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# Sulfur promoted Pt/SiO<sub>2</sub> catalyzed cross-coupling of anilines and amines

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# ABSTRACT

Pt/SiO<sub>2</sub> (Pt = 5 wt%) catalysts with average Pt particle size of 3.3 and 6.8 nm and sulfur-loaded Pt/SiO<sub>2</sub> (S/Pt ratio = 0.1 and 0.13; Pt size = 5.2 and 5.5 nm), prepared by adding ammonium sulfate on Pt/SiO<sub>2</sub> followed by H<sub>2</sub>-reduction at 500 °C, are tested for mono-*N*-alkylation of aniline with di-*iso*-propylamine. The turnover frequency (TOF), defined as the reaction rate per number of surface Pt species, increases with sulfur loading. The catalyst with S/Pt ratio of 0.13 shows more than 5 times higher TOF than unmodified catalysts, and it acts as effective and recyclable catalyst for cross-coupling of various anilines and amines. Combined with kinetic results and characterizations, XAFS (X-ray absorption fine structure), TEM, and CO adsorption IR, a possible reason for the promotion effect of sulfur species (probably sulfidic species) is discussed.

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## 1. Introduction

Pt catalyst has been the most industrially relevant and widely investigated catalysts [1-13]. Recent reports demonstrated some Pt-catalyzed green organic reactions such as selective oxidation [1–3], hydrogenation [4,5] and hydrogenolysis [6]. However, their application to multi-step one-pot organic synthesis is limited. Sulfur is widely recognized as a poison of metallic Pt catalysts for many reactions. Under reducing conditions the presence of sulfur in general decreases the catalytic activity. There are a few reports of promotional effects of sulfur species on Pt catalysts [7-13]. These examples are based on the promotion effects of sulfate species on the activity of Pt catalysts for hydroisomerization of alkanes and combustion of hydrocarbons. For the former system, Hattori and co-workers have established that sulfate species play an important role in the formation of the molecular hydrogen-originated protonic acid site. For the latter system, the formation of acidic site at the Pt/support/sulfate interface is suggested to be important [10]. However, to the best of our knowledge, positive effects of sulfur species on Pt metal catalyzed multistep organic synthesis were not reported.

Amines are intermediates and products of enormous importance for chemical and life science applications. In addition to the well established Pd-catalyzed aminations of aryl halides [14] and the metal-catalyzed amination of alcohols [15,16], the transition-metal-catalyzed alkylation of amines by amines is an attractive alternative method of alkylamine synthesis [15-29]. The reaction proceeds thorough a hydrogen-borrowing (hydrogen auto-transfer) mechanism [15-21]. 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-alkvl imine, which is hvdrogenated by in situ formed hydride species to the secondary amine product. Ru [18,19] and Ir [20] complexes are successful 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 reusable heterogeneous catalysts. There are many reports of heterogeneous catalysis for cross-coupling [16,17,21-24] or self-coupling [25-28] of amines. However, previous examples of cross-coupling reactions suffer from reusability [17], low turnover number (TON), and need of stoichiometric amount of additives [21] or special reaction methods (microwave heating [21,22], electrocatalysis [23], photocatalysis [24]). Recently, we reported that Pt nanocluster-loaded  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Pt/Al<sub>2</sub>O<sub>3</sub>) was effective for mono-N-alkylation of amines with different amines [29]. In this paper, we found that S-loaded Pt/SiO<sub>2</sub> showed higher TOF (per number of surface Pt) than Pt/SiO<sub>2</sub> and Pt/Al<sub>2</sub>O<sub>3</sub>. Kinetic and structural studies are carried out to discuss a possible reason of the promotion effect of sulfur.

# 2. Experimental

Commercially available organic compounds (from Tokyo Chemical Industry or Kishida Chemical) were used without further purification. The GC (Shimadzu GC-14B) and GC-MS (Shimadzu

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Tal	ole	1

Catalysts	S/Pt (precursor) <sup>a</sup>	S/Pt (ICP) <sup>b</sup>	$T_{\rm cal}/^{\circ}{\rm C}^{\rm c}$	D/nm <sup>d</sup>
Pt/SiO <sub>2</sub> -550 Pt/SiO <sub>2</sub> -600	0 0		550 600	$\begin{array}{c} 3.3 \pm 1.5 \\ 6.8 \pm 3.0 \end{array}$
SPt/SiO <sub>2</sub> -0.10 SPt/SiO <sub>2</sub> -0.13	1 5	0.10 0.13	-	$\begin{array}{c} 5.2  \pm  2.4 \\ 5.5  \pm  3.2 \end{array}$

 $^a$  S/Pt molar ratio in the catalyst precursors prepared by impregnation of  $(\rm NH_4)_2SO_4$  to Pt/SiO\_2.

