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Support Effects of Metal Oxides on Gold-Catalyzed One-Pot *N*-Alkylation of Amine with Alcohol

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Abstract

Gold nanoparticles supported on metal oxides catalyzed the *N*-alkylation of aniline with benzyl alcohol to produce secondary amine under the equimolar amounts of substrates without additives under mild conditions. Selectivity to secondary amine was changed by the kinds of supports. Gold on ZrO_2 exhibited the highest catalytic performance and achieved 94% selectivity to secondary amine. Surface hydroxyl groups of ZrO_2 played important roles in the deprotonation of alcohol in the alcohol dehydrogenation step, as the adsorption sites of aniline, and as proton source in the hydrogen transfer step.

Highlights

1) Supported gold nanoparticles catalyzed one-pot *N*-alkylation of aniline with alcohol.

2) Gold on ZrO_2 exhibited the best catalytic activity and the selectivity.

3) Zirconia assisted alcohol dehydrogenation, aniline adsorption, and hydrogen transfer.

Keywords

gold nanoparticles; supported gold catalyst; *N*-alkylation; dehydrogenation

1. Introduction

Secondary amines are one of the important chemicals or intermediates for fine chemical syntheses. They are generally produced by stoichiometric reactions using alkyl halides with primary amines or the reductive amination of aldehydes or ketones with primary amines via the formation of imine [1]. However, the former process has drawbacks that a lot of inorganic salts and undesired different amines are produced as by-products. As to the reductive amination, alcohols are more beneficial than carbonyl compounds because carbonyl compounds are generally produced by the oxidation of alcohols.

The *N*-alkylation of primary amines with alcohols to produce secondary amines has been recently focused as a new efficient method for the production of secondary amines [2]. It consists three steps in one-pot; (i) the dehydrogenation of alcohol to aldehyde, (ii) the dehydrated condensation of aldehyde with primary amine to form imine via hemiaminal intermediate, and (iii) the hydrogen transfer to produce secondary amine (Scheme 1). The hydrogen, generated by the step (i), can be used for the step (iii), so that neither O_2 nor H_2 is required for the alcohol oxidation or hydrogenation of imine. In addition, water is the only by-product. The *N*-alkylation has been mainly studied in the presence of homogeneous metal catalysts [3-7]. More recently, heterogeneous metal catalysts, such as Ru [8], Ag [9-10], Pd [11], and Cu [12] have been reported to be active for the *N*-alkylation. However, high catalytic activity or selectivity to secondary amine has generally been obtained by using excess amount of alcohols or amines or in the presence of acidic or basic additives.

Gold catalysts, that had long been considered to be catalytically inert, have gained prominence since Au exhibits unique size- and support-dependent catalytic activity and selectivity [13]. We reported that Au clusters supported on inert porous coordination polymers could catalyze the *N*-alkylation of amine with alcohol under equimolar amounts of substrates [14]. Although the size effect of Au particles was pronounced especially for Au particles deposited on inert supports, base was required to promote the first dehydrogenation step, even when Au could be deposited as clusters smaller than 2 nm. Later, Cao and co-workers reported that Au clusters deposited on TiO_2 exhibited the highest catalytic activity and selectivity to secondary amine among the metal oxide-supported Au catalysts under the equimolar amount of substrates without additives [15]. However, the reaction was performed under pressurized N_2. On the other hand, Pen et al. synthesized *N*-benzylaniline from nitrobenzene with benzyl alcohol over Au/Fe_2O_3 in the presence of large excess amount of alcohol [16]. These suggested that the catalytic performance of Au could be significantly changed by the kind of supports, however, the role of supports is not fully investigated.

In this work, we have screened a variety of metal oxide-supported Au catalysts in the *N*-alkylation of aniline with benzyl alcohol under the most of atom-economical reaction conditions; using equimolar amounts of substrates without additives under atmospheric pressure of N_2 and investigated the origin of support effects .We also examined the *N*-alkylation with aliphatic alcohol.

