Heterogeneous Ni Catalyst for Direct Synthesis of Primary Amines from Alcohols and Ammonia

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Ⓢ *Supporting Information*

ABSTRACT: This paper reports the synthesis of primary amines from alcohols and NH_3 by an Al_2O_3-supported Ni nanoparticle catalyst as the first example of heterogeneous and noble-metal-free catalytic system for this reaction without additional hydrogen sources under relatively mild conditions. Various aliphatic alcohols are tolerated, and turnover numbers were higher than those of Ru-based homogeneous catalysts. The catalyst was recoverable and was reused. The effects of the Ni oxidation states and the acid—base nature of support oxides on the catalytic activity are studied. It is clarified that the surface metallic Ni sites are the catalytically active species, and the copresence of acidic and basic sites on the support surface is also indispensable for this catalytic system.

KEYWORDS: alcohols, amines, ammonia, heterogeneous catalysis, nickel
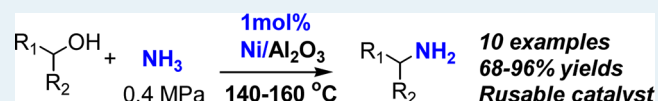
1. INTRODUCTION

Amines are important intermediates in the bulk and fine chemical industries for production of polymers, dyes, pharmaceuticals, agrochemicals, surfactants, and biologically active compounds. Among amines, primary amines are the most useful intermediates for further derivatization reactions. Aliphatic primary amines can be synthesized by the reductive amination of the corresponding carbonyl compounds,[1−3] but their selective synthesis is challenging because of their high reactivity. Although heterogeneous catalysts are used for reductive aminations of simple alcohols under H_2,[2−11] they suffer from drawbacks such as limited substrate scope; low selectivity for primary amines; and the need for high temperature (>200 °C), high H_2 pressure, and high pressure of NH_3 (such as supercritical NH_3[7−9]).

Recently, Mizuno and co-workers developed Ru-[12] and Cu[13]-based heterogeneous catalysts for the direct synthesis of secondary and tertiary amines from alcohols and aqueous ammonia (or urea), but selective formation of primary amines was not reported. As for the homogeneous catalysts, iridium-catalyzed multialkylation of aqueous ammonia with alcohols was reported for the synthesis of secondary and tertiary amines,[14,15] but selective synthesis of primary amines remains as a challenging task. Gunanathan and Milstein[16] reported the first example of the selective synthesis of primary amines from primary alcohols and NH_3 using a Ru PNP pincer complex, although the system was ineffective for the amination of secondary alcohols.[17] Recently, Vogt et al.[17] and Beller et al.[18,19] independently discovered the selective amination of secondary alcohols with NH_3 to give primary amines.

All of these examples are driven by Ru-based organometallic catalysis[16−19] via a borrowing-hydrogen[20] (or hydrogen-autotransfer[21]) mechanism: the carbonyl compound formed by the initial dehydrogenation of the alcohol reacts with NH_3 to form the imine, which is reduced to the amine. For a practical application, these homogeneous catalysts have problems such as difficulty in the catalyst recovery and reuse of catalysts and necessity of noble metals. The development of non-noble-metal-based heterogeneous catalyst for the direct amination is an important research target. To the best of our knowledge, there are no noble-metals-free and ligand-free catalytic systems that are able to aminate various alcohols with NH_3 to primary amines in the absence of additional hydrogen sources (such as H_2). We report herein that alumina-supported a nickel metal nanoparticle catalyst, readily prepared from inexpensive commercial materials, acts as a versatile heterogeneous catalyst for the selective synthesis of primary amines directly from alcohols and ammonia under relatively mild conditions without any additives. To clarify the controlling factors of the catalytic system, the effects of Ni oxidation states and the acid—base character of the support materials on the activity are also discussed on the basis of the results of catalyst characterization.

2. EXPERIMENTAL SECTION

2.1. General. Commercially available organic and inorganic compounds (from Tokyo Chemical Industry, Wako Pure Chemical Industries, Kishida Chemical, or Mitsuwa Chemicals) were used without further purification. The GC (Shimadzu GC-14B) and GC/MS (Shimadzu GCMS-QP2010) analyses were carried out with an Ultra ALLOY capillary column UA⁺-5

(Frontier Laboratories Ltd.) or an Rtx-65 capillary column (Shimadzu) using nitrogen as the carrier gas. ^1H NMR spectra were recorded in $CDCl_3$ with TMS as an internal standard at ambient temperature on a JEOL JNM-ECX 400 operating at 400 MHz.

