

Supplementary Information for

## **Preparation of ternary Pd-Rh-P amorphous alloy and its catalytic performances toward selective hydrogenation of alkynes**

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### **Experimental details:**

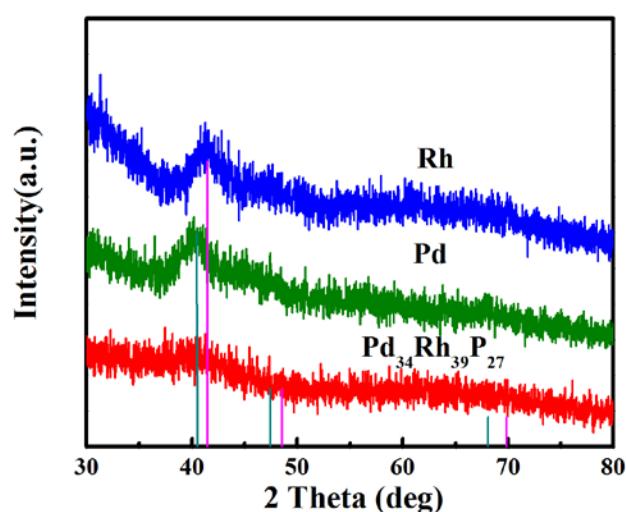
**Materials:** Rh(acac)<sub>3</sub>, Pd(acac)<sub>2</sub>, 1-nitro-4-ethynylbenzene, 1-bromo-4-ethynylbenzene, diphenylacetylene, trioctylphosphine were purchased from Alfa Aesar. Oleylamine and Lindlar catalyst (Pd-Pb/CaCO<sub>3</sub>, Palladium on calcium carbonate, poisoned with 3.5% lead, 5% Pd) were purchased from Acros. Ethanol, cyclohexane, dioxane are of analytical grade from the Beijing Chemical Factory of China. All the reagents were used without further purification.

**Synthesis of alloy NPs:** 2 mg of Rh(acac)<sub>3</sub> and 1.5 mg of Pd(acac)<sub>2</sub> were dissolved in oleylamine (OAm, 5mL) which also serves as the reducing agent. 10-60 μL of trioctylphosphine (TOP) was added in the mixed liquor as capping agent. The mixture solution was sonicated for 20 min and then transferred into a Teflon-lined autoclave, sealed and heated at 220 °C for 16 h. After cooling down to room temperature, the precipitate was separated by centrifugation, washed thoroughly by hot ethanol and cyclohexane (10/1, v/v) for three times and then dispersed in 4 ml of cyclohexane.

Rh and Pd NPs were prepared by the same method except that the bimetal precursor was replaced by same amount of single metal one.

**Characterization:** Powder XRD patterns were recorded with a Bruker D8 ADVANCE X-ray powder diffractometer with Cu K $\alpha$  radiation ( $\lambda=1.5406 \text{ \AA}$ ). Hitachi model H-800 transmission electron microscope, a JEOL-2010F high-resolution transmission electron microscope, and energy dispersive X-Ray spectroscopy (EDX) were carried out on FEI TECNAI F-20 field emission microscope at an accelerating voltage of 200 kV. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was used to determine the content of metal element.

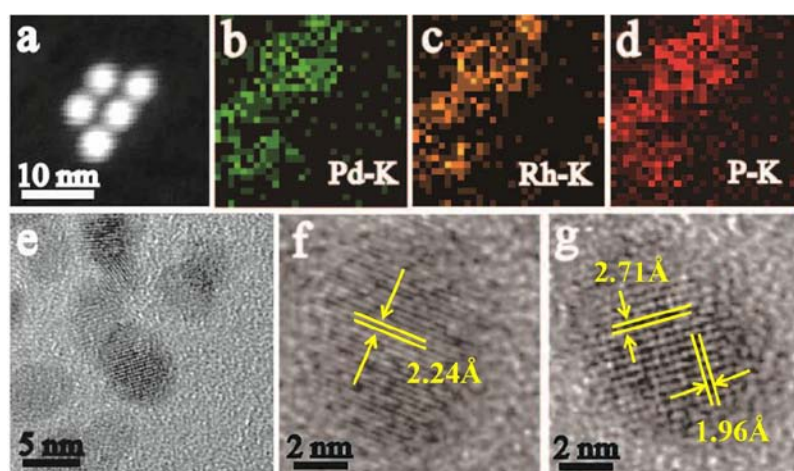
**Catalytic evaluations:** The substrate and catalyst (atomic ratio was 1200:1) were dispersed in 1 ml of dioxane and placed in a 5 ml flask sealed with a rubber stopper. A balloon filled with hydrogen was connected with the flask by a syringe needle after it was purged 3 times with H<sub>2</sub>. The mixture was stirred at 600 rpm at acquired temperature (35 °C) for the required time. After a given reaction time, the reaction product was analyzed off line by gas chromatography (GC, SP-6890) equipped with a flame ionization detector (FID), or by gas chromatography–mass spectrometry (GC–MS, Thermo Fisher, 2012).



