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Electronic effect of Na promotion for selective mono-*N*-alkylation of aniline with di-*iso*-propylamine by Pt/SiO_2 catalysts

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ABSTRACT

Sodium promoted 5 wt.% Pt/SiO_2 catalysts with similar Pt particle size (2.9–3.5 nm) but with different Na loadings (Na/Pt ratio of 0–10) were prepared by a sequential impregnation method. The catalysts were well characterized by Pt L_3-edge XAFS (X-ray absorption fine structure), X-ray photoelectron spectroscopy (XPS), infrared (IR) study of CO adsorption. Their catalytic activity for mono-*N*-alkylation of aniline with $i\mathrm{Pr}_2\mathrm{NH}$, as a test reaction for cross-coupling reaction of different amines, showed a volcano type dependence on the Na/Pt ratio. The catalyst with Na/Pt ratio of 2 showed the highest intrinsic activity. The Na/Pt ratio also affected the electronic states of the support oxide and Pt; the electron densities of Pt and surface oxygen atoms of support oxides increased with the Na/Pt ratio. From the structure–activity relationship, it is shown that the moderate electron densities of Pt and support oxygen atoms lead to the high catalytic activity. Kinetic studies suggest that the present reaction proceeds through a hydrogen-borrowing mechanism that begins with dehydrogenation of $i\mathrm{Pr}_2\mathrm{NH}$ as the rate-limiting step. Based on the mechanistic and structural results, origin of the promotional effect of Na on the catalytic activity of Pt/SiO_2 is discussed.

1. Introduction

Supported metal catalysts play an important role in many heterogeneous catalytic reactions for green organic synthesis. Recent advances in synthetic catalysis established that supported Au, Ru, Rh, Pd, and Ag catalysts catalyze one-pot multi-step organic reactions, which provides a key technology for the green synthesis of fine chemicals [1–4]. Supported Pt metal nanoparticles have been the most industrially relevant and widely investigated catalysts [5–15] and several successful examples have demonstrated Pt-catalyzed green organic reactions such as hydrogenation [5,6] and selective oxidation of alcohols and sugars [7,8]. However, their applications to multi-step one-pot organic synthesis are limited. For developing a new catalyst for the organic synthesis, a fine control of the electronic state of metal centers in organometallic catalysts has been one of the most important design concepts. In the case of supported metal catalysts, alkaline modifiers are widely used as promoters of platinum group metal catalysts for many reactions [9–18]. It is widely recognized that the electron density of a supported noble metal is increased by the addition of alkaline and alkaline earth metals [14–18]. Although fundamental studies on the alkali-promotion effects have been important topics in heterogeneous catalysis, previous studies have focused on conventional reactions such as hydrogenolysis [10,11], oxidation [12,17,18], water gas shift reaction [13], and hydrogenation [14–16]. On the basis of the previous reports by Yoshitake and Iwasawa [14–16] that Na addition on Pt/SiO_2 increased electron density of Pt, we hypothesized that Na-loaded Pt/SiO_2 is a suitable material to discuss the electronic effect on the activity of Pt nanoparticle catalysts for one-pot green organic synthesis.

Amines are intermediates and products of enormous importance for chemical and life science applications. Pd- and Cu-catalyzed aminations of aryl halides [19] and the transition-metal-catalyzed amination of alcohols [20,21] represent attractive approaches for the alkylation of amines. The transition-metal-catalyzed alkylation of amines by amines is an attractive alternative method of alkylamine synthesis [22,29]. The reaction proceeds thorough a hydrogen-borrowing (hydrogen auto-transfer) mechanism [20,22–25]. The process begins with the dehydrogenation of an alkylamine to the corresponding imine. The imine undergoes addition of another nucleophilic amine and elimination of ammonia to form an *N*-alkyl imine, which is hydrogenated by in situ formed hydride species to the secondary amine product. Beller's Ru complexes [23,24] and Williams's Ir complexes [25] are successful

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Table 1
List of catalysts.