(Insert Scheme 1)

2. Experimental

2.1 Materials

High purity microparticulate CeO_2 and ZrO_2 (RC-100) were supplied by Dai-ichi Kigenso Kagaku Kogyo Co. Ltd. Alumina, (Al_2O_3, NEOBEAD 300), and TiO_2 (P-25) were supplied by

Mizusawa Industrial Chemicals, Ltd. and Nippon Aerosil Co., Ltd., respectively. Proprietary WO_3 was used as a support. Reagent grade, $Ni(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, and $Fe(NO_3)_2 \cdot 6H_2O$ were purchased from Wako Pure Chemical Industries, Ltd. and used as received. Cobalt oxide (Co_3O_4) was prepared by the neutralization method from aqueous $Co(NO_3)_2 \cdot 6H_2O$ solution with aqueous Na_2CO_3 solution followed by calcination in air at 300 °C for 4 h. Tetrachloroauric acid tetrahydrate ($HAuCl_4 \cdot 4H_2O$) was purchased from Kishida chemical. Dimethyl gold(III)acetylacetonate, $Me_2Au(acac)$, was purchased from Trichemical Laboratories Inc and used as received. Reagent grade, aniline, benzyl alcohol, *N*-benzylidenbenzylamine, dodecane, and toluene were purchased and used without further purification.

2.2 Instruments

Ball milling was carried out by using Nagao System Planet M2-3 with ZrO_2 pot and ZrO_2 balls ($\phi = 2$ and 5 mm). Transmission electron microscopic (TEM) and high-angle annular dark-field scanning TEM (HAADF-STEM) observations were carried out by using a JEOL JEM-3000F operating at 300 kV. Diffuse reflectance infra-red Fourier transform (DRIFT) spectra were obtained by using a JASCO FT/IR-620. Diffuse reflectance accessory (Spectra Tech, Collector) can be evacuated and heated. Catalyst samples were pretreated at 200 °C for 0.5 h under vacuum ($<10^{-3}$ Pa). After the catalyst was cooled to room temperature, DRIFT spectra were obtained before the introduction of compounds. Then, benzyl alcohol, aniline, and benzaldehyde were adsorbed on the catalyst surfaces at room temperature under vacuum for 30 min and DRIFT spectra were obtained after the adsorption under vacuum. The conversions and product yields of *N*-alkylation were measured by gas chromatography (GC) by using a SHIMADZU GC-14B with a G-Column G-205 (1.2 mm i.d., 40 m, Chemicals Evaluation and

Research Institute Japan) using dodecane as an internal standard. Qualitative analysis was performed with a GC-MS (SHIMADZU PARVUM2 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 ZrO_2 was prepared by the grinding method [17]. A mixture of metal oxide support (3.0 g), $Me_2Au(acac)$ (50 mg for 1 wt% Au loading), and acetone (10 g) was ground by ball milling (350 rpm) in air at room temperature for 30 min. The mixture was filtered, and calcined in air at 300 °C for 4 h. Gold on WO_3 was prepared by mixing WO_3 powder with $Me_2Au(acac)$ in an agate mortar at room temperature for 20 min followed by calcination in air at 300 °C for 4 h [18]. Gold on NiO and Fe_2O_3 were prepared by the co-precipitation [19]. Gold on CeO_2, Al_2O_3, TiO_2, and Co_3O_4 were prepared by the deposition-precipitation (DP) method according to the literature [20]. Gold on MgO was prepared by DP in the presence of Mg citrate according to the literature [21].

2.4 Catalytic tests

A mixture of benzyl alcohol (52 μL, 0.5 mmol), aniline (46 μL, 0.5 mmol), Au catalyst (Au 1.5 mol% to substrate), and toluene (3.0 mL) was stirred under N_2 atmosphere at 110 °C for 22 h. After the reaction, the mixture was extracted with Et_2O and filtered. The filtrate was analyzed by GC using dodecane as an internal standard. In principle, there are two selectivities based on the conversions of benzyl alcohol and of aniline. To simplify the comparison of the support effects, the selectivity to secondary amine was calculated based on the total yields by the following equation: selectivity = yield of sec. amine / total yield of products (sec. amine, imine, aldehyde, and benzyl benzoate).

