

# One-pot *N*-alkylation of primary amines to secondary amines by gold clusters supported on porous coordination polymers

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## Abstract

Gold clusters and nanoparticles were deposited on the three kinds of porous coordination polymers (PCPs), MOF-5, CPL-2, and AI-MIL53 by the solid grinding method. The size of Au particles depended on the kinds of PCPs and increased in the order of AI-MIL53 < CPL-2 < MOF-5. The mean diameter of Au particles supported on AI-MIL53 was estimated to be 1.6 nm by HAADF-STEM. Such small Au clusters on AI-MIL53 can catalyze one-pot synthesis of secondary amines from primary amines by sequential oxidation/hydrogenation owing to the remarkable improvement of hydrogenation efficiency of imine. Gold clusters deposited on AI-MIL53 can also promote *N*-alkylation of amine with alcohol to form a secondary amine under N<sub>2</sub> atmosphere without using O<sub>2</sub> and H<sub>2</sub>.

## Introduction

Gold exhibits unique catalytic properties for a number of vapor and liquid phase reactions when it is deposited as nanoparticles (NPs) smaller than 10 nm on base metal oxides (1). Gold NPs supported on or stabilized by organic polymers, on the other hand, have recently been prepared and have shown that they are catalytically active for liquid phase oxidations (2-6). Since the size sensitivity of the catalysis by Au NPs is stronger over inert supports such as carbons and organic polymers than over metal oxides, it often happens that the critical diameter of Au particles appears at around 2 nm, below which catalytic capability dramatically changes.

Porous coordination polymers (PCPs) with highly ordered nanometer-sized porous structures have been attracting growing interests as supports for metal clusters smaller than 2 nm in diameter (7-11). It has been reported that Pd (7,8), Cu (7), Ru (9) clusters in the range of 1-3 nm could be deposited on or in PCPs by chemical vapor deposition (CVD) whereas Au clusters with diameters of smaller than 2 nm had been hardly obtained by CVD because of the weak interactions of Au with PCP frameworks (7). Recently, we have developed a new deposition technique that enables the deposition of Au as clusters on PCPs and have found that the supported Au clusters and Au NPs smaller than 5 nm are catalytically active for the aerobic oxidation of alcohols (10). However, the kinds of PCP support strongly affected the catalytic activity more significantly than the size of Au particles. We have explored new reactions by using a variety of Au/PCPs as catalysts and have found that Au clusters on PCPs are catalytically more active than larger Au NPs on PCPs in the sequential one-pot *N*-alkylations of primary amines involving (i) oxidation of amine (Scheme 1a) or alcohol (Scheme 1b), (ii) imine formation, and (iii) hydrogenation of imine.

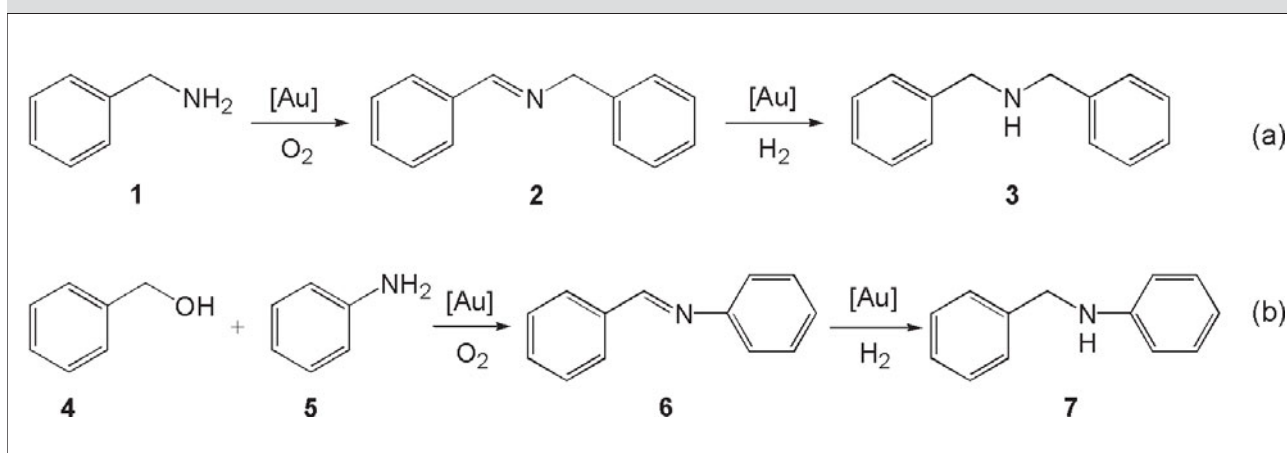
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Scheme 1



