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Supporting Information to

Selective Hydrogenation of Highly Concentrated Acetylene Streams over Mechanochemically-Synthesized PdAg Supported Catalysts

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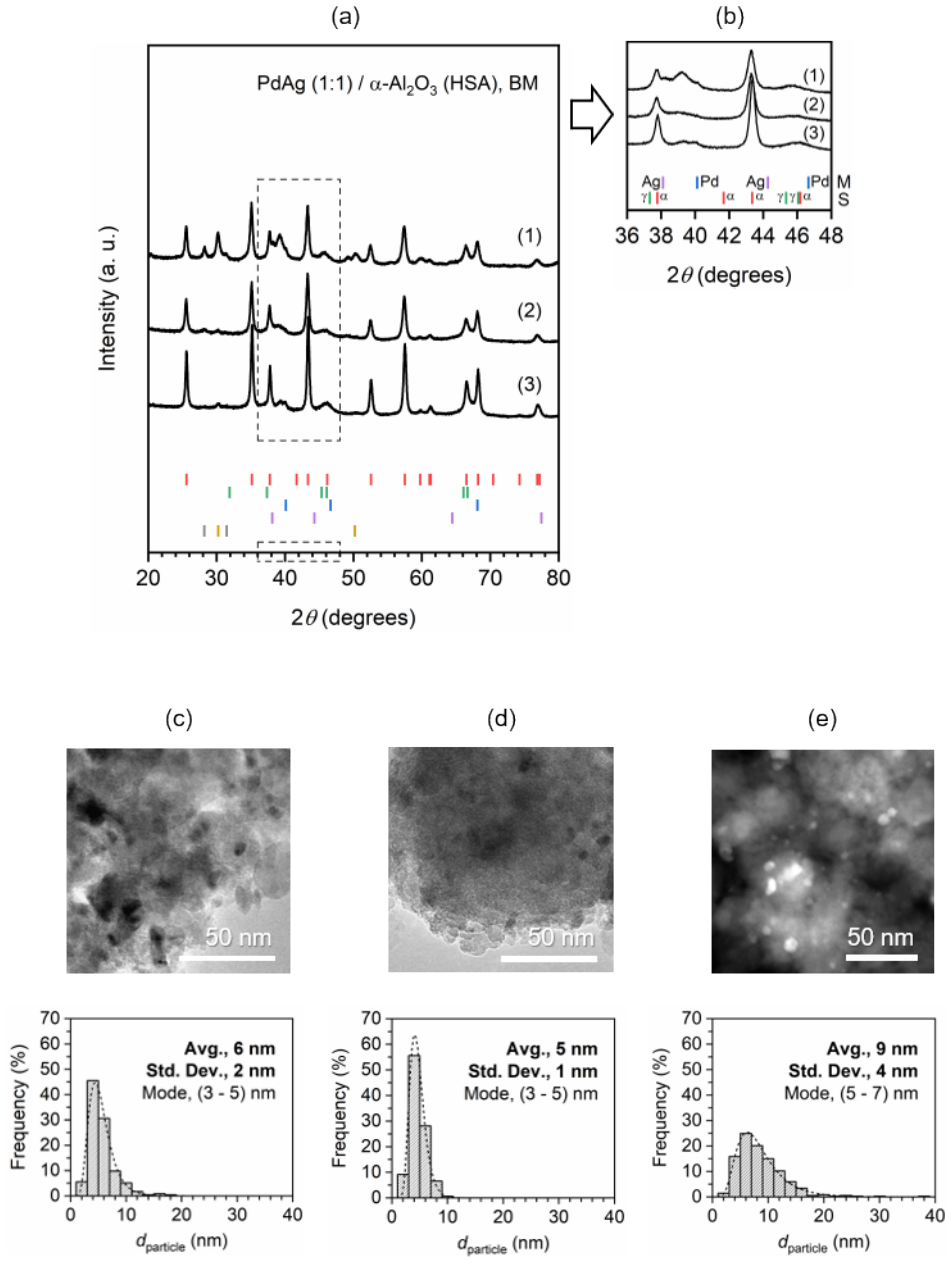

Figure S1. (a) Powder XRD patterns of as-synthesized 5 wt% PdAg (1:1) / HSA-α-Al_2O_3 obtained by ball milling (**1**), after dilution with freshly prepared HSA-α-Al_2O_3 to 1 wt% (**2**), and after dilution and the thermal treatment described in *Experimental Methods* (**3**). In detail (b), magnified powder XRD patterns in the range highlighted in (a). In each case, the reference lines point at the most prominent reflections for α-Al_2O_3 (corundum, in red), γ-Al_2O_3 (corundum, in green), Pd (in blue), Ag (in purple), *t*-ZrO_2 (tetragonal, yttria-stabilized, in grey), and *m*-ZrO_2 (monoclinic, in yellow). The letters M and S in (b) and (d) refer to the metallic components and oxide support. (c-d) Representative HR-TEM and (e) HAADF-STEM micrographs of as-synthesized 5 wt% PdAg (1:1) / HSA-α-Al_2O_3 (c), after dilution to 1 wt% (d), and after dilution and thermal treatment (e), with corresponding metal particle size distribution (histograms). Average particle size, standard deviation, and most probable size range (mode) are specified.

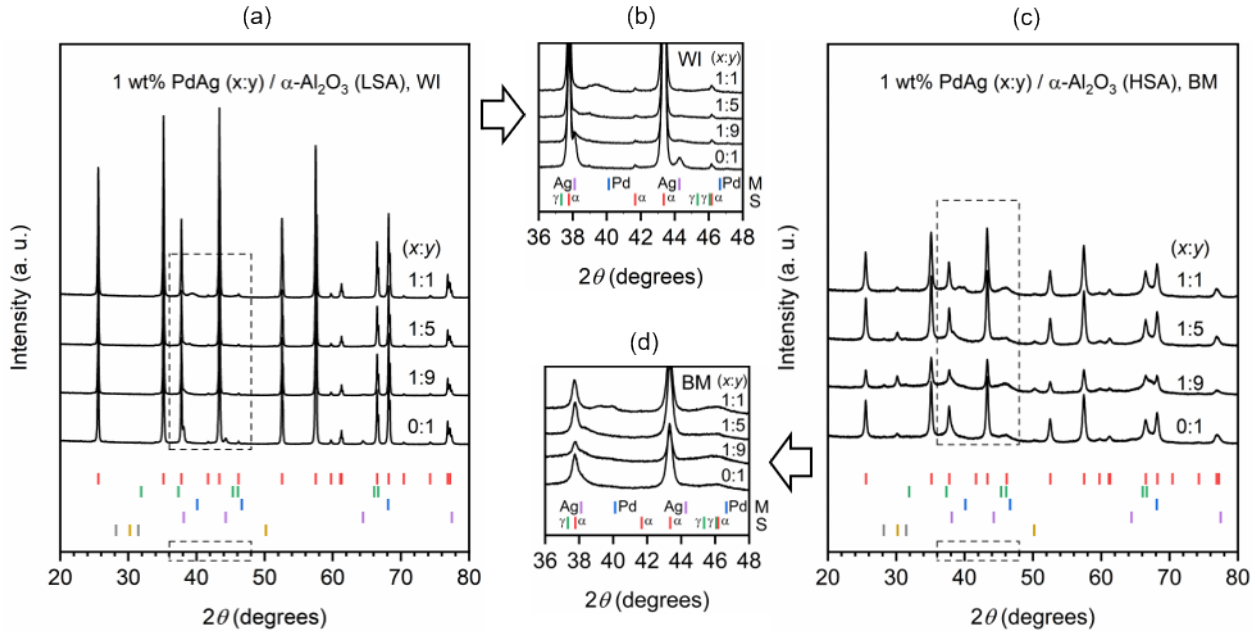

Figure S2. Powder XRD patterns of PdAg (nominal *x*:*y*, as specified) nanoparticles supported on LSA-α-Al_2O_3 obtained via wet impregnation (a-b) and HSA-α-Al_2O_3 obtained by ball milling (c-d). In detail (b) and (d), magnified powder XRD patterns in the range highlighted in (a) and (c), respectively. In each case, the reference lines point at the most prominent reflections for α-Al_2O_3 (corundum, in red), γ-Al_2O_3 (corundum, in green), Pd (in blue), Ag (in purple), *t*-ZrO_2 (tetragonal, yttria-stabilized, in grey), and *m*-ZrO_2 (monoclinic, in yellow). The letters M and S in (b) and (d) refer to the metallic components and oxide support.

