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Highly Efficient Gold Nanoparticle Catalyzed Deoxygenation of Amides, Sulfoxides, and Pyridine N-Oxides

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Selective deoxygenation is one of the most important reactions in the areas of total synthesis, biological chemistry, and transformation of renewable biomass resources.^[1] To date, many useful methods for the selective deoxygenation of oxygen-containing organic molecules, such as amides, nitro compounds, epoxides, sulfoxides, and those with *N*oxide groups, have been developed. However, these methods often include stoichiometric reactions. Some successful catalysts have been reported,^[2–4] but most of them are homogeneous systems and still suffer from low activities and selectivities, harsh reaction conditions, and tedious workup procedures. Therefore, further development of highly efficient heterogeneous catalysts for selective deoxygenations is highly desired.

Gold nanoparticles (Au NPs) have received much attention in the field of catalysis because of their unique and high oxidation ability for various reactions such as oxidation of $CO^{[5]}$ and alcohols,^[6] and selective epoxidation of styrene^[7] and propylene.^[8] On the other hand, the reduction ability of the Au NPs has not yet been widely studied, despite their outstanding catalytic activity compared with other metal NPs. Corma and co-workers have discovered an excellent catalytic activity of TiO₂-supported Au NPs for highly chemoselective reduction of nitro compounds.^[9] Cao and coworkers have reported chemoselective reduction of carbonyl compounds to the corresponding alcohols by TiO₂ or meso-

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porous CeO_2 -supported Au NP catalysts.^[10] We have also discovered a novel Au NP catalytic system for selective deoxygenation of epoxides into alkenes with an alcohol or CO/H_2O as reducing agent.^[11]

From our continuing studies on Au NP catalysis, we herein report that hydroxyapatite-supported Au NPs (hereafter called AuHAP) efficiently catalyze deoxygenation of amides to amines with silanes as reductants. Various tertiary and secondary amides with benzylic, allylic, aliphatic, and heterocyclic amide substituents are selectively deoxygenated to the corresponding amines. Moreover, this AuHAP/silane catalytic system can be applied to deoxygenation of sulfox-ides and pyridine *N*-oxides into sulfides and pyridines, respectively. In these deoxygenations, the AuHAP catalyst achieved excellent turnover numbers (TONs) up to 10000, which is much greater than those of previously reported catalytic systems.^[2-4] The present AuHAP catalyst was easily recovered and reused without any loss of activity or selectivity.

The AuHAP catalyst was synthesized according to a procedure described in our previous paper.^[12] In brief, HAP was mixed into an aqueous solution of HAuCl₄ in the presence of NH₃. The resulting slurry was filtered, washed with distilled water, and dried under vacuum to give a HAP-containing Au^{III} species. The obtained solid was treated with KBH₄ to give AuHAP as a purplish red powder with a mean diameter of 3.0 nm.

We attempted the deoxygenation of *N*,*N*-dimethylbenzamide (**1**) into *N*,*N*-dimethylbenzylamine (**2**) with various supported Au NP catalysts. During the optimization of the reaction conditions, we found that heating AuHAP and **1** at 110 °C in toluene in the presence of dimethylphenylsilane for 3 h afforded complete conversion of **1** to **2** in >99% yield (Table 1, entry 1).^[13,14] Other supports for Au NPs such as TiO₂ and Al₂O₃ also gave good yields of **2** (Table 1, entries 2 and 3). Compared with other metal NPs tested, the Au NPs exhibited the highest catalytic activities; Pd, Ag, and Pt NPs resulted in low yields of **2** and neither Ru nor Rh NPs showed any activity (Table 1, entries 6–10). In addi-

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Table 1. Deoxy genation of N,N-dimethylbenzamide with hydrosilanes by various catalysts.^[a]

	N -		
	1	2	
	Catalyst	Yield [%] ^[b]	Sel. [%] ^[b]
1	AuHAP	>99	> 99
2	AuTiO ₂	88	>99
3	$AuAl_2O_3$	80	>99
4	AuMgO	67	>99
5	AuSiO ₂	55	>99
6	AgHAP	29	>99
7	PdHAP	20	>99
8	PtHAP	7	>99
9	RuHAP	trace	-
10	RhHAP	trace	-
11	$HAuCl_4$	trace	-
12	Au_2O_3	0	-
13	HAP	0	-

[a] Reaction conditions: AuHAP (0.1 g, $1.6 \mod \%$ Au), *N*,*N*-dimethylbenzamide (0.5 mmol), dimethylphenylsilane (2.5 mmol), toluene (5 mL), 110 °C, Ar, 3 h. [b] Selectivity (sel.) was determined by GC using naphthalene as an internal standard.

tion, the use of the gold compounds $HAuCl_4$ and Au_2O_3 , bulk Au, or parent HAP in place of AuHAP did not promote the deoxygenation at all (Table 1, entries 11–13). These results suggested that the high catalytic activity of the AuHAP is derived from the intrinsic activity of the Au NPs.

