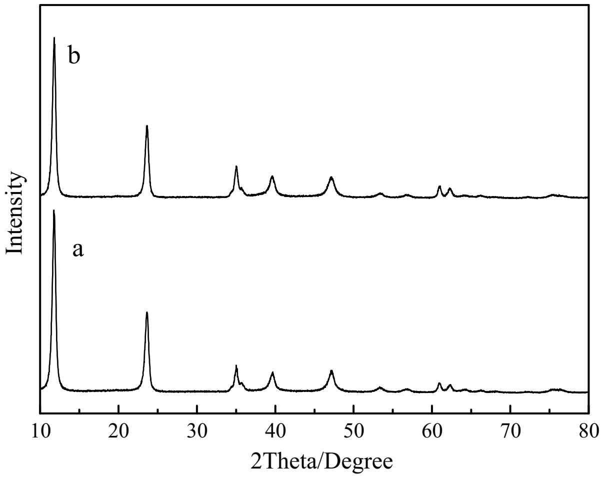


Fig. 1. XRD patterns of (a) LDH support and (b) Au/LDH catalyst.

3. Results and discussion

3.1. *Characterization of Au/LDH catalyst*

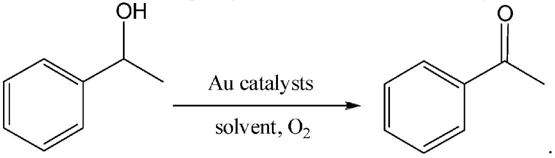
Fig. 1 shows XRD patterns of LDH and Au/LDH samples. They exhibited almost the same XRD peaks, indicating that the layered structure of LDH is well remained after loading of Au nanoparticles. Notably, the diffraction peaks associated with Au nanoparticles were not observed, which might be related to high dispersion of Au nanoparticles on LDH. TEM image of Au/LDH (Fig. 1(a)) confirms the presence of very small Au nanoparticles distributed at 1–5 nm.

3.2. *Oxidation of secondary alcohols*

Table 1 presents catalytic activities and selectivities in oxidation of a typical secondary alcohol of 1-phenylethanol to acetophenone with molecular oxygen at an atmospheric pressure over various catalysts. Clearly, Au/LDH catalyst was very active. After reaction at 80 °C for 2 h in toluene, 1-phenylethanol was completely converted (Table 1, entry 1). When the temperature was decreased down to 45 °C, the complete conversion of 1-phenylethanol took for 4 h (Table 1, entry 2). Interestingly, when the reaction was performed at room temperature for 12 h, the conversion still had 96% (Table 1, entry 3). Compared with toluene, the use of water showed relatively low reaction rate. When the reaction was performed at 45 °C for 4 h, the conversion was 40% (Table 1, entry 4). When the reaction time was increased to 16 h, the conversion was 98% (Table 1, entry 5). In contrast, Pd/LDH and the other Au-based catalysts showed very low conversion for this reaction. For examples, Pd/LDH was almost inactive (Table 1, entry 7). A series of Au-based catalysts with similar Au content with Au/LDH (Au/TiO_2, Au/MgO, Au/Fe_2O_3 and Au/SiO_2) exhibited very low conversion (11–26%, Table 1, entries 9–12). Even if the presence of additional Na_2CO_3, Au/SiO_2 still gave a low conversion (19%, Table 1, entry 13). These results indicate that Au/LDH catalyst is very active, compared with Pd/LDH and the other Au-based catalysts.

More importantly, when Au/LDH catalyst was recycled for 6 times, the conversion still have 97% (Table 1, entry 6), which is still comparable with the fresh catalyst (loss of activity less than 3%, Table 1, entry 1). These results indicate that Au/LDH catalyst was stable and reusable in aerobic oxidation of 1-phenylethanol. Sample TEM images (Fig. 2) showed that Au nanoparticle sizes of the recycled catalyst were similar to those of the fresh catalyst, indicating that Au nanoparticles are basically stable during

Table 1
Aerobic oxidation of 1-phenylethanol over various Au catalysts.



