Promoting gold nanocatalysts in solvent-free selective aerobic oxidation of alcohols†

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A trace amount of metal carbonate, acetate or borate significantly boosts gold nanocatalysts in selective aerobic oxidation of alcohols under mild solvent-free conditions.

Supported gold nanoparticles have been recently extensively studied as catalysts for a wide range of oxidation reactions including low-temperature CO oxidation,[1–4] alkene epoxidation,[5,6] aldehyde oxidation,[7–9] and aerobic oxidation of alcohols in both gas- and liquid-phase under relatively mild conditions.[9–23] Among noble metal nanoparticle catalysts used in the liquid-phase aerobic oxidation of alcohols, properly sized supported gold nanoparticles are the most selective catalysts, the least prone to leaching due to over-oxidation of the metal active sites, and not easily poisoned through ligand chelating.[11,20,23]

The application of supported gold nanoparticles in liquid-phase alcohol oxidation under mild conditions typically requires an aqueous alkaline reaction medium (*e.g.*, excess NaOH, K_2CO_3), which results in carboxylate products.[11–13] The catalytic activity by oxide-supported gold nanoparticles under solvent-free conditions at temperatures less than 100 °C has been demonstrated but is still limited.[14–16] Furthermore, the catalytic performance of oxide-supported gold nanoparticles is very sensitive to the size of the gold nanoparticles and also the physical and chemical nature of the metal oxide support.[15–18]

Here we report a methodology to promote oxide-supported gold nanocatalysts in solvent-free selective aerobic oxidation of alcohols. The significant promotional effect is achieved by a catalytic amount of low-cost promoters such as metal carbonates, acetates or borate, which is applicable to all oxide-supported gold nanoparticles. A turnover-frequency (TOF) as high as 25030 h^{-1} has been obtained in the aerobic selective oxidation of alcohols under solvent-free conditions at 100 °C. By choosing appropriate promoters, product selectivity and alcohol conversion have been simultaneously improved.

Oxide-supported gold nanoparticle catalysts were prepared by the general strategy that we have recently developed.[22] In the absence of a base (*e.g.*, K_2CO_3, Na_2CO_3), these oxide-supported gold nanoparticles do not efficiently catalyze the selective oxidation of alcohols under mild solvent-free conditions (Table 1, entry 1), which is consistent with previous reports.[14–16] At 100 °C and 2 atm O_2, the conversion of benzyl alcohol (10 mL) is only 2.5%. A dramatic improvement in the alcohol conversion is observed, however, when a small amount of K_2CO_3/Na_2CO_3 (see below) is added (Table 1, entries 2 and 3). For example, the addition of K_2CO_3 increases the conversion of benzyl alcohol from 2.5 to 76.6% with benzaldehyde selectivity of 50.9%.

Carbonates (*e.g.*, K_2CO_3, Na_2CO_3) are widely applied as weak bases in many organic syntheses, particularly in reactions involving proton extraction. In most of these syntheses, a stoichiometric excess of carbonate is required to achieve high reaction efficiencies. In the gold-nanoparticle-catalyzed oxidation reactions where we use a carbonate, the molar ratios of carbonate/alcohol were, however, much lower. The promotional effect is effective even if a trace amount of carbonate, with a K_2CO_3/alcohol molar ratio of 1×10^{-3}, is used. Increasing the amount of K_2CO_3 does not linearly increase the alcohol conversion (Fig. 1).

Fig. 2 shows the aerobic oxidation of benzyl alcohol as a function of time with the additions of K_2CO_3 promoter. The promotional effect by carbonates is maximized at the beginning of promoter additions (*i.e.*, at 0 and 75 h) and decays with reaction time. The first addition of K_2CO_3 (1 mol% to alcohol) leads to alcohol conversion up to ∼38% within 2 h. Since the produced benzaldehyde can be further oxidized to form benzoic acid by-product which reacts with K_2CO_3, a decay of reaction rate is observed. However, a further increase in the alcohol conversion is observed when the second K_2CO_3 addition is applied. In addition, it is worth noting that aldehyde is still the key product for the reactions promoted by a small amount of carbonates.

