Electronic Supplementary Material (ESI) for Faraday Discussions.

Supporting Information

The isoprene selective hydrogenation using AgCu-promoted Pd nanoalloys

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Experimental section

1 Preparation of catalyst

The process steps for the preparation of PdAgCu ternary alloy catalyst are described as follows. Support pretreatment: we used ϒ-Al_2O_3 with a size of 0.85-1 mm as the support. First, the support was soaked and rinsed 3-5 times using deionized water to make the water molecules occupy the support pore channels, then the support was placed in deionized water, heated and boiled. And repeated 3-5 times to remove the air bubbles inside the support pore channels. Next, 30 mL of chloropalladium acid solution (concentration of 0.01005 g/ml) was added with 100 mL of deionized water, and potassium carbonate was used to adjust the pH range between 2.3-2.4. Subsequently, the precursor liquid was heated and the support was poured into it; the beaker was shaken every 2-3 minutes for uniform impregnation, and the heating was ended when the upper layer of liquid in the beaker changed to clear liquid. After the temperature dropped to room temperature, the Pd catalyst was removed from the beaker. The Pd catalyst was aged in a glass dish for 4 hours, dried in an oven at 120°C for 4 hours, and then calcined in a muffle furnace at 450°C for 4 hours to obtain a Pd/Al_2O_3 catalyst with a loading of 0.3 wt%. Finally, we prepared a series of PdAgCu ternary alloy nanocatalysts with different molar ratios by the equal volume impregnation method. For comparison, we also prepared PdAg and PdCu bimetallic catalysts (Pd loading of 0.3 wt% and molar ratio of Pd to Ag and Cu of 1:1) using the above method.

2 Catalyst characterization

H_2-TPR experiments were performed on a Micromeritics AutoChem 2900. First, 50 mg of 0.25-0.43 mm sized catalyst was pretreated in a helium atmosphere (30 mL/min) for 0.5 h; simultaneously air was turned on to purge the environment around the sample tube and cooled down to 30°C. After waiting for the baseline to stabilize, the temperature increase was started and the support gas was switched to 10% H_2/Ar (30 mL/min). Then, the temperature was increased from 30°C to 800°C at a rate of 10 °C/min. H_2 consumption was monitored by a thermal conductivity detector (TCD). Finally, the position and size of the reduction peak of the metal were derived. The NH_3-TPD experiment used the same apparatus as the H_2-TPR experiment. TEM images, elemental mapping images, and line scan profiles were obtained on an electron microscope model FEI Tecnai G2 F20 equipped with an EDS attachment. X-ray powder diffraction (XRD) was measured on a JBruker D8 advanced X-ray diffractometer equipped with CuKα radiation (1.5405 Å) at a scan rate of 2°min^{-1} from 5° to 90°. XPS spectra were recorded on Thermo Scientific spectrometer equipped with monochrome Al-K radiation source.

3 Catalytic performance test

The samples were hydrogenated in a fixed-bed four-channel continuous flow reactor. Firstly, 5 mL of sample was mixed well with 5 mL of quartz sand and then loaded into the reaction tube. After checking the gas tightness of the reactor was intact, hydrogen gas was introduced and the reaction tube was heated to reduce the catalyst sample. The reduction conditions were 1.5 MPa pressure, 300°C for 4 hours and a hydrogen flow rate of 1 L/h. A mixture of n-heptane (Tianjin Yongda Chemical Reagent Co., Ltd.) and isoprene (Yanfeng Technology Co., Ltd.) was used as raw material, in which the content of isoprene was 5.67% (mass fraction). Then, after the reactor operation was stabilized we started sampling and testing. To ensure the authenticity of the data, three sets of experiments were taken for each data point. Finally, the raw oil and the hydrogenated product were analyzed using an Agilent 7890B fully automated liquid chromatograph.

Figure and table captions

Fig. S1 EDS Mapping and line scan image of PdAg catalyst.