2.2. Catalyst Preparation. γ-Al_2O_3 (with surface area of 124 m^2 g^{-1}), θ-Al_2O_3 (112 m^2 g^{-1}) and α-Al_2O_3 (17 m^2 g^{-1}) were prepared by calcination of γ-AlOOH (Catapal B Alumina purchased from Sasol) for 3 h at 900, 1000, and 1200 °C, respectively. MgO (JRC-MGO-3, 19 m^2 g^{-1}), TiO_2 (JRC-TIO4, 50 m^2 g^{-1}), and CeO_2 (JRC-CEO3, 81.4 m^2 g^{-1}) were supplied by the Catalysis Society of Japan. Hydroxides of Zr, Sn, Y, and La were prepared by hydrolysis of zirconium oxynitrate 2-hydrate, $SnCl_4 \cdot 6H_2O$, or metal nitrates in distilled water by gradually adding an aqueous NH_4OH solution (1.0 mol dm^{-3}), followed by filtration of precipitate, washing with distilled water three times, and drying at 100 °C for 12 h. $Ca(OH)_2$ and $Nb_2O_5 \cdot nH_2O$ (supplied by CBMM) were commercially supplied. CaO, Y_2O_3, La_2O_3, ZrO_2, Nb_2O_5, and SnO_2 were prepared by calcination of these hydroxides at 500 °C for 3 h.

NiO/θ-Al_2O_3 (Ni loading = 10 wt %) was prepared by an impregnation method: A mixture of θ-Al_2O_3 (9.0 g) and an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ (0.17 M, 100 cm^3) was evaporated at 50 °C, followed by drying at 90 °C for 12 h and calcination in air at 300 °C for 1 h. Before each catalytic experiment, Ni/θ-Al_2O_3 was prepared by in situ prereduction of NiO/θ-Al_2O_3 in a glass (pyrex or quartz) tube under a flow of H_2 (20 cm^3 min^{-1}) at a reduction temperature (T_{H_2}) of 500 °C for 0.5 h. Ni/θ-Al_2O_3 with different Ni loadings (5 and 20 wt %) and 5 wt % Ni loaded on various supports (α-Al_2O_3, La_2O_3, Y_2O_3, CeO_2, ZrO_2, TiO_2, Nb_2O_5, SnO_2) were prepared by the impregnation method in the same manner as the preparation of Ni/θ-Al_2O_3 (Ni loading = 10 wt %). CaO and MgO-supported Ni (5 wt %) were prepared by the impregnation method, followed by drying at 90 °C for 12 h, and by in situ prereduction of the precursor under H_2 at 500 °C. γ-Al_2O_3-supported metal catalysts, M/γ-Al_2O_3 (M = Ni, Co, Cu, Ru, Pd, Rh, Ag, Ir, Pt) with a metal loading of 5 wt % were prepared by an impregnation method in a manner similar to the preparation of Ni/θ-Al_2O_3 using an aqueous solution of metal nitrates (for Ni, Co, Cu), $RuCl_3$, or an aqueous HNO_3 solution of $Rh(NO_3)_3$, $Pd(NO_3)_2$, or $Pt(NH_3)_2(NO_3)_2$. Au/γ-Al_2O_3 (Au = 1 wt %) was prepared by the deposition–precipitation method with $HAuCl_4$. Raney Ni (B113W, Ni > 90%) was supplied from Evonik Industries.

2.3. Typical Procedures of Catalytic Reactions. Typically, 10 wt % Ni/θ-Al_2O_3 (Ni/alcohol = 1:100) prereduced at 500 °C was used as a standard catalyst. After the prereduction, the catalyst in the closed glass tube sealed with a septum inlet was cooled to room temperature under H_2 atmosphere. The mixture of o-xylene (4.0 g), alcohol (3.0 mmol), and n-dodecane (0.5 mmol) was injected to the prereduced catalyst inside the glass tube through the septum inlet, then the septum was removed under air, and a magnetic stirrer was put in the tube, followed by inserting the tube inside a stainless autoclave with a dead space of 33 cm^3. Soon after being sealed, the reactor was flushed with NH_3 from a high-pressure gas cylinder and charged with 0.4 MPa NH_3 at room temperature. Note that the secondary pressure was reduced to 0.4 MPa using a regulator. The amount of NH_3 present in the reactor before heating was 6.7 mmol (2.2 equiv with respect to

the alcohol). Then the reactor was heated, typically at 160 °C, under stirring (150 rpm). Conversion and yields of products were determined by GC using n-dodecane as an internal standard. The products were identified by GC/MS equipped with the same column as GC and by comparison with commercially pure products.

