Aqueous-phase aerobic oxidation of alcohols by soluble Pt nanoclusters in the absence of base†

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A soluble Pt nanocluster catalyst (Pt-GLY) is efficient in the absence of base for aqueous-phase aerobic oxidation of, in particular, non-activated alcohols with high recyclability.

Soluble metal nanoclusters (NCs) in ionic liquids or water exhibit superior catalytic performances over traditional supported metal catalysts in many hydrogenation reactions. Examples include hydrogenation of arenes over rhodium nanoclusters,[1] selective hydrogenation of *o*-chloronitrobenzene over platinum nanoclusters,[2] and precise hydrogenative cleavage of the C–O–C bonds in cellobiose over ruthenium nanoclusters,[3] *etc.* Such superiority of the soluble NCs may be closely related to their controllable sizes and unique nature that is freely rotational and three-dimensional, in contrast to the traditional supported metal clusters that are restricted by support surfaces.[4] Recently, soluble metal NCs have been reported to be also applicable to aerobic oxidation of alcohols in water.[5,6]

Oxidation of alcohols to their corresponding carbonyl or carboxyl compounds is one of the most important processes for production of fine and specialty chemicals.[7] Traditional methods involve use of stoichiometric amounts of noxious oxidants such as chromate and permanganate,[8] or non-green organic solvents,[7b,9] or require severe reaction conditions.[10] From an environmental and economic viewpoint, there is an urgent need to develop a green, economic and efficient alcohol oxidation process.[11] In this context, much attention has recently been focused on the aerobic oxidation of alcohols with reusable catalysts in the aqueous phase under mild conditions,[12,13] which is particularly suitable for industrial practices. However, very few catalysts are active for a wide range of alcohols in water, especially for non-activated alcohols, like aliphatic and alicyclic alcohols. In particular, bases such as KOH or K_2CO_3 are frequently required for oxidation of primary aliphatic alcohols (*e.g.* 1-octanol) in water.[6b,11–13] The use of bases is clearly not green and leads to problems such as corrosion and waste base treatment. Herein, we report a soluble platinum nanocluster catalyst exhibiting excellent activities in the absence of any bases for the aqueous-phase aerobic oxidation of non-activated alcohols with high recyclability under mild conditions.

The soluble Pt NC catalyst (designated Pt-GLY) was prepared by reducing $H_2PtCl_6 \cdot 6H_2O$ with glycol,[14] stabilizing the reduced Pt clusters with poly(*N*-vinyl-2-pyrrolidone) (PVP), and then removing glycol *via* dialysis in H_2O.‡Taken together, XPS[15] and TEM characterization shows the formation of metallic Pt nanoclusters with a mean diameter of 1.5 nm and a narrow size distribution (Fig. 1). The oxidation of alcohols was generally carried out in water at 80 °C and 1 atm of O_2 for 24 h without addition of any bases.§ The reactants and products were analyzed by GC and GC-MS. The results are summarized in Table 1. It was found that primary and secondary alcohols were oxidized to the corresponding carboxylic acids and ketones, respectively. Notably, Pt-GLY was capable of catalyzing the aerobic oxidation of various non-activated alcohols. For alicyclic alcohols, they gave ketones in good yields of 78.4–97.1% (Table 1, entries 1–3). Oxidation of a secondary aliphatic alcohol, *i.e.* 2-octanol, afforded a 94.2% yield of 2-octanone (Table 1, entry 4). It is especially noteworthy that Pt-GLY was highly active for the oxidation of primary aliphatic alcohols, the most inactive alcohols, in the absence of any bases (Table 1, entries 5–7). For example, the yield of 1-hexanoic acid in 1-hexanol oxidation was as high as 99.3% at a 100% conversion. It is known that oxidation of such primary alcohols frequently requires bases as cocatalysts, although their presence is not green

