Supporting Information

Selective Hydrogenation of Functionalized Alkynes to (*E*)-Alkenes Using Ordered Alloys as Catalysts

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Experimental procedures

Catalyst preparation

Pd/SiO_2 and Rh/SiO_2 (Pd, Rh: 3 wt%) was prepared by a pore-filling impregnation. Aqueous solution of $Pd(NO_3)_2$ was added to dried SiO_2, 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. A similar procedure was applied for the synthesis of Rh/SiO_2 using $Rh(NO_3)_3$ solution. Most of the Pd-based bimetallic catalysts, Pd_xM_y/SiO_2 (M = Ag, Bi, Cu, Fe, Ga, Pb, Sn and Zn), were prepared by a successive impregnation with Pd/SiO_2. A solution of second metal precursor was added to the reduced Pd/SiO_2 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 1 or 3 h: Pd–Ag (1:1), $AgNO_3$, 600°C, 1 h; Pd–Bi (3:1), $Bi(NO_3)_3\cdot 2H_2O$, 800°C, 1 h; Pd–Cu (1:1), $Cu(NO_3)_2\cdot H_2O$, 800°C, 1 h; Pd–Fe (1:1), $Fe(NO_3)_3\cdot 9H_2O$, 900°C, 3 h; Pd–Ga (2:1), $Ga(NO_3)_2\cdot H_2O$, 800°C, 1 h; Pd–Pb (3:1), $Pb(NO_3)_2\cdot 2H_2O$, 800°C, 1 h; Pd–Sn (1:1), $(NH_4)_2SnCl_6$, 800°C, 1 h; Pd–Zn (1:1), $Zn(NO_3)_2\cdot 6H_2O$, 600°C, 2 h. RhSb/SiO_2 was also prepared by the similar procedure using $SbCl_3\cdot 2H_2O$ (Rh:Sb = 1:1) and reduction at 800°C for 1 h. PdIn/SiO_2 was prepared by co-impregnation method using a 1:1 mixed solution of $Pd(NO_3)_2$ and $In(NO_3)_3$ with reduction at 400°C for 1 h. The crystal phase of the supported alloy or intermetallic nanoparticles was examined by powder X-ray diffraction (XRD) with a Rigaku RINT2400 using an X-ray source of Cu Kα. See our previous report (ref. 8) for further information on RhSb/SiO_2 (TEM, electron diffraction, FT-IR with adsorbed CO, and DFT calculations).

Catalytic reaction

Catalyst(s) (50 or 100 mg) was put into a 50 ml three necked round-bottom flask equipped with a silicone ruber septum, a reflux condensor and a gas storage baloon (2 L) and was pretreated under pure H_2 stream (99.999%, 50 $ml\cdot min^{-1}$) at 400˚C for 0.5 h using a mantle heater. After the pretreatment, the reactor was cooled to room temperature under H_2 atmosphere. Catalytic reaction was initiated at room temperature (25°C) by adding mixture containing solvent (tetrahydrofran, 5 ml), alkyne (0.5 mmol), and internal standard (propylbenzene) into the flask through the septum. Products were quantified by flame-ionization detection-gas chromatograph (FID–GC, Shimadzu GC2010 equipped with a TC-17 capillary column) using the internal standard. For recycling, the spent catalysts were washed with the solvent twice, followed by drying under Ar flow at room temperature. To minimize loss and aerobic oxidation of the catalysts, all recycling procedures (decantation, washing, drying, and reactions) were done in the reaction vessel.

