Supporting Information

Highly Efficient Aerobic Oxidation of Various Amines Using Pd$_3$Pb Intermetallic Compound Catalysts

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Experimental procedures

Catalyst preparation

Pd/SiO₂ (Pd: 3 wt%) was prepared by a pore-filling impregnation. Palladium nitrate solution was added to dried SiO₂, where the solution just filled the pores of the silica gel. The mixture was kept overnight at room temperature and then dried on a boiling water bath with stirring. The sample was calcined in a dry air atmosphere at 403 K for 6 h followed by 600°C for 4 h. The calcined sample was then reduced in a quartz reactor with hydrogen flow (60 ml min⁻¹) at 600°C for 2 h. Intermetallic catalysts, PdₓMᵧ/SiO₂ (M = Bi, Cu, Fe, Ga, In, Pb, Sb, Sn and Zn), were prepared by a successive impregnation with Pd/SiO₂. A solution of second metal precursor was added to the reduced Pd/SiO₂ to achieve the desired molar ratio of x : y. The sample was then dried followed by reduction under hydrogen flow (60 ml min⁻¹) at 400–800°C for 2 h. Other monometallic Pd catalysts for optimization of support (Pd/TiO₂, Pd/Al₂O₃ and Pd/MgO, Pd: 3 wt%, respectively) were prepared by a simple impregnation. Aqueous solution of (NH₄)₂PdCl₄ was added dropwise to a vigorously stirred aqueous slurry of alumina. After a stirring for 15 min in the air, the slurry was completely dried over a hot plate followed by grinding to a fine powder. The sample was then reduced in a quartz reactor with hydrogen flow (50 ml min⁻¹) at 823 K for 1 h. The corresponding intermetallic PdₓPb catalysts (PdₓPb/TiO₂, PdₓPb/Al₂O₃ and PdₓPb/MgO, Pd: 3 wt%, respectively) were prepared by coin-impregnation using mixed solution of (NH₄)₂PdCl₄ and Pb(NO₃)₂ (3:1 molar ratio) in a similar manner to the procedure for the monometallic catalysts. The reduction temperature for each support was adjusted so that the formed intermetallic particles were uniform in size (TiO₂; 450°C, Al₂O₃; 600°C and MgO; 600°C). Liquid phase reduction using LiBH₄ as a reducing agent was employed to prepare nano-PdₓPb/Al₂O₃. As-impregnated PdₓPb/Al₂O₃ (300 mg) was put into a three-necked round bottom flask with a silicone rubber septum. The sample was pre-heated under Ar (20 mL min⁻¹) at 150°C for 0.5 h to remove adsorbed water molecules. After the pretreatment, the flask was cooled to room temperature and quickly equipped with a reflux condenser under a temporary flush of Ar. Dehydrated THF (10 mL) was then added into the flask through the septum followed by stirring and heating at 353 K. A THF solution of LiBH₄ (twenty equimolar to the total amount of metal precursors) was quickly added to the refluxing mixture. The color of the mixture immediately turned black or dark gray. After another stirring for 15 min, the mixture was centrifuged and the resulting supernatant was decanted off, followed by addition of distilled water into the precipitate to quench residual LiBH₄. The sample was then washed three times by distilled water and acetone alternately and dried at 353 K. The crystal structure of supported metal and/or intermetallic particles was examined by powder X-ray diffraction (XRD) with a Rigaku RINT2400 using an X-ray source of Cu Ka.
Preparation of deuterated dibenzylamines

(1) Dibenzylamine-$\alpha,\alpha,\alpha,\alpha$-$d_4$ was prepared by the following procedure. Benzylbromide-$\alpha,\alpha$-$d_2$ (5.5 mmol) in dimethylformamide (4 ml) was slowly added dropwise to vigorously stirred mixture of benzylamine-$\alpha,\alpha$-$d_2$ (5.5 mmol), $\text{Cs}_2\text{CO}_3$ (5.5 mmol) and dimethylformamide (6 ml) at 0°C, followed by stirring at 0°C for 2 h. The reaction mixture was then filtered and the filtrate was concentrated by evaporation of dimethylformamide. A solution of 1 N NaOH (6 ml) and toluene (5 ml) was added to the concentrated residue, followed by extraction by toluene four times. The organic layer was collected, dried by Na$_2$SO$_4$, concentrated and distilled by Kugelrohr to afford 337 mg (31% yield) of colorless oil. $^1$H NMR: (500 MHz, CD$_3$OD) $\delta$ 5.77 (8H, d), 5.70 (2H, m), 3.42 (1H, s). (2) Dibenzylamine-$N$-$d_1$ was prepared by washing dibenzylamine (2.0 g) with D$_2$O (6 mL) three times, followed by extraction using toluene, evaporation, and Kugelrohr distillation. A $^1$H NMR spectrum indicated >90% deuterium content at the $N$-position by comparison of the integrated signal of amino-proton with that of benzyllic-one.

Catalytic reaction
Catalyst (50 or 100 mg) was put into a 50 ml three necked round-bottom flask equipped with a silicone rubber septum, a reflux condensor and a gas storage balloon (2 L) and was pretreated under pure H$_2$ stream (99.999%, 50 ml·min$^{-1}$) at 400°C for 0.5 h using a mantle heater. After the pretreatment, dry Ar was passed into the flask to replace residual H$_2$ and the flask was cooled to room temperature. Reaction mixture containing solvent ($p$-xylene, 5 ml), amine (0.5 or 1.0 mmol) and internal standard (biphenyl) was added into the flask through the septum. The atmosphere was then replaced with 5% O$_2$/Ar. Catalytic reaction was initiated by immersing the reaction apparatus into a preheated oil bath. Temperature of the oil bath was controled to keep actual temperature of the reaction mixture at 110°C. Products were quantified by flame-ionization detection-gas chromatograph (FID-GC, Shimadzu GC14B equipped with a TC-17 capillary column) using biphenyl as an internal standard. Turnover frequencies were estimated based on the total amount of Pd (mmol) and the reaction rates (mmol·h$^{-1}$) under differential reaction conditions (below 30% conversion, excepting the case of indoline oxidation at 100% conversion). Catalyst pretreatment was performed at 150°C when Pd$_3$Pb/Al$_2$O$_3$-L was used as a catalyst.
Figure S1. XRD patterns of silica-supported monmetallic Pd and Pd-based intermetallic compounds.
Figure S2. Time course of conversion in oxidation of N-isopropylbenzylamine over Pd$_3$Pb/SiO$_2$, Pd$_3$Bi/SiO$_2$ and Pd/SiO$_2$. Figure in parenthesis shows selectivity of N-benzylideneisopropylamine at 5 h. Only small amounts of benzaldehyde and banzonitrile were produced as by-products in each case.
Figure S3. XRD patterns of Pd₃Pb supported on various oxide. Figure in parenthesis shows crystallite size determined by using Scherrer’s equation after peak deconvolution.