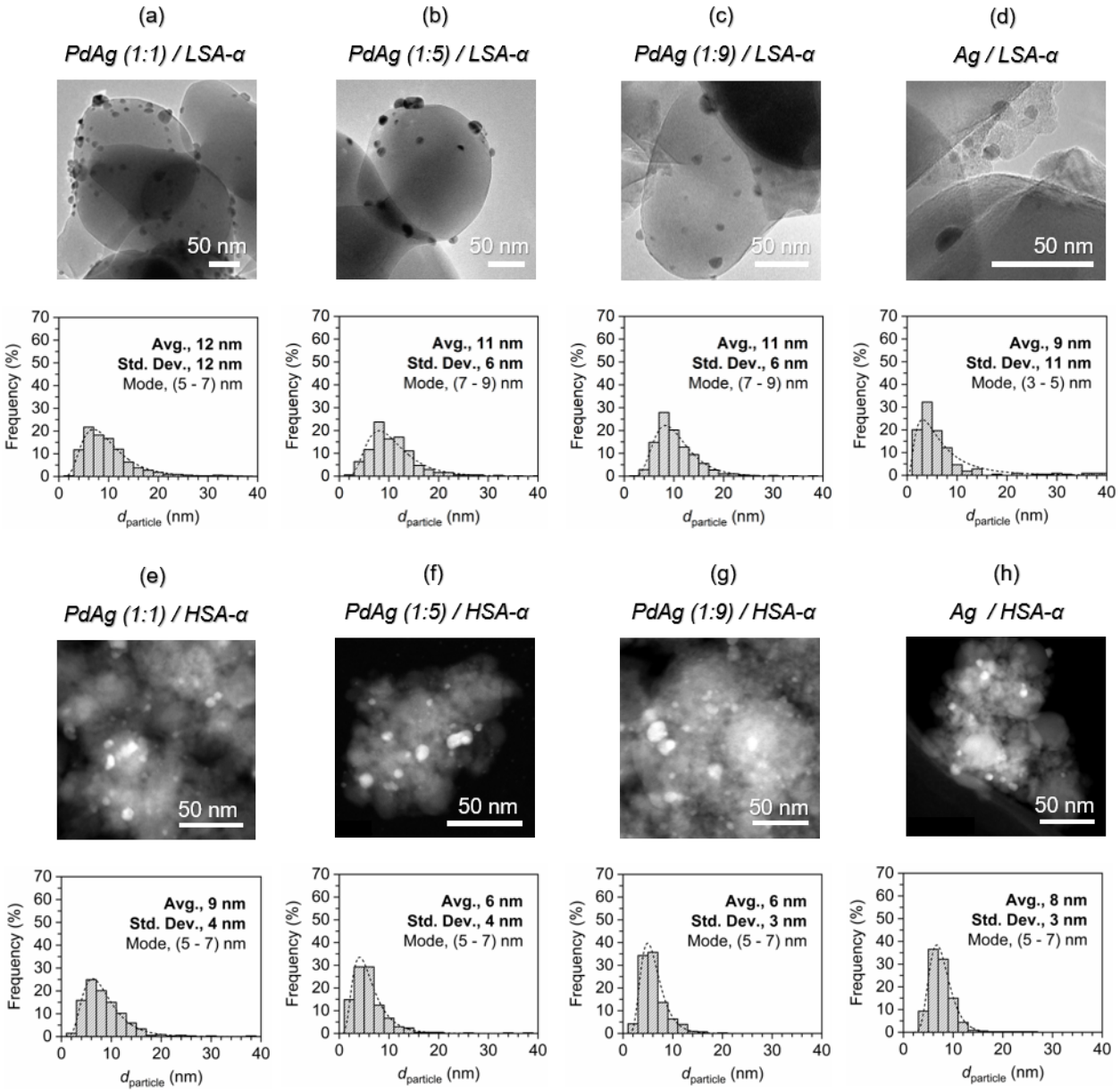

Figure S3. Representative TEM micrographs of PdAg (nominal *x*:*y*, as specified) nanoparticles supported on LSA-α-Al_2O_3 obtained via wet impregnation (a-d) and HSA-α-Al_2O_3 obtained by ball milling (e-h) with corresponding metal particle size distribution (histograms). Average particle size, standard deviation, and most probable size range (mode) are specified.

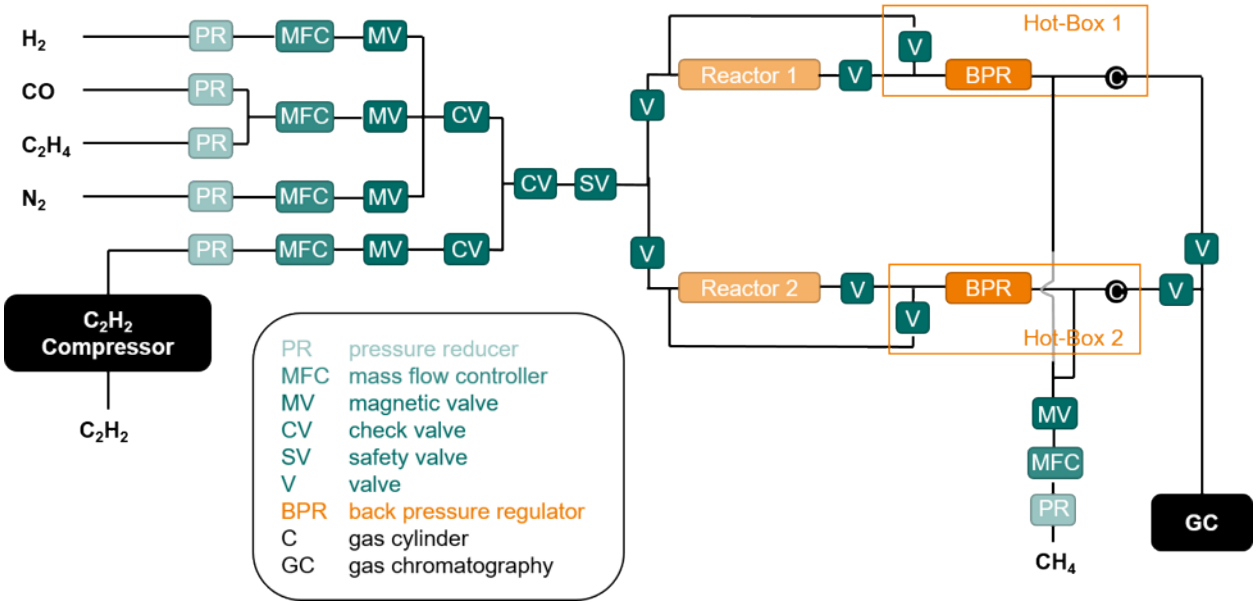

Figure S4. Flow diagram of the setup used for catalytic tests, including piping and instrumentation. The chart shows all gas supplies, including acetylene and dedicated compressor, pressure reducers, mass flow controllers, magnetic valves, check and safety valves, reaction zones (two reactors, not used simultaneously), back pressure regulators (heated), and the gas chromatography device as specified.