Computational details

Periodic DFT calculations except vibrational calculations were performed using the CASTEP code[1] with Vanderbilt-type ultra-soft pseudopotentials[2] and a revised Perdew–Burke–Ernzerhof exchange–correlation functional (RPBE)[3-4] based on the generalised gradient approximation. The plane wave basis set was truncated at a kinetic energy of 370 eV. A Fermi smearing of 0.1 eV was utilised. The reciprocal space was sampled using a k-point mesh with a typical spacing of 0.04 $Å^{-1}$ generated by the Monkhorst−Pack scheme.[5] Atomic coordinates were fully relaxed, whereas lattice constants were fixed. Slabs were modelled typically with 4-atomic-layer-thickness and a 13 Å vacuum spacing between the two surfaces. The most densely packed low Miller-index planes were selected as surfaces most stable and likely to be exposed; Pd(111), Pd_3Pb(111), PdAg(110), PdIn(110), Pd_3Bi(100) (space group: Pd, $Fm\bar{3}m$; Pd_3Pb, PdAg, and PdIn, $Pm\bar{3}m$; Pd_3Bi, *Pmma*). Although PdAg is generally of a solid solution alloy, an intermetallic body centered cubic (CsCl-type) structure was considered for simplification in this study. As a model of Lindlar catalyst's surface, Pd(111) surface where Pb atoms were deposited on fcc hollow sites with a (3×3)–2Pb structure was considered. Ethylene and acetylene were adsorbed on the surface typically with (2×2)–C_2H_x structures (Pd(111), Pd_3Pb(111), PdAg(110), and PdIn(110)). For Pd_3Bi(100) and Pb-deposited Pd(111) surfaces, c(4×2)–2C_2H_x and (3×3)–2Pb+C_2H_x structures were employed for the molecular adsorption. For all cases, di-σ adsorption modes were considered for both ethylene and acetylene. The geometry optimization was performed with the following convergence criteria: (a) a self-consistent field tolerance of 2.0×10^{-6} eV/atom, (b) an energy tolerance of 2.0×10^{-5} eV/atom, (c) a maximum force tolerance of 0.05 eV/Å and (d) a maximum displacement tolerance of 2.0×10^{-3} Å. The adsorption energy was defined with the following equation, $\Delta E_{\mathrm{ad}} = E_{\mathrm{A-S}} - (E_{\mathrm{S}} + E_{\mathrm{A}})$, where $E_{\mathrm{A-S}}$ is the total energy of the slab with the adsorbate, E_{A} is the energy of the free adsorbate, and E_{S} is the energy of the bare slab.

Table S1. Result of recycling tests for ethyl phenylpropiolate hydrogenation with Pd_3Pb/SiO_2 and $RhSb/SiO_2$ catalysts.

run	time / min	alkyne conv. (%)	alkene sel. (%)	E : Z
1	110	100	85	99 : 1
2	150	100	85	98 : 2
3	220	100	84	96 : 4
4	400	100	85	95 : 5

Reaction condition: alkyne, 0.5 mmol; catalyst, Pd_3Pb/SiO_2 (Pd: 3 wt%) 100 mg, $RhSb/SiO_2$ (Rh: 3 wt%) 100 mg; solvent (THF), 5 ml; atmosphere, 1 atm H_2; temperature, 25°C.