Entry	Catalyst	Solvent	Temperature (°C)	Time (h)	Conversion (%)	Selectivity (%)
1	Au/LDH	Toluene	80	2	>99	>99.5
2	Au/LDH	Toluene	45	4	>99	>99.5
3	Au/LDH	Toluene	R.T.	12	96	>99.5
4	Au/LDH	H_2O	45	4	40	>99.5
5	Au/LDH	H_2O	45	16	98	>99.5
6[a]	Au/LDH	Toluene	80	2.5	97	>99.5
7	Pd/LDH	Toluene	80	12	<1	>99.5
8[b]	Pd/LDH	Toluene	80	12	7	77[c]
9	Au/TiO_2	Toluene	80	2	24	>99.5
10	Au/MgO	Toluene	80	2	11	>99.5
11	Au/Fe_2O_3	Toluene	80	2	26	>99.5
12	Au/SiO_2	Toluene	80	2	4	>99.5
13[d]	Au/SiO_2	Toluene	80	2	19	>99.5

Reaction conditions: 0.6 mmol of 1-phenylethanol, 80 mg of catalyst, 10 ml of solvent, O_2 with rate 30 ml/min, room temperature at 26 °C.

[a] Recycled for 6 times.

[b] Addition of t-butyl hydroperoxide (TBHP, 5 mol% based on substrate) as initiator.

[c] Formation of benzaldehyde by-product.

[d] Addition of 1 mmol of Na_2CO_3 base.

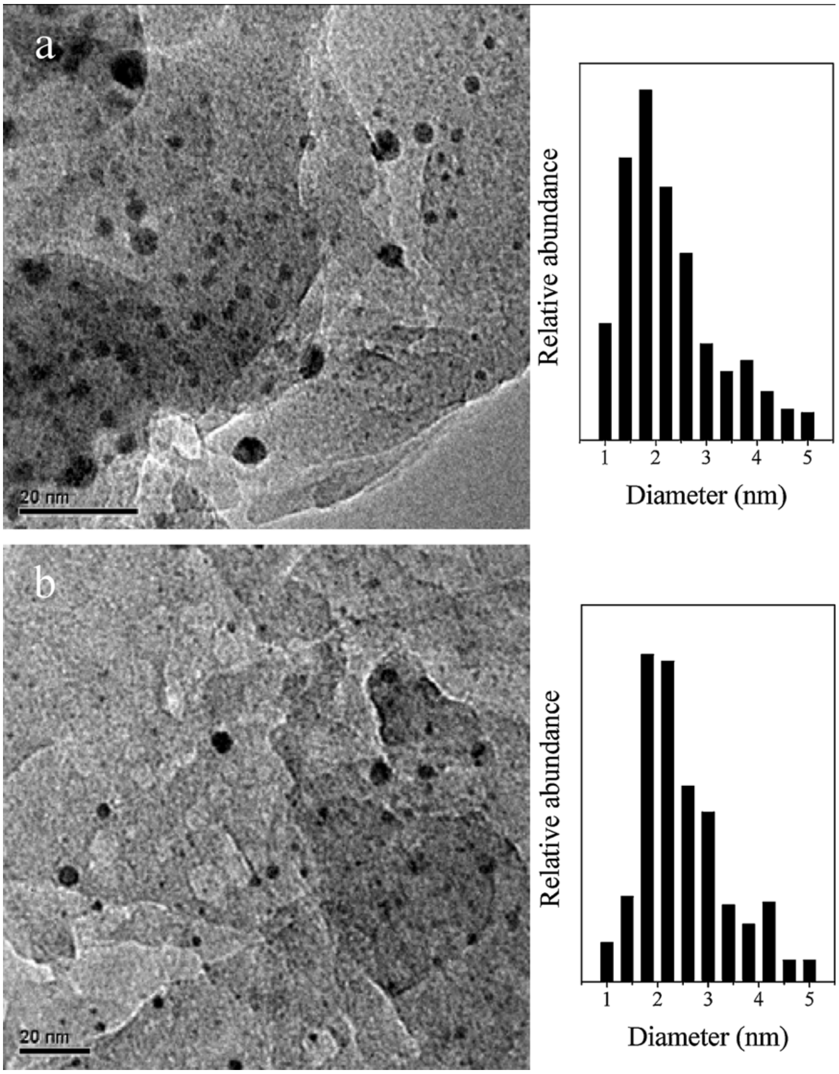


Fig. 2. TEM images and Au size distribution of (a) Au/LDH catalyst and (b) Au/LDH catalyst recycled for 6 times.