Catalysts	Na/Pt ratio	T_{cal}/°C[a]	T_{H_2}/°C[b]	D_{CO}/nm[c]	D_{TEM}/nm[d]
Pt/SiO_2	0	550	500	2.9	3.3
$NaPt/SiO_2$-0.2	0.2	500	200	3.0	–
$NaPt/SiO_2$-1	1	–	400	3.5	2.6
$NaPt/SiO_2$-2	2	–	300	3.1	–
$NaPt/SiO_2$-5	5	–	200	3.2	–
$NaPt/SiO_2$-10	10	–	200	3.3	2.4

[a] Temperatures of calcination.
[b] Temperatures of reduction in H_2.
[c] Average particle size of Pt estimated by CO adsorption experiment.
[d] Average particle size of Pt estimated by TEM.

catalytic systems for selective amine cross-coupling of different amines, leaving ammonia as the only by-product. From the environmental and economic viewpoints, it is preferable to accomplish the selective cross-coupling reaction using heterogeneous catalysts. Previous examples of Pt- and Pd-based heterogeneous systems for amine cross-coupling suffer from low selectivity for cross-coupling of different amines [26], reusability, low turnover number (TON), and need of stoichiometric amount of additives [29] or special reaction methods (microwave heating [29,30], electrocatalysis [27], photocatalysis [28]). In this paper, we found that Na-loaded Pt/SiO_2 showed higher turnover frequency (TOF), defined as the activity per unit of exposed metal surface, than Pt/SiO_2. Combined with various characterization results, the promoting effect of Na is discussed in terms of the support ionicity (electron density of support oxygen) and electron density of Pt, and a catalyst design concept is proposed.

2. Experimental

Commercially available organic compounds (from Tokyo Chemical Industry or Kishida Chemical) were used without further purification. The GC (Shimadzu GC-14B) and GCMS (Shimadzu GCMS-QP5000) analyses were carried out with a Rtx-65 capillary column (Shimadzu) using nitrogen as the carrier gas.

SiO_2-supported Pt (Pt/SiO_2 with Pt loading of 5 wt.%) was prepared by impregnating SiO_2 (Q-10, 300 $m^2\,g^{-1}$, supplied from Fuji Silysia Chemical Ltd.) with an aqueous HNO_3 solution of $Pt(NH_3)_2(NO_3)_2$ (Tanaka Kikinzoku), followed by evaporation to dryness at 80 °C, drying at 120 °C for 12 h, calcination in air at 500 °C, and reduction in a flow of 100% H_2 at 550 °C for 10 min. Sodium-loaded Pt/SiO_2 catalysts were prepared by impregnating Pt/SiO_2 with aqueous solution of $NaNO_3$, followed by evaporation to dryness at 80 °C, drying at 120 °C for 12 h, and reduction in a flow of H_2 for 10 min. To prepare a series of catalyst with different Na/Pt ratios but with similar Pt particle size, temperatures of reduction (T_{H_2}) were changed as summarized in Table 1. The catalysts are designated as $NaPt/SiO_2$-*x*, where *x* is the Na/Pt ratio. $NaPt/SiO_2$-2 was used as a standard catalyst.

The number of surface Pt atom in the Pt catalysts, pre-reduced in H_2 at 200 °C, was estimated with the CO uptake of the samples using the pulse-adsorption of CO in a flow of He. The average particle size was calculated from the CO uptake assuming that CO was adsorbed on the surface of semi-spherical Pt particles at CO/(surface Pt atom) = 1/1 stoichiometry.