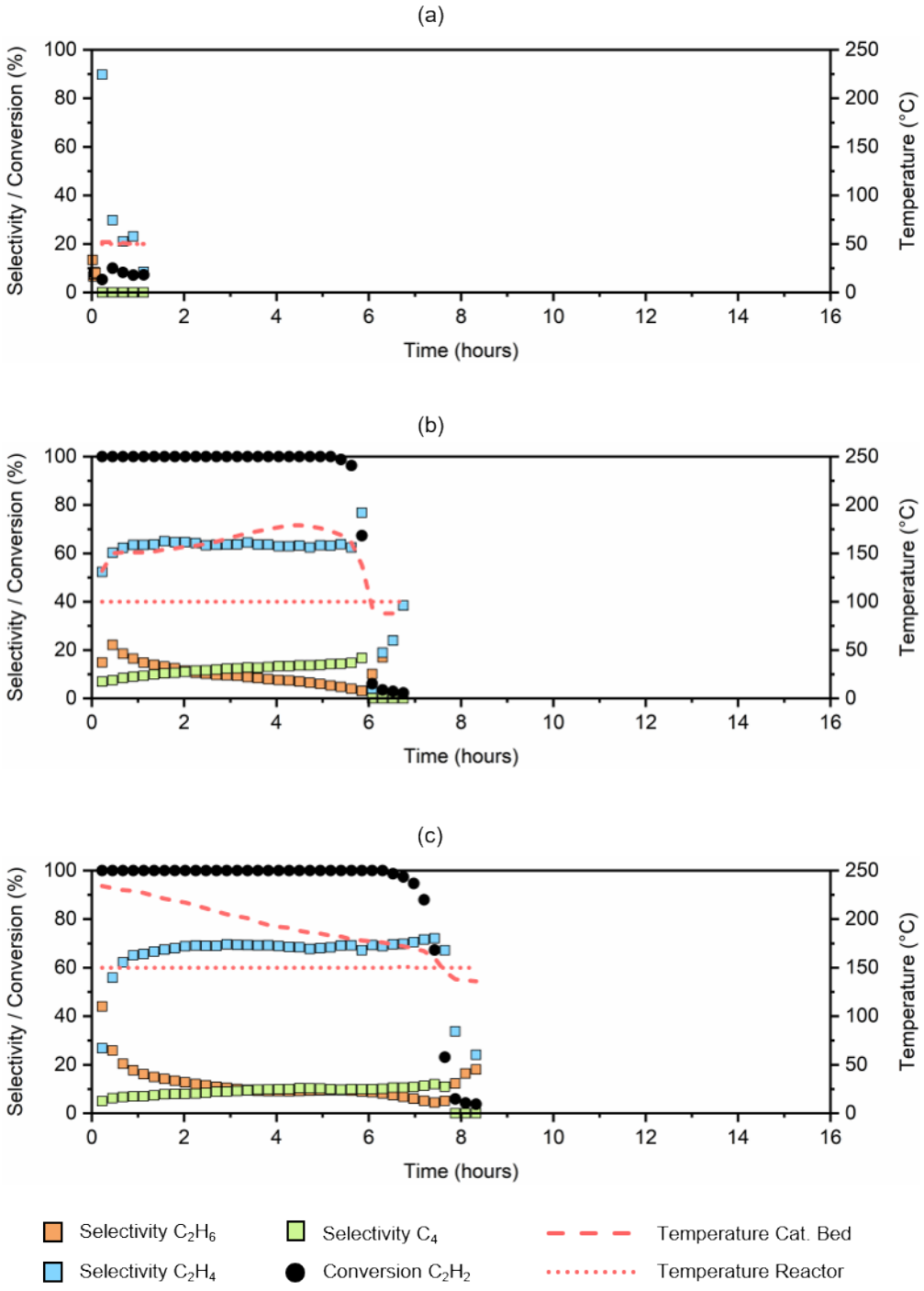

Figure S5. Conversion of acetylene (C_2H_2) and selectivity to ethylene (C_2H_4), ethane (C_2H_6), and C_4-hydrocarbons *vs.* time on stream for 1 wt% PdAg (1:9) / LSA-α-Al_2O_3 prepared by wet impregnation (WI) given a reactor temperature around 50 °C (a), 100 °C (b), and 150 °C (c), respectively. The catalyst bed temperature is similarly plotted against the time on stream.

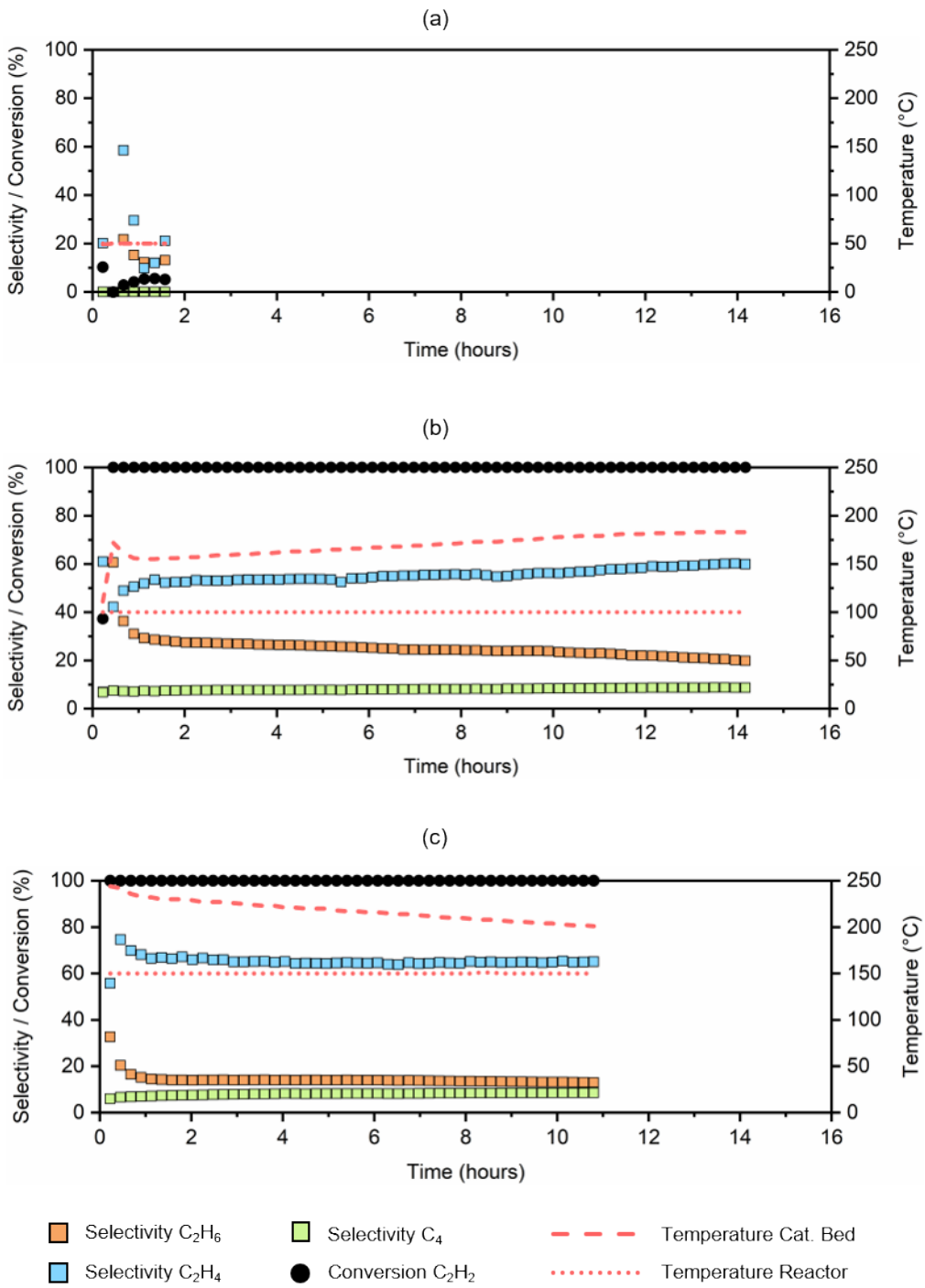

Figure S6. Conversion of acetylene (C_2H_2) and selectivity to ethylene (C_2H_4), ethane (C_2H_6), and C_4-hydrocarbons *vs.* time on stream for 1 wt% PdAg (1:9) / HSA-α-Al_2O_3 prepared by ball milling (BM) given a reactor temperature around 50 °C (a), 100 °C (b), and 150 °C (c), respectively. The catalyst bed temperature is similarly plotted against the time on stream.

