

# Atomically Dispersed Pd-Ru Dual Sites in Amorphous Matrix towards Efficient Phenylacetylene semi-Hydrogenation

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## Methods

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### Preparation of PdRu-ZPO catalyst

In a typical synthesis of Pd<sub>5</sub>Ru<sub>95</sub>-ZPO, 50  $\mu$ L of PdCl<sub>2</sub> stock solution (6 g/L) and 1.425 mL RuCl<sub>2</sub> stock solution (3.6 g/L) were added into the beaker with 3.4 mL 1.93 g ZrOCl<sub>2</sub>·8H<sub>2</sub>O and 50 mL ethanol. The beaker was kept stirring while another beaker with 0.52 mL H<sub>3</sub>PO<sub>4</sub>, 4 mL triethylamine, and 20 mL ethanol slowly poured in and the solution turned from clear to slightly brown-ish opaque. The reaction was allowed to age for 30 min. A gel-like precipitate was collected by centrifuge the solution and washed with pure ethanol. The wash-centrifuge process was repeated for three times. The pale brown gel was then dissolved in distilled water to form a homogeneous solution, which was freeze-dried to obtain the final product.

### Catalyst Characterization

XRD characterization of the samples was carried out on a German Bruker D8 Advance X-ray diffractometer using the Ni-filtered Cu K $\alpha$  radiation at 40 kV and 40 mA. XPS data

were recorded with the Axis Ultra Photoelectron Spectrometer (Kratos Analytical Ltd.) by means of a monochromatized Al K $\alpha$  anode (225 W, 15 mA, 15 kV). The C 1s peak at 284.8 eV was used as the reference to calibrate the binding energies (BE). A Tecnai F20 electron microscope operating at 200 kV equipped with an EDS unit (Si(Li) detector) was used for the TEM investigations. The samples for electron microscopy were prepared by grinding and subsequent dispersing the powder in ethanol and applying a drop of very dilute suspension on carbon-coated grids. High resolution TEM, EDS mapping, and HADDF-STEM were performed on an FEI Titan G2 (60-300) probe-corrected TEM system with a field emission gun operated at 300 kV. A micromeritics ASAP 2460 system was used to measure the nitrogen adsorption-desorption isotherms of the samples at 77 K. Before test, the samples were dried at 200 °C for 12 h at vacuum condition. Specific surface area was calculated by Brunauer-Emmett-Teller (BET) method, and pore size distribution was determined by non-linear DFT model.

### **Catalytic Activity Test**

The selective hydrogenations were carried out in a high-pressure stainless autoclave reactor (Parr Instrument Co., 4790, 50 mL). Typically, 2 mL ethanol, 0.5 mL phenylacetylene, and 40 mg of catalyst were placed in the autoclave equipped with a stir bar. The autoclave was sealed and flushed several times with 0.5 MPa H<sub>2</sub> to remove the air in the reactor; then, 2 MPa H<sub>2</sub> was charged. The heating was started and maintained at 60 °C for 2 hours. The autoclave was then removed from the heating plate and allowed to cool down naturally. 0.3 mL of internal standard 1,4-dioxane was added into the aqueous product in autoclave. The reaction mixture was transferred into a centrifuge tube, and the solid catalyst was separated by centrifugation. The product solution was quantitatively analyzed using a GC Agilent 7820A equipped with a HP-5 capillary column connected to a flame ionization detector. Identification of the products was performed by using a GC-MS spectrometer. Noted that the total carbon balance was >95%. For the recycling experiment, the centrifuged catalysts from parallel tests were collected and washed with ethanol/distilled water mixture for several times, followed by air drying at 120°C for 8 h.

## Diffuse reflectance FTIR characterizations

In-situ DRIFT-IR was carried out by using Pd5Ru95-ZPO which was pressed into a small disc and then transferred into an in-situ chamber of FTIR. The chamber was flushed with 1 bar Ar at room temperature ten times. Then, 5% H<sub>2</sub>/Ar and phenylacetylene vapor were charged into the chamber for several minutes and recorded by FTIR (Thermo Fisher IS50). The blank chamber with Ar was used for background correction.