Fig. S2 EDS Mapping and line scan image of PdCu catalyst.

Fig. S3 Hydrogenation performance diagram of different catalysts.

Fig. S4 Hydrogenation performance graphs of PdAgCu catalysts.

Fig. S5 XPS image of PdAgCu ternary alloy catalyst.

Table S1 Hydrogenation performance of PdAgCu ternary alloy catalysts with different compositions.

Table S2 Atomic ratios of surface composition and chemical valence states of PdAgCu ternary alloy catalysts.

Table S3 Pd/AgCu atomic ratio of catalysts measured by XPS and ICP.

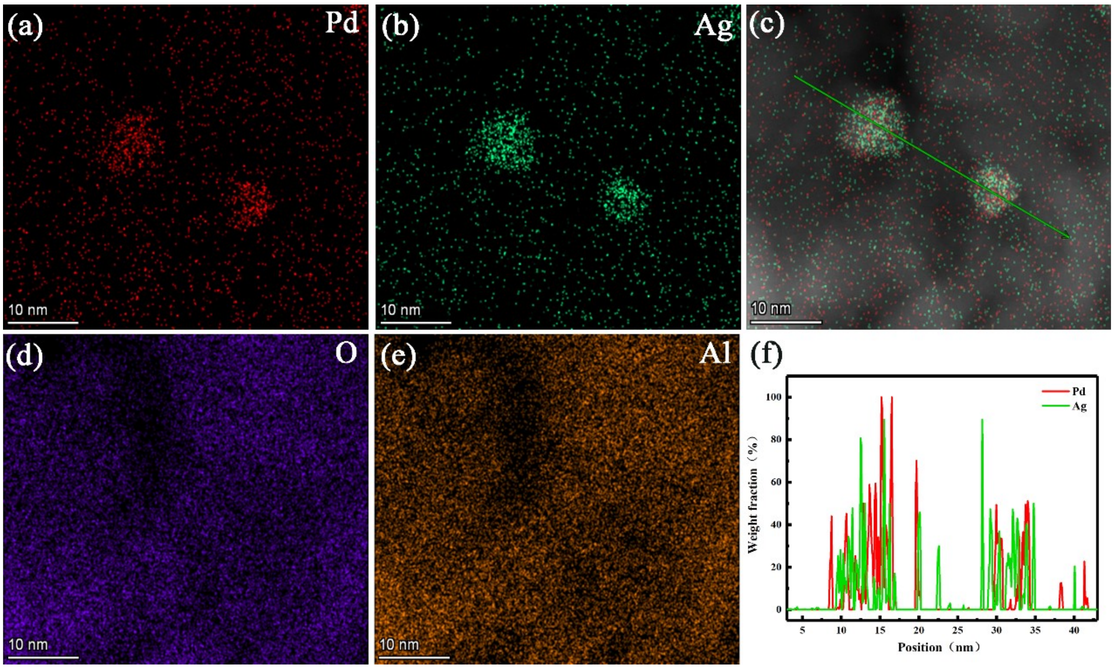

Fig. S1 EDS Mapping and line scan image of PdAg catalyst.

