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Aerobic oxidation of hydroxylamines with nanoporous gold catalyst as an efficient synthetic method of nitrones

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ABSTRACT

A facile preparation of nitrones has been achieved by use of unsupported nanoporous gold (AuNPore) as a heterogeneous catalyst through aerobic oxidation of *N*,*N*-disubstituted hydroxylamines with molecular oxygen as an oxidizing agent under mild conditions. A variety of amines were oxidized to the corresponding nitrones in high chemical yields. The catalyst is robust enough to be reused without leaching.

1. Introduction

Selective oxidation of organic molecules, such as alcohols and amines, is one of the most fundamental and important transformations in organic synthesis. For this purpose, it is highly desirable to develop an effective and reusable heterogeneous catalyst together with cheap and environmentally friendly oxidizing agent.[1] During the last decade, gold nanoparticles supported on suitable oxides have been studied well as efficient heterogeneous catalysts for such oxidation reactions.[2] However, they have drawbacks on the stability because they have tendency to agglomerate to become larger particles by repeating the reactions, resulting in the deactivation. Recently, we were successful in using a monolithic nanoporous gold material (AuNPore) as an efficient catalyst for aerobic oxidation of alcohols with molecular oxygen.[3] The reaction proceeded smoothly with a variety of secondary alcohols under mild conditions, and the corresponding ketone products were obtained in good to high yields. The catalyst is reusable at least four times without leaching as well as any significant loss of the catalytic activity. In comparison with supported gold nanoparticle catalysts, the nanoporous gold catalyst can be fabricated easily by selective leaching of Ag from commercially available or handmade gold–silver alloys by just immersion in nitric acid.[4] Particularly, due to the robust 3D network structure composed of ligaments, it shows high durability and reusability.[5,6] These results encouraged us to explore the catalytic performance of AuNPore in other reactions, and we focused on the oxidation of *N*,*N*-disubstituted hydroxylamines, which are nitrogen-analogues of secondary alcohols. The expected products are nitrone compounds, which are valuable building blocks in organic synthesis.[7] They can be used as electrophiles in reactions of organometallic reagents[8] as well as in 1,3-dipolar cycloaddition reactions.[9] Furthermore, they are useful as spin-trap reagents[10] and therapeutic agents.[11] Although a number of preparation methods have been reported so far,[12–16] effective methods with recyclable heterogeneous catalysts are still limited.[17] In this article, we report that AuNPore exhibits a remarkable catalytic activity in the aerobic oxidation of hydroxylamines with molecular oxygen at atmospheric pressure, leading to nitrone compounds in good to high yields.[18] The catalyst is recoverable and reusable many times with no leaching of gold.

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2. Results and discussion

The fabrication of AuNPore catalysts was performed through a selective dealloying of silver as the less noble metal from $Au_{30}Ag_{70}$ alloy with a thickness of 40 μm using 70 wt % of nitric acid for 18 h at room temperature.[4] A scanning electron microscopy (SEM) image in Fig. 1a showed that the ligaments with average size of 30 nm as well as nanoporous channels are formed uniformly across the entire AuNPore. The result of energy dispersive X-ray (EDX) analysis showed that the composition of AuNPore is $Au_{98}Ag_2$ (in atomic %), in which the residual silver usually gives an effect in the catalytic activity of AuNPore.

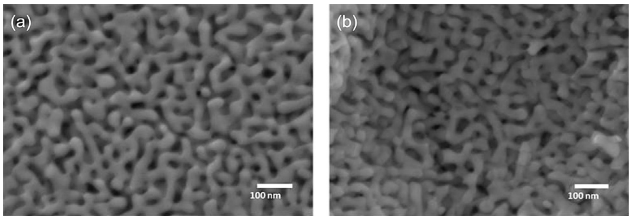
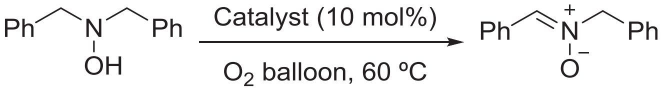


Fig. 1. The Scanning electronic microscopy (SEM) images. (a) The freshly prepared AuNPore. (b) The reused AuNpore in the reaction of **1a**.