 $^{\rm b}\,$  S/Pt molar ratio in the catalysts after calcination and H\_2-reduction of the precursors.

<sup>c</sup> Temperatures of calcination.

<sup>d</sup> Average particle size of Pt estimated by TEM.

GCMS-QP5000) analyses were carried out with a Rtx-65 capillary column (Shimadzu) using nitrogen as the carrier gas.

SiO<sub>2</sub>-supported Pt (Pt/SiO<sub>2</sub> with Pt loading of 5 wt%) was prepared by impregnating SiO<sub>2</sub> (Q-10,  $300 \text{ m}^2 \text{ g}^{-1}$ , supplied from Fuji Silysia Chemical Ltd.) with an aqueous HNO<sub>3</sub> solution of Pt(NH<sub>3</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> (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. This sample is named Pt/SiO<sub>2</sub>-550. The sample named Pt/SiO<sub>2</sub>-600 was prepared by the similar method and reduced in H<sub>2</sub> at 600 °C for 10 min. Sulfur-loaded Pt/SiO<sub>2</sub> catalysts were prepared by impregnating Pt/SiO<sub>2</sub>-550 with aqueous solution of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, followed by evaporation to dryness at 80°C, drying at 120°C for 12 h, and reduction in a flow of 100% H<sub>2</sub> at 500 °C for 10 min. Table 1 includes the relative amount of  $(NH_4)_2SO_4$  in the solution to that of Pt atoms in Pt/SiO<sub>2</sub> and the S/Pt ratio of the catalyst after the H<sub>2</sub>-reduction at 500 °C determined by ICP analysis. The catalysts are designated as SPt/SiO<sub>2</sub>-*x*, where *x* is the S/Pt ratio. SPt/SiO<sub>2</sub>-0.13 is used as a standard catalyst.

XRD patterns of the powdered catalysts were recorded with a Rigaku MiniFlex II/AP diffractometer with Cu K $\alpha$  radiation. Transmission electron microscopy (TEM) measurements were carried out using a JEOL JEM-2100F TEM operated at 200 kV.

In situ IR 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. Samples were pressed into a 22 mg of self-supporting wafer and mounted into the quartz IR cell with CaF<sub>2</sub> windows, and the spectrum was measured at room temperature in He flow accumulating 15 scans at a resolution of 4 cm<sup>-1</sup>. For the CO adsorption IR experiments, 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<sub>2</sub>(2%)/He flow (100 cm<sup>3</sup> min<sup>-1</sup>) at 500 °C 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.

Pt L<sub>3</sub>-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<sub>2</sub> (100 cm<sup>3</sup> min<sup>-1</sup>) for 30 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). The Fourier transformation of the  $k^3$ -weighted EXAFS from k space to R space was carried out over the k range 3–15 Å<sup>-1</sup> 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 3.3–14.7 Å<sup>-1</sup> using the empirical phase shift and amplitude functions for Pt-Pt and Pt-O shells extracted from the data for Pt foil and PtO<sub>2</sub>, respectively.

#### Table 2

Curve-fitting analysis of Pt L<sub>3</sub>-edge in situ EXAFS.

Sample	Shell	N <sup>a</sup>	R/Å <sup>b</sup>	$\sigma/{ m \AA^c}$	$R_{\rm f}/\%^{\rm d}$
SPt/SiO <sub>2</sub> -0.13	Pt	9.6	2.74	0.088	2.6
Pt/SiO <sub>2</sub> -550	Pt	10.6	2.75	0.083	0.9

<sup>a</sup> Coordination numbers.

<sup>b</sup> Bond distance.

<sup>c</sup> Debye-Waller factor.

<sup>d</sup> Residual factor.

In a typical catalytic test, SPt/SiO<sub>2</sub>-0.13 (1 mol% Pt with respect to aniline) was 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<sub>2</sub> was filled. The resulting mixture was vigorously stirred under reflux condition (heating temperature = 155 °C) for 4 h. Products were identified with GC–MS and <sup>1</sup>H NMR [29]. 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

Pt/SiO<sub>2</sub>-550 (as a precursor of S-loaded catalysts), Pt/SiO<sub>2</sub>-600, and SPt/SiO<sub>2</sub>-x (x=0.1, 0.13) were characterized by various spectroscopic methods. The S/Pt ratio of the catalyst was determined by ICP analysis as listed in Table 1. XRD pattern of these samples showed lines due to Pt metal. TEM measurements of these samples were carried out, and the particle size analysis was conducted on 98–124 particles. The size distribution of Pt/SiO<sub>2</sub> samples and SPt/SiO<sub>2</sub>-0.13 are illustrated in Fig. 1. As listed in Table 1, the average particle size of SPt/SiO<sub>2</sub>-x (x=0.1, 0.13) and Pt/SiO<sub>2</sub>-600 are in a range 5.2–6.8 nm. Pt/SiO<sub>2</sub>-550 has a relatively smaller Pt size (3.3 nm).