One-pot synthesis of symmetric secondary amine (a) and of asymmetric secondary amine (b)

During the course of our investigation, the sequential one-pot synthesis of secondary amine in Scheme 1a by Au/TiO<sub>2</sub> and Au/C was demonstrated by Gurrane et al. (12) and the one-pot synthesis of imine in Scheme 1b by Au/hydroxyapatite was reported by Sun et al. (13). However, the effect of the size of Au NPs on the reactions was studied only for the first oxidation step by using Au NPs larger than 3.5 nm. In addition, catalytic performance of polymer supported Au catalysts for hydrogenation reactions has not yet been explored. Herein, we demonstrate that one-pot *N*-alkylations can be performed by using PCP-supported Au clusters owing to the markedly improved catalytic activity for hydrogenation. It has also been found that Au clusters catalyzed the one-pot *N*-alkylation of amine with alcohol even under inert atmosphere.

## 2 Experimental section

### 2.1 Materials

Porous coordination polymers, Al-MIL53 ([Al(OH)(bdc)]<sub>n</sub>, bdc = benzene-1,4-dicarboxylate) (14) and MOF-5 ([Zn<sub>4</sub>O(bdc)<sub>3</sub>]<sub>n</sub>) (15) were supplied by BASF. CPL-2 ([Cu<sub>2</sub>(pzdc)<sub>2</sub>(bpy)]<sub>n</sub>, pzdc = pyrazine-2,3-dicarboxylate, bpy = 4,4'-bipyridine) was prepared according to the literature (16). Dimethyl acetylacetonatogold(III) complex (Me<sub>2</sub>Au(acac)) was purchased from Tri Chemical Laboratories Inc. and was used without further purification. Benzylamine, benzylalcohol, aniline, *N*-benzylidenebenzylamine, *N*-benzylideneaniline, anisole, toluene (dehydrated), diethyl ether, Cs<sub>2</sub>CO<sub>3</sub>, and 2-propanol, all reagent grades, were purchased and used as received.

### 2.2 Instruments

Gold clusters and NPs were observed with a high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) using a JEOL JEM-3000F operating at 300 kV. Particle size distributions were taken from more than 200 particles. Quantitative analysis was performed by a gas chromatography (SHIMADZU GC-14B with a G-Column G-205, 1.2 mm i.d., 40 m, Chemicals Evaluation and Research Institute Japan) using anisole as an internal standard. Qualitative analysis was performed with a GC-MS (SHIMADZU PARVUM and GC-2010 with a Shinwa Chemical ULBON HR-1 capillary column, 0.25 mm i.d., 30 m).