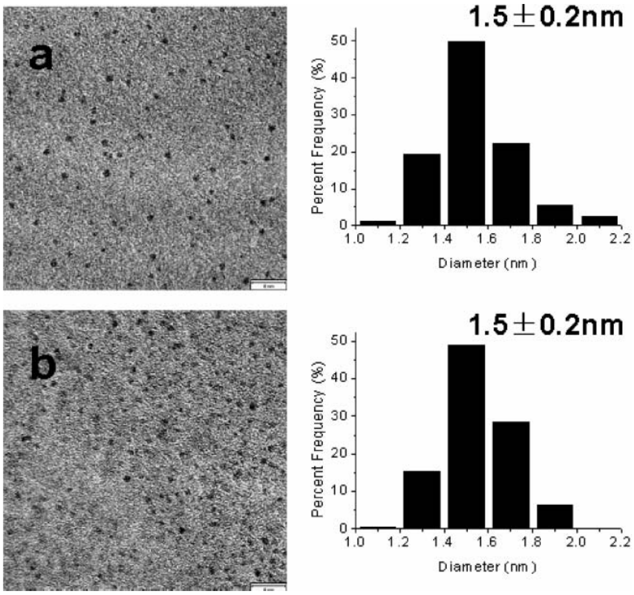

Fig. 1 TEM micrographs and particle size distribution histograms of Pt-GLY catalyst (a) before and (b) after five runs (more than 200 particles were measured for the histograms; scale bar: 8 nm).

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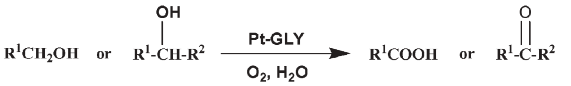
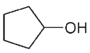
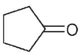
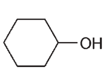
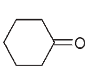
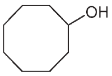
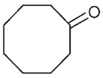
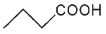
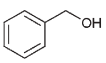
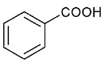
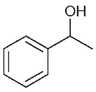
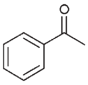
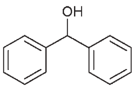
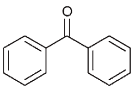
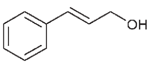
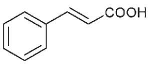
Table 1 Aerobic oxidation of alcohols in water by Pt-GLY catalyst[a]



Entry	Substrate	Product	Conv.[b] (%)	Yield[b] (%)
1			100	97.1
2			88.4	78.4
3			99.1	88.8
4			95.2	94.2
5			100	99.7
6			100	99.3
7			96.0	94.5
8			100	98.6
9			98.5	97.9
10			98.3	98.3
11			100	53.5[c]

[a] All oxidations were performed as follows unless otherwise noted. A mixture of 0.579 mmol alcohol and 15 mL Pt-GLY (0.0290 mmol Pt in 15 mL water) was stirred at 80 °C under atmospheric pressure of oxygen for 24 h. [b] Determined by GC analysis. [c] The other product was mainly cinnamaldehyde (37.5%).

and desirable.[6b,11–13] For example, Uozumi and coworkers reported that Pt NCs supported on amphiphilic resin catalyzed oxidation of 1-octanol with equimolar K_2CO_3.[13a,13b]

In order to examine the versatility of the Pt-GLY catalyst, activated alcohol oxidation was also carried out simply under the same conditions. Like most of the catalysts reported previously, Pt-GLY efficiently catalyzed the oxidation of various aromatic alcohols, such as benzyl alcohol, 1-phenylethanol and benzhydrol (Table 1, entries 8–10), almost quantitatively to their target products (~98% yields). An allylic alcohol, cinnamyl alcohol, was oxidized to cinnamic acid at a 100% conversion, although with a selectivity of only 53.5% (Table 1, entry 11; the other product was mainly cinnamaldehyde). These results clearly show the efficiency of the Pt-GLY catalyst in the aerobic oxidation of both activated and non-activated alcohols in water.