Fig. 2A shows  $k^3$ -weighted in situ extended X-ray absorption fine structure (EXAFS) data of SPt/SiO<sub>2</sub>-0.13 acquired at room temperature in a flow of He after H<sub>2</sub>-reduction at 200 °C. The Pt-Pt coordination number and the distance are determined by curvefitting analysis and are listed in Table 2. The EXAFS consists of a Pt-Pt contribution with coordination number of 9.6 at bond distance of 2.74 Å. These values are not markedly different from those of Pt/SiO<sub>2</sub>-550: Pt-Pt coordination number of 10.6 at bond distance of 2.75 Å. This indicates that the presence of sulfur species on Pt/SiO<sub>2</sub> does not change the bulk structure of metallic Pt. The EXAFS result showed no Pt-S bond in the SPt/SiO<sub>2</sub>-0.13 sample. In the IR spectrum of the unreduced precursor, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>-loaded Pt/SiO<sub>2</sub>-550 with S/Pt ratio of 5, a band due to sulfate species  $(1420 \text{ cm}^{-1})$ was observed (result not shown). This band was not observed for the H<sub>2</sub>-reduced sample, SPt/SiO<sub>2</sub>-0.13. Taking into account the fact that the catalyst exhibits the S/Pt ratio of 0.13 (ICP result in Table 1), it is reasonable to assume that sulfidic sulfur species are present on the catalyst and some of them may present on the surface of Pt.

As shown in Table 2, the coordination number for the Pt–Pt bond in  $Pt/SiO_2-550$  (10.6) was larger than that of  $SPt/SiO_2-0.13$  (9.6). On the other hand, the Pt particle size of  $Pt/SiO_2-550$  (3.3 nm) was smaller than that of  $SPt/SiO_2-0.13$  (5.2 nm). Assuming that the shape of Pt particle does not depend on the presence of sulfur, it is likely that EXAFS data is not consistent with the average size of Pt particles measured by TEM. This inconsistency might be explained as follows. Some of the sulfur species in  $SPt/SiO_2-0.13$  interact strongly with Pt surface, which results in an increased disorder in the local structure of the Pt metals.

Fig. 2B shows in situ X-ray absorption near-edge structures (XANES) for SPt/SiO<sub>2</sub>-0.13. It is clear that the XANES spectrum of SPt/SiO<sub>2</sub>-0.13 is nearly identical to that of Pt/SiO<sub>2</sub>-550, which



Fig. 1. Particle size distribution of from TEM analysis.



Fig. 2. In situ Pt L<sub>3</sub>-edge (A) EXAFS and (B) XANES spectra of (dashed lines) Pt/SiO<sub>2</sub>-550 and (solid lines) SPt/SiO<sub>2</sub>-0.13 recorded under He at 40 °C after flowing H<sub>2</sub> at 200 °C for 10 min.

indicates that the presence of S on  $Pt/SiO_2$  does not change the bulk electronic state of metallic Pt.

XANES reflects the average oxidation states of Pt located at bulk and surface of metal particles. IR spectroscopy with CO as a probe molecule allows monitoring of the changes in the electronic states of surface Pt. Fig. 3 shows IR spectra of CO adsorbed on the Pt catalysts in a region characteristic to linearly coordinated CO on metallic Pt (2100–2000 cm<sup>-1</sup>). It is widely recognized that the wavenumber of the band due to the linear CO adspecies increases with an increase in the electron deficiency of the metal. The result showed that the addition of S did not markedly change the wavenumber of the maximum intensity; the wavenumber for SPt/SiO<sub>2</sub>-0.13 (2085 cm<sup>-1</sup>) is in between those of Pt/SiO<sub>2</sub>-550 (2090 cm<sup>-1</sup>) and Pt/SiO<sub>2</sub>-600 (2078 cm<sup>-1</sup>). This suggests that the addition of S does not change the surface electronic state of Pt.