Without the promoter, the catalytic performance of oxide-supported gold nanoparticles is highly dependent on the metal oxide support. To study the effect of metal-oxide supports with the use of K_2CO_3, we deposited the same-sized (6.3 nm) gold nanoparticles on different metal oxides ranging from semiconducting (*i.e.*, TiO_2, ZnO), acidic (*i.e.*, SiO_2, zeolite), to basic (*i.e.*, Co_3O_4, ZnO, MgO) oxides. With the help of a small amount of promoter (*e.g.*, K_2CO_3), all of the prepared oxide-supported gold nanoparticles efficiently catalyze the oxidation of alcohols under mild conditions (Table 1, entries 10–15).

Recently, Hutchings and co-workers demonstrated that Au/Pd-TiO_2 catalysts exhibit very high activity of alcohol oxidation under mild solvent-less conditions.[14] For solvent-free oxidation of benzyl alcohol, the reported Au/Pd-TiO_2 catalyst gives a TOF of 6440 h^{-1} (measured from the first 0.5 h of reaction) at 100 °C and 2 atm O_2. With the use of low-cost promoting agent (*i.e.*, K_2CO_3) instead of Pd and under similar catalysis conditions, we have found that oxide-supported pure gold nanoparticles (*e.g.*, Au–TiO_2) can catalyze the oxidation of alcohols even more efficiently (Table 1, entry 16) with a TOF of 7851 h^{-1} (based on a 5 h reaction) at 100 °C. It should be pointed out that a TOF of 25030 h^{-1} is

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Table 1 Selected catalytic results of selective oxidation of alcohols by using supported gold nanoparticles as catalysts

Entry[a]	Alcohol	Catalyst[b]	Au/alcohol[c] ($\times 10^{-6}$)	Promoter	Promoter/ alcohol	Conversion (%)	Selectivity[d] (%)	TOF[e]/h^{-1}
1	Benzyl alcohol	2.5% on TiO_2	262	None	NA	2.5	>99.9	19
2	Benzyl alcohol	2.5% on TiO_2	262	K_2CO_3	0.10	76.6	50.9	584
3	Benzyl alcohol	2.5% on TiO_2	262	Na_2CO_3	0.10	75.3	51.6	574
4	Benzyl alcohol	2.5% on TiO_2	131	NaOH	0.02	9.3	58.1	142
5	Benzyl alcohol	2.5% on TiO_2	131	NEt_3	0.02	8.7	90.5	137
6	Benzyl alcohol	2.5% on TiO_2	131	$NaCH_3COO$	0.01	42.5	74.6	648
7	Benzyl alcohol	2.5% on TiO_2	131	KCH_3COO	0.01	40.7	72.9	620
8	Benzyl alcohol	2.5% on TiO_2	131	$Na_2B_4O_7$	0.005	38.3	80.4	584
9	Benzyl alcohol	2.5% on TiO_2	131	$K_2B_4O_7$	0.005	39.6	82.1	604
10	Benzyl alcohol	2.5% on TiO_2	131	K_2CO_3	0.01	35.0	55.0	534
11	Benzyl alcohol	2.5% on ZnO	131	K_2CO_3	0.01	38.1	81.5	581
12	Benzyl alcohol	2.5% on Zeolite[f]	131	K_2CO_3	0.01	31.8	65.8	485
13	Benzyl alcohol	2.5% on SiO_2	131	K_2CO_3	0.01	33.6	59.3	512
14	Benzyl alcohol	2.5% on Co_3O_4	131	K_2CO_3	0.01	65.8	55.7	1003
15	Benzyl alcohol	2.5% on MgO	131	K_2CO_3	0.01	47.4	58.0	723
16	Benzyl alcohol	2.5% on TiO_2	2.6	K_2CO_3	0.002	10.3	78.7	7851
17	Benzyl alcohol	2.5% on TiO_2	262	$Co(CH_3COO)_2$	0.01	46.2	93.8	352
18	Benzyl alcohol	2.5% on TiO_2	262	$CoCl_2$	0.01	3.8	>99.9	29
19	Ethanol	2.5% on TiO_2	74	K_2CO_3	0.1	38.0	>99.9	1026
20	1-Propanol	2.5% on TiO_2	95	K_2CO_3	0.1	35.1	>99.9	739
21	1-Butanol	2.5% on TiO_2	116	K_2CO_3	0.1	58.9	>99.9	1014
22	2-Propanol	2.5% on TiO_2	97	K_2CO_3	0.1	15.3	>99.9	315
23	2-Octanol	2.5% on TiO_2	202	K_2CO_3	0.1	64.8	>99.9	643