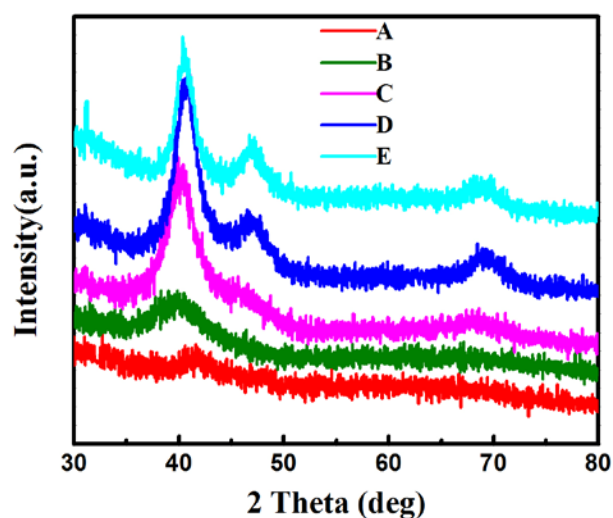
**Fig. S1** XRD patterns of the PdRhP alloy NPs, pristine Pd and Rh NPs, respectively.

**Table S1. Elemental composition of the as-synthesized amorphous alloy NPs**

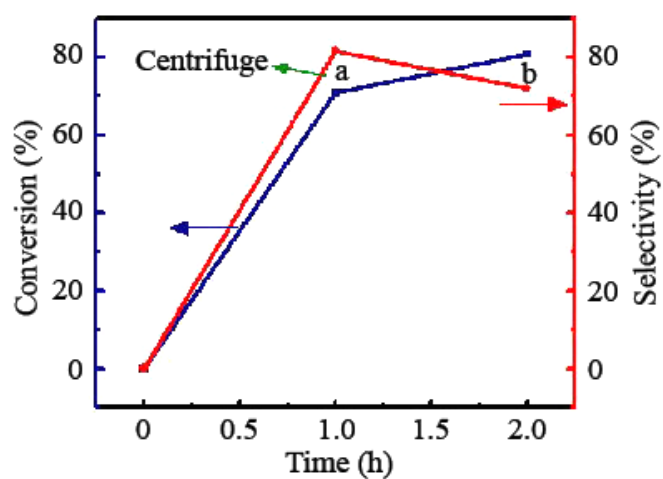
Element	ICP analysis(Atom% )
Rh	39.58
Pd	33.82
P	26.60
Total	100



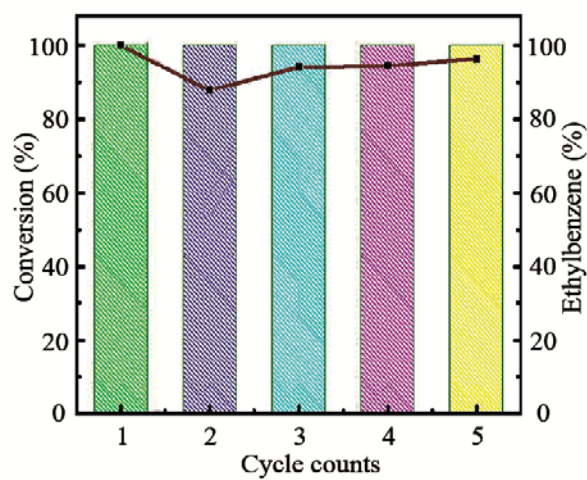
**Fig. S2** (a) HAADF-STEM image of the amorphous alloy NPs; EDX mapping images of (b) Pd-K, (c) Rh-K, (d) P-K; (e) HRTEM image of alloy NPs supported on SiO<sub>2</sub> after calcination in which separate Pd (f) and Rh<sub>2</sub>P (g) phase can be identified.



**Fig. S3** XRD patterns of the obtained alloy NPs with various P/metal ratios: (A) P/metal=14/1, (B) P/metal=11/1, (C) P/metal=9/1, (D) P/metal=7/1, (E) P/metal=2/1.



**Fig. S4** The conversion of phenylacetylene and selectivity toward styrene over the PdRhP alloy catalyst before (a) and after centrifugation (b). Reaction conditions: dioxane (1 ml),  $H_2$  (1 bar), 35 °C.



**Fig. S5** Recycle capability of the PdRhP alloy catalyst toward the hydrogenation of phenylacetylene.