Supporting Information

Aerobic Oxidative Esterification of Aldehydes with Alcohols by Gold–Nickel Oxide Nanoparticle Catalysts with a Core-Shell Structure

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EXPERIMENTAL SECTION

General Methods. The aldehyde **1a**, **b** and alcohol **3** were purchased from Wako Pure Chemical Industries, Ltd. and used after purification. HAuCl_4 and $\text{Pd/SiO}_2\text{--Al}_2\text{O}_3$ were purchased from N.E. CHEMCAT Corporation. $\text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Pb(OAc)_2 , methanol, ethanol and *n*-butanol were purchased from Wako Pure Chemical Industries, Ltd. $\text{NiO}_2 \cdot n\text{H}_2\text{O}$ was purchased from Sigma-Aldrich Corporation. All other reagents were obtained from commercial suppliers. GC measurements were carried out using a Shimadzu GC-14B gas chromatograph (FID) equipped with a DB-1701 glass capillary column (0.25 mm $\times$ 30 m). GC-MS analyses were performed on a Hewlett Packard 6890 Plus-5973N mass spectrometer equipped with a DB-1701 glass capillary column (0.25 mm $\times$ 30 m). The known products **2a–2e** and **4** were identified by comparison of GC and GC-MS spectra with those of the authentic samples obtained from the commercially available compounds. The amounts of Au and Ni in the leaching solution were estimated using inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

Support Preparation. An aqueous solution (5.0 L) of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (3.75 kg), $\text{Mg}(\text{NO}_3)_2$ (2.56 kg), and 60% HNO_3 (540 g) was gradually added to silica sol (20 kg, Snowtex N-30 (SiO_2 content: 30 % by mass), Nissan Chemical Industries, Ltd.) under stirring at 15 °C to obtain a mixed slurry of silica sol, aluminum nitrate and magnesium nitrate. The silica sol had a colloidal particle diameter of 10–20 nm. The mixed slurry was subsequently aged by holding at 50 °C for 24 h. After cooling to room temperature, the mixed slurry was spray-dried with a spray dryer, set to an outlet temperature of 130 °C, to obtain a solid. Next, the resulting solid was filled to a thickness of about 1 cm into a top-open stainless steel container followed by heating in an electric oven from room temperature to 300 °C over the course of 2 hours and then holding at that temperature for an additional 3 hours. After further heating to 600 °C over the course of 2 hours followed by holding at that temperature for an additional 3 hours, the solid was cooled gradually to obtain the $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--MgO}$ support. The amounts of silicon, aluminum, and magnesium in the support were 83 mol%, 8 mol% and 9 mol%, respectively. The specific surface area, pore volume, and average pore diameter were determined to be 149 m^2/g , 0.26 mL/g , and 8 nm, respectively, using nitrogen adsorption isotherms. The average particle diameter of the support was determined to be 60 μm using a laser diffraction particle size analyzer. In addition, the shape of the support was found to be nearly spherical based on observations with a scanning electron microscope (SEM).

Catalyst Preparation. The $\text{AuNiO}_x/\text{SiO}_2\text{--Al}_2\text{O}_3\text{--MgO}$ catalyst was prepared by co-precipitation. An aqueous solution (1000 mL) containing $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (16.35 g) and 1.3 mol/L HAuCl_4 (12 mL) was heated at 90 °C. The $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--MgO}$ support (300 g) obtained above was added to this solution followed by stirring for 30 min, thereby precipitating gold hydroxide–nickel hydroxide components onto the support. Next, this mixture was allowed to stand undisturbed and the supernatant was removed followed by washing with distilled water until chloride ions were no longer detected. The liquid was subsequently filtered. The resultant material was

dried in vacuo at 110 °C overnight and then calcined at 450 °C for 5 h to afford AuNO_x/SiO₂–Al₂O₃–MgO as a brown powder. The Au and Ni contents were determined to be 0.9 and 1.1 wt% respectively, by ICP-AES.

General Procedure for the Catalytic Oxidative Esterification of Aldehydes with Alcohols in the presence of Molecular Oxygen. A stainless-steel autoclave (120 mL) equipped with a magnetic stirring bar was charged with a mixture of AuNiO_x/SiO₂–Al₂O₃–MgO (328 mg, Au: 0.015 mmol, Ni: 0.06 mol), methacrolein (15 mmol, containing 50 ppm hydroquinone inhibitor), and tetradecane (internal standard for GC analysis, 0.25 mmol) in methanol (10 mL). The autoclave was pressurized to 3 MPa with an oxygen–nitrogen mixture (7:93 v/v), and the mixture was stirred (600 rpm) at 60 °C for 2 h. After the reaction, the flask was cooled to room temperature and carefully depressurized. AuNiO_x/SiO₂–Al₂O₃–MgO was separated from the reaction mixture by filtration. The reaction mixture was analysed by GC. The conversion of methacrolein (58%) and the selectivity of methyl methacrylate (98%) were determined using tetradecane as an internal standard (mass balance based on methacrolein: 99.6 %) and the products were identified by GC-MS.

Methyl methacrylate (2a). Table 2, entry 1: m/z = 41 (100), 69 (63), 39 (37), 100 (M+, 27).

Ethyl methacrylate (2b). Table 2, entry 2: m/z = 69 (100), 41 (96), 329 (35), 39 (28), 86 (20), 114 (M+, 12).

Butyl methacrylate (2c). Table 2, entry 3: m/z = 41 (100), 69 (97), 87 (77), 56 (52), 39 (49), 29 (31), 27 (22).

Methyl benzoate (2d). Table 2, entry 4: m/z = 105 (100), 77 (62), 136 (M+, 39), 51 (25).