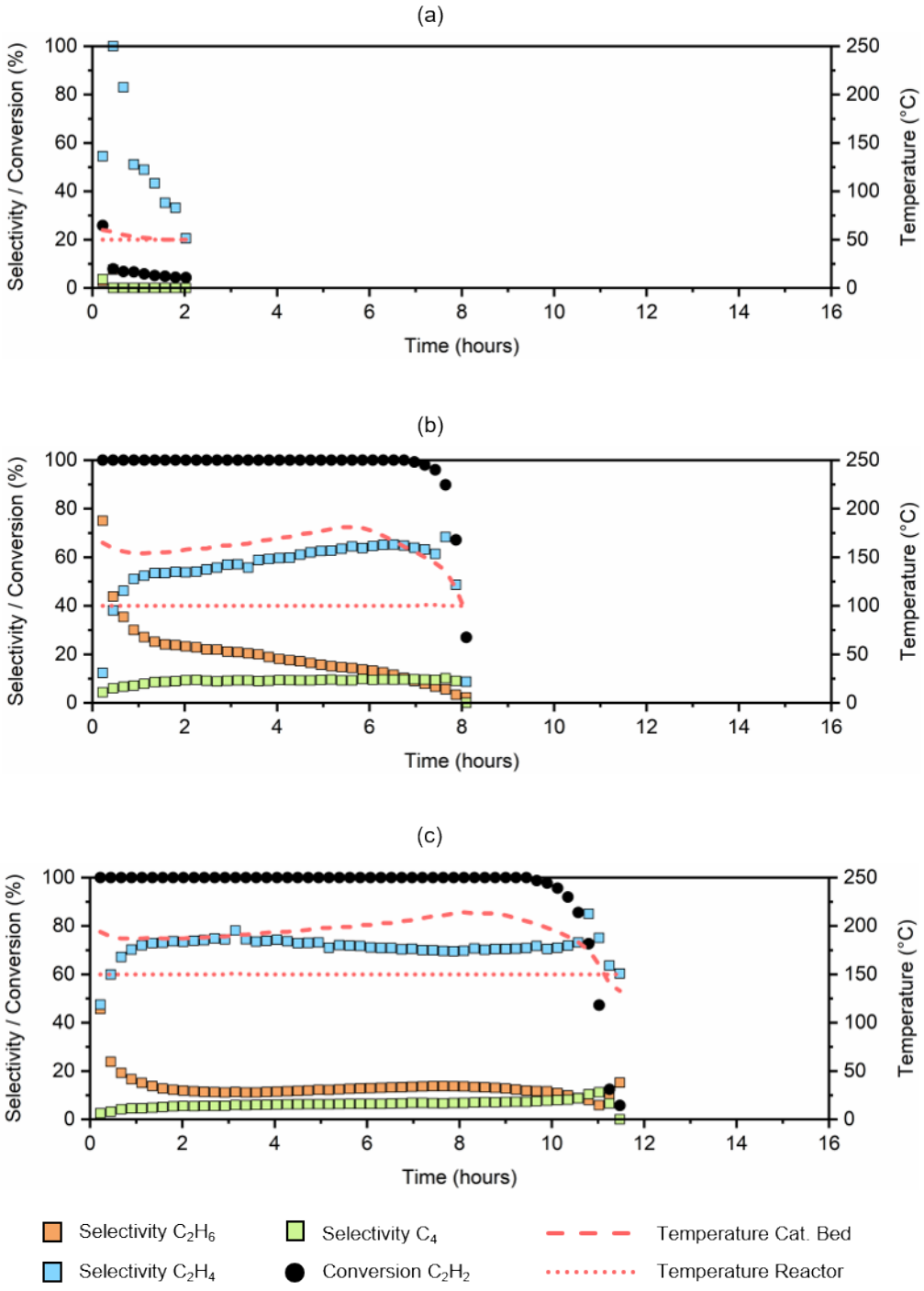

Figure S7. Conversion of acetylene (C_2H_2) and selectivity to ethylene (C_2H_4), ethane (C_2H_6), and C_4-hydrocarbons *vs.* time on stream for 1 wt% PdAg (1:5) / LSA-α-Al_2O_3 prepared by wet impregnation (WI) given a reactor temperature around 50 °C (a), 100 °C (b), and 150 °C (c), respectively. The catalyst bed temperature is similarly plotted against the time on stream.

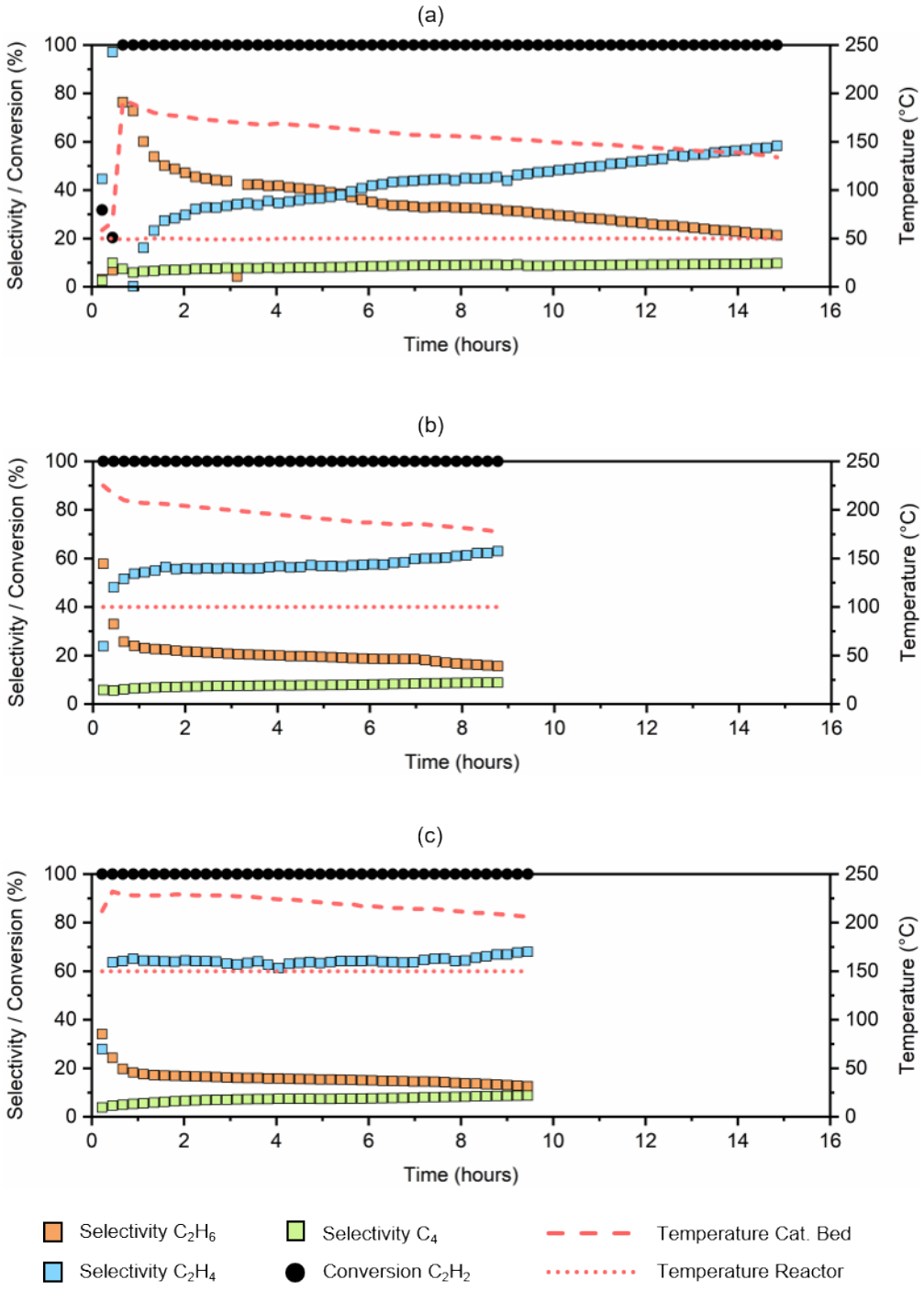

Figure S8. Conversion of acetylene (C_2H_2) and selectivity to ethylene (C_2H_4), ethane (C_2H_6), and C_4-hydrocarbons *vs.* time on stream for 1 wt% PdAg (1:5) / HSA-α-Al_2O_3 prepared by ball milling (BM) given a reactor temperature around 50 °C (a), 100 °C (b), and 150 °C (c), respectively. The catalyst bed temperature is similarly plotted against the time on stream.