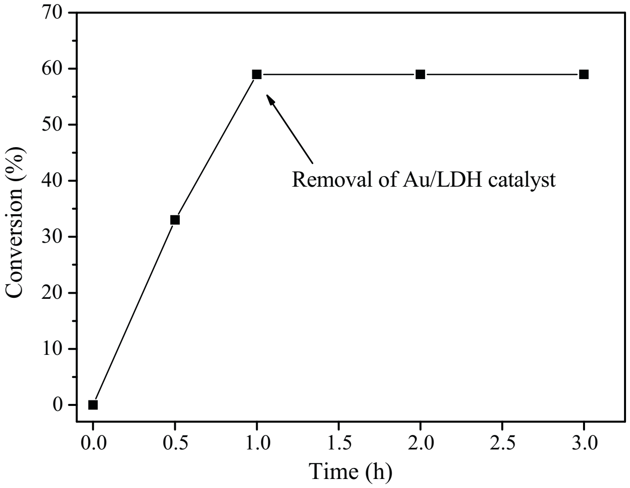


Fig. 3. Dependence of catalytic activity in oxidation of 1-phenylethanol on time for a reaction system before and after separation of Au/LDH catalyst. Reaction conditions: 0.6 mmol of 1-phenylethanol, 80 mg of Au/LDH catalyst, 10 ml of toluene, 80 °C, O_2 with rate 30 ml/min.

catalyst recycles. The excellent stability of Au/LDH catalyst is potentially important for its industrial applications for production of fine chemicals.

It is worth noting that aerobic oxidation of 1-phenylethanol could occur in the absence of solvent. When a reaction system (160 mmol and 10 mg of Au/LDH) was performed for 0.5 h at 160 °C, Au/LDH gives a extremely high turnover frequency (TOF) of 21,040 h^{-1}, which is comparable with the most active Au species reported in literature [16b,23].

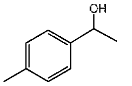
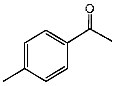
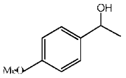
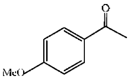
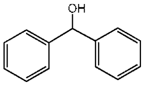
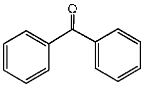
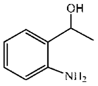
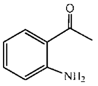
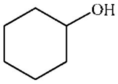
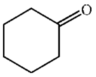
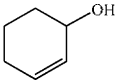
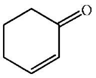
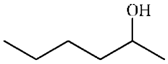
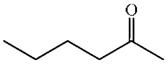
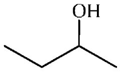
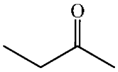
Fig. 3 shows dependence of catalytic conversion on time for a reaction system before and after separation of Au/LDH catalyst. Before the removal of Au/LDH catalyst, the conversion increased with time. However, after separation of Au/LDH catalyst from the reaction system, the conversion became a constant. These results indicate that there is no leaching of active sites from Au/LDH catalyst during heterogeneous oxidation of 1-phenylethanol to acetophenone with molecular oxygen.