[a] *Catalysis conditions*: solvent-free reactions; 100 °C for entries 1–18, and 80 °C for entries 19–23; 2 atm oxygen; 5 h. [b] All are based on 6.3 nm gold nanoparticles. [c] Calculated for all gold atoms, both on the surface and in the core of the nanoparticles. [d] Selectivity to benzaldehyde for entries 1–18, ethyl acetate for entry 19, propyl propionate for entry 20, butyl butanoate for entry 21, acetone for entry 22, and 2-octanone for entry 23. [e] TOF calculations were based on the analysis at the end of 5 h reactions. [f] CBV-600 Zeolite from Zeolyst International.

obtained for our reaction when the calculation is based on the 0.5 h reaction that the Hutchings group used.[14] In contrast to the more complicated Au/Pd–TiO_2 catalysts which are inactive for the oxidation of 2-octanol, pure supported gold nanoparticles are highly active with the help of a small amount of K_2CO_3 (Table 1, entry 23).

In addition to alkaline carbonates, we found that incorporation of a small amount of acetate (*i.e.*, $NaCH_3COO$, KCH_3COO, Table 1, entries 6–7) and borate (*i.e.*, $Na_2B_4O_7 \cdot 10H_2O$, $K_2B_4O_7 \cdot 10H_2O$, Table 1, entries 8 and 9) also significantly promote the reactions under mild conditions. In comparison, the substitution of carbonates with stronger (*i.e.*, NaOH) or organic (*i.e.*, triethylamine) bases (Table 1, entries 4 and 5) does not lead to the promotional effect as prominent as that from carbonates, acetates and borates. The result suggests that basicity is necessary and the nature of applied bases is critical in promoting alcohol conversion.

For the oxidation of secondary alcohols by supported gold nanoparticles, the only products are ketones (Table 1, entries 22 and 23). The catalytic oxidation of primary alcohols produces the corresponding aldehydes or/and esters. The selectivity of the primary alcohol oxidation depends largely on the oxidative stability of produced aldehydes. For example, esters are the only products from the oxidation of ethanol, 1-propanol, 1-butanol at

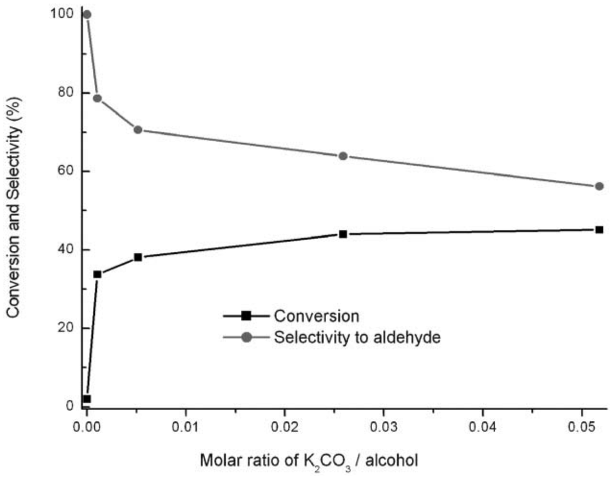

Fig. 1 The effect of amount of K_2CO_3 on the gold-catalyzed aerobic oxidation of benzyl alcohol. *Catalysis conditions*: 0.200 g of 2.5% 6.3 nm Au on TiO_2; 20 mL benzyl alcohol; 2 atm O_2; 5 h.

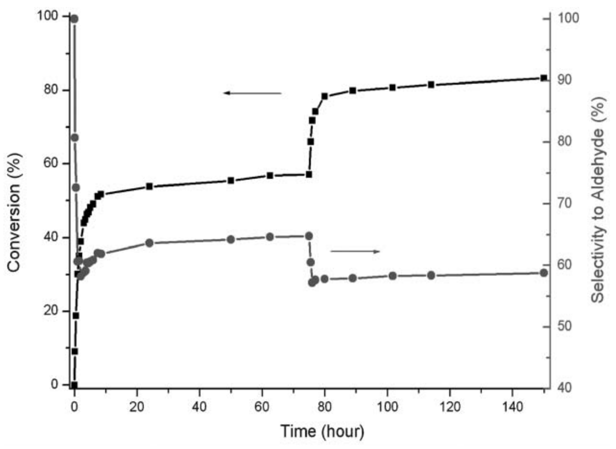

Fig. 2 The catalytic kinetics of benzyl alcohol oxidation with the additions of K_2CO_3. *Catalysis conditions*: 0.250 g of 2.5% 6.3 nm Au on TiO_2; 20 mL benzyl alcohol; 2 atm O_2; 0.280 g K_2CO_3 were added at 0 and 75 h.