2.4. Catalyst Characterization. Temperature-programmed reduction under H_2 (H_2-TPR) was carried out with BELCAT (Bell Japan Inc.). The sample, NiO/θ-Al_2O_3 (Ni loading = 10 wt %, 20 mg) was mounted in a quartz tube, and the sample was heated with a temperature ramp rate of 5 °C min^{-1} in a flow of 5% H_2/Ar (20 cm^3 min^{-1}). The effluent gas was passed through a trap containing MS4 Å to remove water, then through the thermal conductivity detector. The amount of H_2 consumed during the experiment was detected by a thermal conductivity detector. Temperature-programmed desorption (TPD) experiments of CO_2 and NH_3 were carried out using BELCAT. Prior to each experiment, catalyst (0.1 g) was heated in a flow of He (20 cm^3 min^{-1}) at 500 °C for 0.5 h, followed by cooling to 40 °C under He flow. Then the catalyst was exposed to a flow of 100% CO_2 or 5% NH_3/He for 10 min. After being purged in He for 0.5 h, the catalyst was heated linearly at 10 °C min^{-1} to 900 °C in a flow of He, and the CO_2 (m/e = 44) and NH_3 (m/e = 16 and 17) in the outlet gas were analyzed by a mass spectrometer (Belmass). The BET surface area was obtained by measuring the N_2 adsorption at −196 °C by BELCAT.

Transmission electron microscopy (TEM) measurements were carried out by using a JEOL JEM-2100F TEM operated at 200 kV. Ni K-edge X-ray absorption fine structure (EXAFS) was measured in transmission mode at the BL01B1 in the SPring-8 (Proposal No. 2011B1137). The storage ring was operated at 8 GeV. A Si(111) single crystal was used to obtain a monochromatic X-ray beam. The catalyst prereduced in a flow of 100% H_2 (20 cm^3 min^{-1}) for 0.5 h at 500 °C was cooled to room temperature in the flow of H_2 and was sealed in cells made of polyethylene under N_2, and then the EXAFS spectrum was taken at room temperature. The EXAFS analysis was performed using the REX version 2.5 program (Rigaku). The Fourier transformation of the k^3-weighted EXAFS oscillation from k space to R space was performed over the range 3.0−16.0 $Å^{-1}$ to obtain a radial distribution function. The inversely Fourier filtered data were analyzed with a usual curve fitting method in the k range of 3.0−16.0 $Å^{-1}$. The parameters for the Ni−O and Ni−Ni shells were provided by the FEFF6. The number of free parameters for curve-fitting can be estimated as P_{free} = $2\Delta k \Delta R/\pi \approx 13$, indicating that we can model the EXAFS data with three shells.

IR (infrared) spectra were obtained by use of a Jasco Fourier transform infrared (FT-IR) 4100 spectrometer equipped with an MCT detector at 4 cm^{-1} resolution. A total of 64 scans were collected to obtain each spectrum. The real temperature of the sample was estimated from a calibration curve of temperatures measured inside and outside the IR cell. A catalyst disc was prereduced under H_2 (20 kPa) at 500 °C for 0.5 h, followed by evacuation at the same temperature for 0.5 h. IR spectra of clean samples before CO adsorption experiments were measured under evacuation at −180 °C and were used as background spectra. Subtracted IR spectra of adsorbed CO were measured after the sample was exposed to CO (500 Pa) at −180 °C.