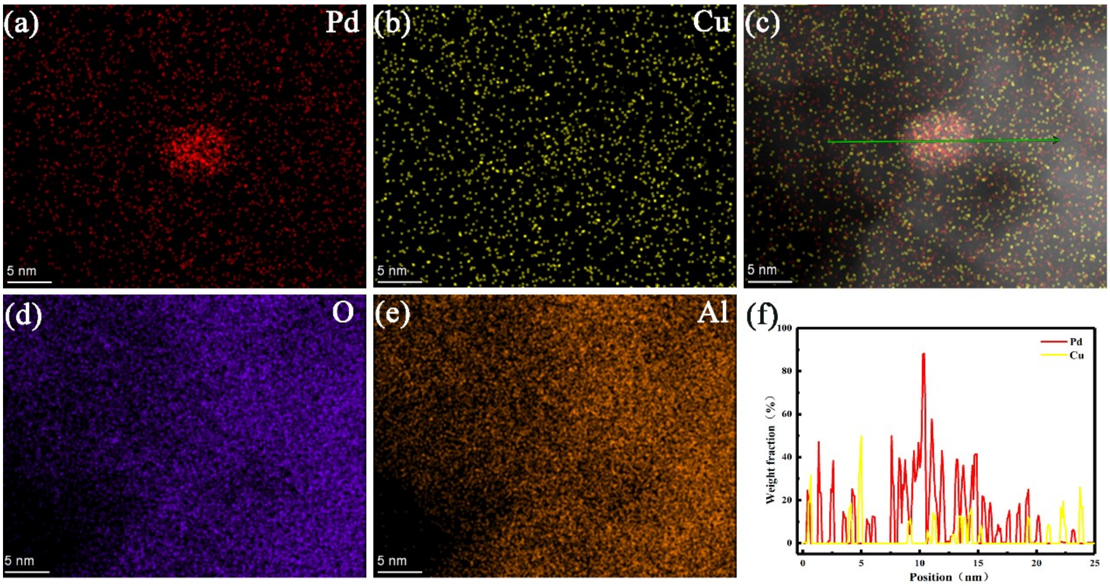

Fig. S2 EDS Mapping and line scan image of PdCu catalyst.

