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Acceptorless dehydrogenation of *N*-heterocycles by supported Pt catalysts

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ABSTRACT

Pt metal nanoparticles loaded on various supports and carbon-supported various metal catalysts are tested for dehydrogenation of 6-methyl-1,2,3,4- tetrahydroquinoline to 6-methyl-quinoline under oxidant-free conditions. In the 20 types of the catalysts screened, carbon-supported Pt catalyst (Pt/C) shows the highest activity. Pt/C is reusable after the reaction and is effective for dehydrogenation of various *N*- heterocycles (tetrahydroquinolines and indoline). Pt/C is also effective for hydrogenation of quinoline under 3 bar H_2. The results demonstrate that this catalytic method may be useful for an organic hidride–based hydrogen storage system.

1. Introduction

Catalytic dehydrogenation [1–9] and oxidation [10–21] of saturated *N*-heterocycles are of fundamental importance in the synthesis of nitrogen-containing aromatics. Previous methods [10–21] are based on the catalytic oxidation of *N*-heterocycles using an external oxidant such as O_2 and stoichiometric oxidants, but use of the oxidant potentially limits selectivity and functional group tolerance. An alternative method is the catalytic dehydrogenation of *N*-heterocycles in the absence of oxidants [1–9]. Recently reported homogeneous catalytic methods with Ir [4,5,7], Ru [8], Co [6] and Fe [9] catalysts were effective for the reaction, but most of these methods have drawbacks such as low turnover number (TON) and difficulties in catalyst/product separation and reuse of the homogeneous catalyst [5–9]. A few reports showed acceptorless dehydrogenation of *N*-heterocycles with heterogeneous catalysts [1–3]. For example, Kaneda et al. developed Pd [1] and Cu catalysts [2] for dehydrogenation of indolines and tetrahydroquinoline, respectively. For a model dehydrogenation of 1,2,3,4-tetrahydroquinoline, the previous homogeneous [4,7,8,6,9] and heterogeneous [2,3] catalysts showed limited TON in a range of 3.3–87. Among these examples, a few studies have succeeded in the reversible dehydrogenation-hydrogenation reactions of *N*-heterocycles with a single catalyst [2,4–6,9]. This reversible transformation is of particular importance from a viewpoint of organic hydrides for hydrogen storage system. As a part of our continuous studies in heterogeneous catalysis for oxidant-free dehydrogenation reactions [22], we report herein dehydrogenation of saturated *N*-heterocycles by a Pt/C catalyst, which shows higher TON for dehydrogenation of tetrahydroquinoline than previous catalytic systems. Additionally, Pt/C is effective for the reverse reaction, that is hydrogenation of quinoline into tetrahydroquinoline under 3 bar H_2.

2. Experimental

2.1. Catalyst preparation

Commercially available organic and inorganic compounds (Tokyo Chemical Industry, Kanto Chemical) were used without further purification. The standard carbon support, Vulcan XC72 (210 $m^2\,g^{-1}$), was commercially supplied. γ-Al_2O_3 (124 $m^2\,g^{-1}$) was prepared by calcination of γ-AlOOH (Catapal B Alumina from Sasol) at 900 °C for 3 h. SiO_2 (Q-10, 300 $m^2\,g^{-1}$) was supplied from Fuji Silysia Chemical Ltd. TiO_2 (JRC-TIO-4, 50 $m^2\,g^{-1}$), MgO (JRC-MGO-3, 19 $m^2\,g^{-1}$), SiO_2- Al_2O_3 (JRC-SAL-2, Al_2O_3 = 13.75 wt%, 560 $m^2\,g^{-1}$) and HBEA zeolite ($SiO_2/Al_2O_3 = 25 \pm 5$, JRC-Z-HB25) were supplied from Catalysis Society of Japan. Nb_2O_5 (54 $m^2\,g^{-1}$), ZrO_2 and SnO_2 were prepared by calcination of $Nb_2O_5{\cdot}nH_2O$

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(CBMM), $ZrO_2 \cdot nH_2O$ and H_2SnO_3 (Kojundo Chemical Laboratory Co., Ltd.), respectively, at 500 °C for 3 h.