Table 2 presents aerobic oxidation of various secondary alcohols over Au/LDH catalyst. The conversion of *p*-methyl-α-phenylethanol and *p*-methoxy-α-phenylethanol was very high, giving at 95% and 99%, respectively (Table 2, entries 1 and 2). Diphenylmethanol also had good conversion (92%) (Table 2, entry 3), but 1-(2-aminophenyl)ethanol showed relatively low conversion (81%, Table 2, entry 4), which might be related to the presence of amine groups in 1-(2-aminophenyl)ethanol. Compared with these aromatic secondary alcohols, aliphatic secondary alcohols exhibit low activities (Table 2, entries 5–8). For example, cyclohexanol had conversion at 60% at room temperature (Table 2, entry 5), and 2-cyclohexan-1-ol gave conversion at 74%. Normally, the oxidation of olefinic alcohols is considered as a model reaction because side reactions such as hydrogenation, hydrogenolysis, and decarbonylation exist during the oxidative process. Interestingly, a typical olefinic alcohol of 2-cyclohexan-1-ol exhibited very high selectivity for 2-cyclohexan-1-one (>99.5%, Table 2, entry 6), suggesting that the side reactions are free in the oxidation. For straight-chain alcohols, 2-hexanol and 2-butanol still had conversion of 43 and 33% at 80 °C (Table 2, entries 7 and 8). These results indicate that Au/LDH catalyst is very active for aerobic oxidation of a wide range of secondary alcohols.

3.3. Oxidation of primary alcohols

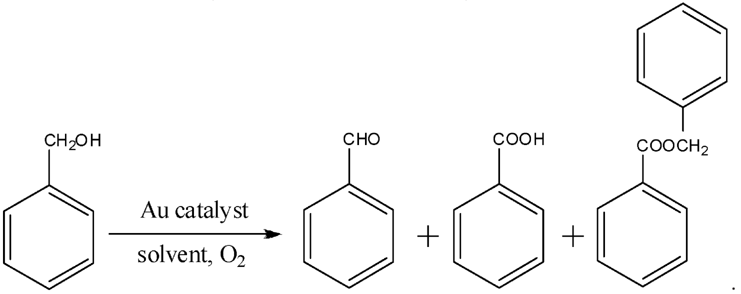
Generally, compared with secondary alcohols, the oxidation of primary alcohols shows relatively low activities [16]. Table 3 presents catalytic activities and selectivities in aerobic oxidation of benzyl alcohol over Au/LDH catalyst, and the choice of benzyl alcohol as a model reaction is due to the presence of side reactions such as over-oxidation of benzaldehyde and esterification of benzyl alcohol with benzoic acid. Notably, Au/LDH catalyst was very active and selective for the formation of benzaldehyde in the presence of toluene solvent (Table 3, entries 1–3). When the temperature was

Table 2
Aerobic oxidation of secondary alcohols over Au/LDH catalyst.

Entry	Substrate	Product	Temperature (°C)	Solvent	Time (h)	Conversion (%)	Selectivity (%)
1			R.T.	Toluene	20	95	>99.5
2			R.T.	Toluene	20	99	>99.5
3			45	Toluene	8	92	>99.5
4			80	Toluene	8	81	92
5			R.T.	Toluene	24	60	>99.5
6			45	Toluene	12	74	>99.5
7			80	Toluene	24	43	>99.5
8			80	Toluene	40	33	>99.5

Reaction conditions: 0.6 mmol of alcohol, 80 mg of catalyst, 10 ml of solvent, O_2 with rate 30 ml/min, room temperature at 26 °C.

Table 3
Aerobic oxidation of benzyl alcohol over various Au catalysts.



Entry	Catalyst	Solvent	Temperature (°C)	Time (h)	Conversion (%)	Selectivity[a] (%)
1	Au/LDH	Toluene	80	20	89	93
2	Au/LDH	Toluene	45	20	77	96
3	Au/LDH	Toluene	R.T.	20	49	99
4	Au/LDH	H_2O	80	20	96	71
5	Au/LDH	H_2O	45	20	90	71
6	Au/LDH	H_2O	R.T.	40	69	82
7	Pd/LDH	Toluene	45	24	<1	–
8[b]	Pd/LDH	Toluene	45	24	3	98
9	Au/TiO_2	Toluene	80	20	14	99
10	Au/MgO	Toluene	80	20	26	97
11	Au/Fe_2O_3	Toluene	80	20	6	99
12	Au/SiO_2	Toluene	80	20	<1	–
13[c]	Au/SiO_2	Toluene	80	20	6	91