### 2.3 Catalyst preparation

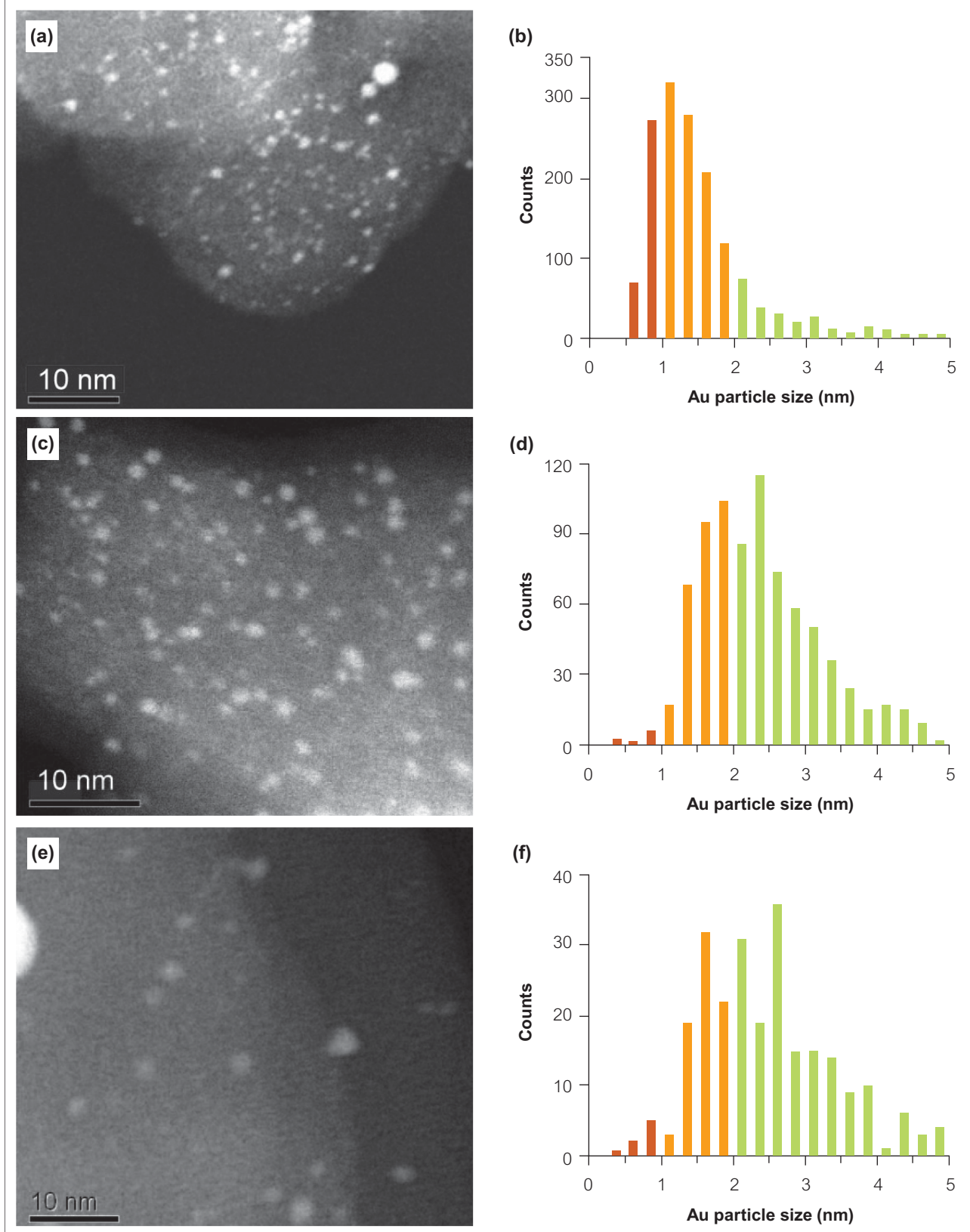
Gold on PCPs were prepared by the solid grinding method (10). Support (300 mg) and Me<sub>2</sub>Au(acac) (10 mg, 2 wt% of Au loading) were ground in an agate mortar in air at room temperature for 20 min. The gold(III) precursor adsorbed on the support was reduced in a stream of 10 vol% H<sub>2</sub> in N<sub>2</sub> at a flow rate of 50 mL/min at 120°C for 2 h to yield Au/PCP. Gold on TiO<sub>2</sub> (1 wt% of theoretical Au loading) was prepared by the deposition-precipitation method according to the procedures described in the literature (17).