A precursor of the 5 wt% Pt/C catalyst was prepared by impregnation method; a mixture of carbon (Vulcan XC72) and aqueous HNO_3 solution of $Pt(NH_3)_2(NO_3)_2$ (Furuya Metal Co., Ltd.) was evaporated at 50 °C, followed by drying at 90 °C for 12 h. The reduced Pt/C catalyst, designated as Pt/C, was prepared by reduction of the precursor ($Pt(NH_3)_2(NO_3)_2$-loaded carbon) in a pyrex tube under H_2 flow (20 cm^3 min^{-1}) at 300 °C for 0.5 h. The other Pt catalysts were prepared by the same method as Pt/C. Carbon-supported metal catalysts, designated as M/C (M = Rh, Pd, Ir, Ru, Ni, Cu, Co, Ag), with metal loading of 5 wt% were prepared by impregnation method by the similar manner as Pt/C using aqueous solution of metal nitrates (for Ni, Cu, Co, Ag) or $IrCl_3 \cdot nH_2O$ or aqueous HNO_3 solution of $Rh(NO_3)_3$ (Furuya Metal Co., Ltd.) or Pd $(NH_3)_2(NO_3)_2$ (Kojima Chemicals Co., Ltd.). These catalysts were reduced under H_2 flow at 300 °C for 0.5 h. Platinum oxides-loaded carbon (PtOx/C) was prepared by calcination of the $Pt(NH_3)_2(NO_3)_2$-loaded C in air at 300 °C for 0.5 h.

2.2. Catalyst characterization

Temperature programmed reduction by H_2 (H_2-TPR) was carried out by BELCAT (MicrotracBEL). PtOx/C (20 mg) in a quartz tube was heated with a temperature ramp-rate of 10 °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, which detected the amount of H_2 consumed during the experiment. The number of surface Pt^0 atoms on Pt/C, pre- reduced in H_2 at 300 °C for 0.5 h, was estimated from the CO uptake of the samples at room temperature using the pulse-adsorption of CO in a flow of He by BELCAT (MicrotracBEL). The average Pt particle size was calculated from the CO uptake assuming that CO was adsorbed on the surface of spherical Pt particles at a stoichiometry of CO/(surface Pt atom) = 1/1. Transmission electron microscopy (TEM) observation of Pt/C was carried out by a JEOL JEM–2100 F TEM operated at 200 kV.

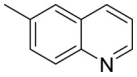
2.3. Catalytic tests

Typically, 5 wt% Pt/C was used as the standard catalyst. After the H_2-reduction of the catalyst at 300 °C, catalytic tests were carried out using a batch-type reactor without exposing the catalyst to air as follows. A mixture of 6-methyl 1,2,3,4-tetrahydroquinoline (1.0 mmol) and *n*-dodecane (0.29 mmol) in *o*-xylene (1.5 mL) was injected to the pre-reduced catalyst inside the reactor (cylindrical glass tube) through a septum inlet, followed by filling N_2. Then, the resulting mixture in a 15 mL of closed reflux system under 1 atm N_2 was magnetically stirred and was heated to reflux temperature; the bath temperature was 160 °C and reaction temperature was *ca.* 144 °C. The yield of 6-methyl-quinoline was determined by GC (Shimadzu GC–14 B with Ultra ALLOY capillary column UA^+-1 of Frontier Laboratories Ltd., N_2) using *n*-dodecane as an internal standard. Typically, the error in the yield determined by GC was ±1.5%. To determine the isolated yield of 6-methyl-quinoline, 6-methyl-quinoline was isolated by column chromatography using silica gel 60 (spherical, 63–210 μm, Kanto Chemical Co. Ltd.) with hexane/ethylacetate (90/10) as the eluting solvent, followed by analyses by GC–MS and ^1H and ^{13}C NMR. The hydrogenation of quinoline was carried out by a stainless autoclave (28 cm^3) at 160 °C under 3 bar H_2.