Reaction conditions: 0.6 mmol of benzyl alcohol, 80 mg of catalyst, 10 ml of solvent, O_2 with rate 30 ml/min.
[a] Selectivity for benzaldehyde.
[b] Addition of t-butyl hydroperoxide (TBHP, 5 mol% based on substrate) as initiator.
[c] Addition of 1 mmol of Na_2CO_3 base.

80 °C, the catalyst gave the conversion at 89% and selectivity at 93% (Table 3, entry 1); when the temperature was reduced to 45 °C, the catalyst showed lower conversion (77%) but higher selectivity (96%) (Table 3, entry 2); when the reaction was performed at room temperature, the conversion was much lower (49%) and the benzaldehyde was selectively formed (>99%) (Table 3, entry 3). In contrast, Pd/LDH and the other Au-based catalysts exhibited very low conversion (1–25%, Table 3, entries 7–13).

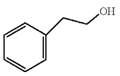
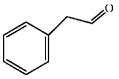
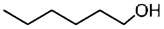
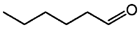
Interestingly, when water was used as solvent in the oxidation, Au/LDH catalyst showed high conversion and low selectivity (Table 3, entries 4–6), compared with toluene solvent. For example, the conversion of benzyl alcohol at 45 °C in water can reach 90%, which is much higher than that in toluene solvent (77%). On the contrary, the selectivity in water was only 71%, which is less than that in toluene solvent (96%). This phenomenon is possibly assigned to the difference in solubility of alcohols [6a,20] and in reactivity of products [19b]. For example, primary alcohols have better solubility in water than secondary alcohols, resulting in higher conversion of primary alcohols than secondary alcohols [6a,20]. However, water could react with aldehyde oxidized by primary alcohols to form aldehyde hydrate, which could be easily oxidized into carboxylic acid, a major by-product of primary alcohol oxidations [19b]. In contrast, the acetones oxidized by secondary alcohols in water are basically stable.

Table 4 presents catalytic activities and selectivities in oxidation of 2-phenylethanol and 1-hexanol in the presence of water. 2-phenylethanol had good conversion (87%) and selectivity for phenylacetaldehyde (81%), while 1-hexanol showed low activity (14%) and selectivity for *n*-hexaldehyde (22%).

3.4. XPS spectra of Au/LDH, Au/TiO$_2$, and Au/SiO$_2$ catalysts

To understand the highly active Au nanoparticles on the surface of LDH support, XPS spectra of Au/LDH, Au/TiO_2, and Au/SiO_2 catalysts have been compared, as shown in Fig. 4. Au/LDH catalyst showed Au $4f_{7/2}$ binding energy at 83.2 eV (Fig. 4(a)), which is obviously lower than that of Au/TiO_2 (83.5 eV, Fig. 4(b)) and of Au/SiO_2 catalyst (84.0 eV, Fig. 4(c)). Compared with Au/TiO_2 and Au/SiO_2, the downshift of Au $4f_{7/2}$ over Au/LDH indicates that Au nanoparticles are negative charged, which might be resulted from the strong interaction between Au nanoparticles with LDH support [17a,21,22]. The negatively charged Au nanoparticles are favorable for activation of molecular oxygen in aerobic oxidation of alcohols [23]. It was reported that a hydrogenation step is key step for the oxidation of alcohols [19b,24,25]. In addition, the support alkalinity is important to facilitate the dehydrogenation step [19b,24]. This conclusion is also confirmed by the fact that the addition of solid base (Na_2CO_3) could effectively enhance catalytic activities in this

Table 4
Aerobic oxidation of primary alcohols over Au/LDH catalyst.

