1 Supplementary Information

2 Pd-Ag/SiO₂ bimetallic catalysts prepared by galvanic displacement for 3 selective hydrogenation of acetylene in excess ethylene

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7 **1.** The Ag dispersion of 2 wt% Ag/SiO₂was measured by chemisorption using H₂ titration of Oprecovered Ag sites at 170 °C.³² The sample was reduced at 250 °C in 10% H₂/balance Ar for 2 8 h and then purged with pure Ar for 30 min, before cooling to 170 °C in flowing Ar. Next, 10% 9 O₂/balance He was passed over the catalyst for 30 min at 170 °C to form Ag-O surface species 10 before being purged with pure Ar for 30 min to remove residual, gas phase oxygen and oxygen 11 weakly adsorbed on the support. Finally, 10% H₂/balance Ar was dosed at 170 °C until all 12 surface Ag-O species reacted with hydrogen to form water and Ag° sites. For each Ag atom, a 13 single H₂ molecule is consumed. H₂ titration uptake curves are shown in Fig. S1. The average Ag 14 dispersion was 4.9%, which corresponds to an average Ag particle size of 23.8 nm and 5.52 \times 15 10^{18} Ag surface sites per gram of catalyst, assuming spherical particle shape. 16



18 Fig. S1 Uptake curves for H₂ titration of O-precovered Ag sites at 170 °C for 2 wt% Ag/SiO₂.

2. For further reference, powder X-ray diffraction (XRD) on 2 wt% Ag/SiO₂ was conducted using a Rigaku Miniflex II benchtop diffractometer with a CuK α radiation source ($\lambda = 1.5406$ Å) operated at 30 kV and 15 mA. Powder sample was loaded on an amorphous glass-backed, low background holder. Scanning was done over the 20 range of 10-80° with sampling width of 0.02° and dwell time of 1°/min. The diffractometer was fitted with a Rigaku D/tex Ultra silicon strip detector which is capable of detecting nanoparticles in samples with metal loadings as low as 1 wt% and particles as small as 1 nm. The profile was shown in Fig. S2, and the Ag particle size obtained from XRD was 19.6 nm.



10 Fig. S2 XRD pattern of 2 wt% Ag/SiO₂.

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3. The blank experiment to check the physisorption of Pd^{2+} on the silica support was conducted under the same conditions that were used for the preparation of Pd-Ag/SiO₂ bimetallic catalysts. As stated in the experimental section, $Pd(NO_3)_2$ was used as the metal source of Pd^{2+} , and the support was AEROSIL® OX 50 hydrophilic, fumed silica (Evonik Degussa Corporation) with a specific surface area of $50 \pm 15 \text{ m}^2/\text{g}$. A concentrated solution of nitric acid was added dropwise to the bath to maintain its pH at ~2.0 ± 0.1 during the entire experiment. The concentration of 1 Pd^{2+} was chosen as ~19.0 µmoles/g. cat which was corresponding to 0.19 wt% Pd on silica if all 2 the Pd²⁺ was adsorbed. From Fig. S3, it can be seen that there was no observed physisorption of 3 Pd^{2+} on the silica support in this case. Besides, for all the preparation experiments of bimetallic 4 catalysts, 2 L of de-ionized water was used to wash the fresh catalysts thoroughly after 1 h of 5 reaction time to remove all soluble salts including weakly adsorbed Pd²⁺ from the catalysts.



7 Fig. S3 Time-dependent blank experiment of Pd²⁺ on silica support under pH 2 and at room
8 temperature.

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4. The time-dependent metal displacement profiles are illustrated in Fig. 2 in manuscript. Both 10 the concentrations of deposited Pd²⁺ and corrected displaced Ag⁺ were monitored during the 11 experiments. It can be seen in Fig. 2A that the displacement reaction is initially first order in Pd²⁺. 12 To show the reaction order relation more clearly, explicit plots of first order reaction for Pd²⁺ 13 disappearance vs. time were shown in Fig. S4. A straight line correlation for ln [Pd²⁺] 14 disappearance vs. time confirms that the displacement reaction is initially first order in Pd²⁺. 15 Because the deposition for 0.03 wt% Pd has just a few points, here we only show the plots for 16 0.09, 0.28 and 0.32 wt% Pd samples. Taking liquid aliquot sample at t = 0 min, along with 17

