

## Selective cross-coupling of amines by alumina-supported palladium nanocluster catalysts

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### 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.

Pd/C (Pd = 5 wt%) was purchased from Kawaken Fine Chemicals. Pd black and PdO were purchased from Mitsuwa Chemical.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (with surface area of 124 m<sup>2</sup> g<sup>-1</sup>) was prepared by calcination of  $\gamma$ -AlOOH (Catapal B Alumina purchased from Sasol) at 900 °C for 3 h. CeO<sub>2</sub> (140 m<sup>2</sup> g<sup>-1</sup>) was purchased from Rhodia Electronics Catalysis. MgO (JRC-MGO-3, 19 m<sup>2</sup> g<sup>-1</sup>) was supplied from Catalysis Society of Japan. SiO<sub>2</sub> (Q-10, 300 m<sup>2</sup> g<sup>-1</sup>) was supplied from Fuji Silysia Chemical Ltd. ZrO<sub>2</sub> (60 m<sup>2</sup> g<sup>-1</sup>) was prepared by hydrolysis of zirconium oxynitrate 2-hydrate in distilled water by gradually adding an aqueous NH<sub>4</sub>OH solution (1.0 mol dm<sup>-3</sup>), filtration of precipitate, washing with distilled water three times, drying at 100 °C, and calcining at 500 °C.

Metal oxide-supported Pd catalysts (1 or 5 wt% Pd) were prepared by impregnating metal oxide with aqueous HNO<sub>3</sub> solution of Pd(NO<sub>3</sub>)<sub>2</sub>, followed by evaporation to dryness at 80 °C, drying at 120 °C for 12 h, calcination in air for 1 h, and reduction in H<sub>2</sub> for 0.5 h. Metal(M) loaded  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (M= Rh, Pd, Pt, Ag) catalysts were prepared by the impregnating method using the following metal sources: aqueous HNO<sub>3</sub> solution of Rh(NO<sub>3</sub>)<sub>3</sub>, Pd(NO<sub>3</sub>)<sub>2</sub> and Pt(NH<sub>3</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>, aqueous solution of silver nitrates or ruthenium chloride. To control the metal particle size, temperatures of calcination ( $T_{\text{cal}}$ ) and reduction ( $T_{\text{H}_2}$ ) were changed as summarized in Table 1. The catalysts are designated as Mx/Al<sub>2</sub>O<sub>3</sub>-D, where x is the metal content (wt%) and D is the metal particle sizes (nm). Pd1/Al<sub>2</sub>O<sub>3</sub>-1.8 was used as a standard catalyst.

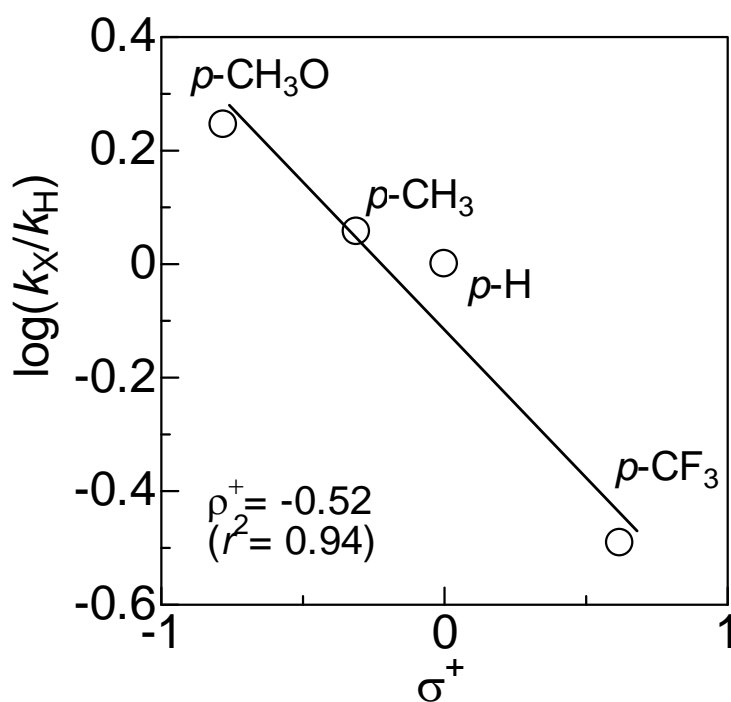
The number of surface metal atom in Pt, Pd, Rh, and Ru catalysts, pre-reduced in H<sub>2</sub> at 200 °C, were estimated with the CO uptake of the samples using the pulse-adsorption of CO in a flow of He at room temperature. CO adsorption experiments for the Pd loaded basic oxides (MgO and CeO<sub>2</sub>) were carried out at -78 °C. The average particle size was calculated from the CO uptake assuming that CO was adsorbed on the surface of spherical Pt particles at CO/(surface Pt atom) = 1/1 stoichiometry.

