

# Gold nanoparticles on hydrotalcites as efficient catalysts for oxidant-free dehydrogenation of alcohols†

Wenhao Fang, Qinghong Zhang,\* Jing Chen, Weiping Deng and Ye Wang\*

Received (in Cambridge, UK) 3rd November 2009, Accepted 6th January 2010

First published as an Advance Article on the web 27th January 2010

DOI: 10.1039/b923047e

**Hydrotalcite-supported gold nanoparticles with sizes of less than 5 nm are highly efficient and reusable catalysts for the oxidant-free dehydrogenation of alcohols to carbonyl compounds and hydrogen.**

Highly dispersed gold species have been demonstrated to be active catalysts in many hydrogenation and oxidation reactions such as hydrogenation of alkenes and aldehydes, CO oxidation, propylene epoxidation, hydrogen peroxide synthesis, and aerobic oxidation of alcohols.<sup>1</sup> For some reactions, supported gold catalysts even show performances superior to those of platinum group metal catalysts. It is widely accepted that the size of gold plays a dominating role in catalysis although many other factors such as the chemical state of gold (metallic, cationic or anionic), the morphology of gold particles, and the interaction between gold and a support may also influence the catalytic behaviours. Gold catalysis has become an exciting research area, showing magic changes of catalytic behaviours with size of particles.

On the other hand, the dehydrogenation of alcohols to carbonyl compounds is one of the most essential transformations in organic synthesis. A number of heterogeneous catalysts including supported Au nanoparticles have been developed for the selective oxidation of alcohols by O<sub>2</sub> to replace the stoichiometric reactions using dichromate or permanganate oxidants.<sup>2,3</sup> From the viewpoints of safety and avoiding possible over-oxidation of products, the oxidant-free dehydrogenation of alcohols to aldehydes or ketones and H<sub>2</sub> is a more desirable route. A few platinum group catalysts, especially Ru complexes and supported Ru catalysts, could catalyse the dehydrogenation of alcohols in the absence of any oxidants or hydrogen acceptors.<sup>4</sup> Recently, it has been disclosed that supported Ag and Cu nanoparticles can also catalyse the oxidant-free dehydrogenation of alcohols with good efficiency.<sup>5,6</sup> To date, only one report has mentioned the Au-catalysed oxidant-free dehydrogenation of benzyl alcohol to benzaldehyde, but toluene was formed with a high selectivity (~47%) over the catalyst (Au–Pd/TiO<sub>2</sub>) with a high activity and the Au/TiO<sub>2</sub> alone gave a very low activity.<sup>7</sup> Moreover, there is little knowledge about the Au-catalysed

dehydrogenation reactions although a few studies have shown that supported Au could catalyse the decomposition of ammonia or formic acid or the dehydrogenation of propane in the presence of H<sub>2</sub> and O<sub>2</sub>.<sup>1b,e,8,9</sup> Herein, we demonstrate that the supported Au nanoparticles are highly active and selective catalysts for the oxidant-free dehydrogenation of various alcohols. We have clarified that the size of Au nanoparticles plays a pivotal role in this dehydrogenation catalysis.

Table 1 shows the catalytic performances of Au catalysts loaded on various supports, which have been prepared by an impregnation method, followed by H<sub>2</sub> reduction at 250 °C (see the ESI† for experimental details), for the dehydrogenation of benzyl alcohol in the absence of any oxidant or hydrogen acceptor at 120 °C. Among these supported Au catalysts, the Au/hydrotalcite (Au/HT) exhibited the highest activity and selectivity. Au/Al<sub>2</sub>O<sub>3</sub> possessed relatively higher activity but slightly lower selectivity, while Au/MgO possessed relatively higher selectivity but lower activity. Other supported Au catalysts were much less active for the dehydrogenation of benzyl alcohol (conversion <10%). We have also compared the catalytic performance of the Au/HT with those of the Ag/HT and Cu/HT, because the latter two catalysts have been reported to be efficient for the dehydrogenation of alcohols.<sup>5</sup> Under the same reaction conditions, the Au/HT exhibits a better performance than the Ag/HT and Cu/HT (Table 1).