The solid AuHAP catalyst was filtered off from the reaction mixture after 50% conversion of **1**. Further stirring of the filtrate under identical reaction conditions did not afford any products. Inductively coupled plasma (ICP) analysis of the filtrate did not show any leaching of Au species into the solution (detection limit: 0.007 ppm), confirming that the present deoxygenation proceeds on the solid AuHAP catalyst.

The AuHAP catalyst could deoxygenate a wide range of amides to amines. Typical results are shown in Table 2. Most of the tested benzamides exhibited high reactivities (Table 2, entries 1 and 6-9). The derivative with an electron-donating group was more reactive than one with an electron-withdrawing group (Table 2, entry 5 versus 6). The ester-containing amide was converted to the amine without reduction of the ester group (Table 2, entry 7). Benzamides substituted with piperidine and morpholine moieties were deoxygenated efficiently (Table 2, entries 8 and 9). Furthermore, allylic, aliphatic, and heterocyclic tertiary amides all underwent deoxygenation sufficiently, providing the corresponding amines in excellent to good yields (Table 2, entries 10-15). Interestingly, the deoxygenation of the secondary amide of N-methylbenzamide by the AuHAP also occurred to give N-methyl-N-benzylamine in good yield when TMDS was used as a reducing agent instead of dimethylphenylsilane (Table 2, entry 16).^[15]

The deoxygenation of 1 by the AuHAP could be performed on a two-gram scale. Thus, compound 2 was obtained as the sole product in 95% isolated yield (1.9 g) and Table 2. Deoxygenation of amides by AuHAP in the presence of dimethylphenylsilane. $^{\left[a\right] }$

0	_ □ ³
R ¹ ^M N ^{-R3}	 R ¹ Ņ
R ²	R ²
1	2

	1		2		
	Amide	Amine	<i>t</i> [h]	Yield [%] ^[b]	Sel. [%] ^[b]
$1 \\ 2^{[c]} \\ 3^{[d]} \\ 4^{[e]}$	O N I	N ⁻	3 3 3 24	99 (92) 99 99 99 99 (96)	>99 >99 >99 >99 >99
5	NC N	NC	10	80	>99
6	MeO	MeO	3	99 (93)	>99
7	MeO N	MeO N	6	95	>99
8	O N	N	4	91 (85)	>99
9		N O	4	90 (84)	>99
10	O N	N N	6	92	>99
11	° N N	N	6	93	>99
12	∽∽∽∽ ^O N_	N_	8	95	>99
13		Ň	8	95	>99
14	N N	N N	12	91	>99
15	S N	S N	12	90	>99
16 ^[f]	O N H	N H	12	80	>99

[a] Reaction conditions: AuHAP (0.1 g, 1.6 mol% Au), amide (0.5 mmol), dimethylphenylsilane (2.5 mmol), toluene (5 mL), 110 °C, Ar.
[b] Determined by GC by an internal standard technique. Values in parentheses are the isolated yields. [c] First recycle of the catalyst.
[d] Second recycle of the catalyst. [e] AuHAP (0.015 g), amide (2 g).
[f] 1,1,3,3-Tetramethyldisiloxane (TMDS) (1.25 mmol) was used as a reductant.

the TON and turnover frequency (TOF) reached 10000 and 416 h⁻¹, respectively (Table 2, entry 4). This TON value is two orders of magnitude larger than those of previously reported catalytic systems such as $[Ru_3(\mu_3,\eta^2,\eta^3,\eta^5\text{-acenaph-thylene})(CO)_7]/PMHS$ (PMHS = polymethylhydrosiloxane) (TON=77, TOF=5 h⁻¹),^[2k] [H₂PtCl₆]/PMHS (TON=83, TOF=17 h⁻¹),^[2d] [Fe₃(CO)₁₂]/Ph₂SiH₂ (TON=50, TOF= 2 h⁻¹),^[2c] [Os₃(CO)₁₂]/Et₂NH/Et₃SiH (TON=100, TOF=

