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A green and efficient oxidation of alcohols by amphiphilic resin-supported gold nanoparticles in aqueous H_2O_2

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A green and highly efficient oxidation of alcohols in aqueous H_2O_2 using amphiphilic resin (PS-PEG-NH_2)-supported gold nanoparticles is described. The reaction proceeded with excellent yields and selectivities, in particular, for non-activated alcohols without base. The catalyst, in addition, could be readily recovered by simple work-up and reused several times without significant loss of its catalytic activity.

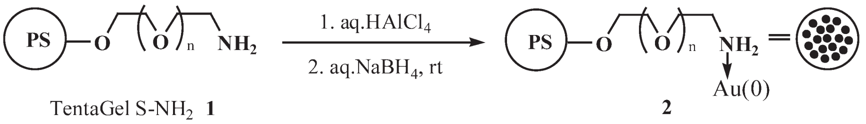
Keywords: oxidation, heterogeneous catalysis, gold nanoparticles, hydrogen peroxide, aqueous medium

The selective oxidation of alcohols to their corresponding carbonyl compounds is an important and challenging processes in organic chemistry.[1] Current methods for alcohol oxidation are mainly based on the use of stoichiometric amounts of toxic or corrosive reagents such as heavy metal salts.[2] Hence there is a desire for their replacement by environmentally more benign approaches. Recently, numerous efforts have been made to develop new catalytic protocols for the green oxidation of alcohols due to the evergrowing concerns over green chemical processes. Among these studies, oxidation of alcohols using green oxidants such as H_2O_2 is notable since it leads to water as the sole by-product.[3–8] Also, the high content of oxygen and simplicity of handling make it more advantageous than its counterparts. Most importantly, it has been found to be particularly effective for non-activated alcohols, such as aliphatic and alicyclic alcohols, without employing base additives (*e.g.* KOH, Na_2CO_3).[9] Although several facile and economical oxidations of alcohols using H_2O_2 as oxidant have been developed, these protocols are invariably associated with one or more disadvantages, such as non-recyclability of the catalyst, long reaction time, low selectivity as well as the use of organic solvents.

Since the discovery that gold nanoparticles can be very active for alcohol oxidation reactions by Haruta and coworkers,[10,11] a series of protocols have been established.[12–15] Of particular interest is the use of supported gold nanoparticles due to the obvious advantages of these catalysts in product isolation, product selectivity and catalyst recycling. However, organic solvents and/or bases are generally required to achieve high yield and selectivity. While acknowledging the pioneering work in this area, we believe the development of a novel catalyst system exhibiting a wide range of substrate tolerance under mild and aqueous conditions remains a major challenge. Here we report a successful oxidation protocol in aqueous H_2O_2 under base-free conditions with reusable amphiphilic resin (PS-PEG-NH_2)-supported gold nanoparticles.

Catalyst **2** was readily accessible by complexation of commercially available PS-PEG-NH_2 (TentaGel S NH_2) with $HAlCl_4.3H_2O$ in water followed by reduction with $NaBH_4$ (Scheme 1). The Au loading was 2.28 wt % according to the ICP analysis. The catalyst was also characterised by high-resolution transmission electron microscopy (TEM) and X-ray diffraction (XRD). The TEM analysis revealed that the gold nanoparticles have a mean diameter of 2.7 nm with a narrow size distribution throughout the resin (Fig. 1a). Also, the characteristic diffraction peaks at (111), (200), (220) and (311) indicate the successful formation of gold nanoparticles on the support (Fig. 1b).

Using the amphiphilic resin-supported gold nanoparticles, we conducted the oxidation of a variety of primary and secondary alcohols to the corresponding carbonyl compounds. The representative data are summarised in Table 1. The results showed that all the reactions took place smoothly to afford the corresponding products in excellent yields and selectivities. The benzylic alcohols were much more active, providing the products in excellent yields and selectivities in short times with only a slight excess of H_2O_2 (entries 11–14). The nonactivated alcohols, such as aliphatic and alicyclic alcohols could also be efficiently oxidised (Table 1, entries 1–10). For cyclopentanol, a conversion of 93% (99% selectivity) was obtained within 6 h in presence of 1 equiv. of H_2O_2 (entry 1). By increasing the amounts of H_2O_2, the reaction proceeded faster and nearly full conversion and selectivity was obtained when a five-fold molar excess of H_2O_2 was employed within 1 h (entry 3). Although cyclopentanol was very active in this catalytic system, the control experiment clearly showed that no product was detected without adding catalyst (entry 4). The effect of temperature was also studied. When the reaction was conducted at room temperature, only 23% of conversion was obtained after 6 h (entry 5), which could be explained by the fact that the H_2O_2 decomposed slowly at low temperature. For comparison, it was found that linear aliphatic alcohols were more difficult to oxidise than alicyclic alcohols, so more H_2O_2 and longer reaction times were generally required for the oxidation process (entries 7–10). The selective oxidation of primary alcohols was then investigated. The results clearly showed that a lower amount of H_2O_2 benefitted the formation of aldehyde. For example, 1-octanol and benzyl alcohol were oxidised to the corresponding aldehydes with 2 equiv. and 1.2 equiv. of H_2O_2, respectively (entries 9 and 11). When a