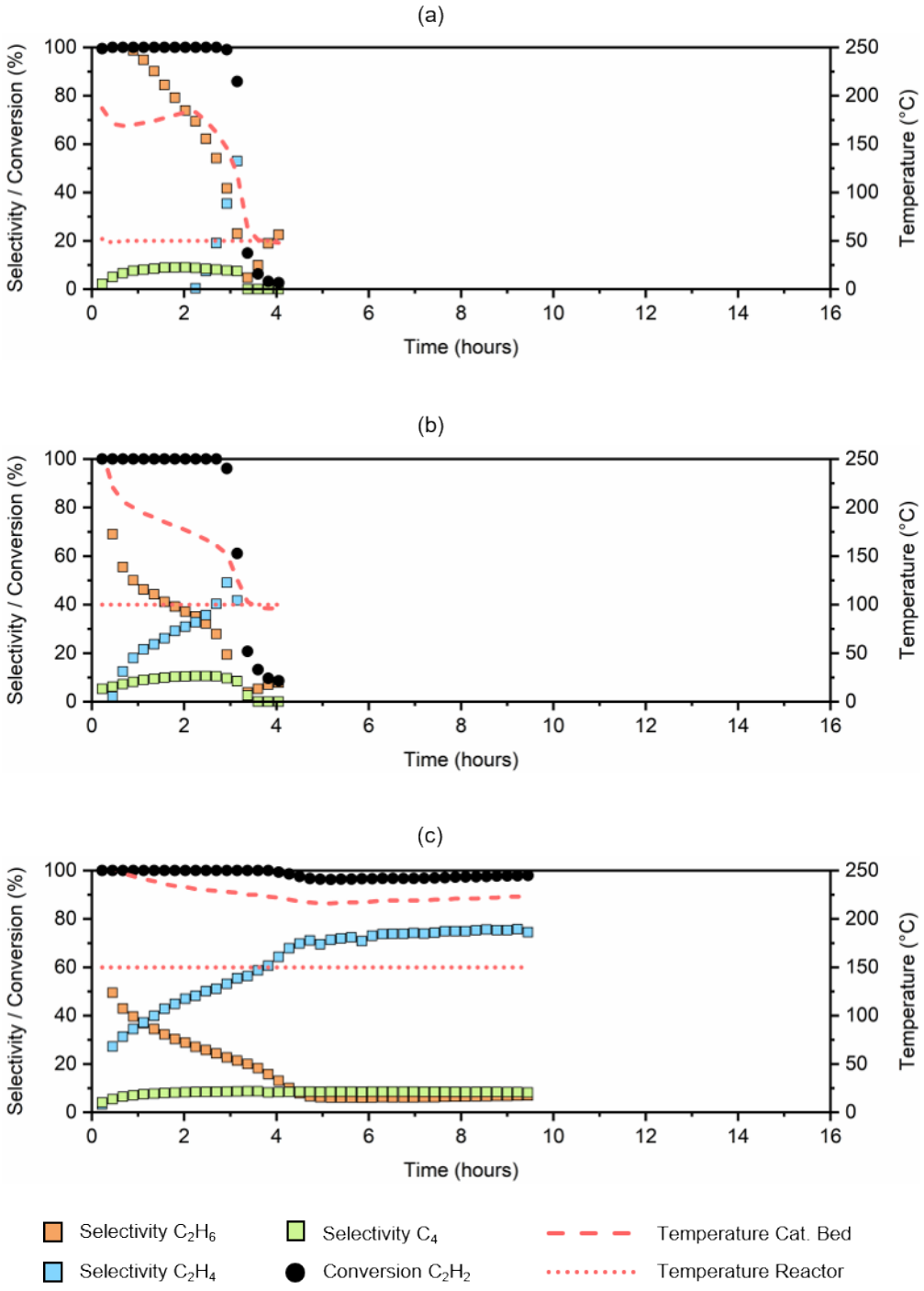

Figure S9. Conversion of acetylene (C_2H_2) and selectivity to ethylene (C_2H_4), ethane (C_2H_6), and C_4-hydrocarbons *vs.* time on stream for 1 wt% PdAg (1:1) / LSA-α-Al_2O_3 prepared by wet impregnation (WI) given a reactor temperature around 50 °C (a), 100 °C (b), and 150 °C (c), respectively. The catalyst bed temperature is similarly plotted against the time on stream.

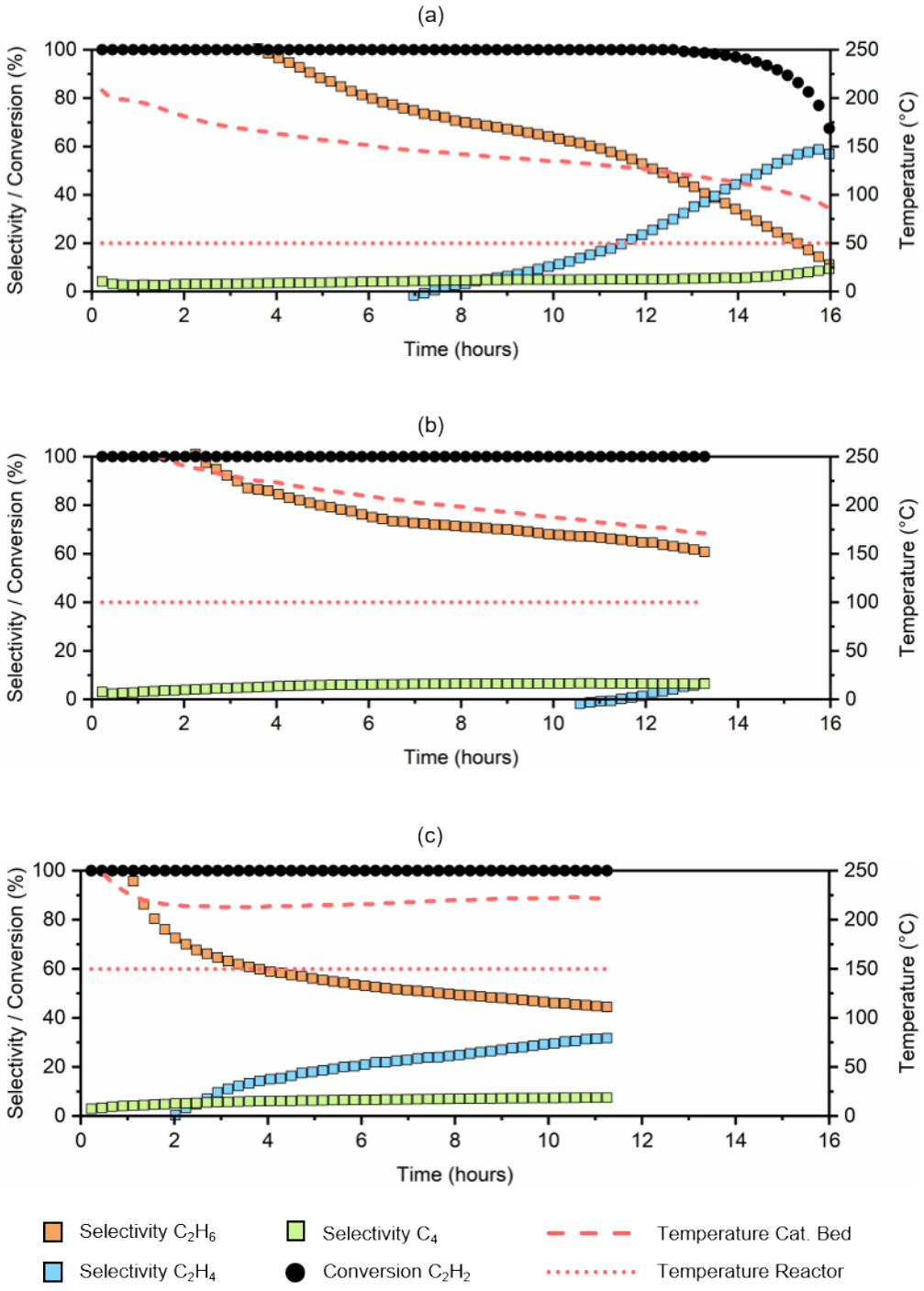

Figure S10. Conversion of acetylene (C_2H_2) and selectivity to ethylene (C_2H_4), ethane (C_2H_6), and C_4-hydrocarbons *vs.* time on stream for 1 wt% PdAg (1:1) / HSA-α-Al_2O_3 prepared by ball milling (BM) given a reactor temperature around 50 °C (a), 100 °C (b), and 150 °C (c), respectively. The catalyst bed temperature is similarly plotted against the time on stream.