3. RESULTS AND DISCUSSION

As summarized in Table 1, we first screened the effect of various catalyst parameters on the catalytic activity for the

Table 1. Amination of 2-Octanol with NH_3[a]

entry	catalyst	conv (%)	yield (%)		
			2a	3a	4a
1	$NiO/\theta\text{-}Al_2O_3$	0	0	0	0
2	$Ni/\theta\text{-}Al_2O_3$	83	80	3	0
3	$Ni/\alpha\text{-}Al_2O_3$	0	0	0	0
4	$Ni/\gamma\text{-}Al_2O_3$	83	81	0	2
5[b]	$Cu/\gamma\text{-}Al_2O_3$	18	14	0	2
6	$Co/\gamma\text{-}Al_2O_3$	10	5	0	2
7	$Pt/\gamma\text{-}Al_2O_3$	95	41	9	16
8	$Ir/\gamma\text{-}Al_2O_3$	80	46	11	4
9	$Re/\gamma\text{-}Al_2O_3$	6	1	0	1
10	$Au/\gamma\text{-}Al_2O_3$	0	0	0	0
11	$Ru/\gamma\text{-}Al_2O_3$	37	28	1	3
12	$Rh/\gamma\text{-}Al_2O_3$	12	2	0	0
13[b]	$Ag/\gamma\text{-}Al_2O_3$	3	3	0	0
14	$Pd/\gamma\text{-}Al_2O_3$	2	1	0	1
15[c]	$\gamma\text{-}Al_2O_3$	0	0	0	0
16[d]	Ni powder	0	0	0	0
17[d]	Raney Ni	22	22	0	0
18	Ni/CaO	25	0	0	1
19	Ni/MgO	0	0	0	0
20	Ni/La_2O_3	52	42	1	8
21	Ni/Y_2O_3	66	56	1	8
22	Ni/CeO_2	74	68	1	3
23	Ni/ZrO_2	71	54	1	6
24	Ni/TiO_2	1	0	0	0
25	Ni/Nb_2O_5	0	0	0	0
26	Ni/SnO_2	0	0	0	0
27[e]	$Ni/\theta\text{-}Al_2O_3\text{-}air$	0	0	0	0

[a]Conversion of **1a** and yields of **2a**, **3a**, and **4a** were determined by GC based on **1a**. [b]T_{H_2} = 300 °C [c]Al_2O_3 = 0.1 g. [d]Ni = 10 mol % [e]Prereduced Ni/θ-Al_2O_3 was exposed to air at room temperature for 0.5 h.

amination of 2-octanol **1a** with NH_3 (P = 0.4 MPa, 6.7 mmol) to the corresponding primary amine **2a** and byproducts (secondary amine **3a** and 2-octanone **4a**) under the same conditions (Ni = 1 mol % with respect to alcohol, T = 160 °C, t = 4 h). Note that the metal-loaded catalysts ($M/M'O_x$) were prepared by H_2 reduction (500 °C) of metal oxide-loaded precursors ($MO_y/M'O_x$), and then the catalytic tests were carried out without exposing the catalyst to air. First, various transition metal (5 wt %)-loaded γ-Al_2O_3 catalysts were tested (entries 4−14). Among the first-row transition metals (entries 4−6), only Ni/γ-Al_2O_3 showed high yield of **2a** (81%), and Co and Cu catalysts showed low activity. Noble metal (Pt, Ir, Re, Au, Ru, Rh, Pd, Ag)-loaded γ-Al_2O_3 catalysts (entries 7−14) showed a lower yield of **2a** (0−46%) than Ni/γ-Al_2O_3. The Cu- and Ag-loaded catalysts prereduced at lower temperature (300 °C) were also tested, but the yield of **2a** was lower than 14%. Use of a large amount (10 mol %) of conventional Ni catalysts

(Ni powder and Raney Ni; entries 16, 17) resulted in a lower yield than Ni/γ-Al_2O_3 (1 mol %).

Next, we tested the reaction with 1 mol % of various Ni (5 wt %)-loaded catalysts (Ni/alcohol = 1:100). Alumina with different crystal phases was tested as a support of Ni (entries 2−4). The alumina with spinel structure (θ-Al_2O_3 and γ-Al_2O_3) gave similar yields (80−81%), whereas that with a corundum structure (α-Al_2O_3) was ineffective. To study the support effects on the activity of Ni catalysts, purely basic (MgO, CaO), amphoteric (γ-Al_2O_3, Y_2O_3, La_2O_3, CeO_2, ZrO_2), and relatively acidic (TiO_2, Nb_2O_5, SnO_2) supports were selected according to well-known classifications of acid−base character of metal oxides.[22−24] Amphoteric supports (entries 4, 20−23) gave good to moderate yields of **2a** (42−81%), and purely basic supports (entries 18, 19) and relatively acidic supports (entries 24−26) showed no activity. For these catalysts, the initial rate of **2a** formation was measured under the conditions where conversion was below 30%, and the rate was converted to the turnover frequency (TOF) on the basis of the total number of Ni atom.