We examined the catalytic aerobic oxidation of *N*,*N*-dibenzylhydroxylamines **1a** with AuNPore catalyst, and the results were summarized in Table 1. Treatment of **1a** in CH_3CN with 10 mol % of AuNPore at 60 °C for 15 h under oxygen balloon resulted in the formation of *N*-benzyl-1-phenylmethanimine oxide **2a** in 63% yield (entry 1). The chemical yield was increased to 98–99 % by using nitromethane or toluene as solvents (entries 2–3). Furthermore, the reaction rate was dramatically improved by use of MeOH as a solvent and **2a** was obtained in 99% yield after only 2 h (entry 4). From these results, MeOH was confirmed as the best choice for solvent in this reaction. Since no reaction occurred with Au–Ag mother alloy, it is obvious that the nanostructure of AuNPore is necessary to create the catalytic activity (entry 5). The reaction proceeded even under air although the reaction became sluggish (entry 6). On the other hand, **2a** was not produced under Ar (entry 7). These results clearly showed that molecular oxygen behaved as an oxidizing agent in this reaction, and ordinary stoichiometric oxidants, such as H_2O_2 and *N*-methylmorpholine-*N*-oxide (NMO), are not necessary.[12–16]

Table 1
Aerobic oxidation of *N*,*N*-dibenzylhydroxylamine **1a** with AuNPore catalyst[a]

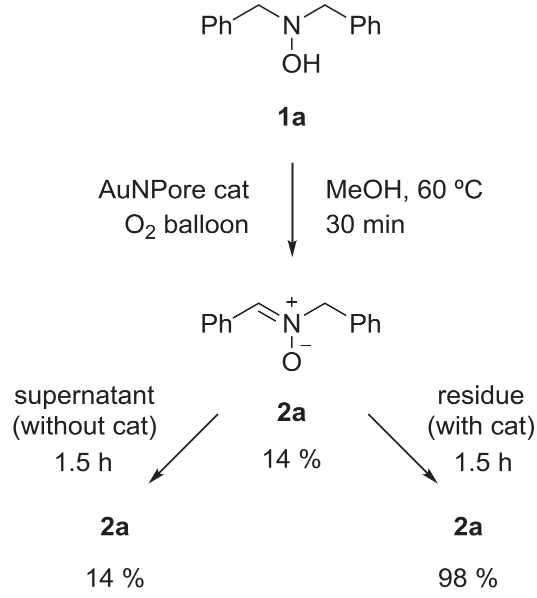


1a **2a**

Entry	Catalyst	Solvent	Time	Yield of **2a** (%)[b]
1	AuNPore	CH_3CN	15 h	63
2	AuNPore	CH_3NO_2	15 h	98
3	AuNPore	Toluene	15 h	99
4	AuNPore	MeOH	2 h	99
5	Au–Ag alloy	MeOH	2 h	0
6[c]	AuNPore	MeOH	2 h	34
7[d]	AuNPore	MeOH	2 h	Trace

[a] Reaction conditions: **1a** (0.15 mmol), catalyst (10 mol %), solvent (2 mL), at 60 °C under O_2.
[b] Determined by NMR using CH_2Br_2 as an internal standard.
[c] The reaction was conducted under air.
[d] The reaction was conducted under Ar.

In order to verify whether this catalytic performance in this reaction comes from the solid phase of gold or the dissolved ones, leaching experiment was conducted as described in Scheme 1. Initially, AuNPore catalysed aerobic oxidation under standard conditions was carried out using substrate **1a** along with 1,3,5-trimethoxybenzene as an internal standard, and allowed to react for 30 min. At this stage, nitrone **2a** was produced in 14% yield. Then, a half volume of supernatant (without solid AuNPore catalyst) was transferred into different reaction vial using syringe equipped with filter unit, and both reaction solutions were allowed to react under the same conditions for 1.5 h. In the reaction without the catalyst, the chemical yield of **2a** was unchanged from 14%. On the other hand, **2a** was produced nearly quantitatively in the reaction with the catalyst. These results clearly showed that heterogeneous phase of gold catalyst became the active species for catalytic performance, not the leached ones. This observation was also supported by induced coupled plasma–mass spectrometry (ICP-MS) analysis that showed the presence of leached species of gold in reaction solution could be negligible (50 ppb only).



Scheme 1. The leaching experiment.