TentaGel S-NH_2 **1**

2

Scheme 1 Preparation of polymer-supported gold nanoparticles.

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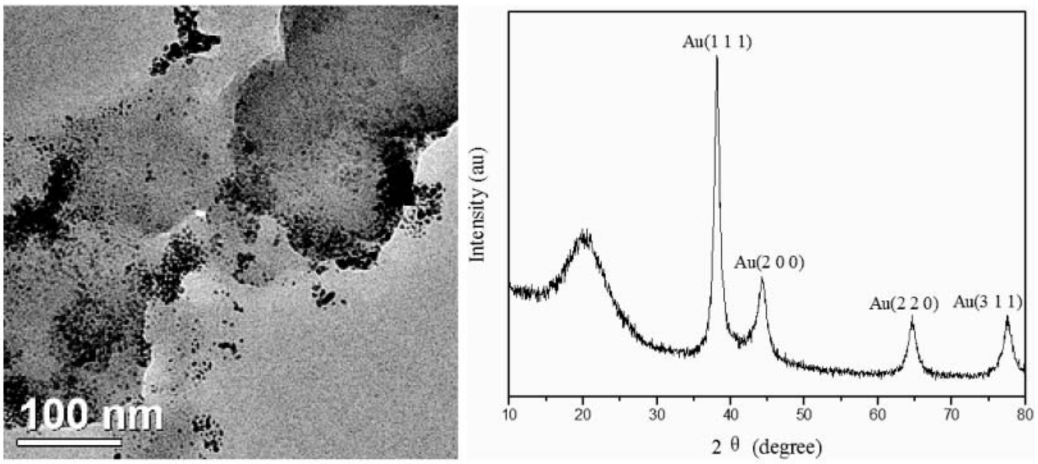
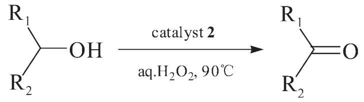
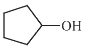
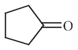
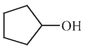
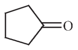
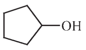
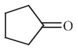
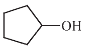
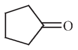
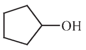
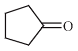
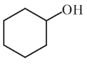
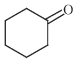
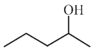
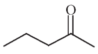
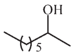
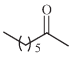
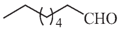
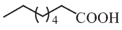
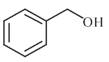
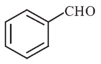
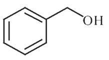
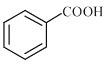
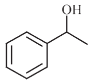
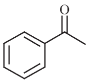
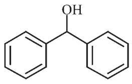
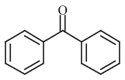


Fig. 1 Characterisation of catalyst **2**: (a) TEM image; (b) XRD pattern.

Table 1 Selective oxidation of various alcohols with catalyst 2 in aqueous H_2O_2[a]



Entry	Substrate	Product	H_2O_2/substrate molar ratio	Time /h	Conversion /%	Selectivity /%
1			1	6	93	99
2			2	2	95	99
3			5	1	>99	99
4[b]			2	2	0	0
5[c]			2	6	23	99
6			2	3	96	99
7			5	3	95	99
8			5	3	93	97
9			2	6	91	96
10			5	6	>99	99
11			1.2	1	>99	94
12			2.5	2	>99	99
13			1.2	2	>99	99
14			1.2	2	>99	99

[a] Reaction conditions: substrate (1 mmol), catalyst (0.5 mol%%, 30% H_2O_2, water (3 mL), 90°C; Conversion was based on GC and GC-MS analysis.
[b] No catalyst was added.
[c] Room temperature.