Figure 1 plots TOF as a function of the electronegativity of the support metal oxide, which is generally used as a parameter
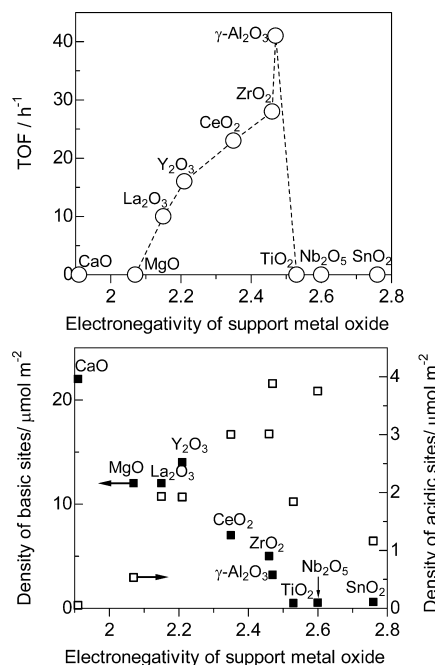

Figure 1. TOF (○) and the surface densities of basic (■) and acidic (□) sites vs electronegativity of the support metal oxide.

of acidity of metal oxides.[25−28] The electronegativity of the metal oxide is calculated according to the concept of Sanderson[29] on the basis of the electronegativity of the element.[30] Among the supports with basic to amphoteric nature (MgO ∼ γ-Al_2O_3), the activity increases with the electronegativity of the support oxide. These results suggest that both acidic and basic sites in the support are necessary for this reaction. As listed in Table S1 (in the Supporting Information), the densities of the surface acidic and basic site on each catalyst was estimated on the basis of the surface area of the catalyst and the number of desorbed NH_3 and CO_2 molecules during NH_3- and CO_2-TPD experiments. In Figure 1, the densities of acidic and basic site as experimental indexes of the acid−basicity of the catalyst are plotted versus the support electronegativity. For

the supports with basic to amphoteric nature (CaO ∼ γ-Al$_2$O$_3$), the increase in the electronegativity generally results in a decrease in the density of the basic sites and an increase in the acid site density. The supports with the electronegativity higher than 2.5 (TiO$_2$ ∼ SnO$_2$) show a negligible value of basic site density. Comparing the catalytic and characterization results in Figure 1, we can conclude that the copresence of acidic and basic sites on the surface of the support oxides is indispensable for this reaction.

Ni/θ-Al$_2$O$_3$ with various Ni loadings (1−20 wt %) were also tested (Figure S1 in the Supporting Information), and the catalysts with 5 or 10 wt % Ni were found to be optimal. From the above results, θ- or γ-Al$_2$O$_3$-supported Ni (5 or 10 wt %) catalysts were found to be the optimal catalysts.

To discuss the relationship between the structure of Ni species and catalytic activity, we carried out various spectroscopic characterization of the standard catalyst, Ni/θ-Al$_2$O$_3$ (10 wt % Ni). Transmission electron microscopy (TEM) analysis of Ni/θ-Al$_2$O$_3$ (10 wt % Ni) showed spherical or semispherical Ni particles with average particle sizes of 6.5 ± 2.2 nm (Figure 2). Next, we studied the effect of oxidation
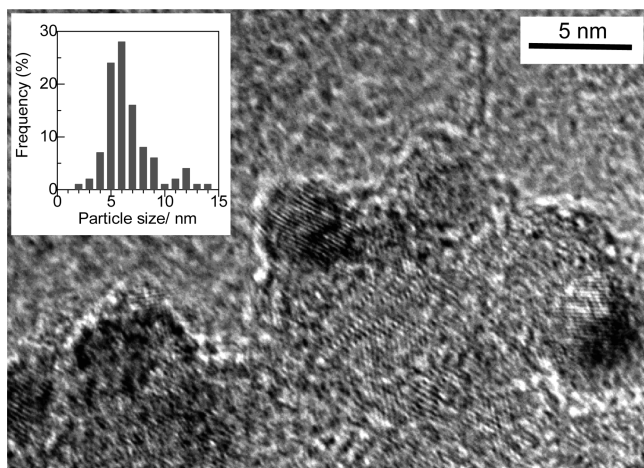
Figure 2. A representative TEM image and particle size distribution of Ni/θ-Al$_2$O$_3$ (Ni loading = 10 wt %, T_{H_2} = 500 °C).