80 °C (Table 1, entries 19–21). The selective oxidation of benzyl alcohol gives both benzaldehyde and benzyl benzoate. For example, the use of $NaCH_3COO$ gives a benzaldehyde selectivity of 74.6% (Table 1, entry 6). With the use of $Co(CH_3COO)_2 \cdot 4H_2O$ instead of $NaCH_3COO$, however, a much higher selectivity to aldehyde (93.8%) has been achieved together with the high efficiency (TOF = 353 h^{-1}) at 100 °C (Table 1, entry 17). Such an improvement in both alcohol conversion and product selectivity is not achievable by CH_3COO^- or Co^{2+} alone (Table 1, entries 6 and 18).

In conclusion, we have discovered that low-cost and non-toxic promoters dramatically boost the catalytic activity of gold nanocatalysts in the selective oxidation of alcohols by using oxygen as the ultimate oxidant under mild solvent-free conditions. The promoted gold catalysis is an environmentally and economically viable process for producing a wide range of useful chemicals from alcohols. Further spectroscopic studies are needed for a complete elucidation of the role of promotors in the oxidative process.

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Notes and references

1 M. Haruta, *Chem. Rec.*, 2003, **3**, 75–87.
2 M. Haruta, *CATTECH*, 2002, **6**, 102–115.
3 M. S. Chen and D. W. Goodman, *Science*, 2004, **306**, 252–255.
4 T. V. Choudhary and D. W. Goodman, *Top. Catal.*, 2002, **21**, 25–34.
5 B. Chowdhitry, J. J. Bravo-Suarez, M. Date, S. Tsubota and M. Haruta, *Angew. Chem., Int. Ed.*, 2006, **45**, 412–415.
6 T. Hayashi, K. Tanaka and M. Haruta, *J. Catal.*, 1998, **178**, 566–575.
7 S. Biella, L. Prati and M. Rossi, *J. Catal.*, 2002, **206**, 242–247.
8 S. Biella, L. Prati and M. Rossi, *J. Mol. Catal. A: Chem.*, 2003, **197**, 207–212.
9 S. Biella, G. L. Castiglioni, C. Fumagalli, L. Prati and M. Rossi, *Catal. Today*, 2002, **72**, 43–49.
10 S. Biella and M. Rossi, *Chem. Commun.*, 2003, 378–379.
11 L. Prati and M. Rossi, *J. Catal.*, 1998, **176**, 552–560.
12 L. Prati and F. Porta, *Appl. Catal., A*, 2005, **291**, 199–203.
13 G. J. Hutchings, S. Carrettin, P. Landon, J. K. Edwards, D. Enache, D. W. Knight, Y. J. Xu and A. F. Carley, *Top. Catal.*, 2006, **38**, 223–230.
14 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 and G. J. Hutchings, *Science*, 2006, **311**, 362–365.
15 D. I. Enache, D. W. Knight and G. J. Hutchings, *Catal. Lett.*, 2005, **103**, 43–52.
16 G. Li, D. I. Enache, J. Edwards, A. F. Carley, D. W. Knight and G. J. Hutchings, *Catal. Lett.*, 2006, **110**, 7–13.
17 V. R. Choudhary, A. Dhar, P. Jana, R. Jha and B. S. Uphade, *Green Chem.*, 2005, **7**, 768–770.
18 A. Abad, P. Concepcion, A. Corma and H. Garcia, *Angew. Chem., Int. Ed.*, 2005, **44**, 4066–4069.
19 A. Abad, C. Almela, A. Corma and H. Garcia, *Chem. Commun.*, 2006, 3178–3180.
20 A. Abad, C. Almela, A. Corma and H. Garcia, *Tetrahedron*, 2006, **62**, 6666–6672.
21 C. H. Christensen, B. Jorgensen, J. Rass-Hansen, K. Egeblad, R. Madsen, S. K. Klitgaard, S. M. Hansen, M. R. Hansen, H. C. Andersen and A. Riisager, *Angew. Chem., Int. Ed.*, 2006, **45**, 4648–4651.
22 N. Zheng and G. D. Stucky, *J. Am. Chem. Soc.*, 2006, **128**, 14278–14280.
23 T. Mallat and A. Baiker, *Chem. Rev.*, 2004, **104**, 3037–3058.