We next examined the reusability of the catalyst. After completion of the reaction of **1a**, the catalyst was recovered by simple filtration of the reaction mixture, followed by washing the catalyst with acetone several times. After dryness under vacuum conditions, the catalyst was reused. The reaction proceeded with the recovered catalyst, and the corresponding product **2a** was obtained in high yields even after repeating the reaction 8 times (Fig. 2). This

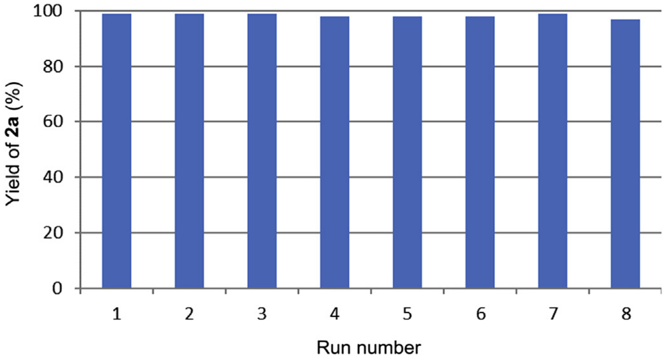


Fig. 2. Reusability of AuNPore in the oxidation of **1a**.

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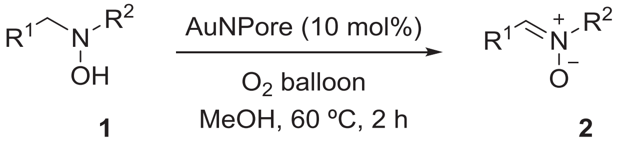
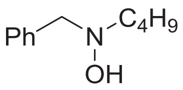
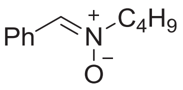
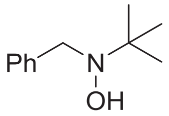
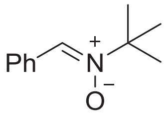
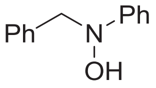
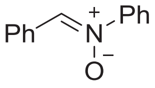
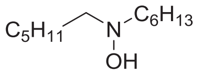
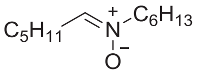
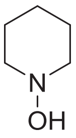
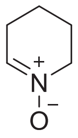
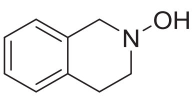
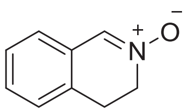
observation clearly showed that AuNPore was a robust catalyst with high durability in this reaction. The SEM image of the recovered catalyst also showed that the nanostructure of AuNPore was unchanged even after 8 times reuse (Fig. 1b).

With the optimized reaction condition established in entry 4 of Table 1, we investigated the scope of this catalytic reaction with other hydroxylamines, and the results are summarized in Table 2. The reaction of *N*-benzyl-*N*-butylhydroxylamine **1b** proceeded smoothly, and *N*-butyl-1-phenylmethanimine oxide **2b** was obtained selectively in high yield, and the regioisomer, *N*-benzylbutan-1-imine oxide, was not produced (entry 1). A bulky *t*-butyl group of **1c** has no influence on this reaction, and the corresponding **2c** was obtained in high yield (entry 2). Not only aliphatic but also aromatic group is tolerant in this reaction, and benzyl phenyl hydroxylamine **1d** was oxidized in high yield (entry 3). *N*,*N*-dialkyl substituted symmetric substrate **1e** gave **2e** in good yield (entry 4). The 6-membered cyclic hydroxylamine **1f** gave the corresponding nitrone **2f** in good yield (entry 5). In the reaction of 3,4-dihydroisoquinolin-2(1H)-ol **1g**, 3,4-dihydroisoquinoline 2-oxide **2g** was obtained in 91% yield, and the unconjugated regioisomer was not produced (entry 6).

Table 2
Aerobic oxidation of a variety of hydroxylamines with AuNPore catalyst[a]



Entry	Hydroxylamines		Nitrones		Yield of **2** (%)[b]
1		**1b**		**2b**	85
2		**1c**		**2c**	91
3		**1d**		**2d**	93
4		**1e**		**2e**	89
5		**1f**		**2f**	86
6		**1g**		**2g**	91

[a] Reaction conditions: **1a** (0.15 mmol), solvent (2 mL), under O_2.
[b] Isolated yield.

3. Conclusion

In conclusion, the aerobic oxidation of secondary hydroxylamines into their corresponding nitrones catalysed by nanoporous gold has been demonstrated for the first time. The oxidation reaction proceeded smoothly in high chemical yields with tolerance to different functional groups under mild conditions. Furthermore, the gold catalyst was recoverable and reusable many times with no leaching of gold.