X-Ray diffraction (XRD) patterns of the powdered catalysts were recorded with a Rigaku

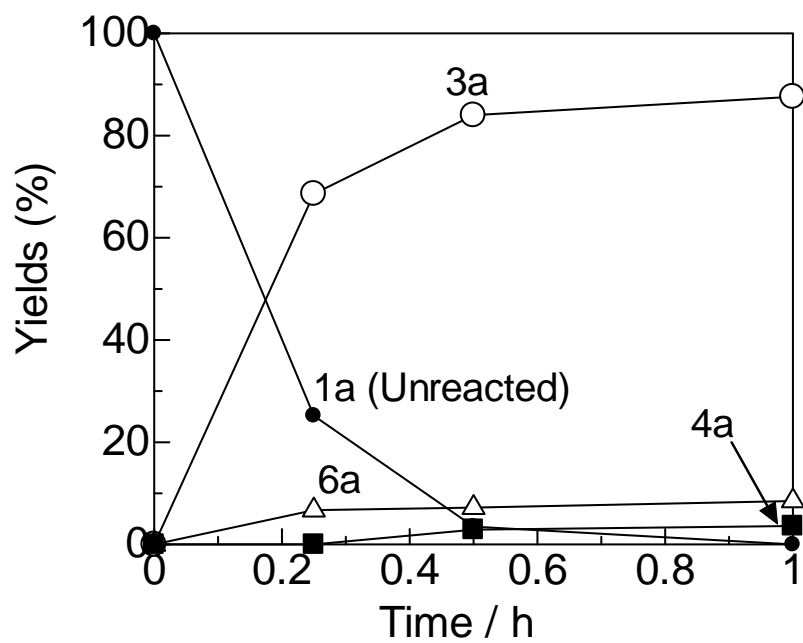
MiniFlex II/AP diffractometer with Cu K $\alpha$  radiation. Average metal particle size was calculated from the half-width of the peak from the XRD pattern using Scherrer equation.

The X-ray photoelectron spectroscopy (XPS) measurements were carried out using a JEOL JPS-900MC with AlK $\alpha$  anode operated at 20 mA and 10 kV. The oxygen 1s core electron levels in support oxides were recorded. Binding energies were calibrated with respect to C<sub>1s</sub> at 285.0 eV.

Pd1/Al<sub>2</sub>O<sub>3</sub>-1.8 (1 mol% Pd with respect to benzyl amine) were added to the mixture of benzyl amine (1.0 mmol), cyclic amines (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 1 h. The reaction mixture was analyzed by GC (Rtx-65 capillary column, 30 m). Conversion of aniline and yields of products were determined by GC using *n*-dodecane as an internal standard.



**Fig. S1.** Brown–Okamoto plot for the reaction of **2a** with *p*-substituted benzyl amines by Pd1/Al<sub>2</sub>O<sub>3</sub>-1.8. Reaction conditions are shown in Table 2.



**Fig. S2.** Time course of the yields of **1a**, **3a**, **4a** and **6a** for the reaction of **1a** with **2a** by Pd1/Al<sub>2</sub>O<sub>3</sub>-1.8 (Table 2, entry 1).