Pt L_3-edge in situ XAFS measurement was carried out at BL01B1 of SPring-8 (Hyogo, Japan). The storage ring energy was operated at 8 GeV with a typical current of 100 mA. A self-supported wafer form (pressed pellet) of the pre-reduced Pt catalyst with 10 mm diameter was placed in a quartz in situ cell in a flow of 100% H_2 (100 $cm^3\,min^{-1}$) for 10 min at 200 °C under atmospheric pressure, and the sample was cooled to 40 °C under a flow of He, then the spectra were recorded in situ. The analyses of the extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structures (XANES) were performed using the REX version 2.5 program (RIGAKU). For EXAFS analysis, the spectra were extracted by utilizing the cubic spline method and normalized to the edge height. The Fourier transformation of the k^3-weighted EXAFS from *k* pace to *R* space was carried out over the *k* range 3.3–14.3 Å^{-1} to obtain a radial distribution function. The inversely Fourier filtered data (in the *R* range of 1.5–3.3 Å) were analyzed with a usual curve fitting method in the *k* range of 3.3–14.3 Å^{-1} using the empirical phase shift and amplitude functions for Pt–Pt and Pt–O shells extracted from the data for Pt foil and PtO_2, respectively. During the fitting procedure the absorber–scatterer distances, Debye–Waller factors or the coordination numbers were refined using a least squares refinement procedure.

Transmission electron microscopy (TEM) measurements were investigated using a JEOL JEM-2100F TEM operated at 200 kV.

The X-ray photoelectron spectroscopy (XPS) measurements were carried out using a JEOL JPS-900MC with Al Kα anode operated at 20 W and 10 kV. The oxygen 1s core electron levels in support oxides were recorded. Binding energies were calibrated with respect to C 1s at 285.0 eV.

In situ FTIR spectra were recorded at room temperature on a JASCO FT/IR-620 equipped with a quartz IR cell connected to a conventional flow reaction system. The sample was pressed into a 10 mg of self-supporting wafer and mounted into the quartz IR cell with CaF_2 windows. Spectra were measured accumulating 15 scans at a resolution of 4 cm^{-1}. A reference spectrum of the catalyst wafer in He was subtracted from each spectrum. Prior to each experiment the catalyst disk was heated in H_2 (2%)/He flow (100 $cm^3\,min^{-1}$) at temperatures shown in Table 1 for 10 min, followed by cooling to room temperature under He flow. Then, the catalyst was exposed to a flow of CO (0.9%)/He for 180 s.

$NaPt/SiO_2$-2 (1 mol.% Pt with respect to aniline) were added to the mixture of aniline (1.0 mmol), di-*iso*-propylamine (2.0 mmol) and *o*-xylene (2 mL) in a reaction vessel equipped with a condenser and N_2 was filled. Note that the aniline/di-*iso*-propylamine ratio of 2 was adopted because the reaction rate increased with the ratio as shown in Fig. 5. The resulting mixture was vigorously stirred under reflux condition (heating temperature = 155 °C) for 4 h. The reaction mixture was analyzed by GC. Conversion of aniline and yields of products were determined by GC using *n*-dodecane as an internal standard.

3. Results and discussion

3.1. Characterization

X-ray diffraction (XRD) pattern of $NaPt/SiO_2$-*x* (*x* = 0, 0.2, 1, 2, 5, 10) catalysts showed lines assignable to Pt metal (not shown). The number of surface metallic Pt atoms in these catalysts was estimated by the CO adsorption method, and the average size of metallic Pt particles was estimated by assuming that CO was adsorbed on the surface of semi-spherical Pt particles at CO/(surface Pt atom) = 1/1 stoichiometry. As summarized in Table 1, the Pt particle sizes, which did not markedly depend on the Na/Pt ratio, were in a range of 2.9–3.5 nm. The average Pt particle size of selected samples, $NaPt/SiO_2$-*x* (*x* = 0, 1, 10), was estimated from TEM analysis. As listed in Table 1, the particle size of these samples did not markedly depend on the Na/Pt ratio, but slightly decreased with the Na/Pt ratio. The Pt particle sizes from TEM (2.4–3.3 nm) were approximately close to those from CO adsorption. However, it should be noted that the particle size for Pt/SiO_2 from TEM (3.3 nm) is slightly larger than that from CO adsorption (2.9 nm), while those for $NaPt/SiO_2$-1 (2.6 nm) and $NaPt/SiO_2$-10 (2.4 nm) from TEM are slightly smaller than those from CO adsorption (3.5 and 3.3 nm). Considering a generally observed tendency that the