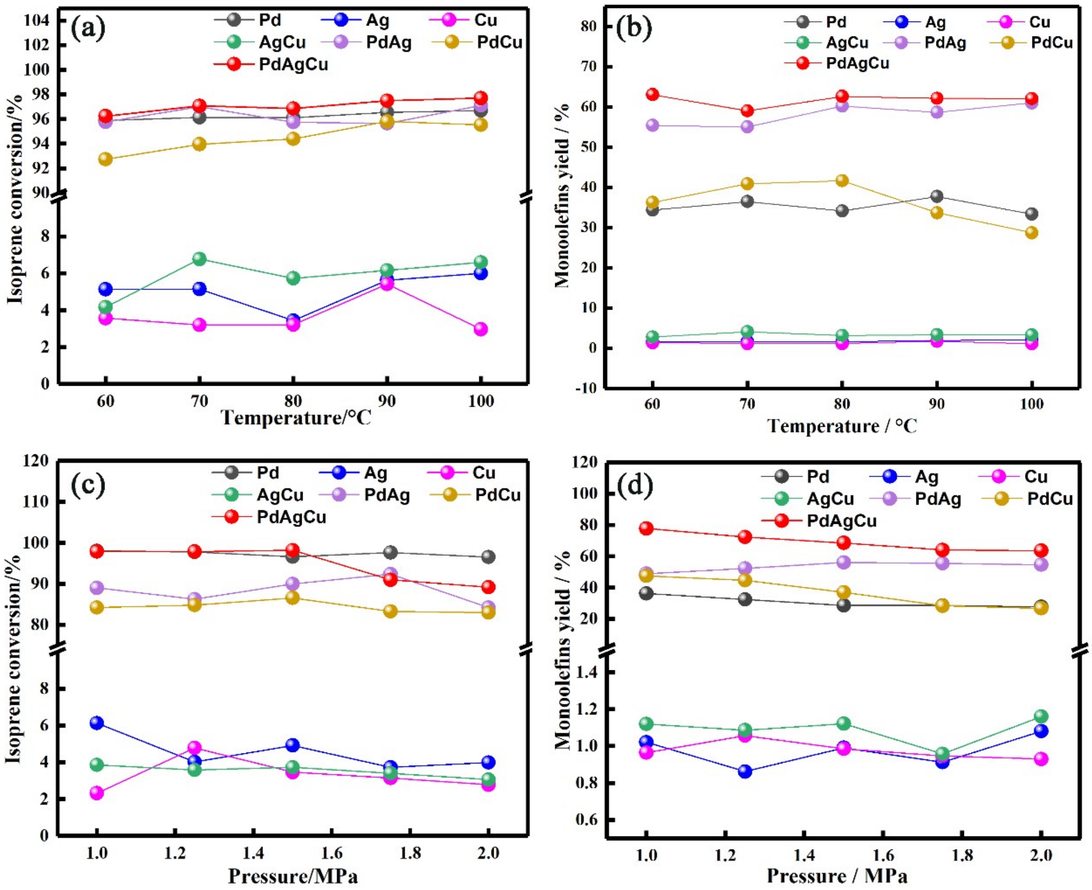

Fig. S3 Hydrogenation performance graphs of different catalysts. (a~b)The reaction conditions are 1.5 Mpa, 12 h-1, and the temperature is changed; (c~d) the reaction conditions are 60 °C, 12 h-1, and the pressure is changed.

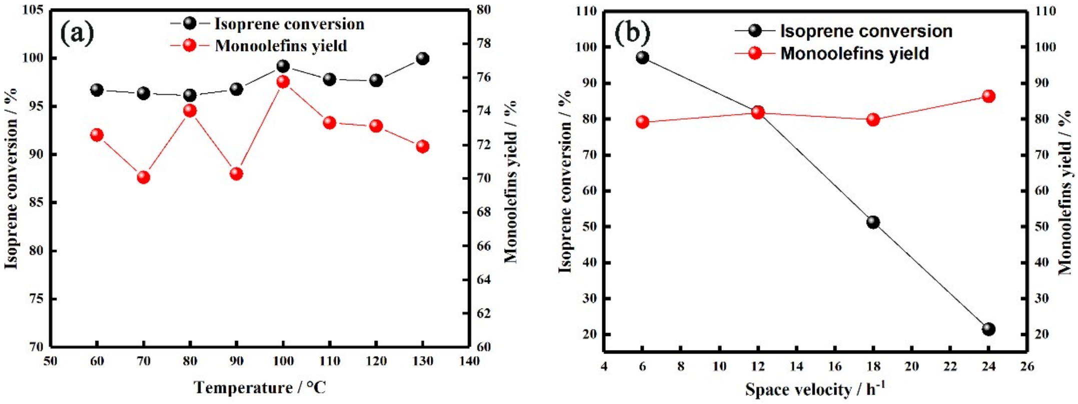

Fig. S4 Hydrogenation performance graphs of PdAgCu catalysts, (a) reaction conditions of 1 Mpa, 12 h-1, varying the temperature; (b) reaction conditions of 1 Mpa, 100 °C, varying the space velocity.