adding monometallic Ag/SiO2 catalyst and starting time clock were all conducted at same point,
 which led to some error for actual beginning time. Thus, the following plots start from t = 2 min.
 Besides, the displacement essentially stops after t = 10 min for 0.09 wt% Pd and t = 20 min for
 0.28 and 0.32 wt% Pd, so the plots only show points over these time intervals.





2 Fig. S4 First order plots for Pd²⁺ disappearance vs. time for (A) 0.09, (B) 0.28, (C) 0.32 wt% Pd
3 on Ag/SiO₂. A straight line correlation confirms first order dependency.

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5. The concentrations of surface Pd on Ag for the series of Pd-Ag/SiO₂ catalysts were measured 5 by chemisorption using H₂ titration of O-precovered Pd sites at 40 °C.^{7,8} The sample was 6 reduced at 200 °C in 10% H₂/balance Ar for 2 h and then purged with pure Ar for 30 min before 7 cooling to 40 °C in flowing Ar. Next, 10% O₂/balance He was passed over the catalyst for 30 8 min at 40 °C to form Pd-O surface species before being purged with pure Ar for 30 min to 9 remove residual, gas phase oxygen and oxygen weakly adsorbed on the support. Finally, 10% 10 H₂/balance Ar was dosed at 40 °C until all surface Pd-O species reacted with hydrogen to form 11 water and Pd-H sites. For each Pd atom, 1.5 H₂ molecules are consumed. H₂ titration uptake 12 curves are shown in Fig. S5. There was no significant H₂ uptake for this sample as well as for all 13 other samples. 14





3 Fig. S5 Uptake curves for H₂ titration of O-precovered Pd sites at 40 °C for (A) 0.03, (B) 0.09,
4 (C) 0.28, (D) 0.32, (E) 0.39, and (F) 0.44 wt% Pd on Ag/SiO₂.

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6. Because of the uncertainty of Ag 3d binding energies of supported Ag catalysts, presumably 6 due to the charging effects of the insulating silica support and possible Ag particle size effects, 7 8 comparisons of Ag binding energies are valid only within a given study for similar Ag morphologies and particle size. To confirm the Ag $3d_{5/2}$ binding energies for Ag^o and Ag⁺ (or 9 Ag^{δ^+}) species in this study, the XPS spectra for 2 wt% Ag/SiO₂ shown in Fig. S6 were taken 10 after reduction in 100% H₂ at 200 °C for 2 h and after calcination in 100% O₂ at 200 °C for 2 h. 11 Both H₂ and O₂ pretreatment were performed in situ in catalysis cell attached to XPS chamber, 12 and the parameters were set same as those during XPS of Pd-Ag/SiO₂ (Fig. 5 in the manuscript). 13 The Ag 3d_{5/2} values are 367.9 eV after reduction (red) and 368.7 eV after calcination (blue), 14 corresponding to Ag° and Ag^{+} respectively. Thus, the shift to higher Ag $3d_{5/2}$ binding energy 15

value indicates electron transfer away from Ag. The similar trend on 12 wt% Ag/Al₂O₃ sample
was observed in a previous study from our group.⁴⁵ The XPS spectrum was also taken for the
fresh prepared 2 wt% Ag/SiO₂ sample (black) that was ex situ calcined and reduced before being
loaded into XPS. It shows that the base Ag/SiO₂ was well reduced before the preparation of PdAg/SiO₂ bimetallic catalysts.



Fig. S6 Ag 3d spectra of 2 wt% Ag/SiO₂ for (1) *ex situ* pretreatment in air at 300 °C for 2 h and
in 10% H₂/He at 300 °C for 2 h, (2) *in situ* pretreatment in 100% H₂ at 200 °C for 2 h, and (3) *in situ* pretreatment in 100% O₂ at 200 °C for 2 h.