3. Results

3.1. Support screening

Acid-base properties of metal oxides can be correlated to the electronegativity of metal element or metal ions (χ_i) in metal oxide support and an increase in electronegativity increased acidity of metal oxide surfaces [23]. χ_i is expressed as $\chi_i = (1+2z)\chi_0$, where χ_0 is the Pauling's electronegativity of metal element and z is the valence of metal ions [23]. Table 1 shows the results of the *N*-alkylation of aniline (**1**) with benzyl alcohol (**2**) over Au NPs supported on metal oxides. Gold on basic (entries 1-3) and neutral metal oxides (entries 4-8) showed relatively higher alcohol conversions than Au on acidic WO_3 (entry 9) except for Au/NiO (entry 2) and Au/Fe_2O_3 (entry 7). Among the catalysts, Au/ZrO_2 gave both appreciable high catalytic activity and the highest selectivity to secondary amine (**5**) (entry 6). While Au/NiO (entry 2) and Au/WO_3 (entry 9) gave relatively low alcohol conversions, they exhibited better selectivity to sec. amine than others. We have reported that Au/NiO was highly active for aerobic oxidation of methanol in the presence of amine and preferentially oxidized alcohol to give formamide [22], whereas it showed relatively lower catalytic activity but better selectivity to sec. amine than others in *N*-alkylation. This result implies that the catalytic nature of Au/NiO for alcohol transformation was altered by the presence of O_2. Gold on CeO_2 gave not only sec. amine but also benzaldehyde (**3**) and benzyl benzoate (**6**) as by-products, lowering the selectivity to sec. amine (entry 3). Benzyl benzoate was formed from benzaldehyde and benzyl alcohol via the formation of hemiacetal followed by the dehydrogenation (Scheme 2). Gold on Co_3O_4 and Au/Fe_2O_3 gave only imine (**4**) and did not promote the hydrogen transfer even when the amount of Au was increased (entries 5 and 7). Cao et al. reported that Au/TiO_2 exhibited high catalytic activity and selectivity in the *N*-alkylation [15]. However, Au/TiO_2 did not show high selectivity to sec. amine under our conditions (entry 8) probably due to the relatively larger Au NPs (2.8 nm) in our catalysts than 1.8 nm in Au/TiO_2 prepared by Cao et al.

(Insert Table 1, Scheme 2, and Figure 1)

In the *N*-alkylation, Shimizu et al. demonstrated that the yield of secondary amine could be correlated to the electronegativity of metal element in metal oxides, showing that volcano type relationships with Al_2O_3 support at the top for Ag clusters catalysts [9]. Figure 1a and 1b show the relationships between the electronegativity of metal ions (χ_i) and the conversion of benzyl alcohol and the selectivity to sec. amine, respectively. It has been reported in the reaction mechanism of Au NPs-catalyzed alcohol oxidation that the deprotonation of alcohols to form alkoxide takes place at the basic sites of metal oxide surfaces [24]. Therefore, basic oxides have been recognized as efficient supports. It is reasonable that basic and neutral oxides gave higher alcohol conversion than acidic WO_3 (Figure 1a). On the contrary, the relationships between acid-base properties and the selectivity to sec. amine were not observed under our conditions (Figure 1b).

3.2. Dehydrogenation of alcohol over gold catalysts

Catalytic performance of Au catalysts for the dehydrogenation of benzyl alcohol was studied (Table 2). The reaction proceeded in the absence of aniline and the formation of molecular hydrogen was confirmed. The catalytic activity order was similar to the one for the

N-alkylation. However, the conversion of benzyl alcohol were decreased; for example, from 82% to 46% over Au/ZrO_2 (entry 3). It is likely that imine acted as a hydrogen acceptor to remove hydrogen or hydride from the Au surfaces in a similar manner to O_2 in the catalytic cycle of oxidative dehydrogenation over Au catalysts [24]. Again, Au/NiO showed poor catalytic activity in the absence of O_2 (entry 1). The catalytic activity of Au/CeO_2 for the dehydrogenation was not affected by the absence of aniline (entry 2).

(Insert Table 2)

Fang et al. demonstrated that Au NPs supported on hydrotalcite possessing both acidity and basicity exhibited the best catalytic performance among the other supports such as acidic or basic metal oxides for the dehydrogenation of alcohol in the absence of hydrogen acceptor [25]. They proposed that H^+ would be supplied from acidic sites of hydrotalcite. However, taking into account that Au NPs supported on basic CeO_2 catalyzed the dehydrogenation of alcohol, CeO_2 possesses an ability to supply H^+ although there are no acidic sites on CeO_2. These results implied that hydrogen transfer efficiency from imine to sec. amine did not directly correlate to the surface acidity of metal oxide supports.

3.3. Optimization of reaction conditions

We further searched better reaction conditions by using Au/ZrO_2 (Table 3). To use excess amount of alcohol or amine has usually been adopted in order to achieve higher selectivity to sec. amines [8-12]. The fact, that the conversion of benzyl alcohol exceeded the conversion of aniline, suggested that side reactions of alcohol might occur such as disproportionation to benzaldehyde and toluene [25] and toluene formation by the hydrogenolysis with H_2 generated by the dehydrogenation of alcohol [11]. Accordingly, 2-propanol was added as a hydrogen donor but not effective to improve the selectivity to sec. amine (entry 2). It was probably due to the inhibition when an excess amount of aniline (2 eq.) was used. The hydrogen transfer efficiency was improved to give 78% selectivity to sec. amine whereas the dehydrogenation of alcohol was inhibited (entry 3). An increase in the gold content appreciably improved the selectivity to sec. amine and 4 mol% of Au achieved the selectivity of 94% under equimolar amount of alcohol and aniline without additives (entry 4).