2.4. NMR and GC–MS analysis

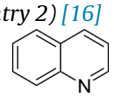
^1H and ^{13}C NMR spectra were recorded at ambient temperature by JEOL-ECX 600 operating at 600.17 and 150.92 MHz, respectively with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. All chemical shifts are reported relative to tetramethylsilane and *d*-solvent peaks (77.00 ppm, chloroform), respectively. Abbreviations used in the NMR experiments: s, singlet d, doublet; t, triplet; m, multiplet. GC–MS spectra were recorded by SHIMADZU QP2010.

2.4.1. 6-Methyl-quinoline (Table 3, entry 1) [18]



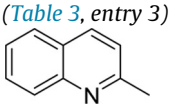
^1H NMR (600.17 MHz, $CDCl_3$), TMS: δ 8.51 (d, J = 2.70 Hz, 1H), 7.73 (d, J = 8.94 Hz, 1H), 7.54 (d, J = 7.56 Hz, 1H), 7.12 (d, J = 8.22 Hz, 1H), 7.05 (s, 1H), 6.98-6.87 (m, 1H), 2.09 (s, 3H); ^{13}C NMR (150.91 MHz, $CDCl_3$) δ 148.63, 146.11, 135.36, 134.39, 130.82, 128.27, 127.44, 125.79, 120.17, 20.66; MS m/e 143.07.

2.4.2. Quinoline (Table 3, entry 2) [16]



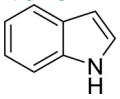
^1H NMR (600.17 MHz, $CDCl_3$), TMS: δ 8.89 (d, J = 2.76 Hz, 1H), 8.12-8.07 (m, 2H), 7.76 (d, J = 8.22 Hz, 1H), 7.68 (t, J = 7.56 Hz, 1H), 7.50 (t, J = 7.56 Hz, 1H), 7.33–7.32 (m, 1H); ^{13}C NMR (150.91 MHz, $CDCl_3$) δ 150.15, 148.02, 135.81, 129.22, 129.19, 128.03, 127.57, 126.30, 120.83; MS m/e 129.04.

2.4.3. 2-Methyl-quinoline (Table 3, entry 3) [23]



^1H NMR (600.17 MHz, $CDCl_3$), TMS: δ 8.03 (d, J = 8.28 Hz, 1H), 7.80 (d, J = 8.28 Hz, 1H), 7.59 (d, J = 7.56 Hz, 2H), 7.34 (t, J = 6.90 Hz, 1H), 7.05 (t, J = 6.18 Hz, 1H), 2.64 (s, 3H); ^{13}C NMR (150.91 MHz, $CDCl_3$) δ 158.13, 147.18, 135.35, 128.68, 127.95, 126.82, 125.77, 124.93, 121.22, 24.65; MS m/e 143.07.

2.4.4. Indole (Table 3, entry 4) [14]



^1H NMR (600.17 MHz, $CDCl_3$), TMS: δ 8.09 (s, NH, 1H), 7.65 (d, J = 8.28 Hz, 1H), 7.38 (d, J = 8.28 Hz, 1H), 7.19 (m, 2H), 7.12 (t, J = 7.20 Hz, 1H), 6.55 (s, 1H); ^{13}C NMR (150.91 MHz, $CDCl_3$) δ 135.74, 127.82, 124.10, 121.96, 120.71, 119.79, 111.00, 102.60; MS m/e 117.10.

3. Result and discussion

3.1. Catalyst characterization

Fig. 1 shows temperature programmed H_2-reduction (H_2-TPR) profile of $Pt(NH_3)_2(NO_3)_2$- loaded carbon as the precursor of Pt/C. The H_2-TPR profile shows H_2 consumption peaks below 250 °C assignable to the reduction of Pt(II) to metallic Pt. This indicates that the standard Pt/C catalyst pre-reduced at 300 °C contains metallic Pt. Fig. 2 shows a representative TEM image and Pt size distribution of Pt/C. The average diameter of Pt particles for 98 particles was 2.9 ± 0.8 nm, and the volume-area mean diameter of Pt particles was 3.5 ± 0.8 nm. The volume-area mean diameter (TEM analysis) was consistent with the mean diameter estimated by the CO adsorption experiment (3.2 nm) within the experimental error of TEM analysis, which supprted the TEM reults. Summarizing the above characterization results, we conclude that Pt species in the standard Pt/C catalyst are present as 3.5 nm sized Pt metal nanoparticles.

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