**Table 1** Catalytic performances of Au catalysts loaded on various supports (Au loading, 0.1 wt%) and HT-supported Ag and Cu catalysts (Ag and Cu loadings, 0.1 wt%) for the oxidant-free dehydrogenation of benzyl alcohol<sup>a</sup>

| Catalyst                          | Mean size of metal particles <sup>b</sup> /nm |     | Selectivity/% |         |         |
|-----------------------------------|---|-----|---------------|---------|---------|
|                                   | Conv./%                                       |     | Aldehyde      | Toluene | Benzene |
| Au/Cab-O-Sil                      | 9.0   | 0.5 | 47            | 40      | 13      |
| Au/SBA-15                         | 4.3   | 0.4 | 53            | 29      | 18      |
| Au/CNT <sup>c</sup>               | 8.2   | 4.6 | 95            | 4.8     | 0.7     |
| Au/TiO <sub>2</sub>               | 5.8   | 1.5 | 90            | 6.5     | 3.2     |
| Au/ZrO <sub>2</sub>               | 18  | 1.4 | 88            | 9.3     | 2.5     |
| Au/La <sub>2</sub> O <sub>3</sub> | n.d. <sup>d</sup>                             | 5.3 | 97            | 1.8     | 0.8     |
| Au/CeO <sub>2</sub>               | 8.7   | 4.6 | 97            | 2.4     | 0.9     |
| Au/HAP <sup>e</sup>               | 28  | 4.3 | 84            | 1.9     | 1.0     |
| Au/MgO                            | 11  | 37  | >99           | 0.4     | 0.2     |
| Au/Al <sub>2</sub> O <sub>3</sub> | 5.1   | 59  | 96            | 2.9     | 0.5     |
| Au/HT                             | 8.0   | 61  | >99           | 0.3     | 0       |
| Cu/HT                             | n.d.  | 14  | 85            | 14      | 1.0     |
| Ag/HT                             | n.d.  | 51  | >99           | 0.3     | 0.2     |

<sup>a</sup> Reaction conditions: catalyst (prepared by impregnation), 0.20 g; T = 120 °C; benzyl alcohol, 1.0 mmol; *p*-xylene, 5.0 cm<sup>3</sup>; Ar, 3 cm<sup>3</sup> min<sup>-1</sup>; time, 6 h. <sup>b</sup> See Fig. S1 in the ESI† for TEM micrographs and particle size distributions. <sup>c</sup> CNT denotes carbon nanotube. <sup>d</sup> Not detected. <sup>e</sup> HAP denotes hydroxyapatite.

State Key Laboratory of Physical Chemistry of Solid Surfaces, National Engineering Laboratory for Green Chemical Productions of Alcohols, Ethers and Esters, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China.

E-mail: zhangqh@xmu.edu.cn, wangye@xmu.edu.cn;  
Fax: +86-592-2183047; Tel: +86-592-2186156

† Electronic supplementary information (ESI) available: Experimental details, TEM micrographs and particle size distributions for supported Au catalysts and recycling uses of the Au/HT. See DOI: 10.1039/b923047e

Recently, Shimizu *et al.*<sup>6</sup> reported that the nature of the support played a key role in the Ag-catalysed dehydrogenation of 4-methylbenzyl alcohol and they proposed that the acid–base bifunctional support (*e.g.*, Al<sub>2</sub>O<sub>3</sub>) was superior to the basic or the acidic supports. Our present results also suggest that the choice of a proper support is important for obtaining high activity and selectivity for the Au-catalysed oxidant-free dehydrogenation of benzyl alcohol. Future studies are needed to clarify the functions of the support in our Au-catalysed dehydrogenation of alcohols.

It can be expected that the size of Au nanoparticles may significantly affect the catalytic performances. We have performed TEM measurements for some typical catalysts listed in Table 1. The mean size of Au nanoparticles for the Au/HT was 8.0 nm, which was larger than those for the Au/SBA-15, Au/TiO<sub>2</sub> and Au/Al<sub>2</sub>O<sub>3</sub>, and was similar to those for the Au/Cab-O-Sil, Au/CNT and Au/CeO<sub>2</sub> (Table 1). By using a deposition–precipitation (DP) method (see the ESI† for details), we have succeeded in preparing Au/HT catalysts with smaller Au nanoparticles. TEM observations for the 0.06 wt% Au/HT prepared by the DP method showed that the Au nanoparticles were 1.5–4.5 nm in size and the mean size of Au was calculated to be 2.8 nm by counting ~200 Au nanoparticles (Fig. 1). This catalyst gave a significantly higher benzyl alcohol conversion (94%) under the reaction conditions of Table 1. We have investigated the catalytic performances of the Au/HT catalysts prepared by the DP method with different Au loadings. HTs without Au could not catalyse the dehydrogenation of benzyl alcohol, suggesting that Au was the active phase. The variation of Au loadings between 0.03 and 12 wt% provided variable benzyl alcohol conversions between 34 and >99%, but consistently high benzaldehyde selectivity (>99%). We observed a unique dependence of benzyl alcohol conversion on the Au loading (Fig. 2). The conversion first increased to 94% as the Au loading rose to 0.06 wt%, and then underwent a decrease with an increase in Au loadings from 0.06 to 0.26 wt%. However, further increases in Au loadings caused increases in benzyl alcohol conversions again, and the catalyst with an Au loading of 12 wt% afforded a conversion of >99%.