#### 3.2. Catalytic and kinetic studies

*N*-Alkylation of aniline (**1**) with 2 equivalent of di-*iso*propylamine (**2**),  $iPr_2NH$ , in  $N_2$  atmosphere was chosen as a test reaction of cross-coupling reaction of amines. Fig. 4 shows changes in the yields of the unreacted aniline **1**, an imine intermediate (isopropylidene-phenylamine **4**) and *N*-isopropylaniline (**3**) as a desired hydrogenated product, which can be produced by



reduction of 4. The S-doped catalyst, SPt/SiO<sub>2</sub>-0.13, gave 100% con-

version of 1, 98% yield of the desired amine 3 and low yield of the

byproduct **4** (2%) after 4 h (entry 1 in Table 3), corresponding to the turnover frequency (TOF) of  $24.5 \text{ h}^{-1}$  based on the total num-

ber of Pt atoms in the catalyst. This value is higher than that of





Fig. 4. Yields of (▽) unreacted 1, (○) *N*-isopropylaniline 3 and (●) isopropylidene-phenylamine 4 for the reaction of aniline with *i*Pr<sub>2</sub>NH vs. reaction time.

homogeneous Ir catalyst (TOF =  $9.8 h^{-1}$ ) [20] for the same reaction at the same temperature. This demonstrates a highly efficient feature of the present catalytic system. In contrast, the unmodified catalysts (Pt/SiO<sub>2</sub>-550, Pt/SiO<sub>2</sub>-600) showed lower **1** conversion and **3** yield than SPt/SiO<sub>2</sub>-0.13 but higher yield of the imine intermediate **4**. After the reaction, the SPt/SiO<sub>2</sub>-0.13 catalyst was easily separated from the reaction mixture by centrifugation. The separated catalyst was washed with acetone (5 mL), followed by drying at 200 °C for 1 h, and by reducing in H<sub>2</sub> at 500 °C for 10 min. Then, the reused catalyst showed 90% yield of **3** (entry 2 in Table 3). To study the scope and limitation of the present reaction by SPt/SiO<sub>2</sub>-0.13, the alkylation of anilines with various aliphatic amines were tested (Table 3). Secondary (entries 1 and 3) and primary amines (entries 4–6) acted as effective amine donor. For example, the reaction of aniline 1 with a secondary amine, di-*sec*-butylamine (entry 3), lead to the formation of the corresponding *N*-alkylated amine in high yield (95%). However, the reaction of 1 with a primary amine, *iP*rNH<sub>2</sub> (entry 6) gave lower yield (49%) than the standard reaction of 1 with *i*Pr<sub>2</sub>NH (entry 1). The amination of the aniline derivative with a

# Table 3

NH<sub>2</sub>

N-Alkylation of aniline with various amines.

RNH<sub>2</sub>, SPt/SiO<sub>2</sub>-0.13 (1mol%)

Entry	Amine substrate	Amine donor	Product	Yield/% <sup>a</sup>
1	NH <sub>2</sub>	↓ ↓ H	ſ N Y	98
2 <sup>b</sup> 3				90 95
4		NH <sub>2</sub>		97
5		NH <sub>2</sub>		75
6	NH <sub>2</sub>	NH <sub>2</sub>	₩ ,	49
7	H <sub>2</sub> N	NH <sub>2</sub>		87

<sup>a</sup> Yields of product determined by GC are based on aniline.

<sup>b</sup> Reaction by the reused catalyst after entry 1.



Scheme 1. Proposed mechanism of Pt-catalyzed alkylation of aniline with *i*Pr<sub>2</sub>NH.

sterically hindered substituent at *ortho* position was also successful (entry 7).