### 2.4 Catalytic tests

#### 2.4.1 One-pot synthesis of dibenzylamine from benzylamine

An autoclave was charged with a magnetic stirring bar, benzylamine (110 μL, 1.0 mmol), Au catalyst (Au 1 mol%), and toluene (3.0 mL). Oxygen was introduced into the autoclave until the pressure reached 0.5 MPa. The reaction mixture was stirred

Figure 1



HAADF-STEM images and the size distributions of 2 wt% Au/Al-MIL53 (a, b), 2 wt% Au/CPL-2 (c, d), and 2 wt% Au/MOF-5 (e, f)

at 100°C for 22 h. After the oxidation, O<sub>2</sub> was removed, purged by H<sub>2</sub> several times, and then H<sub>2</sub> was introduced until the pressure reached 0.5 MPa. The reaction mixture was again stirred at 100°C for 22 h. The reaction mixture was extracted with Et<sub>2</sub>O, filtered, and analyzed by GC-MS and GC using anisole as an internal standard.

#### 2.4.2 One-pot synthesis of *N*-phenylbenzylamine from aniline with benzylalcohol

An autoclave was charged with a magnetic stirring bar, benzylalcohol (52 μL, 0.5 mmol), aniline (46 μL, 0.5 mmol), Au catalyst (Au 1 mol%), and toluene (3.0 mL). The following procedures were the same as in 2.4.1 except for the reaction temperature at 120°C.

#### 2.4.3 One-pot *N*-alkylation of aniline with benzylalcohol under N<sub>2</sub> atmosphere

A glass reactor was charged with a magnetic stirring bar, benzylalcohol (52 μL, 0.5 mmol), aniline (46 μL, 0.5 mmol), Au catalyst (74 mg, Au 1.5 mol%), Cs<sub>2</sub>CO<sub>3</sub> (168 mg, 0.5 mmol), and toluene (3.0 mL). Then the mixture was stirred under N<sub>2</sub> atmosphere at 110°C for 22 h. The reaction mixture was washed with H<sub>2</sub>O, extracted with Et<sub>2</sub>O, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and analyzed by GC-MS and GC using anisole as an internal standard.

#### 2.4.4 Hydrogen transfer reaction of *N*-benzylideneaniline with 2-propanol

A glass reactor was charged with a magnetic stirring bar, *N*-benzylideneaniline (91 mg, 0.5 mmol), 2-propanol (0.38 mL, 5 mmol), 2 wt% Au/Al-MIL53 (99 mg, Au 2 mol%), Cs<sub>2</sub>CO<sub>3</sub> (163 mg, 0.5 mmol), and toluene (2.0 mL). The following procedures were the same as in 2.4.3 except for the reaction temperature at 120°C and time for 24 h.

## 3 Results

### 3.1 Deposition of gold clusters onto porous coordination polymers

Figure 1 shows the HAADF-STEM images and the size distributions of Au particles deposited on PCPs. All the three kinds of PCPs could support Au NPs smaller than 5 nm. In particular, over Al-MIL53, 80% of Au particles could be deposited as clusters with diameters below 2 nm. The mean diameter of Au particles could be minimized to 1.6±1.0 nm (Figure 1a, b, and Table 1), whereas the mean diameters of Au particles in Au/CPL-2 and Au/MOF-5 were larger than that in Au/Al-MIL53 and estimated to be 2.4±1.0 and 3.3±2.3 nm, respectively (Figure 1c-f and Table 1).