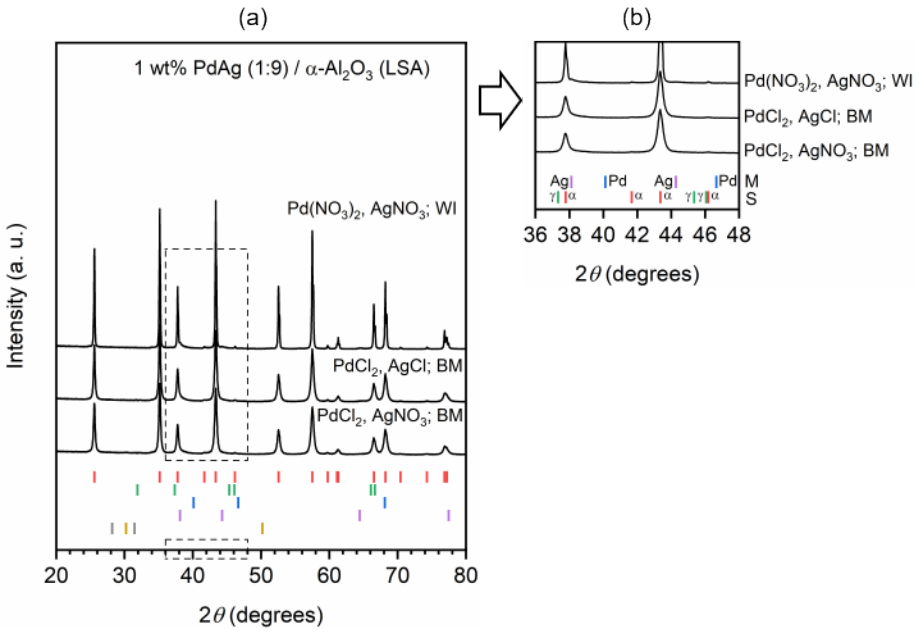

Figure S11. (a) Powder XRD patterns of PdAg (1:9) nanoparticles supported on LSA-α-Al_2O_3 obtained by impregnating Pd and Ag nitrates over LSA-α-Al_2O_3 or by depositing Pd chloride and Ag chloride/nitrate on LSA-α-Al_2O_3 upon ball milling, followed by the thermal treatment described in *Experimental Methods*, as specified. (b) Magnification of the powder XRD patterns in the range defined in (a). In each case, the reference lines point at the most prominent reflections for α-Al_2O_3 (corundum, in red), γ-Al_2O_3 (corundum, in green), Pd (in blue), Ag (in purple), *t*-ZrO_2 (tetragonal, yttria-stabilized, in grey), and *m*-ZrO_2 (monoclinic, in yellow). The letters M and S in (b) refer to the metallic components and oxide support.

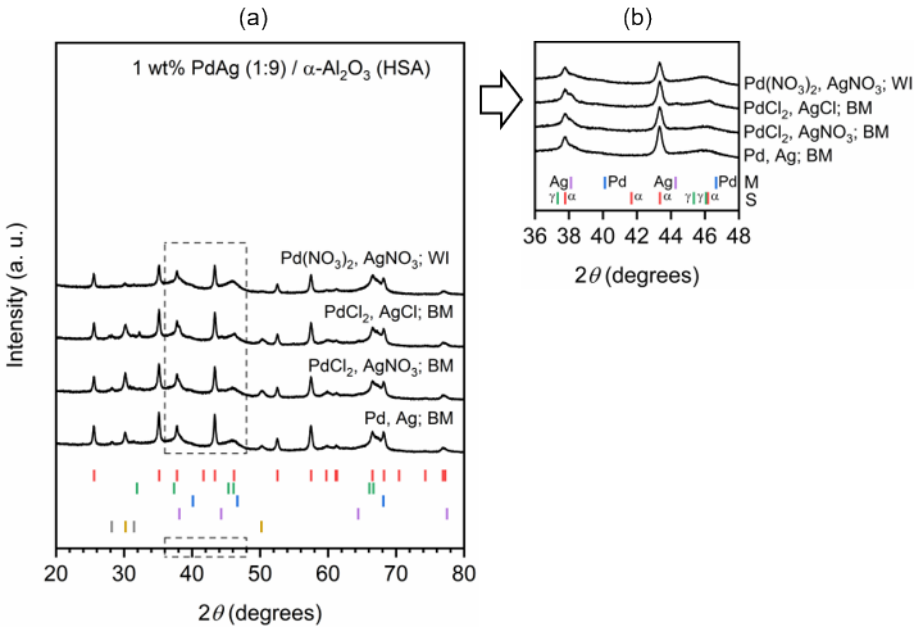

Figure S12. (a) Powder XRD patterns of PdAg (1:9) nanoparticles supported on HSA-α-Al_2O_3 obtained by impregnating Pd and Ag nitrates over HSA-α-Al_2O_3 or by depositing Pd chloride and Ag chloride/nitrate on HSA-α-Al_2O_3 upon ball milling, followed by the thermal treatment described in *Experimental Methods*, as specified. Magnification of the powder XRD patterns in the range defined in (a). In each case, the reference lines point at the most prominent reflections for α-Al_2O_3 (corundum, in red), γ-Al_2O_3 (corundum, in green), Pd (in blue), Ag (in purple), *t*-ZrO_2 (tetragonal, yttria-stabilized, in grey), and *m*-ZrO_2 (monoclinic, in yellow). The letters M and S in (b) refer to the metallic components and oxide support.

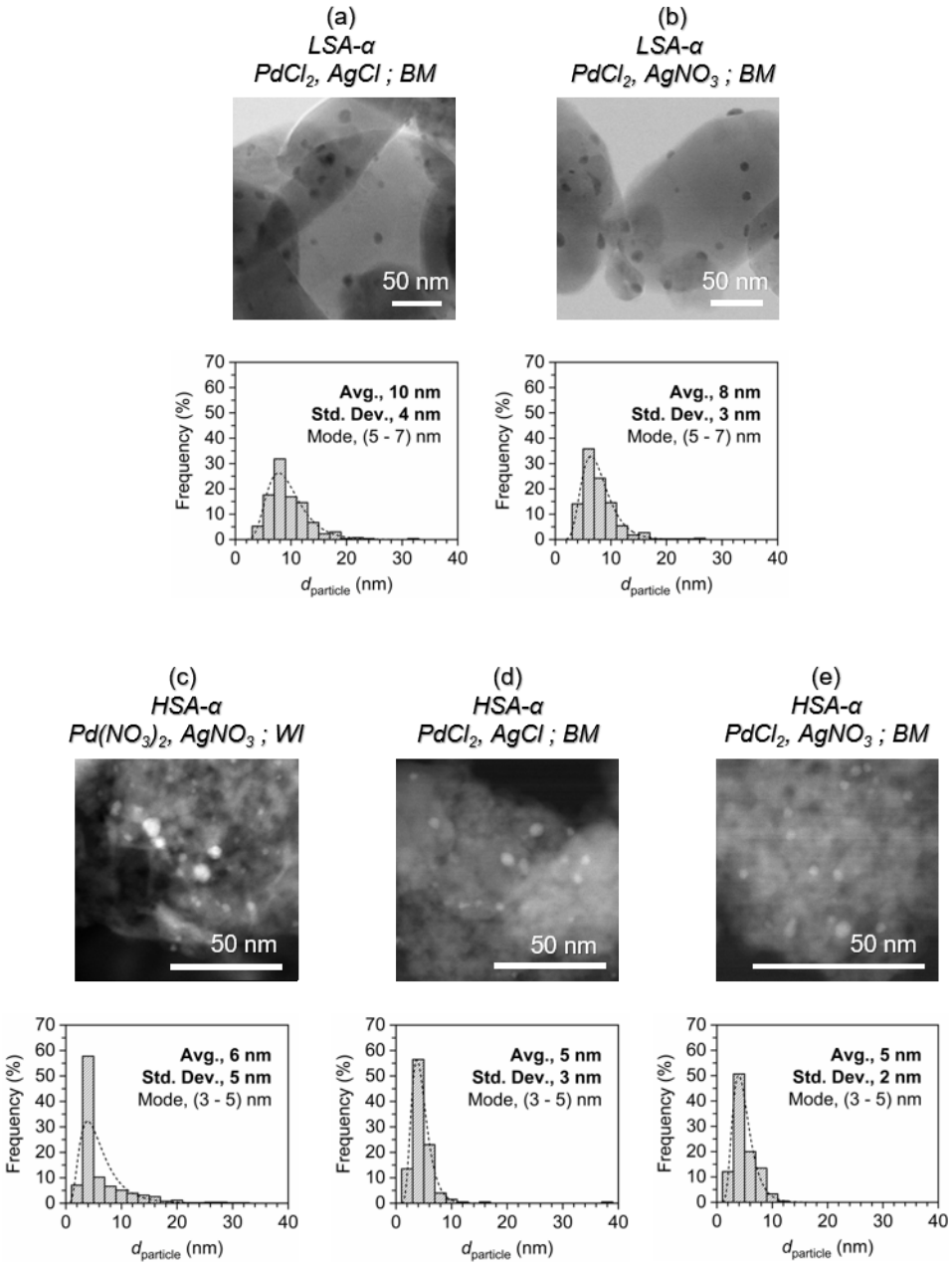

Figure S13. Representative TEM micrographs of PdAg (1:9) nanoparticles supported on LSA-α-Al_2O_3 (a-b) or HSA-α-Al_2O_3 (c-e) with corresponding metal particle size distribution (histograms). Average particle size, standard deviation, and most probable size range (mode) are specified. The catalysts were obtained either by impregnating Pd and Ag nitrates over HSA-α-Al_2O_3 or by depositing Pd chloride and Ag chloride/nitrate over LSA/HSA-α-Al_2O_3, followed by the thermal treatment described in *Experimental Methods*, as specified.