Entry	Substrate	Product	Temperature (°C)	Solvent	Time (h)	Conversion (%)	Selectivity (%)
1			45	H_2O	24	87	81
2[a]			80	H_2O	24	14	22

Reaction conditions: 0.6 mmol of alcohol, 80 mg of catalyst, 10 ml of solvent, O_2 with rate 30 ml/min.
[a] O_2 pressure at 0.5 MP.

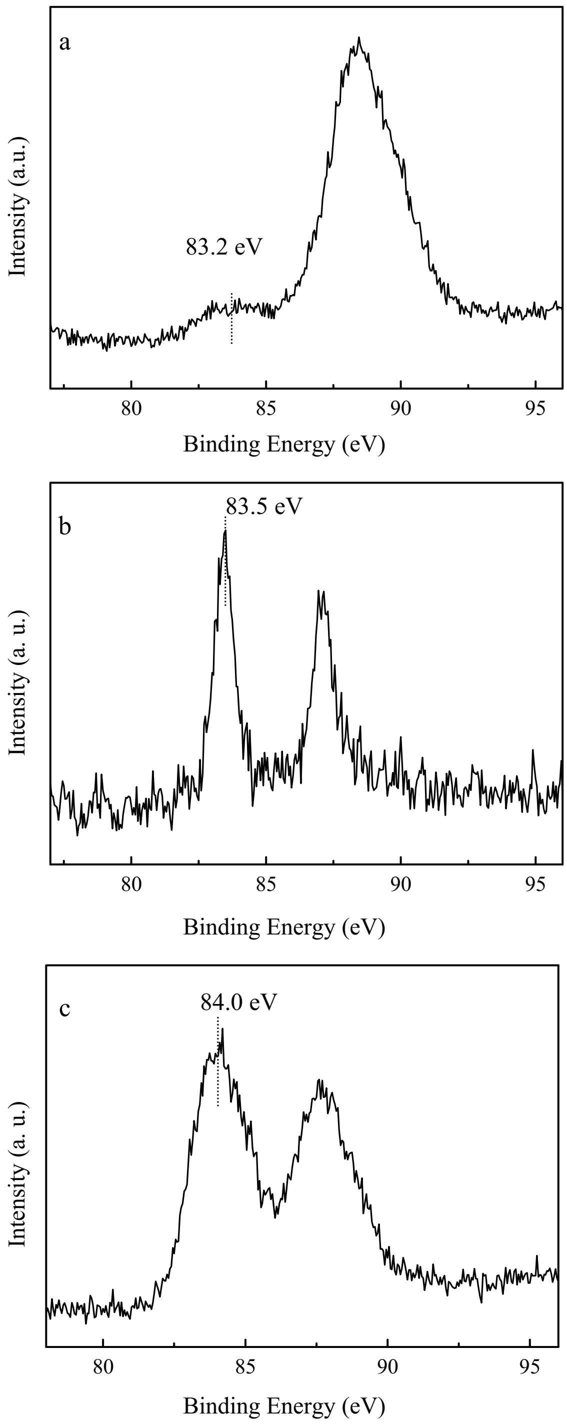


Fig. 4. Au4f XPS spectra of (a) Au/LDH, (b) Au/TiO_2, and (c) Au/SiO_2 catalysts.

work (Table 1, entries 11 and 12; Table 2, entries 12 and 13). Hence, the dehydrogenation abilities of various samples were systemically investigated. Fig. 5 shows the temperature programmed surface reaction (TPSR) curves of 2-propanol on Au/TiO_2, Au/SiO_2, LDH, and Au/LDH samples for H_2 mass intensity. Notably, no H_2 signals could be detected for Au/TiO_2 and Au/SiO_2 samples. However, two obvious peaks assigned to H_2 signals appeared at 294 and 420 °C, when the TPSR processes were carried out by adsorption 2-propanol on LDH sample. Interestingly, Au/LDH gives a H_2 peak with stronger intensity at much lower temperature of 270 °C. These results suggest that LDH support has excellent dehydrogenation abilities for adsorbed 2-propanol, and the presence of Au nanoparticles on LDH can greatly facilitate this process, which could be the reason of high activities of Au/LDH for the alcohol oxidations.