(Insert Table 3)

3.4. N-Alkylation of aliphatic substrates

We examined *N*-alkylation by using aliphatic amine and alcohol (Table 4). The combination of butyl amine with 1-hexanol did not give the corresponding sec. amine but butylidene butyl amine via the dehydrogenative homo-coupling of butyl amine (entry 1). The coupling of butyl amine was prevented when reactive benzyl alcohol was used and the corresponding sec. amine was obtained (entry 2). Entry 3 demonstrated that 1-hexanol could be converted and reacted with aniline to give sec. amine. Although the selectivity to sec. amine was not satisfied at this stage, this result proved that Au/ZrO_2 could promote the dehydrogenation of aliphatic alcohol and followed the *N*-alkylation.

(Insert Table 4)

3.5. Adsorption behavior of metal oxide supported gold catalysts

In order to investigate the support effects on the secondary amine selectivity, we studied the adsorption behavior of benzyl alcohol, aniline, and benzaldehyde onto the catalysts by DRIFT spectra (Figure 2-4). Benzyl alcohol was adsorbed on Au/CeO_2 and Au/ZrO_2, but not on Au/WO_3 judging from the adsorption peaks at 3060, 3024, 2954, and 2910 cm^{-1} which were ascribed to the C-H stretching (Figure 2). These results were in a good agreement with the surface acidity of metal oxides and the catalytic activity order for alcohol conversion.

(Insert Figure 2)

On the aniline adsorption experiments, new adsorption peaks were not observed for Au/CeO_2 but for Au/ZrO_2 and Au/WO_3 (Figure 3). In Figure 3b and 3c, the peaks at 3076 and 3020 cm^{-1} were assigned as C-H stretching. The peaks at 1605 and 1496 cm^{-1} were assigned as C=C ring stretching [26-28].

Vijayraj et al. reported that N-H stretching peaks of adsorbed aniline were higher wavenumber shift (3228 and 3320 cm^{-1} from pure aniline at 3290 and 3355 cm^{-1}, respectively) [28]. They also mentioned that the peak between 3500-3800 cm^{-1} was observed due to the interaction of polarized NH_2 with surface oxygen, leading to the formation of surface OH groups [28]. The other report mentioned that a broad O-H stretching band between 3600 and 3700 cm^{-1} indicated the OH/π interaction [26]. In Figure 3, the broad N-H stretching peaks at 3220-3330 and 3590-3630 cm^{-1} were observed for Au/ZrO_2 and ZrO_2, suggesting the adsorption of aniline on their surfaces.

Tanaka and Ogasawara reported that the peak was observed at 2570 cm^{-1} (NH_3^+

deformation) when aniline was adsorbed at acidic sites [26]. They also proposed that the lower wavenumber shift of N-H deformation band from 1630 cm^{-1} (pure aniline) to 1575 cm^{-1} was due to aniline adsorbed on Lewis acid sites or by hydrogen bonds [26]. However, we did not observed peaks at around 2570 cm^{-1} for all the catalysts, meaning that aniline was adsorbed on the strong acid sites. In contrast, the N-H deformation band was considered to be overlapped at 1605 cm^{-1}, suggesting that aniline was weakly adsorbed on Au/ ZrO_2 and ZrO_2 (Figure 3b and 3c). These results implied that the presence of strong acid sites was not necessary since aniline was weakly adsorbed on the Lewis acid sites or by hydrogen bonds. In addition, the adsorption peaks of aniline were also observed for ZrO_2 without Au (Figure 3c), indicating that adsorption ability was come from metal oxide properties. For Au/WO_3, adsorption peak at 1492 cm^{-1} was observed although the peaks were very weak, indicating that aniline was adsorbed on Au/WO_3 (Figure 3d).

It was also found that Au/CeO_2 and Au/ZrO_2 adsorbed benzaldehyde on their surfaces (Figure 4). Due to the lack of aniline adsorption ability for Au/CeO_2, benzaldehyde reacted with benzyl alcohol to form hemiacetal followed by the dehydrogenation to produce benzyl benzoate as a by-product (Scheme 2). Among these catalysts, only Au/ZrO_2, which could adsorb benzyl alcohol, aniline, benzaldehyde on the surfaces, showed the highest catalytic activity and the selectivity, indicating that the adsorption of benzaldehyde on Au/ZrO_2 enabled the rapid condensation of aniline with aldehyde into imine or hemiaminal intermediate on the Au surfaces.