### 3.2 One-pot synthesis of symmetric secondary amine from primary amine

Table 1 summarizes the experimental results of one-pot synthesis of dibenzylamine (**3**) from benzylamine (**1**) by sequential oxidation/hydrogenation via the formation of *N*-benzylidenebenzylamine (**2**) (18) (Scheme 1a). In terms of yields of **2** and **3**, the catalytic activity of Au/PCPs for the first oxidation step increased with a decrease in the mean diameter of Au particles but only slightly. In contrast, Au/Al-MIL53 exhibited much higher catalytic activity (entry 1) than Au/CPL-2 (entry 3) and Au/MOF-5 (entry 4) for the second hydrogenation step, indicating that hydrogenation is more sensitive to the diameter of Au particles than oxidation. An increase in reaction temperature and the amount of Au catalyst improved the yield of **3** up to 91% (entry 2). Grirrane et al. reported that Au/TiO<sub>2</sub> catalyzed one-pot synthesis of **3** at 100°C according to Scheme 1a (12), however, Au/TiO<sub>2</sub> catalysts prepared by us did not produce **3** under our reaction conditions (entry 5).

Table 1: One-pot synthesis of dibenzylamine (**3**)<sup>a</sup>

Entry	Catalyst	Au size (nm) <sup>b</sup>	Conv. (%) <sup>c</sup>	Yield <b>2</b> (%) <sup>c</sup>	Yield <b>3</b> (%) <sup>c</sup>
1	Au/Al-MIL53	1.6±1.0	67	0	51
2 <sup>d</sup>	Au/Al-MIL53	1.6±1.0	>99	0	91
3	Au/CPL-2	2.4±1.0	81 <sup>e</sup>	38	1
4	Au/MOF-5	3.3±2.3	90 <sup>e</sup>	22	2
5	Au/TiO <sub>2</sub>	2.9±0.5 <sup>f</sup>	60	43	trace

<sup>a</sup> Reaction conditions: benzylamine (1.0 mmol), Au catalyst (Au 1 mol%), toluene (3.0 mL), 100°C. O<sub>2</sub> 0.5 MPa for 22 h and then H<sub>2</sub> 0.5 MPa for 22 h.

<sup>b</sup> Observed by HAADF-STEM. <sup>c</sup> GC conversions and yields after the hydrogenation obtained by using anisole as an internal standard.

<sup>d</sup> The reaction was carried out at 120°C over 2 mol% of Au. <sup>e</sup> High conversions and low yields were due to poor mass balances.

<sup>f</sup> Observed by TEM



### 3.3 One-pot synthesis of asymmetric secondary amine by *N*-alkylation of alcohol with amine

We have also investigated the one-pot synthesis of an asymmetric secondary amine, *N*-phenylbenzylamine (**7**), from benzylalcohol (**4**) with aniline (**5**) via the formation of *N*-benzylideneaniline (**6**) (Scheme 1b and Table 2). Although all Au/PCP catalysts were selective to benzylalcohol oxidation to produce benzaldehyde, leading to the formation of **6** (entry 1-3), only Au/Al-MIL53 could promote the hydrogenation to give **7** (entry 1). Gold on TiO<sub>2</sub> showed lower selectivity to **7** due to the competitive oxidation of **5** to form azobenzene (entry 4) (19).

It is worth noting that Au clusters supported on Al-MIL53 could promote the one-pot *N*-alkylation of **4** with **5** under inert atmosphere without O<sub>2</sub> and H<sub>2</sub> to produce **7** in the co-presence of base (entry 5), whereas Au NPs on CPL-2 and on MOF-5 could not (entry 7, 8). It can be assumed that hydrogen atoms

generated by the dehydrogenation of **4** are used for the hydrogenation of **6** to give **7**. Gold on TiO<sub>2</sub> also gave **7** but substantial amounts of by-products were also formed (entry 9). The modification of reaction conditions (C) improved the selectivity to **7** up to 72% and 76% based on **4** and **5**, respectively, over Au/Al-MIL53 (entry 6).