As previously postulated in the literature [17–20], it is most probable that the amine cross-coupling reaction proceeds through the hydrogen borrowing pathway (Scheme 1), in which the reaction is initiated by a temporary removal of hydrogen from  $iPr_2NH 2$ to generate imine 2' and Pt-H species. The following kinetic results give further evidences on the mechanism of the Pt-catalyzed Nalkylation of aniline 1 with *i*Pr<sub>2</sub>NH 2. As shown in Fig. 4, a typical time-conversion profile of the consecutive reaction was observed for the reaction by SPt/SiO<sub>2</sub>-0.13; the imine intermediate 4, formed at an initial period, was consumed, and then the yield of the hydrogenated product **3** increased with time. This indicates that *N*-isopropylaniline **3** is produced through a consecutive pathway via the *N*-alkylimine **4**. Since the reaction was performed under N<sub>2</sub>, it is reasonable to assume that imine **4** is hydrogenated by hydrogen species formed by the dehydrogenation of iPr<sub>2</sub>NH. iPrNH<sub>2</sub> formed as a byproduct could be dehydrogenated by Pt sites and could act as an alkylating agent. However, considering the result that *i*PrNH<sub>2</sub> shows lower reactivity than *i*Pr<sub>2</sub>NH (Table 3), the reaction of 1 with *i*PrNH<sub>2</sub> should be the minor root in the reaction of **1** with *i*Pr<sub>2</sub>NH. The effect of reactant concentration on the activity was tested for SPt/SiO<sub>2</sub>-0.13 and Pt/SiO<sub>2</sub>-550. In Fig. 5, the reaction rates are plotted as a function of the initial concentration of *i*Pr<sub>2</sub>NH and aniline. The rate dependence on the *i*Pr<sub>2</sub>NH concentration (Fig. 5A) showed the reaction order (n) of 0.91 and 2.0 for SPt/SiO<sub>2</sub>-0.13 and Pt/SiO<sub>2</sub>-550, respectively. The reaction orders with respect to *i*Pr<sub>2</sub>NH (Fig. 5A) are higher than the reaction orders with respect to



**Fig. 6.** ( $\bigcirc$ ) TOF based on the number of surface Pt atom vs. S/Pt ratio in Pt/SiO<sub>2</sub>-600, SPt/SiO<sub>2</sub>-0.10, and SPt/SiO<sub>2</sub>-0.13. Closed triangle ( $\blacktriangle$ ) denotes TOF for Pt/SiO<sub>2</sub>-550.

aniline (Fig. 5B), which suggests that  $iPr_2NH$  is involved in a ratelimiting step and aniline is not involved in the rate-limiting step for both catalysts. The results also rule out a possibility that hydrogenation of imine **4** by Pt–H species is the rate-limiting step. The result in Fig. 5A shows that the addition of S decreases the reaction orders with respect to  $iPr_2NH$ . This indicates that sulfur species promote the rate-limiting  $iPr_2NH$  dehydrogenation step.

To quantify the effect of S-addition on the activity, the rate of **3** formation was measured under the condition where conversion of 1 was below 40%, and TOF per surface Pt species was calculated using the number of surface Pt atom (from TEM results) and the reaction rate. The TOF is plotted as a function of the S/Pt ratio in Fig. 6. For the SPt/SiO<sub>2</sub>-x (x = 0.1, 0.13) catalysts with different S/Pt ratio but with the same Pt loading (5 wt%) and similar Pt particle size (Table 1), TOF increased with S/Pt ratio. SPt/SiO<sub>2</sub>-0.13 showed more than 5 times higher TOF than the undoped Pt/SiO<sub>2</sub> catalysts. It is important to note that the TOF SPt/SiO<sub>2</sub>-0.13 (256  $h^{-1}$ ) is higher than that of  $Pt/Al_2O_3$  (101 h<sup>-1</sup>) shown in our recent report [29]. Combined with the XANES and EXAFS results that the addition of S does not essentially change the structure and electronic state Pt species, a possible reason of the enhanced catalytic activity may be a cooperation of sulfur and Pt species in the *i*Pr<sub>2</sub>NH dehydrogenation step as the rate-limiting step of the catalytic cycle.



**Fig. 5.** Formation rate of **3** (as a function of the concentration of (A)  $iPr_2NH$  and (B) aniline for the reaction of aniline with  $iPr_2NH$  by ( $\triangle$ , dashed lines)  $Pt/SiO_2$ -550 and ( $\bigcirc$ , solid lines)  $SPt/SiO_2$ -0.13.

# 4. Conclusions

Sulfur-promoted 5 wt% Pt/SiO<sub>2</sub> catalysts with similar Pt particle size but with different S loading (S/Pt ratio of 0, 0.1, 0.13) were prepared by a loading of ammonium sulfate on Pt/SiO<sub>2</sub>, followed by H<sub>2</sub>-reduction. It was found that the catalytic activity (TOF per surface Pt) for *N*-alkylation of aniline with *i*Pr<sub>2</sub>NH was linearly increased with sulfur loading, and the catalyst with S/Pt ratio of 0.13 showed more than 5 times higher TOF than undoped Pt/SiO<sub>2</sub> catalysts. Spectroscopic studies show that sulfur species does not change the structure and electronic states of Pt. Kinetic studies suggested that the present reaction proceeds through the hydrogen borrowing pathway. A possible reason of the sulfur-promoted catalytic activity may be a cooperation of sulfur and Pt species in the *i*Pr<sub>2</sub>NH dehydrogenation step as the rate-limiting step of the catalytic cycle.

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