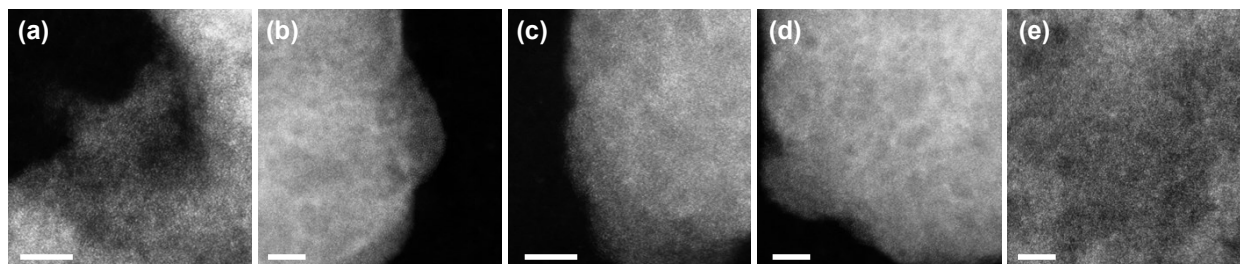


Figure S1 (a–e) HAADF-STEM images of the Pd5Ru95-ZPO. The scale bars in these images are 5 nm.

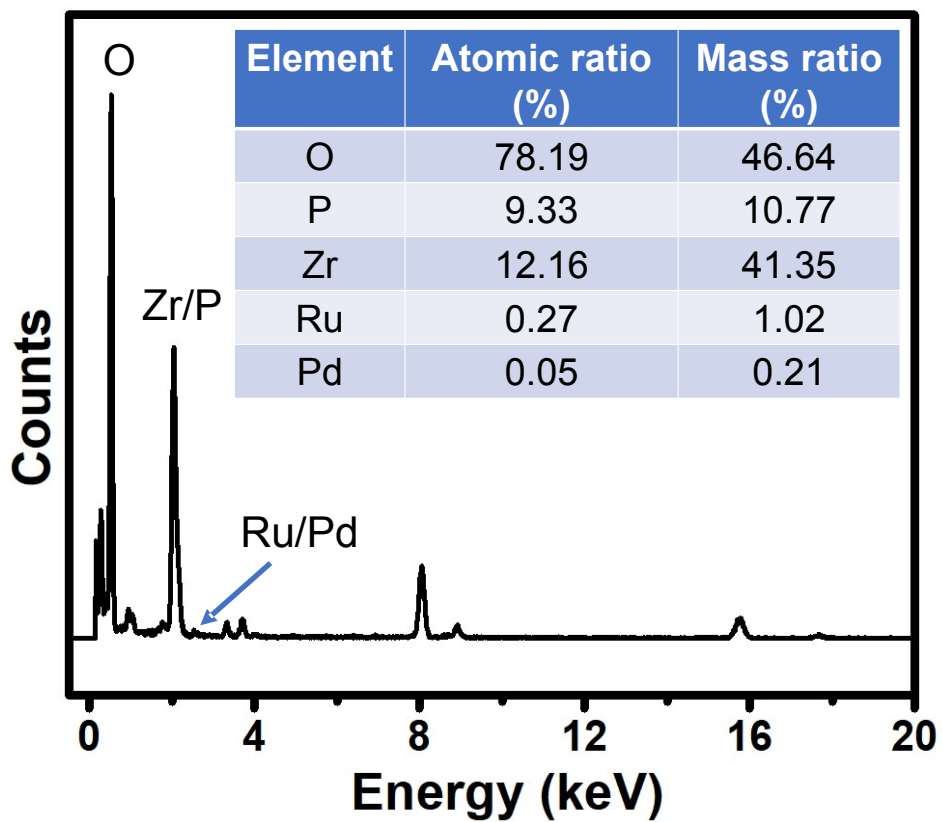


Figure S2 EDS spectrum and the corresponding element ratio analysis.

Table S1 ICP-MS analysis of the Pd5Ru95-ZPO sample.