Ethyl benzoate (2e). Table 2, entry 5: m/z = 105 (100), 77 (41), 122 (31), 150 (M+, 22).

Methyl glycolate (4). m/z = 31 (100), 59 (52), 29 (28), 61 (24), 33 (23), 90 (M+, 16).

Characterization of the Catalyst. The amounts of Au and Ni in the catalyst were determined by ICP-AES using a Thermo Fisher Scientific Model IRIS Intrepid III XDL instrument. Catalyst samples were prepared by weighing out the supporting material into a Teflon decomposition vessel, adding nitric acid and hydrogen fluoride, and heating and decomposing the sample in a microwave decomposition system (Milestone General Model ETHOS-TC). This was followed by evaporation to dryness over a heater, addition of nitric acid and hydrochloric acid to the precipitated residue, heating under an applied pressure with the microwave decomposition system, and using a fixed amount of the resulting pure decomposition product as a test liquid. Quantification was carried out by ICP-AES using an internal standard, and the Au and Ni contents in the catalyst were determined by subtracting a simultaneously determined blank value and calculating the supported amounts and atomic ratio.

Transmission electron microscopy (TEM)/scanning transmission electron microscopy (STEM) measurements were performed with a JEOL Model 3100 FEF microscope operating at 300 kV. The Au–Ni particles were identified using energy-dispersive X-ray (EDX) spectroscopy. The samples were prepared by crushing the particle along with its support using a mortar and pestle, followed by dispersion in ethanol. After ultrasonic cleaning for approximately 1 min, the powder was dropped onto a molybdenum microgrid and air-dried to obtain TEM/STEM samples. Data analysis software Digital Micrograph™ from Gatan was used for TEM and STEM image analyses (length measurement, Fourier transform analysis), and NORAN System SIX from Thermo Fisher Scientific was used for EDS data analyses (mapping image processing, compositional quantification, and calculation).

X-ray diffraction (XRD) measurements of the catalyst were carried out on a Rigaku RINT 2500 diffractometer using monochromated Cu K α radiation at 40 kV and 30 mA. The catalyst sample was prepared by uniformly spraying the sample onto a nonreflective sample plate and fixing it with neoprene rubber.

X-ray photoelectron spectroscopy (XPS) experiments were conducted on a Thermo Electron ESCALAB 250 spectrometer using an Al K α excitation source (15 kV, 10 mA) from 0–1100 eV. The oval surface region considered for the analysis was approximately 1 mm². Narrow scans of Au4f, Ni2p were carried out over the analysis region.

Ultraviolet-visible (UV-vis) measurements were carried out on a Jasco V-550 spectrometer with an integrating sphere unit and a powder sample holder. Spectra were obtained over the wavelength range 200–800 nm at a scanning speed of 400 nm/min. The samples were prepared by crushing the catalyst in an agate mortar and pestle, and the powder was placed in the sample holder for spectral measurements.

Fourier transform-infrared (FT-IR) spectra were recorded on a Shimadzu FTIR-8000 spectrometer. A cell with KBr windows was connected to a conventional vacuum system. Before CO adsorption, the catalyst samples were degassed at 350 °C for 1 h. Then CO (3cc) was introduced into the cell at 15 °C and hold for 30 min. Afterward the sample was evacuated and spectra were recorded.

Electron-probe microanalysis (EPMA) was performed on a Shimadzu Model 1600 microanalyzer at an accelerating voltage of 15 kV. The Ni and Au concentrations in the depth direction from the outer surface were determined from electron-reflected images and X-ray analysis (Ni wavelength: 14.5829, analyzing crystal: RAP; Au wavelength: 5.8419, analyzing crystal: PET).

Life of the Catalyst. The catalytic life of AuNiO_x/SiO₂–Al₂O₃–MgO was evaluated by using a continuous-flow reaction apparatus. The catalyst was packed in a 1.2 L stirring-type stainless-steel continuous reactor provided with a catalyst separator. A 37 wt% solution of **1a** in methanol was then continuously fed into the reactor at 0.6 L/h, and the reaction was carried out by blowing air in the reactor at 80 °C and 0.5 MPa until the exiting O₂ concentration became 4 vol% (equivalent to the oxygen partial pressure of 0.02 MPa). Then, the mixture was stirred (stirrer tip speed: 4 m/s). The reaction product was continuously extracted from the reactor

outlet by overflow; the reactivity was investigated by GC analysis, and the products were identified by GC-MS.

The continuous-flow reaction apparatus

Figure S1. Size distribution histograms of AuNiO_x particles.

Figure S2. X-ray diffraction patterns of (a) AuNiO_x/SiO₂-Al₂O₃-MgO and (b) NiO/SiO₂-Al₂O₃-MgO.

Figure S3. X-ray photoelectron spectroscopy (Au4f and Ni2p spectra) characterization of the $\text{AuNiO}_x/\text{SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ catalyst.

Figure S4. Ultraviolet-visible spectra of (a) Au/SiO₂-Al₂O₃-MgO, (b) AuNiO_x/SiO₂-Al₂O₃-MgO, (c) NiO_x/SiO₂-Al₂O₃-MgO, (d) NiO/SiO₂-Al₂O₃-MgO, and (e) SiO₂-Al₂O₃-MgO.

Figure S5. Fourier transform-infrared spectra for the adsorbed species of CO on AuNiO_x/SiO₂-Al₂O₃-MgO (a) and Au/SiO₂-Al₂O₃-MgO (b) at 15 °C. Spectra 1 and 2 were obtained after adsorption CO then evacuation of the cell for 5 min and 20 min, respectively.

Figure S6. Monitoring of catalytic activity over time using a continuous-flow reaction apparatus.