(Insert Figure 3 and 4)

4. Discussion

4.1. Support effects on the N-alkylation

To elucidate the reaction pathway for the *N*-alkylation, hydrogen transfer reaction from benzyl alcohol to imine over Au/ZrO_2 was examined. The yield of sec. amine decreased to 17% as compared to 46% for the *N*-alkylation (Table 1, entry 6), meaning that imine was only slightly adsorbed on Au/ZrO_2 surfaces. This was in opposite to the case of polymer supported Au clusters [14]. In the case of metal oxide supported Au catalysts, imine could not be easily converted to sec. amine once imine was formed in the reaction solution without catalysts or diffused into the solution from the catalyst surfaces. As Cao et al. [15] and Shimizu et al. [9] have mentioned for the *N*-alkylation over Au/TiO_2 and Ag/Al_2O_3, respectively, it is likely that the hydrogen transfer would occur via hemiaminal intermediates rather than imine on Au/ZrO_2 surface. Therefore, the aniline adsorption ability of metal oxides at the Lewis acidic sites or by OH/π-interactions would play an important role.

4.2. Reaction pathways for N-alkylation

A plausible reaction pathway is shown in Scheme 3. Deprotonation of alcohol was promoted at the basic sites of ZrO_2 to from alkoxide on the Au surfaces. Gold catalyzes the β-hydride elimination to produce benzaldehyde. Aldehyde and aniline, which are adsorbed on the ZrO_2 surfaces beforehand, react to form hemiaminal. Before hemiaminal is converted to imine, hydride on the Au NPs and proton on the surface OH groups on ZrO_2 move to produce sec. amine. Acidic OH groups might contribute as proton sources and as aniline adsorption sites. However, Au NPs supported on basic CeO_2 could also catalyze the dehydrogenation of alcohol, suggesting that protons could be supplied not only from acidic sites but also other surface OH groups. Although the acidic sites of ZrO_2 would be involved in the catalytic reaction, acidity of metal oxides was not a major factor to control the hydrogen transfer efficiency. Furthermore, the addition of 2-propanol as a hydrogen donor lowered the selectivity to sec. amine over Au/ZrO_2 (Table 3, entry 2). It is indicated that excess amount of alcohols inhibited the adsorption of aniline onto ZrO_2 surfaces, resulting the imine formation in the reaction solution. Therefore, it can be concluded that aniline adsorption ability of oxide supports plays an important role to achieve high hydrogen transfer efficiency.

(Insert Scheme 3)

5. Conclusions

We have demonstrated that Au/ZrO_2 worked as an efficient catalyst for the *N*-alkylation of aniline with benzyl alcohol to yield secondary amine using equimolar amount of substrates without additives under N_2 at an atmospheric pressure. Although Au/CeO_2 showed the highest catalytic activity for the dehydrogenation of alcohol in the absence of aniline, the hydrogen transfer efficiency was lower than that of Au/ZrO_2 due to the lack of aniline adsorption ability. It was revealed that not only basic and acidic properties of metal oxide surfaces but also aniline adsorption ability by hydrogen bonding were important in the *N*-alkylation and that aniline adsorption might influence on the hydrogen transfer efficiency to give secondary amine in high yields.

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Figure Captions

Scheme 1 Au-Catalyzed *N*-Alkylation of aniline with benzyl alcohol to produce secondary amine.

Scheme 2 Formation of benzyl benzoate over Au catalysts.

Scheme 3 A possible reaction pathway for the *N*-alkylation of aniline with benzyl alcohol over Au/ZrO_2.

Figure 1 Relationships between the electronegativity of metal ions (χ_i) in metal oxide supports and the conversion of benzyl alcohol (a) and the selectivity to secondary amine (b).

Figure 2 Difference DRIFT spectra of benzyl alcohol adsorbed on Au/CeO_2 (a), Au/ZrO_2 (b), and Au/WO_3 (c).

Figure 3 Difference DRIFT spectra of aniline adsorbed on Au/CeO_2 (a), Au/ZrO_2 (b), ZrO_2 (c), and Au/WO_3 (d).

Figure 4 Difference DRIFT spectra of benzaldehyde adsorbed on Au/CeO_2 (a) and Au/ZrO_2 (b).