4. Experimental

4.1. General

Scanning electron microscopy (SEM) observation was carried out using a JEOL JSM-6500F instrument operated at an accelerating voltage of 30 kV. TEM characterization was performed using a JEM-2100 TEM JEOL (JEOL, 200 kV) equipped with double spherical aberration (Cs) correctors for both the probe-forming and the image-forming lenses. The XPS measurements were carried-out using a VG ESCALAB 250 spectrometer (Thermo Fisher Scientific K. K.) employing monochromatic Al K X-ray radiation. The base pressure of the analysis chamber was less than 10^{-8} Pa. ^1H NMR and ^{13}C NMR spectra were recorded on JEOL JNM AL 400 (400 MHz) spectrometers. Column chromatography was carried out employing neutral silica gel 60 N (spherical, 40–100 µm, KANTO Chemical Co.) and basic silica gel (DM2035, Fuji Silysia Chemical Ltd.). Analytical thin-layer chromatography (TLC) was performed on glass TLC silica gel 60 F254 (neutral, Merck KGaA) and basic TLC plates (Chromatorex, Fuji Silysia Chemical Ltd.). Au (99.99%) and Ag (99.99%) were purchased from Tanaka Kikinzoku Kogyo K.K. and Mitsuwa's Pure Chemicals, respectively. Structures of known products were identified by ^1H and ^{13}C NMR and HRMS (or GC–MS).

4.2. Fabrication of AuNPore catalyst

Au (99.99%) and Ag (99.99%) were melted with electric arc-melting furnace under Ar atmosphere to form Au/Ag alloy (30:70, in at. %), which was milled down to thickness of 40 µm. The resulting foil was annealed at 850 °C for 20 h. The foil was cut into small pieces (3×3 mm^2). Treatment of the resulting chips (50 mg) with 70 wt% nitric acid (5.6 mL) for 18 h at room temperature resulted in the formation of the nanoporous structure by selective leaching of silver. The materials were washed successively with pure water and acetone. Drying of the materials under reduced pressure gave the nanoporous gold (24.3 mg) and its composition was found to be $Au_{98}Ag_2$ from EDX analysis result.

4.3. General procedure for aerobic oxidation of secondary hydroxylamines

31.9 mg (0.15 mmol) of *N*,*N*-dibenzylhydroxylamines **1a** was placed into a 4 mL vial equipped with a magnetic stirrer bar. 2 mL of dehydrated methanol was added and then stirred to obtain a solution. AuNPore (10 mol%, 2.96 mg) was put into the reaction solution, which was placed in the bottom of vial. Oxygen balloon was prepared and then attached into the vial through cap equipped with a septum to make an oxygen atmosphere. Reaction was allowed to proceed for 2 h at 60 °C. The formation of product(s) was monitored by TLC. After completion of reaction, the resulting solution was simply taken using a pipette while the vial was washed several times with methanol. Combined solution was concentrated under vacuum condition to give a residue. Obtained residue was purified by passing it through a basic silica column chromatography with ethyl acetate as the eluent to give 31.1 mg of **2a** in 98% yield. All of products in Tables 1 and 2 are identified with the reported data in the literature: **2a**,[17a] **2b**,[19] **2c**,[12b] **2d**,[20] **2e**,[13j] **2f**,[19] **2g**.[13b]

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4.4. Procedure for leaching experiment

Reaction solution of 31.9 mg (0.15 mmol) of **1a** was prepared with the addition of 1,3,5-trimethoxybenzene as internal standard before reaction started. The reaction was allowed to proceed for 30 min at standard conditions and then stopped. 1 mL of solution was taken using a syringe filter and transferred into a different vial, which contained no catalyst, while a small amount of solution was taken to be analysed by NMR to detect the yield of nitrone **2a**. Both supernatant and residue (the remaining reaction solution contained AuNPore catalyst) were allowed to continue the reaction for 1.5 h with the same conditions. After workup, each residue was analysed by ^{1}H NMR to find out the yield of produced nitrone **2a**.

4.5. Procedure for reusability test

The aerobic oxidation reaction of secondary hydroxylamines **1a** was carried out. After 2 h, reaction solution was taken while the remaining AuNPore catalyst was recovered by a simple filtration through cotton, washed several times with acetone and then dried under a reduced pressure. New reaction solution of **1a** was prepared and allowed to react with the used AuNPore and then treated like the previous one. This treatment was repeated several times and the yield of **2a** in each repetition was analysed by NMR. After the eighth cycle, the porous structure of reused AuNPore was analysed using SEM and compared with the fresh one.

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