	Atomic ratio (%)		
	Pd	Ru	Zr
Pd5Zr95-ZPO	<0.01	0.17	9.9

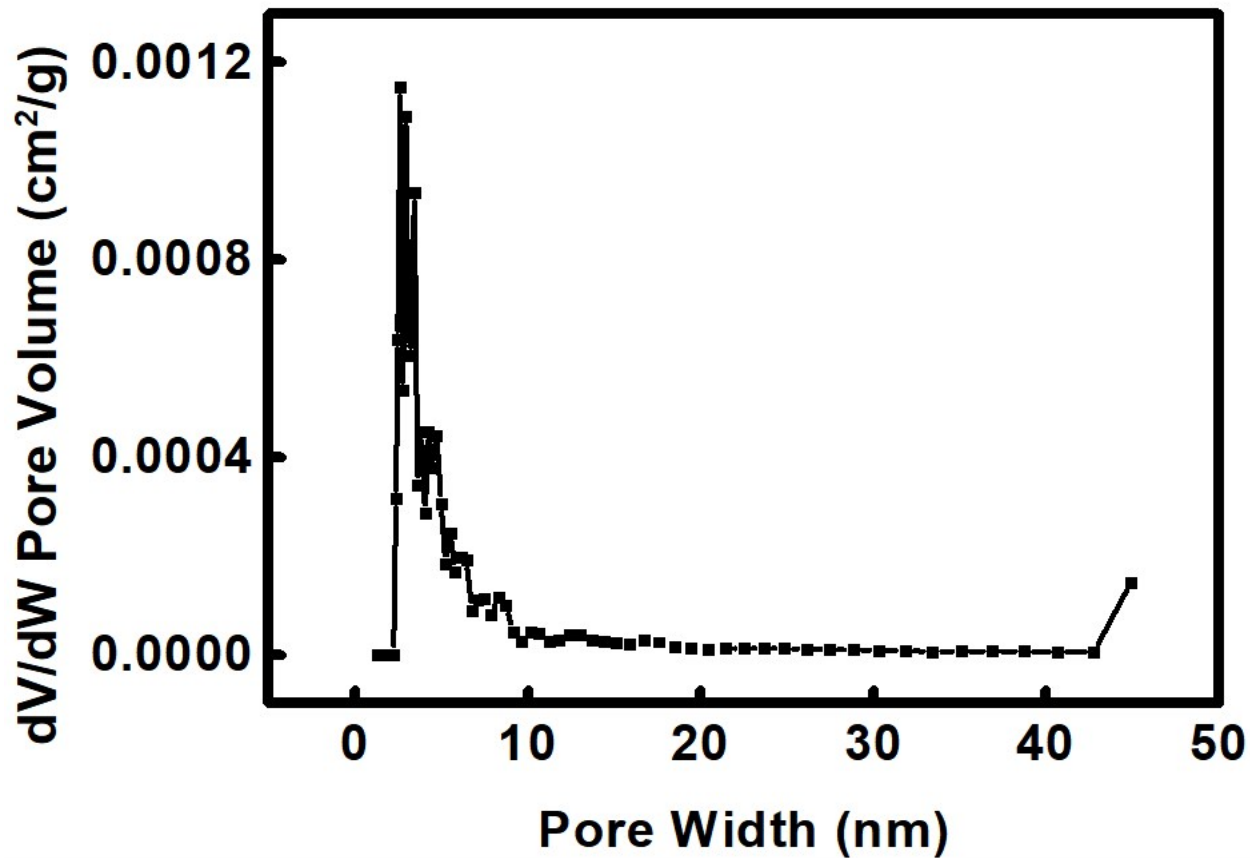


Figure S3 Pore size distributions of the Pd5Ru95-ZPO calculated from BET measurement.