Table 1. *N*-Alkylation of aniline (**1**) with benzyl alcohol (**2**) over Au catalysts.[a]

Entry	Catalyst	χ_i [b]	Conv. **1** (%)[c]	Conv. **2** (%)[c]	Yield (%)[c] **3**	**4**	**5**	**6**	Selec. **5** (%)[d]
1	Au/MgO	6	44	68	19	39	4	0	6
2	Au/NiO	9	29	43	5	15	13	0	39
3	Au/CeO_2	9.9	33	70	20	17	10	17	16
4	Au/Al_2O_3	10.5	59	68	9	51	8	0	12
5	Au/Co_3O_4[d]	11.3	90	>99	0	88	0	0	0
6	Au/ZrO_2	12.6	79	82	0	31	46	0	60
7	Au/Fe_2O_3[d]	12.8	42	42	0	40	0	0	0
8	Au/TiO_2	13.5	81	87	5	72	9	0	10
9	Au/WO_3	22.1	39	34	0	15	19	0	56

[a] Reaction conditions: aniline (0.5 mmol), benzyl alcohol (0.5 mmol), Au catalyst (Au 1.5 mol%), toluene (3.0 mL), 110 °C, 1 atm of N_2, 22 h. [b] Electronegativity of metal ion (χ_i) in metal oxide supports is expressed as $\chi_i = (1+2z)\chi_0$, where χ_0 is the Pauling's electronegativity of metal element and z is the valence of metal ions [23]. [c] Conversions and yields were calculated by GC using dodecane as an internal standard. [c] Selectivity was calculated based on the total yields of all the products detected by GC. [d] Au 5 mol%.

Table 2 Dehydrogenation of benzyl alcohol (**2**)[a]

Entry	Catalyst	Conv. (%)[b]	Yield **3** (%)[b]	Yield **6** (%)[b]
1	Au/NiO	16	14	0
2	Au/CeO_2	66	32	31
3	Au/ZrO_2	46	35	0
5	Au/WO_3	0	0	0

[a] Reaction conditions: benzyl alcohol (0.5 mmol), toluene (3.0 mL), Au 1.5 mol%, 110 °C, 22 h.

[b] Calculated by GC using dodecane as an internal standard.

Table 3 Optimization of reaction conditions for Au/ZrO_2.

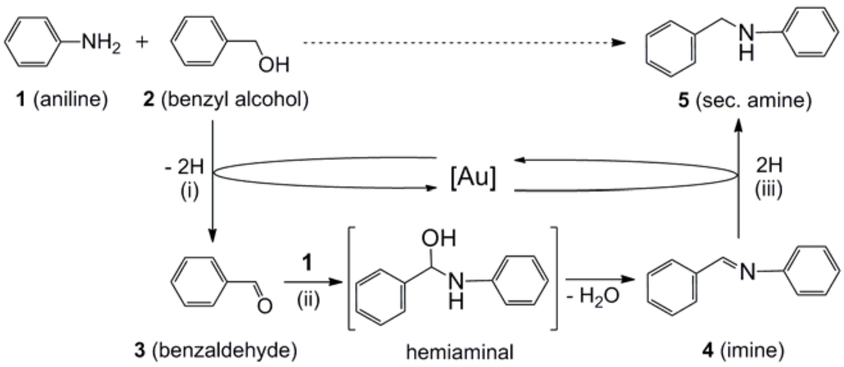
Entry	conditions[a]	Conv. **1** (%)[b]	Conv. **2** (%)[b]	Yield (%)[b]				Selec. **5** (%)[c]
				3	**4**	**5**	**6**	
1	A	79	82	0	31	46	0	60
2	B	91	>99	0	45	45	0	50
3	C	—[d]	42	0	8	30	0	78
4	D	86	99	0	4	80	0	94

[a] Reaction conditions : [A] aniline (0.5 mmol), benzyl alcohol (0.5 mmol), Au catalyst (Au 1.5 mol%), toluene (3.0 mL), 110 °C, under 1 atm of N_2, 22 h. [B] Au 2 mol%, 2-propanol (0.5 mmol) was added. [C] conditions A but aniline (1.0 mmol). [D] Conditions A but Au 4 mol%. [b] Conversions and yields were calculated by GC using dodecane as an internal standard. [c] Selectivity was calculated based on total yields of all products detected by GC. [d] Conversion was not calculated because 2 eq. amount of **1** was used.