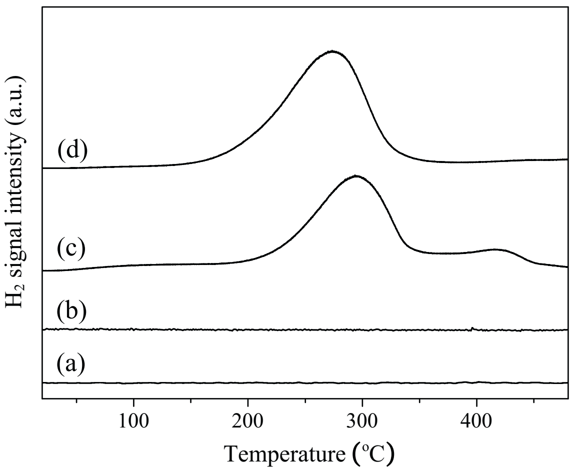


Fig. 5. TPSR spectra of 2-propanol adsorbed on (a) Au/TiO_2, (b) Au/SiO_2, (c) LDH and (d) Au/LDH for H_2 signals.

4. Conclusions

Extremely small Au nanoparticles distributed at 1–5 nm on LDH support (Au/LDH) is successfully prepared by ion-exchange and reduction procedures. Compared with the other Au-based catalysts, Au/LDH catalyst shows good activities, high selectivities, and recyclability in aerobic oxidation of a wide range of primary and secondary alcohols under very mild conditions, which is of great importance for potentially industrial production of fine chemicals.

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References

[1] R.A. Sheldon, J.K. Kochi, Metal-Catalyzed Oxidations of Organic Compounds, Academic Press, New York, 1981.
[2] (a) R.A. Sheldon, J. Dakka, Catal. Today 19 (1994) 215;
(b) R.A. Sheldon, Chemtech (1991) 566;
(c) R.A. Sheldon, I.C.W.R. Arends, A. Dijksman, Catal. Today 57 (2000) 157.
[3] (a) G.A. Barf, R.A. Sheldon, J. Mol. Catal. A: Chem. 102 (1995) 23;
(b) B. Notari, Stud. Surf. Sci. Catal. 60 (1991) 343.
[4] F.A. Luzzio, Organic Reactions, 53, Wiley, New York, 1998, p. 1.
[5] H. Yang, B. Li, Synth. Commun. 21 (1991) 1521.
[6] (a) C.Y. Ma, B.J. Dou, J.J. Li, J. Cheng, Q. Hu, Z.P. Hao, S.Z. Qiao, Appl. Catal. B: Environ. 92 (2009) 202;
(b) G.J. ten Brink, I.W.C.E. Arends, R.A. Sheldon, Science 287 (2000) 1636;
(c) T. Mallat, A. Baiker, Chem. Rev. 104 (2004) 3037;
(d) B.M. Trost, Science 254 (1991) 1471.
[7] T. Wang, H. Shou, Y. Kou, H. Liu, Green Chem. 11 (2009) 562.
[8] T. Inokuchi, K. Nakagawa, S. Torii, Tetrahedron Lett. 36 (1995) 3223.
[9] (a) A. Dijksman, A.M.I. Payeras, I.W.C.E. Arends, R.A. Sheldon, J. Am. Chem. Soc. 123 (2001) 6826;
(b) I.E. Marko, P.R. Giles, M. Tsukazaki, S.M. Brown, C.J. Urch, Science 274 (1996) 2044.
[10] (a) J. Chen, Q.H. Zhang, Y. Wang, H.L. Wan, Adv. Synth. Catal. 350 (2008) 453;
(b) F. Li, Q.H. Zhang, Y. Wang, Appl. Catal. A: Gen. 334 (2008) 217;
(c) R. Tang, S.E. Diamond, N. Nery, F. Mares, J. Chem. Soc. Chem. Commun. (1978) 562.
[11] (a) X. Meng, K. Lin, X. Yang, Z. Sun, D. Jiang, F.-S. Xiao, J. Catal. 218 (2003) 460;
(b) X. Meng, Z. Sun, R. Wang, S. Lin, J. Sun, M. Yang, K. Lin, D. Jiang, F.-S. Xiao, Catal. Lett. 76 (2001) 105.
[12] (a) G.J. Hutchings, J. Catal. 96 (1985) 292;
(b) M. Haruta, T. Koboyashi, H. Sano, N. Yamada, Catal. Lett. 16 (1987) 405.