Concerning applications of soluble metal NC catalysts to the alcohol oxidation in water, to our knowledge, only two kinds of catalysts have been reported to date, *i.e.*, Pd and Au NCs stabilized by microgels and PVP, respectively.[5,6] The Pd catalyst was only active for 1-phenylethanol,[5] and essentially not for non-activated alcohols such as 2-octanol and cyclohexanol, while the Au one was active for a wide range of alcohols but always required the addition of K_2CO_3 or KOH.[6] It is thus apparent that our Pt-GLY catalyst represents the first example of soluble metal NCs being able to catalyze the oxidation of non-activated primary alcohols with high efficiencies in the absence of base.

The recyclability of the Pt-GLY catalyst was examined in the aerobic oxidation of cyclooctanol in water. This catalyst can be readily recycled after simple extraction by diethyl ether. As shown in Fig. 2, the cyclooctanone yields remained essentially constant for the five successive cycles; no Pt deposits were observed, reflecting high stability and reusability of the catalyst. This is consistent with the characterization results for this catalyst. The extracted diethyl ether layers after each run were analyzed by ICP,[16] showing no detectable leaching of Pt. TEM (Fig. 1) and XPS[15] results show essentially no changes in the mean diameters of the Pt NCs and in the metallic state of Pt, respectively, after the five successive runs. Such stability is superior to that reported for the above-mentioned soluble Au and Pd nanocluster catalysts in the alcohol oxidation reactions in water.[5,6]

For comparison with Pt-GLY, three other soluble Pt NCs catalysts were prepared using different reducing agents (see ESI) instead of glycol, including H_2 (the catalyst is designated as Pt-H_2), $NaBH_4$ (Pt-$NaBH_4$) and ethanol (Pt-Ethanol), and then they were examined in the oxidation of cyclooctanol under the same conditions. As shown in Table 2, they exhibited good performances, but they were not stable and recyclable. Pt-H_2 catalyst aggregated even after the first run. Pt-$NaBH_4$ and Pt-Ethanol catalysts formed black Pt deposits after the second run. Generally speaking,[17] PVP plays the crucial role in the stabilization of these Pt NCs. However, the difference in the stability of the four soluble Pt NC catalysts indicates that some other factors may also contribute to the higher stability of the Pt-GLY catalyst. These factors, although they are still not clear, may be related to some glycol-derived products during the process of reduction, which may stabilize the Pt NCs, together with PVP, *via* their strong interactions with the Pt cluster surfaces. These proposed factors may also account for the considerable deactivation of the two reported Au NC and Pd NC catalysts.[5,6]

Soluble metal NCs possess more active sites accessible to reactants than their supported counterparts, they are thus supposed to bear higher catalytic activities.[5] However, our Pt-GLY catalyst indeed exhibits similar activities to those of previous

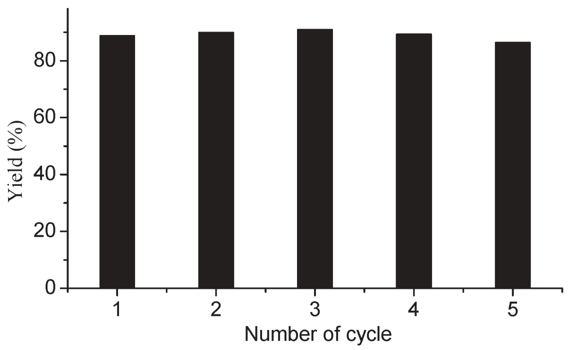


Fig. 2 Recycling of the Pt-GLY catalyst for the aerobic oxidation of cyclooctanol in water at 80 °C for 24 h (0.579 mmol cyclooctanol, 1 atm O_2, 15 mL Pt-GLY (0.0290 mmol Pt in 15 mL water)).