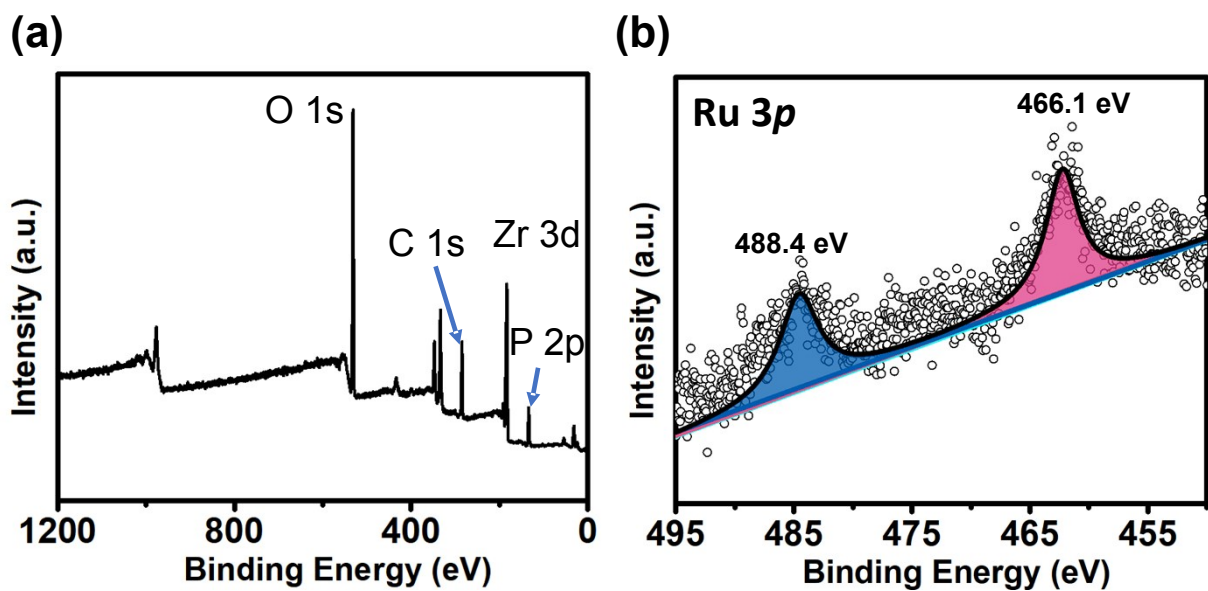


Figure S4 (a) XPS full spectrum and (b) Ru 3p spectra of the Pd5Ru95-ZPO sample.