To understand the unique dependence of catalytic performances on Au loadings, we performed further TEM measurements for the samples with Au loadings of 0.26 and 12 wt%. It is of interest that only larger Au particles (>5 nm)

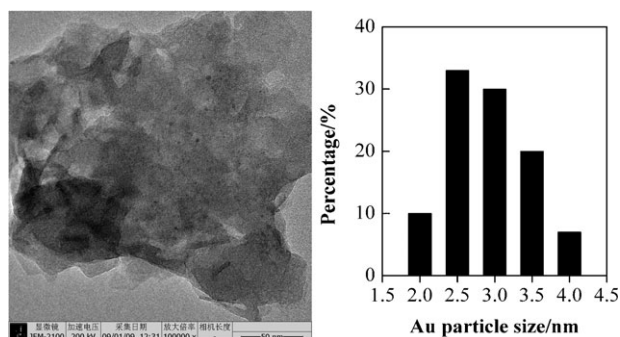


Fig. 1 TEM micrograph and Au particle size distribution for the 0.06 wt% Au/HT catalyst prepared by the DP method.

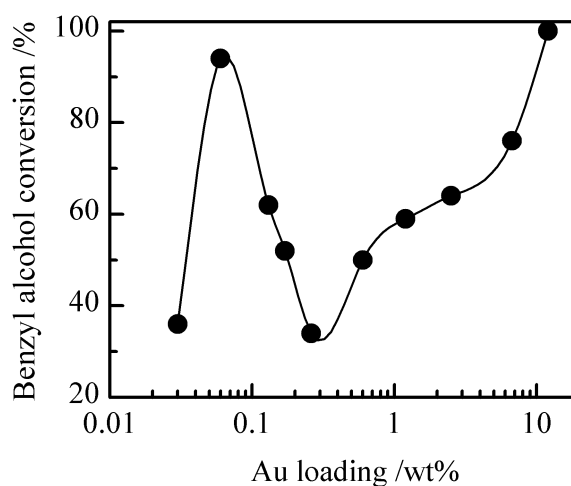


Fig. 2 Dependence of benzyl alcohol conversion on Au loadings for the Au/HT catalysts prepared by the DP method. Reaction conditions: catalyst, 0.20 g;  $T = 120$  °C; benzyl alcohol, 1.0 mmol; *p*-xylene, 5.0 cm<sup>3</sup>; Ar, 3 cm<sup>3</sup> min<sup>-1</sup>; time, 6 h.

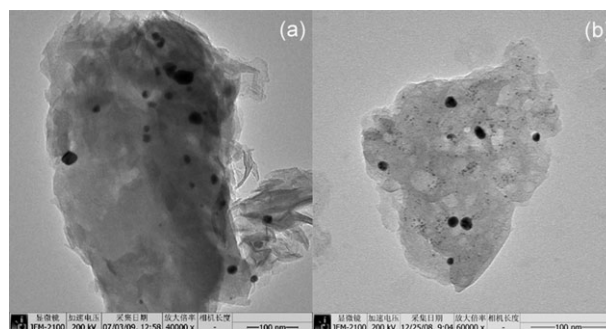
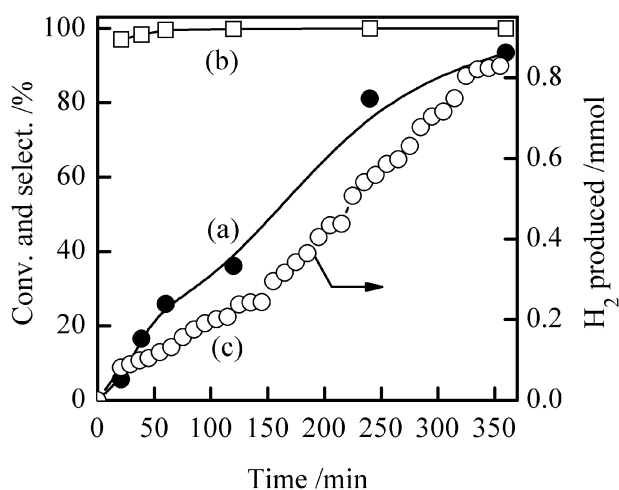