states of Ni on the activity. The catalytic results showed that NiO/θ-Al$_2$O$_3$ as well as the support (θ-Al$_2$O$_3$) showed no activity, indicating that the support and NiO were completely inert. NiO/θ-Al$_2$O$_3$ was reduced in a flow of H$_2$ at various reduction temperatures (T_{H_2} = 300−800 °C), and their TOF for the amination of **1a** was measured. The result showed that TOF increased with T_{H_2} up to 500 °C and did not markedly change with a further increase in T_{H_2} (Supporting Information Figure S2). In Figure 3, TOF is plotted as a function of the fraction of metallic Ni^0 in each catalyst estimated by the temperature programmed reduction under H$_2$ (H$_2$-TPR, Supporting Information Figure S3). It is clear that the activity increases with the fraction of metallic Ni^0, which indicates that the metallic Ni nanoparticles are the active species. The structure of Ni species in the standard catalyst, Ni/θ-Al$_2$O$_3$ (T_{H_2} = 500 °C), was confirmed by EXAFS (Supporting Information Figure S4). The curve-fitting of the EXAFS of Ni/θ-Al$_2$O$_3$ gave the Ni−O shells and two Ni−Ni shells listed in Supporting Information Table S2. By comparison with the crystallographic data of NiO and Ni metal, these are assigned as follows. The
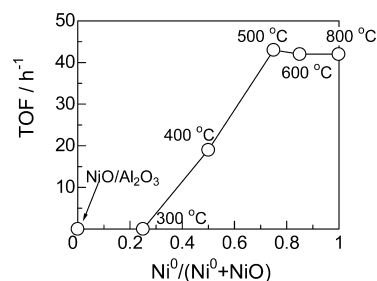
Figure 3. TOF vs the fraction of metallic Ni (from H$_2$-TPR) for 10 wt % Ni/θ-Al$_2$O$_3$ catalysts reduced in H$_2$ at various temperatures.

Ni−Ni shell at a distance (R) of 2.48 Å with coordination number (N) of 5.2 indicates the presence of metallic Ni. The relatively low coordination numbers of the Ni−O shell at 2.00 Å (N = 1.8) and the Ni−Ni shell at 2.94 Å (N = 1.3) indicate the copresence of NiO as a minor Ni species. This result is consistent with the Ni^0/NiO ratio of 0.75/0.25 (Figure 3) for the same catalyst estimated by H$_2$-TPR.

The catalyst named Ni/θ-Al$_2$O$_3$−air (Table 1, entry 32) was prepared by exposing the as-reduced Ni/θ-Al$_2$O$_3$ catalyst to the ambient conditions for 0.5 h. This catalyst showed no activity. This suggests that the metallic Ni^0 species on the surface of Ni nanoparticles are the active species, and reoxidation of them by O$_2$ under ambient conditions results in deactivation of the catalyst. This hypothesis is confirmed by the following results. The EXAFS result (Supporting Information Table S2) showed that air exposure of the Ni/θ-Al$_2$O$_3$ catalyst resulted in an increase in the Ni−O coordination number from 1.8 to 2.3, which indicates that the metallic Ni was partially reoxidized in air. The oxidation states of surface Ni species can be studied by a CO adsorption IR study at −180 °C. IR spectra of adsorbed CO species are shown in Figure 4.
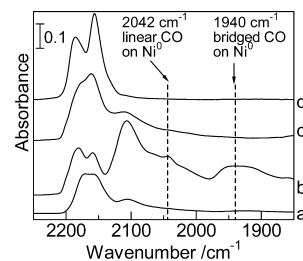
Figure 4. IR spectra of CO adsorbed on 10 wt % Ni-loaded catalysts at −180 °C: (a) NiO/θ-Al$_2$O$_3$, (b) Ni/θ-Al$_2$O$_3$ (T_{H_2} = 500 °C), (c) Ni/θ-Al$_2$O$_3$ after reoxidation in 20 kPa O$_2$ at room temperature, and (d) θ-Al$_2$O$_3$.