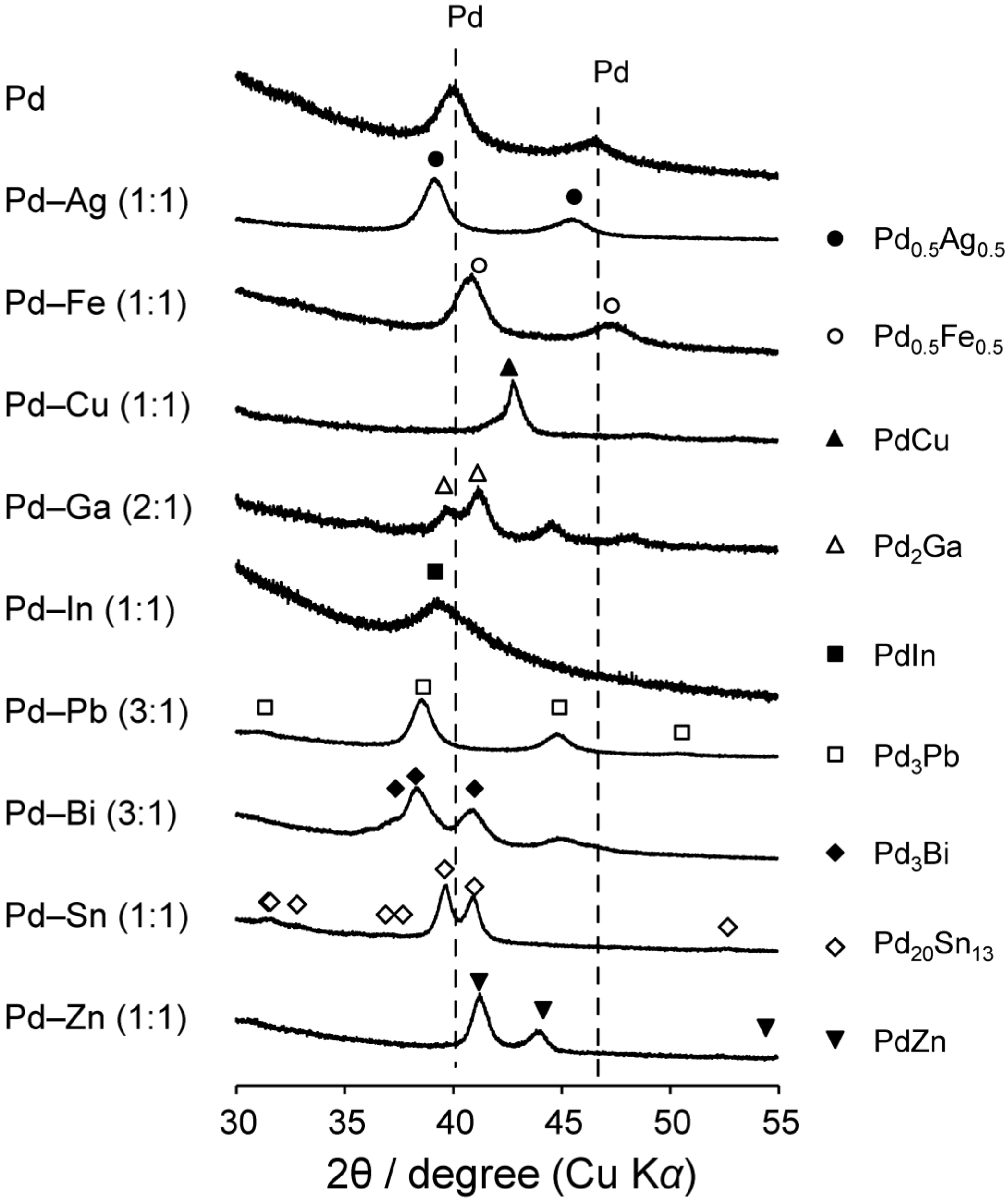

Figure S1. XRD patterns of silica-supported monmetallic Pd and Pd-based alloys.

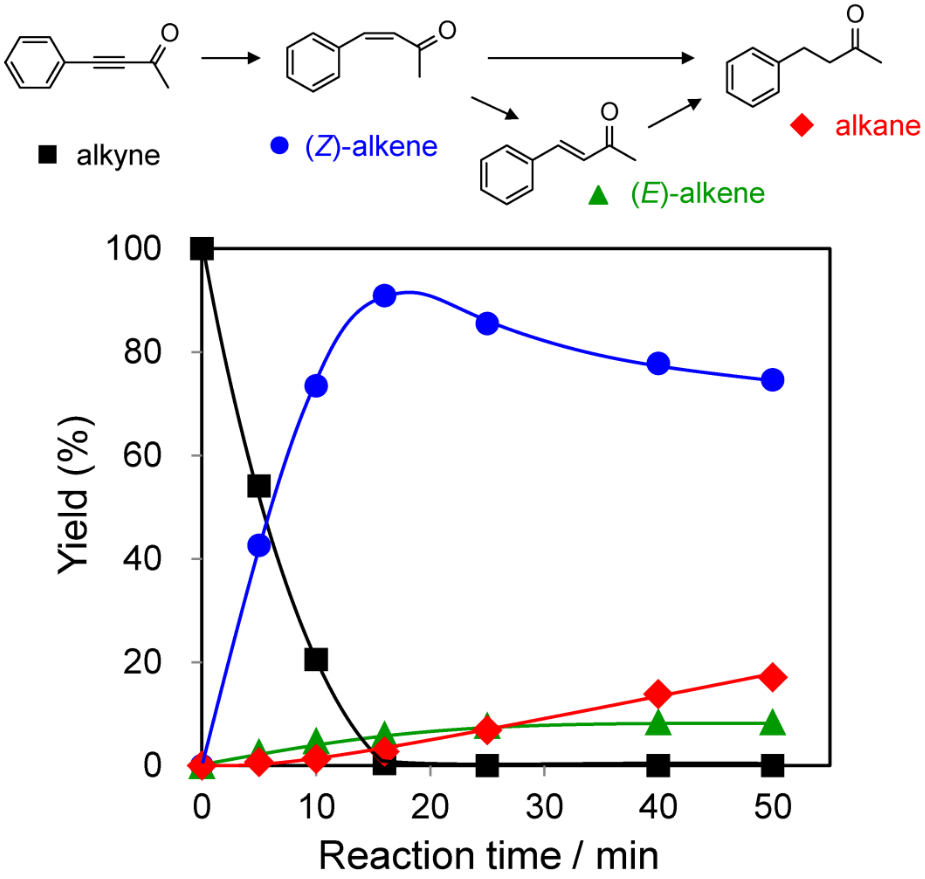

Figure S2. Time course of product yield in the hydrogenation of 4-phenyl-3-butyn-2-one over Pd–Pb/$CaCO_3$ in the presence of quinoline.