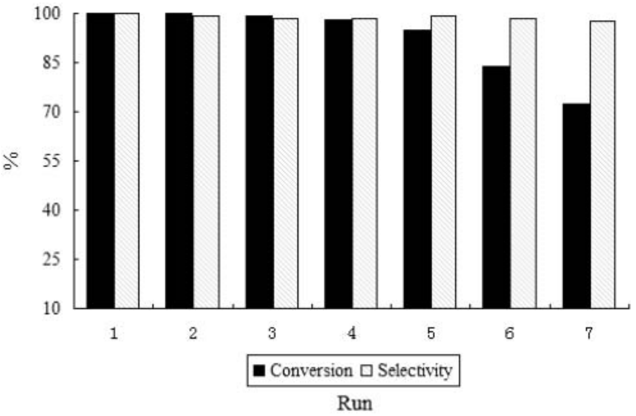


Fig. 2 Recycling experiment.

larger excess of H_2O_2 was employed, the acids were the only products (entries 10 and 12).

Recycling studies were then performed using cyclopentanol as substrate (Fig. 2). Considering the normal loss of catalyst in the recycling and washing processes, the reaction was scaled up to 10 mmol. After reaction, the supported catalyst could be easily recovered by filtration and showed good reusability with slight decrease in its activity after seven runs (1: 99%; 2: 99%; 3: 99%; 4: 97.5%; 5: 94.2%; 6: 84.1%; and 7: 72.7%). The selectivity of the reaction, however, was not affected during the recycling processes. The recovered catalyst was also characterised by ICP analysis. It was found that over 99% of Au was retained in the resin. Meanwhile, the Au leaching in the crude mixture of each recycling process was negligible (<10 ppm) according to the ICP analysis, and the aqueous filtrate did not show any catalytic activity. These observations indicated that the oxidation proceeded in a heterogeneous fashion.

In conclusion, we have successfully demonstrated that amphiphilic resin (PS-PEG-NH_2)-supported gold nanoparticles show excellent activity and selectivity for environmentally benign oxidation of various alcohols, especially for nonactivated alcohols, to the corresponding carbonyl compounds. The reaction could be conducted in aqueous medium without any additives using hydrogen peroxide as oxidant to give only water as the by-product. Moreover, the stability and reusability of the catalyst have also been evaluated by conducting six successive runs, which gave only a slight decrease in its activity.

Experimental

The TentaGel S-NH_2 resin was purchased from Aldrich (amine loading: 0.26 mmol/g; average diameter: 90 μm). All other reagents were obtained from local commercial suppliers and used without further purification. ^1H and ^{13}C NMR spectra were recorded on a Bruker Advance RX300 analyser. GC and MS analyses were performed on a Saturn 2000GC/MS instrument. The gold content was measured by inductively coupled plasma (ICP) on a Varian AA240 analyser. TEM images were collected on a JEOL-2100 transmission electron microscopy at 200 kV and the images were recorded digitally with a Gatan 794 charge-coupled device (CCD) camera. XRD patterns of samples were recorded on a Bruker AXS D8 ADVANCE X-ray diffractometer. All the products are known compounds and were identified by comparing of their physical and spectra data with those reported in the literature.

Preparation of catalyst **2**: A mixture of PS-PEG-NH_2 (3.9 g, total amino capacity: 1 mmol) and $HAuCl_4.3H_2O$ (0.197 g, 0.5 mmol) in water (20 mL) was shaken at room temperature for 2 h. The polymer beads turned from light yellow to intense yellow and then gradually turned into red, which indicated the stabilisation of Au^{3+} in the resin beads. Then a solution of $NaBH_4$ (38.7 mg, 1 mmol) in water (2 mL) was added dropwise over a period of 1 h. The resulting solution was stirred for another 2 h at room temperature. After the reduction of Au^{3+}, the red colour of the beads had completely turned into dark brown and the product was separated by filtration, washed with methanol, water, and acetone and dried to give **2** (4.0 g, 0.12 mmol g^{-1}). The size of the nanoparticles was 2.7 nm, as determined by TEM. Au analysis (ICP): 2.28 wt %.

Catalytic oxidation of alcohols in aqueous H_2O_2; general procedure: The catalytic reactions were performed in a 10 mL two-necked round-bottomed flask equipped with a septum, a magnetic stirring bar, and a reflux condenser. The oxidation was carried out as follows: substrate (1 mmol), water (3 mL), H_2O_2 (30% aq.) and catalyst (0.005 mmol) were charged in the reaction flask. The reaction was carried out at 90 °C and monitored by GC. When the reaction was over, the organic products were separated from the aqueous phase by extraction and then analysed by GC with the internal standard method. The catalyst was removed by simple filtration, washed with methanol, water and acetone, and then dried for next use. Assignments of products were made by comparison with authentic samples. Selected products were also analysed by GC/MS, ^1H NMR and ^{13}C NMR.

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