The bands in the 2150−2210 cm^{-1} region are usually attributed to CO-Al^{3+} or CO-Ni^{2+} species,[31−33] as is confirmed by the experiments on pure θ-Al$_2$O$_3$ and unreduced precursor (NiO/θ-Al$_2$O$_3$). The spectrum for the NiO/θ-Al$_2$O$_3$ showed a weak shoulder at 2106 cm^{-1} due to CO adsorbed on Ni$^+$ species (CO-Ni$^+$).[31−33] The spectrum of the reduced Ni/θ-Al$_2$O$_3$ catalyst exhibits bands around 1940 cm^{-1} due to the bridged CO on the Ni^0 site and a band at 2042 cm^{-1} due to the linear CO on Ni^0 site,[31−33] indicating the presence of metallic Ni^0 species on the surface of Ni/θ-Al$_2$O$_3$. The strong band due to CO−Ni$^+$ species (2106 cm^{-1}) is also observed. Upon exposure to O$_2$ (20 kPa) at room temperature for 0.5 h, the bands due to CO adsorbed on the Ni^0 sites completely
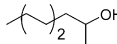
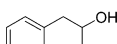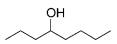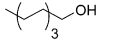disappeared, and the shoulder band due to CO−Ni⁺ (2106 cm^{-1}) remained. Combined with the result of the catalytic test, the result indicates that the surface metallic Ni^0 sites are the catalytically active species. Under ambient conditions, the surface metallic Ni^0 species are completely converted to the inactive Ni^{2+} species.

Next, we examined the catalytic properties of Ni/θ-Al$_2$O$_3$ (10 wt % Ni) under the conditions shown in Table 2. The

Table 2. Amination of Various Alcohols with NH$_3$[a]

R$_1$–CH(OH)–R$_2$ (1, 3.0 mmol) + NH$_3$ (0.4 MPa) → [Ni/Al$_2$O$_3$ (1 mol%), o-xylene (4 g), 160 °C] → R$_1$–CH(NH$_2$)–R$_2$ (2) + R$_1$–CO–R$_2$ (4) + R$_1$R$_2$CH–NH–CHR$_1$R$_2$ (3)

entry	alcohols	t / h	conv. (%)	yield (%) 2	3	4
1[b]	(CH$_2$)$_2$ octanol OH	20	93	88	5	0
2[b]	1st reuse	20	92	88	4	0
3[b]	2nd reuse	20	92	89	4	0
4[c,d]	cyclohexanol OH	28	96	96	5	0
5[c]	cyclooctanol OH	29	94	77	4	12
6[c]	cyclododecanol OH	22	95	82	0	12
7	2-adamantanol OH	63	99	96 (90)[g]	3	0
8[e]	OH	20	100	85	0	4
9	OH	24	81	68	6	0
10[c]	OH	72	94	85	3	6
11[e,f]	OH	72	99	78	11	0
12[e]	(CH$_2$)$_3$ OH	13	90	70	7	0

[a] Conversion and yields were determined by GC based on alcohol. [b] T_{H_2} = 600 °C. [c] T = 140 °C. [d] In n-decane (4 g). [e] Catalyst = 5 mol %. [f] T = 150 °C. [g] Isolated yield.

amination of 2-octanol by Ni/Al$_2$O$_3$ (1 mol %) for 20 h resulted in 88% yield of the corresponding primary amine with a low yield (5%) of the secondary amine. The reaction was completely terminated by removal of the catalyst from the reaction mixture after 32% conversion of **1** (t = 1 h); further heating of the filtrate for 19 h under NH$_3$ (0.4 MPa) at 160 °C did not increase the yield. ICP analysis of the filtrate confirmed that the content of Ni in the solution was below the detection limit. These results confirm that the reaction is attributed to the heterogeneous catalysis of Ni/θ-Al$_2$O$_3$. After the reaction, the catalyst was easily separated from the reaction mixture by centrifugation. The filtered catalyst was washed with acetone, followed by drying in air at 90 °C for 12 h and by reducing in H$_2$ at 600 °C for 0.5 h. As shown in Table 2 (entries 2, 3), the recovered catalyst was reused at least two times.