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6 h⁻¹),^[21] and Zn(OAc)₂/(EtO)₃SiH (TON=10, TOF= 0.5 h⁻¹).^[2a]

To investigate the scope of the deoxygenation ability of the present AuHAP/silane catalytic system, we next applied this system to deoxygenation of sulfoxides.^[13] As exemplified in Table 3, various sulfoxides were selectively deoxygenated

Table 3. Deoxygenation of various sulfoxides by AuHAP.[a]

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R^{1} , $S_{R^{2}}$, R^{1} , R^{2} , R^{2}					
	Sulfoxide	Sulfide	<i>t</i> [h]	Yield [%] ^[b]	Sel. [%] ^{[b}
$1 2^{[c]} 3^{[d]} 4^{[e]}$		\bigcirc ^s \bigcirc	1 1 1 48	>99 >99 99 94 (93)	> 99 > 99 > 99 > 99 > 99
5	¢ s `	C ^s	3	96	>99
6	° S.,	© ^s ≠	4	92 (85)	> 99
7		€ ^s , ⁰ o ⁻	3	96 (90)	>99
8			6	99 (97)	>99
9 ^[f]	°⊓ S∽∽	~~s~~	12	93	>99
10		C) ^s	6	89	>99
11 ^[f]	© [©] ^N	€ ^S [™]	12	98	>99
12		J S S	6	92	> 99

[a] Reaction conditions: AuHAP (0.1 g, 1.6 mol% Au), substrate (0.5 mmol), dimethylphenylsilane (1 mmol), 1,4-dioxane (3 mL), 30 °C, Ar. [b] Determined by GC or LC by an internal standard technique. Values in parentheses are the isolated yields. [c] First recycle of the catalyst. [d] Second recycle of the catalyst. [e] AuHAP (0.01 g, 0.8 mmol Au), substrate (10 mmol), dimethylphenylsilane (20 mmol), 1,4-dioxane (20 mL), 130 °C, Ar. [f] 60 °C.

under mild reaction conditions. Phenyl, benzylic, and aliphatic sulfoxides were converted into the corresponding sulfides in excellent yields with over 99% selectivity. Notably, functionalized sulfoxides were chemoselectively reduced, that is, only the S=O moiety was deoxygenated, whereas olefin, ester, propargyl, cyano, and ketone groups remained intact under the present conditions (Table 3, entries 6, 7, and 10–12). This result is in sharp contrast to that of the reported catalytic system in which hydrogenolysis of an ester moiety and reduction of a sulfoxide occurred.^[3c] Even though the catalytic activity of the AuHAP may be hampered by the strong coordination of the sulfide product, surprisingly, the AuHAP catalyst was active even in higher sulfoxide/AuHAP ratios. An excellent yield of sulfide was obtained with a TOF of $200 h^{-1}$ and a TON of up to 10000, which is three orders of magnitude greater than those of previously reported catalysts (Table 3, entry 4).^[16]

Furthermore, this AuHAP/silane system was effective for the deoxygenation of pyridine *N*-oxides, an important step in the synthesis of functionalized pyridine derivatives.^[1f,h] The catalytic system was revealed to be compatible with various pyridine *N*-oxides with reducible functional groups such as cyano, olefin, and carbonyl, as shown in Table 4.^[13]

Table 4.	Deoxygenation	of various	pyridine	N-oxides by	AuHAP.[a]
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	Pyridine N-oxide	Pyridine	Yield [%] ^[b]	Sel. [%] ^[b]
1			99	>99
2 ^[c]			99	>99
3 ^[d]			99	>99
4 ^[e]			95 (92)	>99
5	N+0	<n< td=""><td>99</td><td>>99</td></n<>	99	>99
6	Ph- N+O	Ph- N	>99 (95)	>99
7	NC→◯N→O	NC – N	99 (92)	>99
8 ^[f]	CCN.		89	>99
9	HO N+O	HO	91	>99
10			96 (90)	>99

[a] Reaction conditions: AuHAP (0.1 g, 1.6 mol% Au), substrate (0.5 mmol), dimethylphenylsilane (1 mmol), 1,4-dioxane (3 mL), 30 °C, Ar, 1 h. [b] Determined by LC by an internal standard technique. Values in parentheses are the isolated yields. [c] First recycle of the catalyst. [d] Second recycle of the catalyst. [e] AuHAP (0.002 g, 0.16 mmol Au), substrate (10 mmol), dimethylphenylsilane (20 mmol), 1,4-dioxane (20 mL), 130 °C, Ar, 60 h. [f] Dimethylphenylsilane (0.75 mmol).