[13] (a) G.J. Hutchings, Catal. Today 122 (2007) 196;
(b) T.V. Choudhary, D.W. Goodman, Top. Catal. 21 (2002) 25;
(c) A.A. Herzing, C.J. Kiely, A.F. Carley, P. Landon, G.J. Huthcings, Science 321 (2008) 1331;
(d) C.Y. Ma, Z. Mu, J.J. Li, Y.G. Jin, J. Cheng, G.Q. Lu, Z.P. Hao, S.Z. Qiao, J. Am. Chem. Soc. 132 (2010) 2608.
[14] (a) A. Corma, H. Garcia, Chem. Soc. Rev. 37 (2008) 2096;
(b) A. Grirrane, A. Corma, H. Garcia, J. Catal. 268 (2009) 350;
(c) W. Yan, S. Brown, Z. Pan, S.M. Mahurin, S.H. Overbury, S. Dai, Angew. Chem. Int. Ed. 45 (2006) 3614;
(d) W. Yan, S.M. Mahurin, S.H. Overbury, S. Dai, Top. Catal. 39 (2006) 199.
[15] (a) X. Zhang, H. Shi, B. Xu, Angew. Chem. Int. Ed. 44 (2005) 7132;
(b) D. He, H. Shi, Y. Wu, B. Xu, Green Chem. 9 (2007) 849;
(c) H. Sun, F.-Z. Su, J. Ni, Y. Cao, H.-Y. He, K.-N. Fan, Angew. Chem. Int. Ed. 48 (2009) 4390.
[16] (a) A. Abad, P. Concepcion, A. Corma, H. Garcia, Angew. Chem. Int. Ed. 44 (2005) 4066;
(b) F.-Z. Su, Y.-M. Liu, L.-C. Wang, Y. Cao, H.-Y. He, K.-N. Fan, Angew. Chem. Int. Ed. 47 (2008) 334.
[17] (a) L. Wang, X. Meng, B. Wang, W. Chi, F.-S. Xiao, Chem. Commun. 46 (2010) 5003;
(b) L. Wang, X. Meng, F.-S. Xiao, Chin. J. Catal. 31 (2010) 943.
[18] H. Tsunoyama, H. Sakurai, Y. Negishi, T. Tsukuda, J. Am. Chem. Soc. 127 (2005) 9374.
[19] (a) S. Biella, L. Prati, M. Rossi, J. Catal. 206 (2002) 242;
(b) S. Carretin, P. McMorn, P. Johnston, K. Griffin, G.J. Hutchings, Chem. Commun. (2002) 696.
[20] N. Dimitratos, A. Villa, D. Wang, F. Porta, D.S. Su, L. Prati, J. Catal. 244 (2006) 113.
[21] Y.F. Han, Z.Y. Zhong, K. Ramesh, F.X. Chen, L.W. Chen, J. Phys. Chem. C 111 (2007) 3163.
[22] F.-Z. Su, M. Chen, L.-C. Wang, X.-S. Huang, Y.-M. Liu, Y. Cao, H.-Y. He, K.-N. Fan, Catal. Commun. 9 (2008) 1027.
[23] H. Tsunoyama, N. Ichikuni, H. Sakurai, T. Tsukuda, J. Am. Chem. Soc. 131 (2009) 7086.
[24] P. Haider, A. Baiker, J. Catal. 248 (2007) 175.
[25] C. Keresszegi, T. Mallat, J.D. Gruwaldt, A. Baiker, J. Catal. 225 (2004) 138.