The scope of the Ni/θ-Al$_2$O$_3$-catalyzed amination of various alcohols with NH$_3$ at 140−160 °C is shown in Table 2. In the presence of Ni/θ-Al$_2$O$_3$ (Ni/alcohol = 1:100), various cyclic aliphatic secondary alcohols were selectively converted to the corresponding primary amines with good to high yield (77−96%), whereas the yields of the secondary amines were below 5%. It should be noted that primary amines were selectively produced even at high conversion level. The amination of 2-adamantanol resulted in 99% conversion of the alcohol. After the reaction, the catalyst was separated from the mixture by a centrifugation, and the solvent was removed under vacuum, then the product (2-adamantylamine) was isolated by column chromatography on silica gel, followed by removal of the solvent under vacuum. The isolated yield was 90%, corresponding to a TON of 90. This value is larger than those of the state-of-the-art homogeneous Ru catalysts for the amination of secondary alcohols: 46 for Ru$_3$(CO)$_{12}$]/CataCXiumPCy[18] and 16 for [Ru(CO)ClH(PPh$_3$)$_3$]/Xant-phos.[19] Note that our heterogeneous system requires an order of magnitude lower amount of ammonia (2.23 equiv) with respect to alcohols than the Ru catalysts (35−59 equiv).[5] To the best of our knowledge, our result represents the first example of heterogeneously catalyzed selective synthesis of primary amines from various alcohols and NH$_3$ without any additives such as H$_2$. For the amination of primary alcohols (benzylalcohol and a linear aliphatic alcohol) with 5 mol % of the catalyst, moderate yields of the corresponding primary amines (70, 78%) were obtained with relatively high yields of secondary amine (11, 7%).

As previously postulated, the present reaction could proceed through the hydrogen-borrowing pathway.[16−21] Thus, the initial stage of the reaction would be the oxidation of alcohol to a carbonyl intermediate accompanied by a transitory generation of Ni hydride species. A time course of the amination of cyclododecanol with NH$_3$ by Ni/θ-Al$_2$O$_3$ is shown in Figure 5. A typical time−conversion profile of the
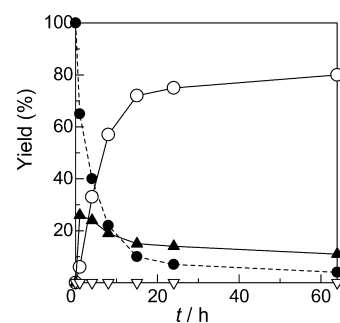
Figure 5. Time−conversion profile for the amination of **1b** (3 mmol) by NH$_3$ with 1 mol % of Ni/θ-Al$_2$O$_3$ (Ni = 10 wt %) at 150 °C in o-xylene (4 g): yields of unreacted **1b** (●), primary amine **2b** (○), secondary amine **3b** (▽) and cyclododecanone **4b** (▲).

consecutive reaction was observed: the carbonyl intermediate **4b**, formed at an initial period, was gradually consumed, and the yield of the primary amine **2b** increased with time. On the basis of the above results, a plausible catalytic cycle is given in Scheme 1. The reaction begins with the dehydrogenation of alcohol by Ni sites to a carbonyl compound, which reacts with ammonia to give an imine. Finally, hydrogen transfer from Ni−H species to the imine gives the primary amine. We tentatively assume that basic sites of the alumina[34,35] promote the dehydrogenation step, possibly by abstraction of a proton

Scheme 1. A Plausible Pathway of Ni-Catalyzed Amination of Alcohols
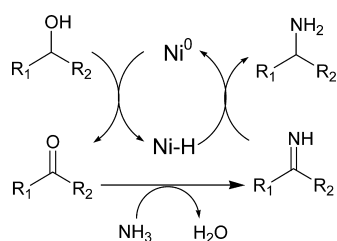
from the alcohol, and the acidic nature of alumina might be relevant to the hydrogen transfer step.

4. CONCLUSIONS

In conclusion, we have reported the selective synthesis of primary amines from alcohols and NH_3 by an Al_2O_3-supported Ni nanoparticle catalyst as the first example of a heterogeneous and noble-metal-free catalytic system for this reaction without additional hydrogen sources. This method provides an atom-efficient, versatile, and economic method for the synthesis of primary amines. Studies on the structure–activity relationship show that the copresence of acid–base sites of alumina and surface metallic Ni^0 species is responsible for the high activity. The fundamental information will lead to a design of ligand- and noble-metal-free recyclable catalysts for environmentally benign and practical production of amines.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Characterization data for catalyst and products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
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