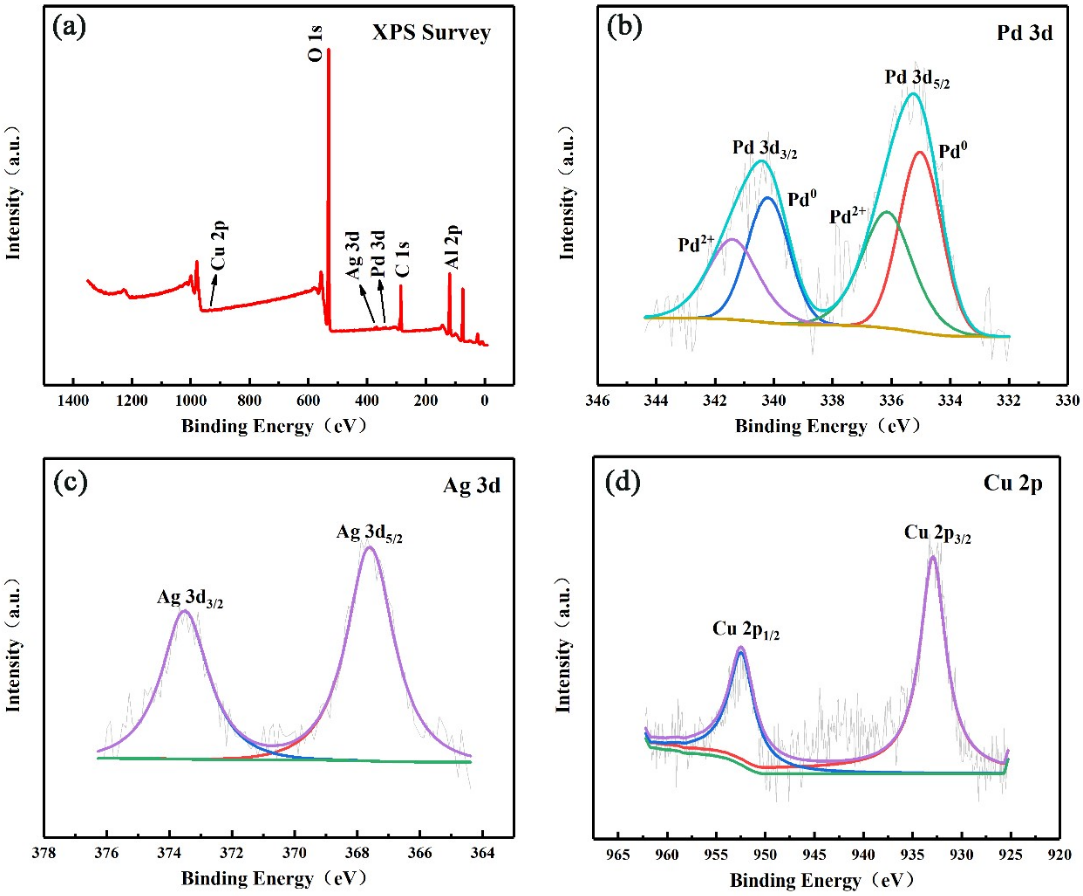

Fig. S5 XPS image of PdAgCu ternary alloy catalyst.