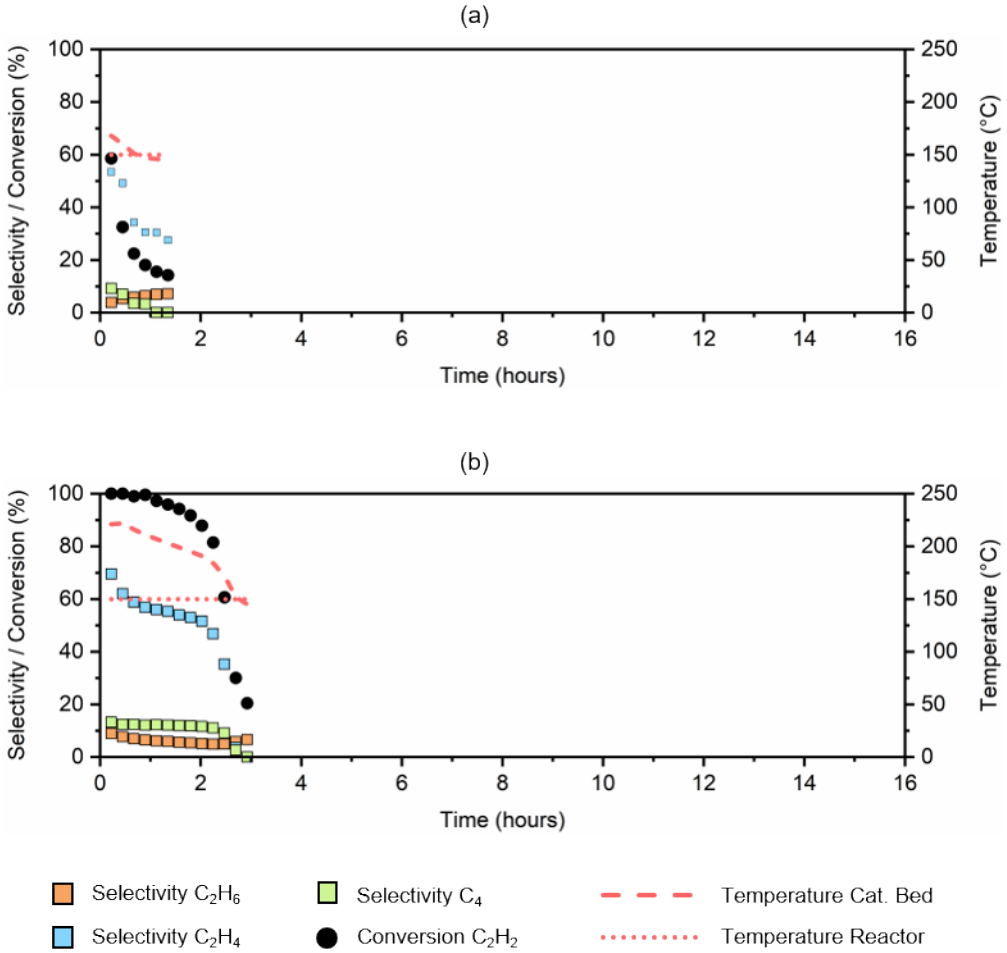

Figure S14. Conversion of acetylene (C_2H_2) and selectivity to ethylene (C_2H_4), ethane (C_2H_6), and C_4-hydrocarbons *vs.* time on stream for 1 wt% PdAg (1:9) / LSA-α-Al_2O_3 obtained by depositing Pd chloride and Ag chloride/nitrate (a/b) upon ball milling, followed by the thermal treatment described in *Experimental Methods,* as specified. In all cases, the reactor temperature was set around 150 °C. The catalyst bed temperature is similarly plotted against the time on stream.

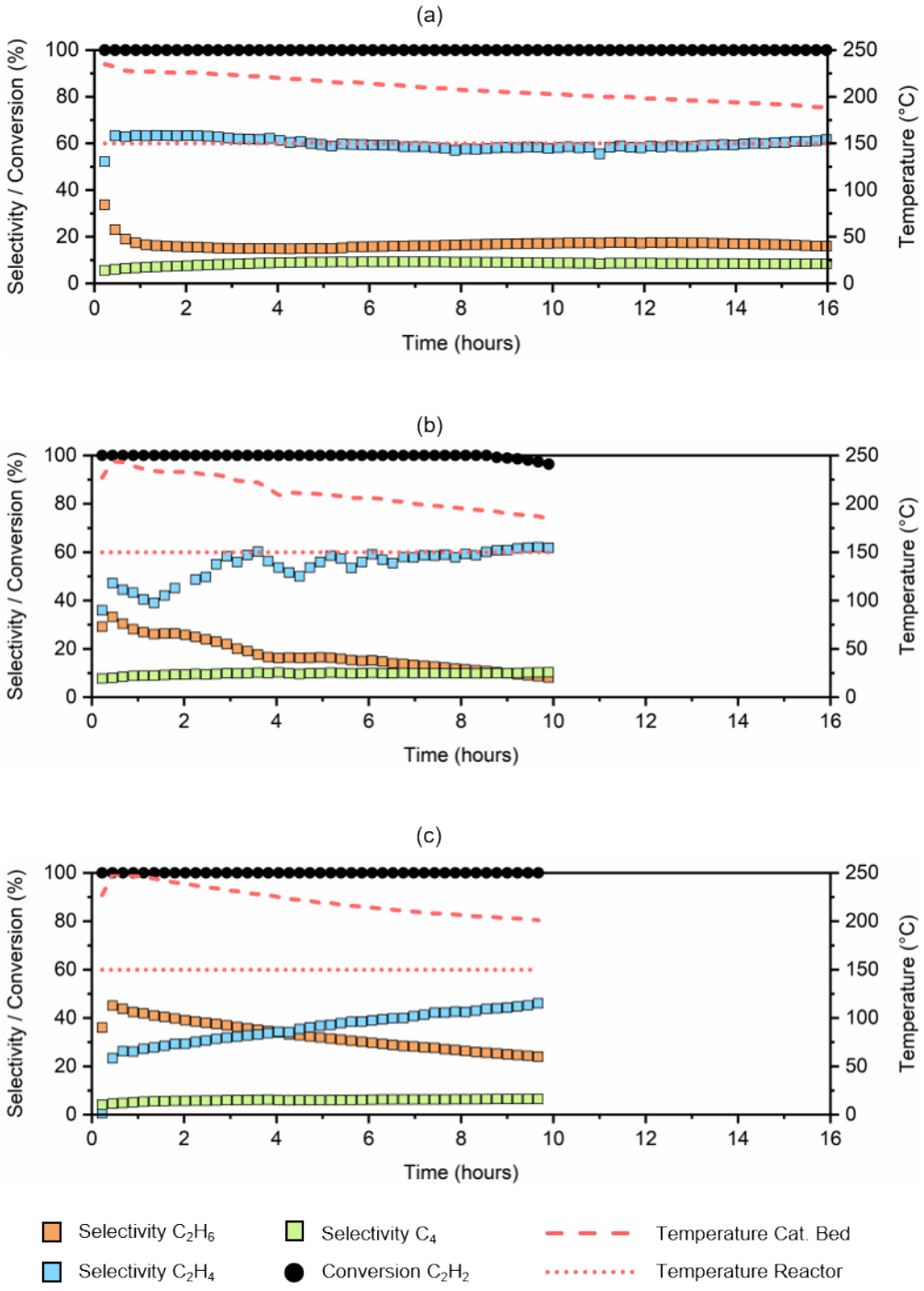

Figure S15. Conversion of acetylene (C_2H_2) and selectivity to ethylene (C_2H_4), ethane (C_2H_6), and C_4-hydrocarbons *vs.* time on stream for 1 wt% PdAg (1:9) / HSA-α-Al_2O_3 obtained by wet impregnation (a) of Pd and Ag nitrates or by deposition Pd chloride and Ag chloride (b) or nitrate (c) upon ball milling, followed by thermal treatment, as described in *Experimental Methods*. In all cases, the reactor temperature was set around 150 °C. The catalyst bed temperature is similarly plotted against the time on stream.