Table 2 Aerobic oxidation of cyclooctanol to cyclooctanone in water by different soluble Pt NC catalysts[a]

Catalyst	Run	Conversion (%)	Yield (%)	Catalyst status
Pt-H_2	1	97.3	95.3	aggregated
Pt-$NaBH_4$	1	100	96.1	black solution
	2[b]	99.7	95.7	aggregated
Pt-Ethanol	1	98.8	90.0	black solution
	2[b]	99.1	94.7	aggregated

[a] Reaction conditions: 0.579 mmol alcohol, 15 mL Pt-GLY (0.0290 mmol Pt in 15 mL water), 80 °C, 1 atm O_2, 24 h. [b] The catalyst was re-used immediately after extraction of the reaction solution with diethyl ether and removal of diethyl ether at room temperature under vacuum.

supported nanoclusters.[13a,13b] This may reflect that PVP is probably not an appropriate stabilizer for such alcohol oxidation reactions by referring to the corresponding reaction mechanism proposed with supported metal catalysts in the literature.[11] This involves dissociative adsorption of the alcohol molecule on the metal surface to form alcoholate and hydrogen species, and subsequently conversion of the alcoholate species to carbonyl products and removal of the hydrogen species in the presence of O_2. This mechanism implies that the coordination and electronic properties of the metal sites would significantly influence the activation of alcohol and oxygen. Accordingly, we anticipate that these properties of the metal sites can be controlled by finely tuning stabilizers and their interactions with the metal nanocluster surfaces, thus leading to improvement in the activities of our soluble Pt NCs; such studies are currently in progress. Furthermore, such a mechanism is proposed with supported metal catalysts, and supports indeed are involved in the alcohol oxidation as well, *via* adsorption and activation of alcohols or O_2 depending on the identity of the supports. Such interference of the supports can be circumvented by using our soluble NCs, from which we can get insight into the exact roles of metal sites in the alcohol oxidation and its mechanism.

In conclusion, we have prepared a soluble Pt nanocluster catalyst (Pt-GLY) which displays a good efficiency in the oxidation of both activated and non-activated alcohols including a wide range of aromatic alcohols, allylic alcohols, alicyclic alcohols, and primary and secondary aliphatic alcohols in water under aerobic conditions without using any bases. It exhibits an excellent stability, and can be reused without detectable deactivation; these features, along with its green nature, show its promising potential for the practical oxidation of alcohols.

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Notes and references

‡ Preparation of the Pt nanocluster catalyst (Pt-GLY): 150 mg of NaOH (3.75 mmol) were added into a glycol solution of $H_2PtCl_6 \cdot 6H_2O$ (0.15 g, 0.290 mmol Pt in 15 mL glycol) with vigorous stirring to obtain a transparent yellow solution. Then the solution was heated at 160 °C for 3 h with pure N_2 flowing through the solution to take away H_2O and some organic products formed during the preparation process. After the solution was cooled to room temperature, 1.288 g PVP (11.6 mmol, MW = 30 000) were dissolved in it with vigorous stirring. Afterwards, the solution was dialyzed overnight using deionized water to completely remove glycol, and then was diluted to 150 mL with deionized H_2O, which led to a transparent black solution of Pt-GLY (1.93×10^{-3} mol Pt/L) for alcohol oxidation reactions. Complete removal of glycol was monitored by GC analysis. The catalyst structures were characterized by TEM and XPS. TEM micrographs were taken on a Hitachi H-9000NAR high resolution transmission electron microscope, and XPS spectra were measured using an Axis Ultra spectrometer (Kratos, UK).

§ Aqueous-phase aerobic oxidation of alcohols: a mixture of 15 mL catalyst solution (1.93×10^{-3} mol L^{-1}, containing 0.0290 mmol Pt) and alcohol (*e.g.* cyclooctanol, 0.579 mmol) was stirred at 80 °C for 24 h under atmospheric pressure of O_2 (1 atm, O_2 balloon). Alcohol reactants and products were analyzed by GC (Agilent 6820) and GC-MS (Agilent 6809/5973i). After cooling to room temperature, the reaction system was extracted with diethyl ether before recycling. The Pt concentrations in the diethyl ether layers were measured on a Profile ICP spectrometer (Leeman US).

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15 The XPS characterization showed binding energies at 71.2 and 71.3 eV for the Pt nanoclusters before and after five oxidation reaction cycles, respectively, which are assigned to Pt $4f_{7/2}$ for metallic Pt.

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