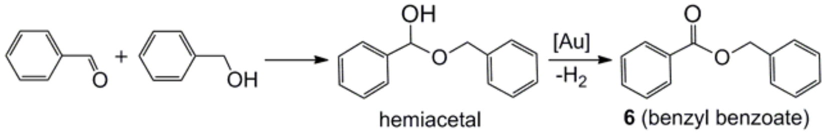
Table 4. *N*-Alkylation of primary amines with primary alcohols over Au/ZrO_2.[a]

Entry	Amine	Alcohol	Conv.		Yield
			Amine (%)[b]	Alcohol (%)[b]	sec. amine (%)[b]
1	Butyl amine	1-Hexanol	95	55	0
2	Butyl amine	Benzyl alcohol	81	76	26
3	Aniline	1-Hexanol	46	72	15

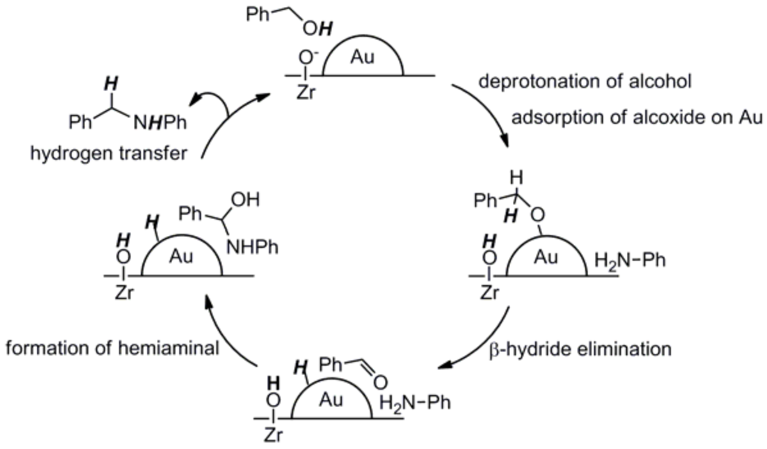
[a] Reaction conditions: amine (0.5 mmol), alcohol (0.5 mmol), Au/ZrO_2 (Au 4 mol%), toluene (3.0 mL), 110 °C, 1 atm of N_2, 22 h. [b] Conversions and yields were calculated by GC using dodecane as an internal standard.