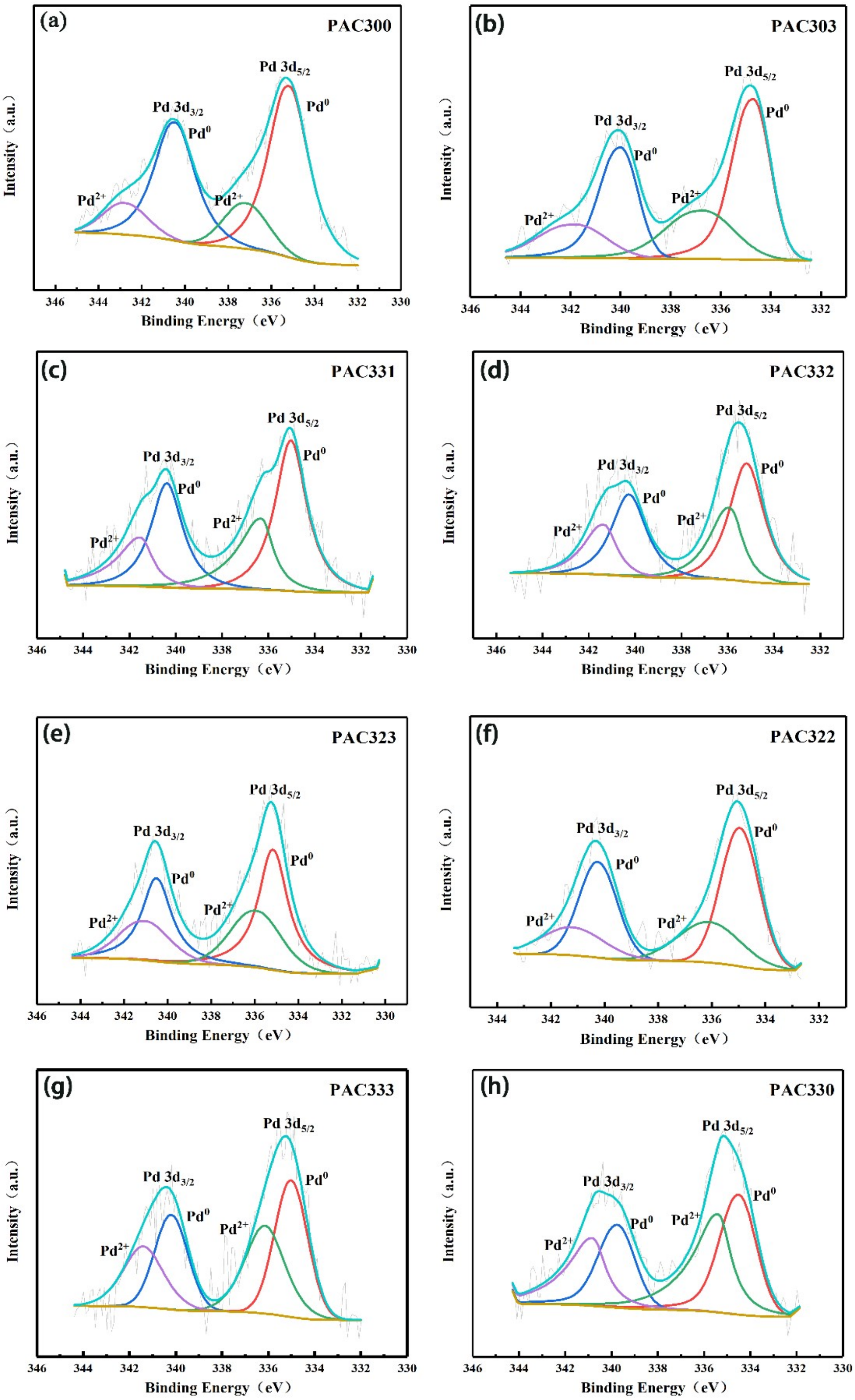

Figure S6. (a-h) Pd 3d XPS spectra of PdAgCu ternary alloy with different composition shown in Table S2.

Table S1 Hydrogenation performance of PdAgCu ternary alloy catalysts with different compositions.

Molar ratio of PdAgCu	Composition/wt% Pd	Ag	Cu	conversion /%	Monoolefin yield /%
3:1:1	0.3	0.101	0.0597	97.78	66.72
3:2:1	0.3	0.203	0.0597	97.19	80.18
3:3:1	0.3	0.304	0.0597	97.10	51.26
3:1:2	0.3	0.101	0.1194	97.22	53.49
3:2:2	0.3	0.203	0.1194	97.91	91.76
3:3:2	0.3	0.304	0.1194	97.73	53.41
3:1:3	0.3	0.101	0.179	97.85	62.58
3:2:3	0.3	0.203	0.179	97.94	91.58
3:3:3	0.3	0.304	0.179	97.57	84.71

Table S2 Atomic ratios of surface composition and chemical valence states of PdAgCu ternary alloy catalysts.

Catalyst	Pd/AgCu(Atomic%)	Pd/AgCu(Atomic%)	Pd^0/Pd^{2+}(Atomic %)
PAC300	0.3	—	3.77:1
PAC303	0.479	1:2.31	1.91:1
PAC331	0.6637	1:2.61	1.85:1
PAC332	0.7234	1:2.86	1.64:1
PAC323	0.7	1:3.20	1.56:1
PAC322	0.6224	1:4.31	1.29:1
PAC333	0.801	1:3.83	1.23:1
PAC330	0.604	1:1.10	1.01:1

PAC323 represents a molar ratio of 3:2:3 for each component of PdAgCu.

Table S3. Pd/AgCu atomic ratio of catalysts measured by XPS and ICP.

Catalyst	Pd/AgCu (atomic ratio [a])	Pd/AgCu (atomic ratio [b])
Pd	-	-
PdAg	2.94:1	1:1.10
PdCu	1.32:1	1:2.31
PdAgCu	0.69:1	1:3.83

[a] As determined by ICP.

[b] As determined by XPS.