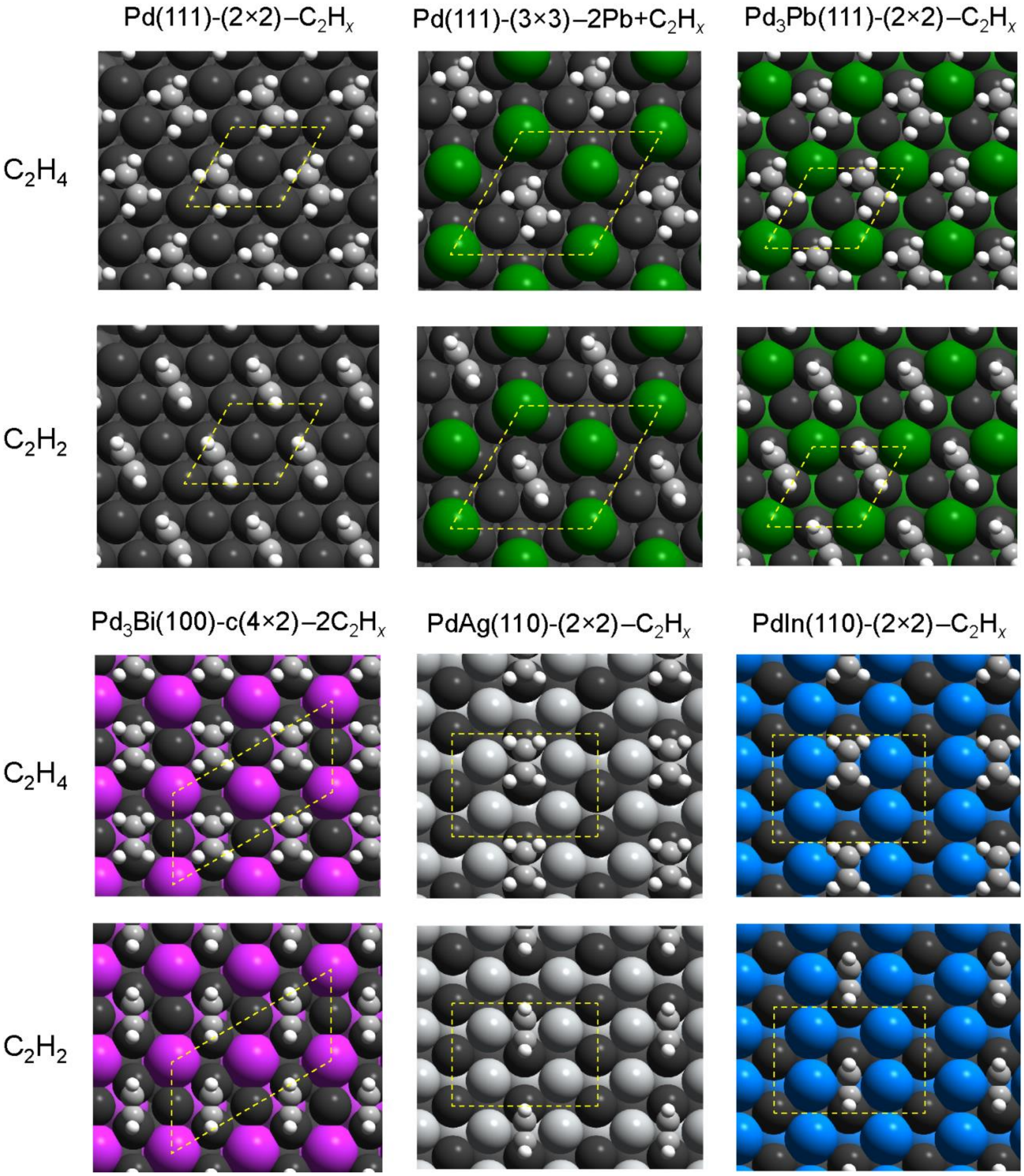

Figure S3. Optimized structures of ethylene and acetylene adsorbed on various Pd-based surfaces with di-σ modes. Yellow dotted tetragons indicate the surface unit cells.

References

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