Fig. 3 TEM micrographs for the 0.26 and 12 wt% Au/HT catalysts prepared by the DP method. (a) 0.26 wt% Au/HT, (b) 12 wt% Au/HT.

exist over the 0.26 wt% Au/HT catalyst (Fig. 3a), indicating the aggregation of Au nanoparticles over this sample. The mean size of Au particles was calculated to be 13.6 nm. On the other hand, the 12 wt% Au/HT catalyst exhibited a bimodal size distribution; smaller Au nanoparticles ( $\leq 4$  nm) could also be observed besides the larger Au particles (Fig. 3b). The mean size of the smaller Au nanoparticles was 2.8 nm. We still cannot make a straightforward interpretation of this phenomenon. Combining this unique observation with the catalytic behaviours shown in Fig. 2, we propose that the smaller Au nanoparticles ( $< 5$  nm) are more active than the larger Au particles ( $> 5$  nm).

We have performed detailed studies for the 0.06 wt% Au/HT catalyst prepared by the DP method, which possesses only smaller Au nanoparticles (1.5–4.5 nm, Fig. 1) and affords a higher benzyl alcohol conversion. Fig. 4 shows the time course for benzyl alcohol conversion. Benzaldehyde selectivity was always >98%. Benzyl alcohol conversion increased almost linearly with time and reached >90% after 6 h of reaction. Accompanying the conversion of benzyl alcohol to benzaldehyde, H<sub>2</sub> was formed, and the formation of H<sub>2</sub> also increased almost linearly with the reaction time. The calculation revealed that the molar ratio of H<sub>2</sub> to benzaldehyde produced in 6 h was about 0.95 : 1, showing that H<sub>2</sub>



**Fig. 4** Time course for the dehydrogenation of benzyl alcohol over the 0.06 wt% Au/HT catalyst prepared by the DP method. (a) Benzyl alcohol conversion, (b) benzaldehyde selectivity, (c) H<sub>2</sub> produced. Reaction conditions: catalyst, 0.20 g; *T* = 120 °C; benzyl alcohol, 1.0 mmol; *p*-xylene, 5.0 cm<sup>3</sup>; N<sub>2</sub>, 10 cm<sup>3</sup> min<sup>-1</sup>.

**Table 2** Catalytic behaviours of the 0.06 wt% Au/HT catalyst prepared by the DP method for dehydrogenation of various alcohols<sup>a</sup>

| Entry | Substrate | Time/h | Conversion/% | Carbonyl compound selectivity/% |
|-------|-----------|--------|--------------|---------------------------------|
| 1     |           | 9      | >99          | >99                             |
| 2     |           | 9      | >99          | >99                             |
| 3     |           | 24     | >99          | >99                             |
| 4     |           | 12     | 97           | >99                             |
| 5     |           | 12     | >99          | >99                             |
| 6     |           | 24     | 90           | >99                             |
| 7     |           | 12     | 96           | >99                             |
| 8     |           | 18     | >99          | >99                             |
| 9     |           | 24     | >99          | >99                             |
| 10    |           | 48     | >99          | >99                             |
| 11    |           | 48     | 61           | >99                             |
| 12    |           | 48     | 31           | >99                             |

<sup>a</sup> Reaction conditions: catalyst, 0.20 g; *T* = 120 °C; substrate, 1.0 mmol; *p*-xylene, 5.0 cm<sup>3</sup>; Ar, 3 cm<sup>3</sup> min<sup>-1</sup>.

was generated stoichiometrically during the dehydrogenation of benzyl alcohol.

We confirmed that no leaching of Au from the 0.06 wt% Au/HT catalyst prepared by the DP method occurred during

the dehydrogenation of benzyl alcohol. No Au can be detected in the filtrate after the reaction. The recycling uses of this sample showed no significant decreases in benzyl alcohol conversion and benzaldehyde selectivity (see Fig. S2, ESI†). Thus, the present Au/HT catalyst could be used repeatedly.

We have further examined the catalytic behaviours of the 0.06 wt% Au/HT catalyst prepared by the DP method for the oxidant-free dehydrogenation of various alcohols. The results in Table 2 show that the present catalyst is effective for the dehydrogenation of benzylic alcohols with different substituents (entries 1–7), alicyclic alcohols (entries 8 and 9) and heterocyclic alcohols containing a nitrogen atom (entry 10). The present catalyst could also catalyse the dehydrogenation of less active linear aliphatic alcohols although the efficiency was lower (entries 11 and 12).