## 4 Discussion

### 4.1 Hydrogenation efficiency in the one-pot synthesis of dibenzylamine

In order to evaluate the hydrogenation efficiency of Au/PCPs, the hydrogenation of **2** to **3** was carried out by using freshly prepared Au catalysts (Table 3). Gold on CPL-2 and Au/MOF-5 produced **3** in yields of only 2 and 25%, respectively (entry 2 and 3). In contrast, Au/Al-MIL53 achieved a full conversion of **2** (entry 1). Therefore, the low catalytic activity of Au/CPL-2 and Au/MOF-5 in the one-pot synthesis can

Table 2: One-pot *N*-alkylation of aniline (**5**) with benzylalcohol (**4**) to *N*-phenylbenzylamine (**7**)

Entry	Catalyst	Reaction conditions <sup>a</sup>	Conv. <b>4</b> (%) <sup>b</sup>	Conv. <b>5</b> (%) <sup>b</sup>	Yield(%) <sup>b</sup>				
					<b>6</b>	<b>7</b>	PhCHO	PhCO <sub>2</sub> Bn	Benzanilide
1	Au/Al-MIL53	A	41	45	21	16	1	0	0
2	Au/CPL-2	A	27	49	21	trace	trace	0	0
3	Au/MOF-5	A	31	31	27	trace	trace	0	0
4 <sup>c</sup>	Au/TiO <sub>2</sub>	A	53	90	45	1	1	trace	0
5	Au/Al-MIL53	B	62	42	19	22	6	6	0
6	Au/Al-MIL53	C	67	63	11	48	trace	trace	0
7	Au/CPL-2	B	14	18	12	0	trace	0	0
8	Au/MOF-5	B	89	62	62	trace	23	trace	trace
9	Au/TiO <sub>2</sub>	B	>99	54	22	15	3	12	12

<sup>a</sup> Reaction conditions A: benzylalcohol (0.5 mmol), aniline (0.5 mmol), 2 wt% Au/PCP or 1 wt% Au/TiO<sub>2</sub> (Au 1 mol%), toluene (3.0 mL), 120°C. O<sub>2</sub> 0.5 MPa for 22 h and then H<sub>2</sub> 0.5 MPa for 22 h. Reaction conditions B: benzylalcohol (0.5 mmol), aniline (0.5 mmol), Cs<sub>2</sub>CO<sub>3</sub> (0.5 mmol), Au catalyst (1.5 mol%), toluene (3.0 mL), N<sub>2</sub> 0.1 MPa, 110°C for 22 h. Reaction conditions C: conditions B but Au catalyst (2 mol%), toluene (2.0 mL), N<sub>2</sub> 0.1 MPa, 130°C for 48 h.

<sup>b</sup> GC conversions and yields obtained by using anisole as an internal standard

<sup>c</sup> Azobenzene was formed as a by-product

Table 3: Hydrogenation of *N*-benzylidenebenzylamine (**2**)<sup>a</sup>

Entry	Catalyst	Conv. (%) <sup>b</sup>	Yield (%) <sup>b</sup>			
			<b>3</b>	PhCHO	PhCH <sub>2</sub> OH	PhCH <sub>2</sub> NH <sub>2</sub>
1	Au/Al-MIL53	>99	>99	0	0	0
2	Au/CPL-2	10	2	5	1	1
3	Au/MOF-5	41	25	7	6	3
4	Au/TiO <sub>2</sub>	>99	>99	0	0	0

<sup>a</sup> Reaction conditions: *N*-benzylidenebenzylamine (0.5 mmol), Au catalyst (Au 1 mol%), toluene (3.0 mL), H<sub>2</sub> 0.5 MPa, 100°C for 22 h.

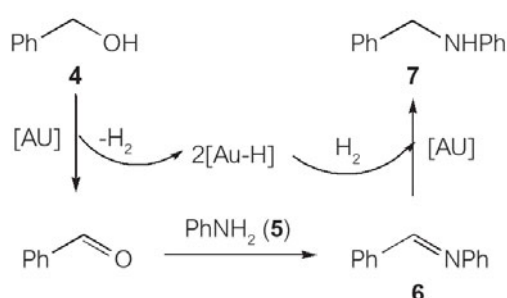
<sup>b</sup> GC conversions and yields obtained by using anisole as an internal standard