Scheme 1



Scheme 2



Scheme 3

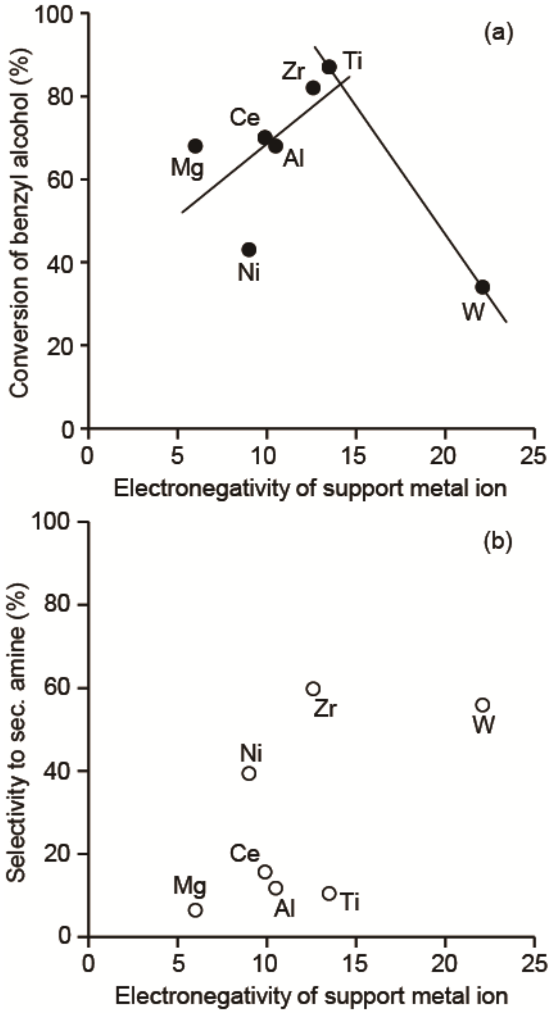


Fig. 1

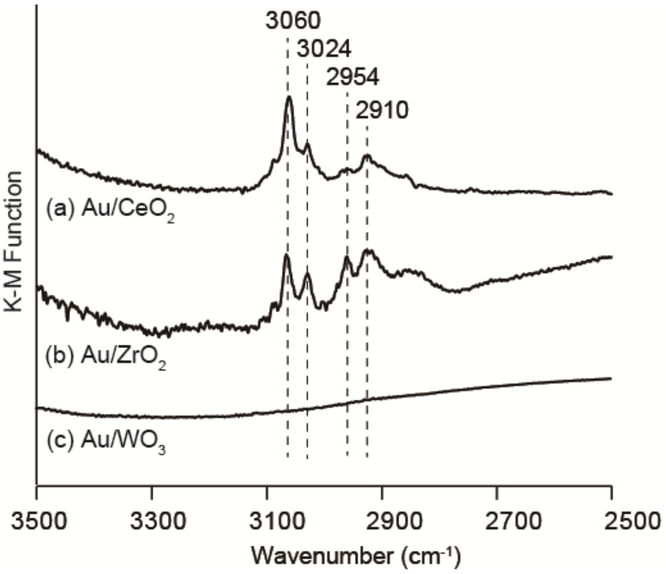

3060
3024
2954
2910
K-M Function
(a) Au/CeO$_2$
(b) Au/ZrO$_2$
(c) Au/WO$_3$
3500
3300
3100
2900
2700
2500
Wavenumber (cm^{-1})

Fig. 2

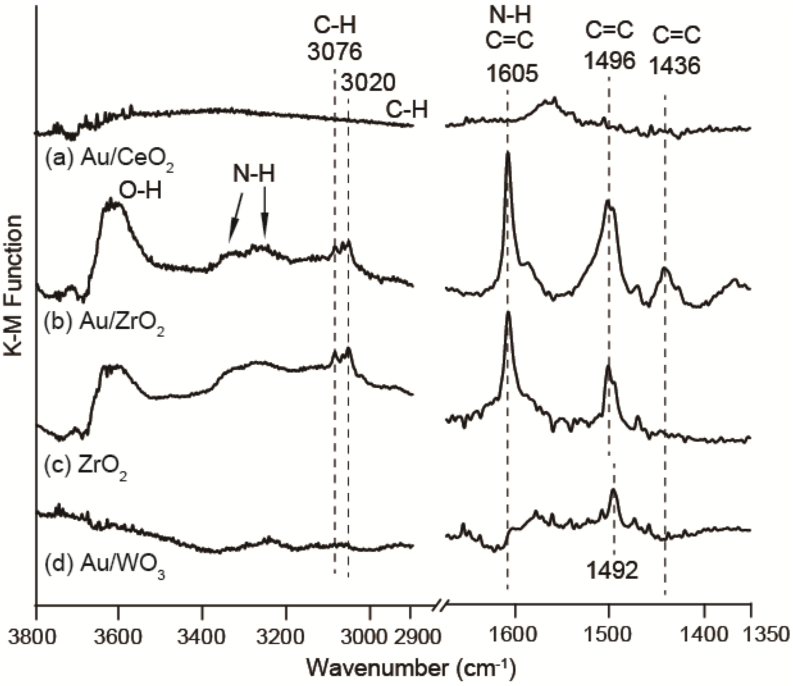

C-H
3076
3020
C-H
N-H
C=C
1605
C=C
1496
C=C
1436
K-M Function
(a) Au/CeO$_2$
O-H
N-H
(b) Au/ZrO$_2$
(c) ZrO$_2$
(d) Au/WO$_3$
1492
3800
3600
3400
3200
3000
2900
1600
1500
1400
1350
Wavenumber (cm^{-1})

Fig. 3

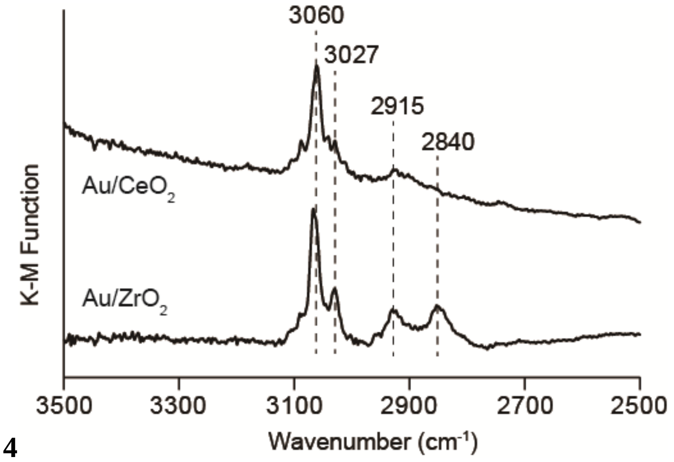

3060
3027
2915
2840
Au/CeO$_2$
Au/ZrO$_2$
K-M Function
3500
3300
3100
2900
2700
2500
Wavenumber (cm^{-1})

Fig. 4