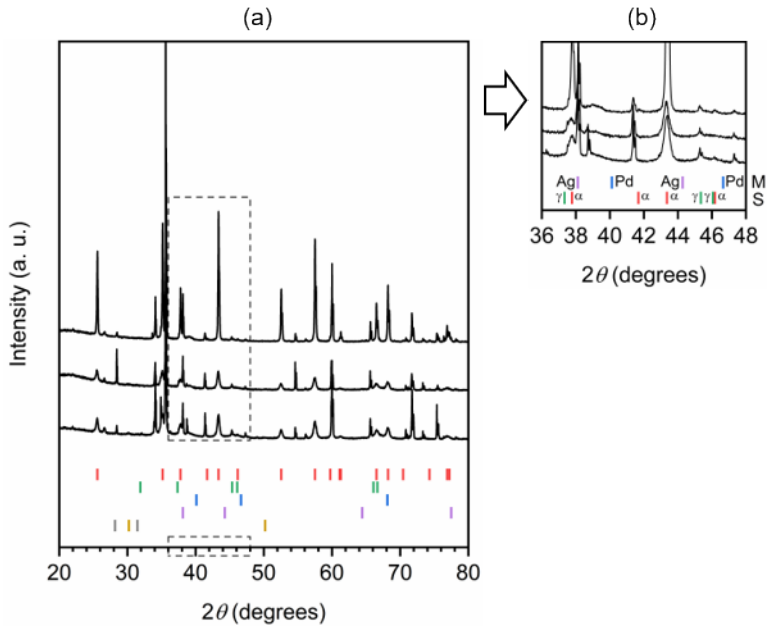

Figure S16. From top to bottom, powder XRD patterns of PdAg (1:1) nanoparticles supported on LSA-α-Al_2O_3 tested at 100°C in the catalytic reaction or HSA-α-Al_2O_3 tested at 50°C and 100°C, respectively. (b) Magnification of the powder XRD patterns in the range defined in (a). In each case, the reference lines point at the most prominent reflections for α-Al_2O_3 (corundum, in red), γ-Al_2O_3 (corundum, in green), Pd (in blue), Ag (in purple), *t*-ZrO_2 (tetragonal, yttria-stabilized, in grey), and *m*-ZrO_2 (monoclinic, in yellow). Additional diffraction lines correspond to SiC impurities. The letters M and S in (b) refer to the metallic components and oxide support.

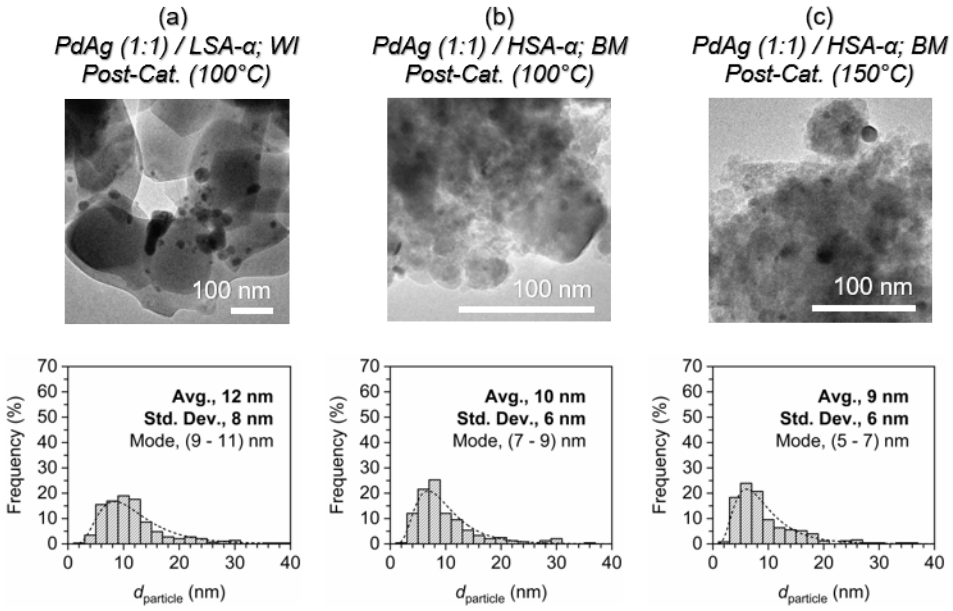

Figure S17. Representative TEM micrographs of PdAg (1:1) nanoparticles supported on LSA-α-Al_2O_3 (a) or HSA-α-Al_2O_3 (b-c) after the catalytic reaction with corresponding metal particle size distribution (histograms). Average particle size, standard deviation, and most probable size range (mode) are specified. While the catalysts (a), tested at 100 °C, and (b), tested at 50 °C, eventually deactivated under reaction conditions, the catalyst (c) was still active when the reaction was interrupted and the material recovered (the reactor was set at 100 °C).

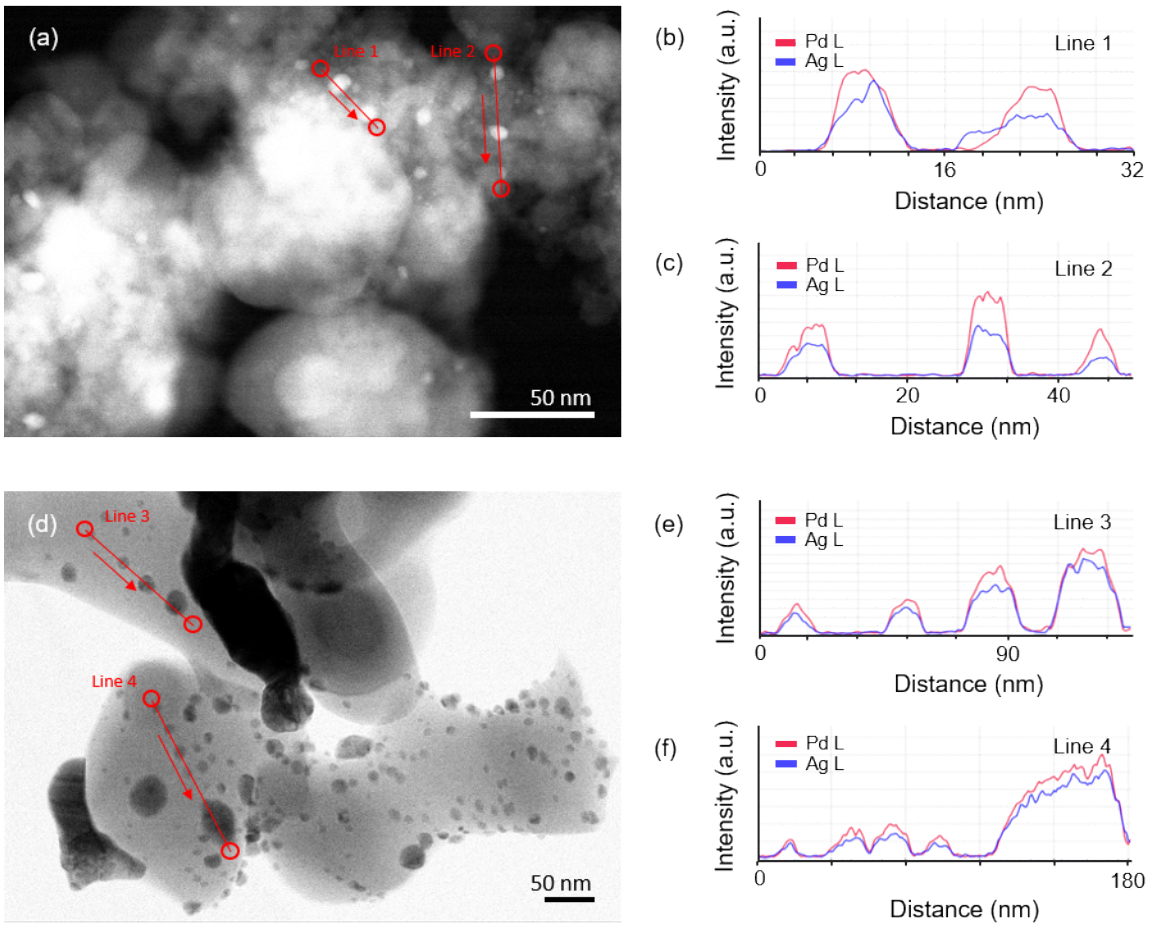

Figure S18. (a) Representative HAADF-STEM micrograph and (b-c) EDX line scan intensity plots, i.e., where the signal intensity for Pd L and Ag L is plotted against the relative position along the given line, measured over selected PdAg nanoparticles of PdAg (1:1) / HSA-α-Al_2O_3. (d) Representative HR-TEM micrograph and (e-f) EDX line scan intensity plots measured over selected PdAg nanoparticles of PdAg (1:1) / LSA-α-Al_2O_3.