be mainly ascribed to intrinsically low hydrogenation efficiency. Bus et al. proposed based on hydrogen chemisorption measurements that hydrogen molecules were dissociated and adsorbed on the corners and the edges of Au particles (20). Thus, higher catalytic activity of Au/Al-MIL53 for hydrogenation could be mainly attributed to an increase in the fraction of Au atoms on the corners and the edges with a decrease in the size of Au,

although support effect cannot be ruled out. Gold on  $\text{TiO}_2$  afforded **3** quantitatively, thus, the low catalytic activity in the one-pot reaction could be ascribed to the deactivation during oxidation (entry 4).

Although Au/Al-MIL53 showed better catalytic performance for one-pot oxidation/hydrogenation, its recycled use was difficult, failed at this stage of our research due to the aggregation of Au clusters to form larger NPs (>10 nm) after the one-pot reactions.

Scheme 2

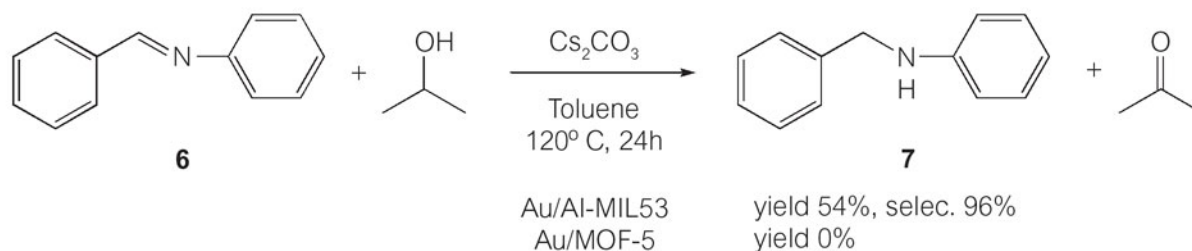


Proposed pathway for the N-Alkylation of **5** with **4** over Au/MIL-53 under inert atmosphere

#### 4.2 Reaction pathway for N-alkylation of alcohol with aniline under inert atmosphere

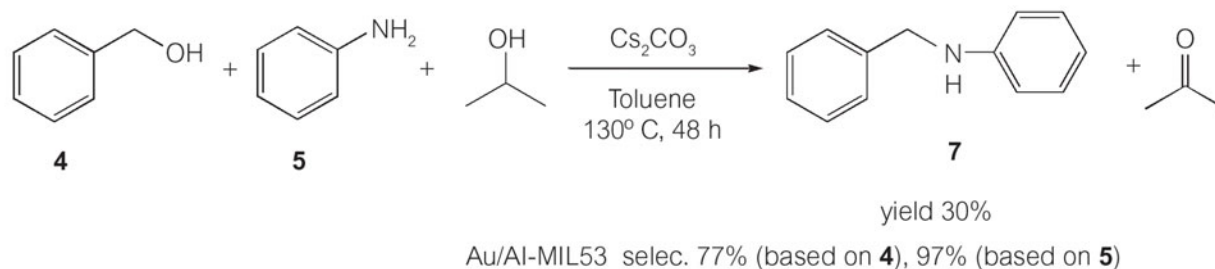
Abad et al. proposed that Au-H species were intermediates formed by the cleavage of the benzylic C-H bond in benzyl alcohol oxidation (21). Hydrogen atoms or hydride species adsorbed on the Au surfaces are considered to be converted with O<sub>2</sub> into water to regenerate the Au catalytic sites. This means that O<sub>2</sub> works as a hydrogen acceptor. This pathway was also proposed by Fristrup et al. by isotope labeling experiments (22) and was supported by ESR study by Conte et al (23).