In summary, we have demonstrated that the HT-supported Au nanoparticles can efficiently catalyse the oxidant-free dehydrogenation of alcohols to the corresponding carbonyl compounds. The size of the Au nanoparticles plays a key role in the dehydrogenation reaction. The present Au/HT catalyst can be used repeatedly, and can be applied to the synthesis of various carbonyl compounds.

This work was supported by the NSFC (Nos. 20625310, 20773099 and 20873110), the National Basic Research Program of China (Nos. 2010CB732303 and 2005CB221408) and the Key Scientific Project of Fujian Province of China (2009HZ0002-1).

## Notes and references

- For typical reviews of gold-catalysed heterogeneous reactions: (a) M. Haruta, *Catal. Today*, 1997, **36**, 153; (b) G. C. Bond and D. T. Thompson, *Catal. Rev. Sci. Eng.*, 1999, **41**, 319; (c) M. Haruta, *Chem. Rec.*, 2003, **3**, 75; (d) M. Haruta, *Gold Bull.*, 2004, **37**, 27; (e) A. S. K. Hashmi and G. J. Hutchings, *Angew. Chem., Int. Ed.*, 2006, **45**, 7896; (f) T. Ishida and M. Haruta, *Angew. Chem., Int. Ed.*, 2007, **46**, 7154; (g) G. J. Hutchings, *Chem. Commun.*, 2008, 1148; (h) G. J. Hutchings, M. Brust and H. Schmidbaur, *Chem. Soc. Rev.*, 2008, **37**, 1759.
- For recent reviews on heterogeneous aerobic oxidation of alcohols, see: (a) T. Mallat and A. Baiker, *Chem. Rev.*, 2004, **104**, 3037; (b) B.-Z. Zhan and A. Thompson, *Tetrahedron*, 2004, **60**, 2917; (c) K. Kaneda, K. Ebitani, T. Mizugaki and K. Mori, *Bull. Chem. Soc. Jpn.*, 2006, **79**, 981; (d) T. Matsumoto, M. Ueno, N. Wang and S. Kobayashi, *Chem.-Asian J.*, 2008, **3**, 196.
- For gold-catalysed aerobic oxidation of alcohols, see: (a) A. Abad, P. Concepción, A. Corma and H. García, *Angew. Chem., Int. Ed.*, 2005, **44**, 4066; (b) D. I. Enache, J. K. Edwards, P. Landon, B. Solsna-Espriu, A. F. Carely, A. A. Herzing, M. Watanabe, C. J. Kiely, D. W. Knight and G. J. Hutchings, *Science*, 2006, **311**, 362; (c) F.-Z. Su, Y.-M. Liu, L.-C. Wang, Y. Cao, H.-Y. He and K.-N. Fan, *Angew. Chem., Int. Ed.*, 2008, **47**, 334.
- (a) J. H. Choi, N. Kim, Y. J. Shin, J. H. Park and J. Park, *Tetrahedron Lett.*, 2004, **45**, 4607; (b) W.-H. Kim, I. S. Park and J. Park, *Org. Lett.*, 2006, **8**, 2543; (c) R. Karvembu and R. Priyarega, *React. Kinet. Catal. Lett.*, 2006, **88**, 333.
- (a) T. Mitsudome, Y. Mikami, H. Funai, T. Mizugaki, K. Jitsukawa and K. Kaneda, *Angew. Chem., Int. Ed.*, 2008, **47**, 138; (b) T. Mitsudome, Y. Mikami, K. Ebata, T. Mizugaki, K. Jitsukawa and K. Kaneda, *Chem. Commun.*, 2008, 4804.
- K. Shimizu, K. Sugino, K. Sawabe and A. Satsuma, *Chem.-Eur. J.*, 2009, **15**, 2341.
- S. Meenakshisundaram, E. Nowicka, P. J. Miedziak, G. L. Brett, R. L. Jenkins, N. Dimitratos, S. H. Taylor, D. W. Knight, D. Bethell and G. J. Hutchings, *Faraday Discuss.*, 2010, DOI: 10.1039/b908172k.
- M. Ojeda and E. Iglesia, *Angew. Chem., Int. Ed.*, 2009, **48**, 4800.
- J. J. Bravo-Suárez, K. K. Bando, J. Lu, T. Fujitani and S. T. Oyama, *J. Catal.*, 2008, **255**, 114.