After the above deoxygenations, the AuHAP catalyst was easily recovered and reused without any loss of catalytic activity, for example, 99% yields were obtained in the two recycling reactions (Table 2, entries 2 and 3; Table 3, entries 2 and 3; and Table 4, entries 2 and 3). TEM and extended Xray absorption fine structure (EXAFS) analysis of both fresh and reused AuHAP revealed that the size and oxidation state of the Au NPs on HAP did not change significantly,^[17] suggesting that the HAP support might play an important role in dispersing and stabilizing the Au NPs.^[18]

In a preliminary study by FTIR spectroscopy, interactions between Au NPs on HAP and silane were investigated. Dimethylphenylsilane was treated with AuHAP and an absorption band assigned to a Si-H stretching vibration of the adsorbed silane shifted to lower frequencies with respect to that of the HAP-adsorbed silane.^[19] No change in the C=O stretching frequency of **1** was observed when AuHAP was treated with **1**. Based on these phenomena, the present AuHAP-catalyzed deoxygenation may proceed through a pathway initiated by the Au–silane interaction, which is similar to that proposed by Beller and co-workers (Figure 4S in the Supporting Information).^[2a]

In conclusion, the present AuHAP system serves as an efficient heterogeneous catalyst for deoxygenation of amides, sulfoxides, and pyridine *N*-oxides. The methodology described herein is a useful protocol for removing oxygen because of the following advantages: 1) excellent catalytic activities and selectivities; 2) the use of easy-to-handle catalysts; 3) applicability to a wide range of amides, sulfoxides, and pyridine *N*-oxides; and 4) reusability of the catalyst without any loss in its efficiency.

Experimental Section

Characterization of AuHAP: Elemental analysis revealed gold loadings of 1.65%. X-ray absorption spectra and TEM showed that the mean diameter (d) and the standard deviation (σ) of the Au NPs formed on the HAP support were d=3.0 nm and $\sigma=0.9$ nm, respectively.

General protocol for deoxygenation by AuHAP: All manipulations were conducted under Ar atmosphere. AuHAP (0.10 g, Au: 0.0083 mmol) and solvent (3-5 mL) were introduced into a Schlenk tube followed by the addition of amide, sulfoxide, or *N*-oxide (0.5 mmol). Then dimethylphenylsilane (1-2.5 mmol) was added. The reaction mixture was vigorously stirred at the selected temperature in a silicone oil bath. After the deoxygenation reaction, the AuHAP was filtered and the reaction mixture was analyzed by GC or LC with naphthalene as an internal standard to determine the conversions and yields.

Acknowledgements

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Keywords: amides • deoxygenation • gold • heterogeneous catalysis • nanoparticles

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- [13] See the Supporting Information for detailed results of the optimization studies.
- [14] Our previously reported catalytic system, in which Au NPs catalyzed the deoxygenation of epoxides with an alcohol or CO as a reductant, could not be applied to the present deoxygenation of amides, sulfoxides, and N-oxides.
- [15] It is reported that two proximate Si–H bonds of TMDS are effective in the deoxygenation of secondary amides. See ref. 2.
- [17] See Figures 1S and 2S in the Supporting Information for EXAFS and TEM analysis of AuHAP.
- [18] Our continuing studies on HAP-supported catalysts revealed that HAP can strongly stabilize metal NPs during various transformation reactions, see: a) N. Hashimoto, Y. Takahashi, T. Hara, S. Shimazu, T. Mitsudome, T. Mizugaki, K. Jitsukawa, K. Kaneda, *Chem. Lett.* **2010**, 39, 832; b) T. Mitsudome, Y. Mikami, H. Mori, S. Arita, T. Mizugaki, K. Jitsukawa, K. Kaneda, *Chem. Commun.* **2009**, 3258; c) T. Mitsudome, S. Arita, H. Mori, T. Mizugaki, K. Jitsukawa, K. Kaneda, *Angew. Chem.* **2008**, *120*, 8056; *Angew. Chem. Int. Ed.* **2008**, 47, 7938; d) K. Mori, T. Hara, T. Mizugaki, K. Ebitani, K. Kaneda, *J. Asm. Chem. Soc.* **2004**, *126*, 10657.
- [19] See Figure 3S in the Supporting Information for the FTIR study.

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