Scheme 3



Hydrogen transfer reaction of 2-propanol with **6** under N<sub>2</sub>. Reaction conditions: **6** (0.5 mmol), 2-propanol (5 mmol), 2 wt% Au cat. (100 mg, Au 2 mol%), Cs<sub>2</sub>CO<sub>3</sub> (0.5 mmol), and toluene (2.0 mL). 120 °C for 24 h under N<sub>2</sub> atmosphere. Yields were determined by GC

Scheme 4



N-Alkylation of **5** with **4** in the presence of 2-propanol and Cs<sub>2</sub>CO<sub>3</sub> under N<sub>2</sub> atmosphere. Reaction conditions: **4** (0.5 mmol), **5** (0.5 mmol), 2-propanol (3 mmol), 2 wt% Au cat. (100 mg, Au 2 mol%), Cs<sub>2</sub>CO<sub>3</sub> (0.5 mmol), and toluene (2.0 mL). 130 °C for 48 h under N<sub>2</sub> atmosphere. Yield was determined by GC

In *N*-alkylation, **6** could act as a hydrogen acceptor with a similar role of  $O_2$  in alcohol oxidations. Therefore, it is most likely that Au-catalyzed *N*-alkylation is composed of three reactions: (i) the dehydrogenation of alcohol to aldehyde with the formation of Au-H species, (ii) the formation of imine from aldehyde with amine, and (iii) the hydrogen transfer from Au-H to imine, yielding secondary amine (Scheme 2).

In order to confirm this assumption, the hydrogen transfer reaction from 2-propanol to **6** was studied under  $N_2$  atmosphere (Scheme 3). Over Au/Al-MIL53, 2-propanol was dehydrogenated to produce acetone, leading to hydrogenation of **6** to **7** with a selectivity of 96%. This result excluded the possibility of direct dehydration of **4** with **5**. Recently, Su et al. reported hydrogen transfer reaction of carbonyl and nitro groups into alcohol and amino groups, respectively, over Au/TiO<sub>2</sub> with 2-propanol as a hydrogen donor (24). Gold NPs supported on carbon showed much lower catalytic activity than Au/TiO<sub>2</sub> in spite of similar size of Au NPs owing to the lack of support effect. In addition, imine is more stable than nitro compounds under hydrogenation conditions (25). It should be noticed again that *N*-alkylation and hydrogen transfer reaction of imine can be performed over Au clusters but not over Au NPs when Au was deposited on PCPs. Although the support effect of Al-MIL53 cannot be fully excluded, the existence of Au clusters smaller than 2 nm as the majority over the surfaces of PCPs might be an important factor to use Au-H species as reducing agents (26).

Finally, *N*-alkylation of **4** with **5** over Au/Al-MIL53 was investigated in the presence of excess amount of 2-propanol as a hydrogen donor (Scheme 4). Although the yield of **7** decreased, the selectivity was appreciably improved to 77% and 97% based on **4** and **5**, respectively. This result suggested that excess amount of Au-H, which was supplied from 2-propanol, enhanced the hydrogen transfer efficiency.

## 5 Conclusions

Gold clusters smaller than 2 nm in diameter supported on Al-MIL53 enabled one-pot synthesis of secondary amines from primary amines by sequential oxidation/hydrogenation. Such Au clusters could also promote the *N*-alkylation of aniline with benzylalcohol in the co-presence of base without  $O_2$  and  $H_2$ . It was found that the hydrogenation of imine to amine was significantly enhanced when Au

clusters are smaller than 2 nm, leading to high catalytic performance for one-pot, two-steps synthesis of secondary amines. Furthermore, Au clusters on Al-MIL53 could use Au-H species generated by the dehydrogenation of alcohol for the hydrogenation of imine by hydrogen transfer.

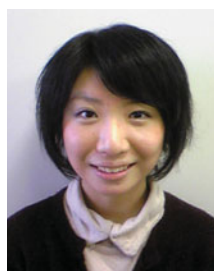
## Acknowledgement

We thank Dr. U. Müller and Mr. N. Takenaka of BASF for supplying Al-MIL53 and MOF-5 samples. This work was supported by JST-CREST and a Grant-in-Aid for Young Scientists (B) (no. 21750160) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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