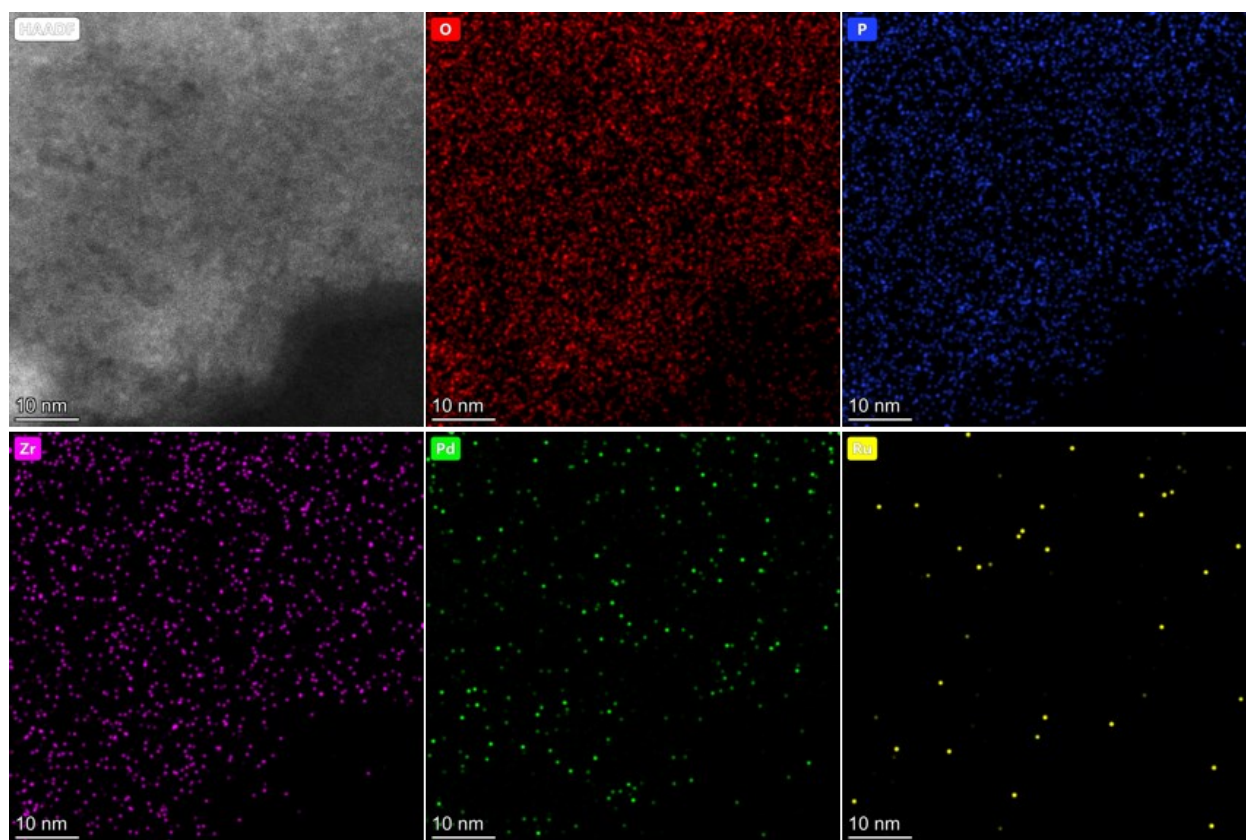


Figure S5 HADDF-STEM images of the sample after five cycles.

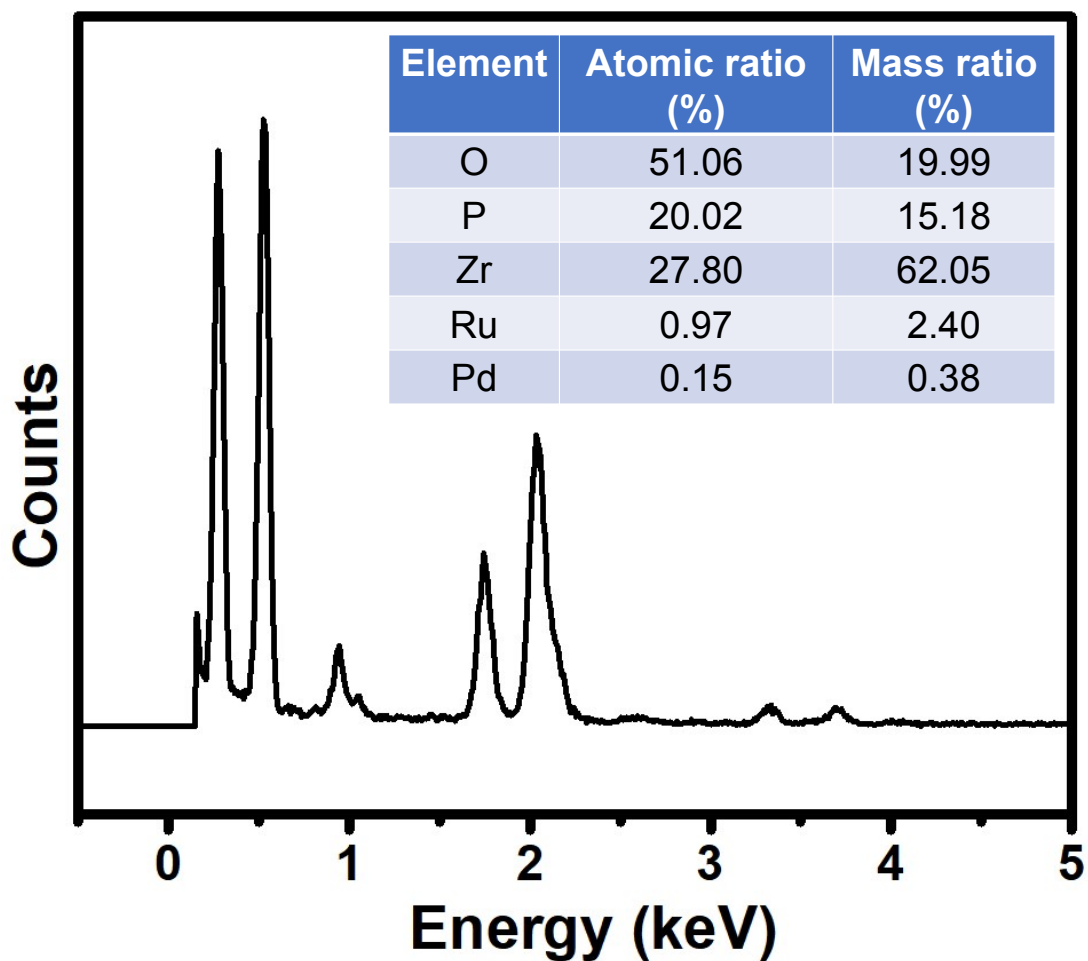


Figure S6 EDS spectrum and the corresponding element ratio analysis of the sample after five cycles.

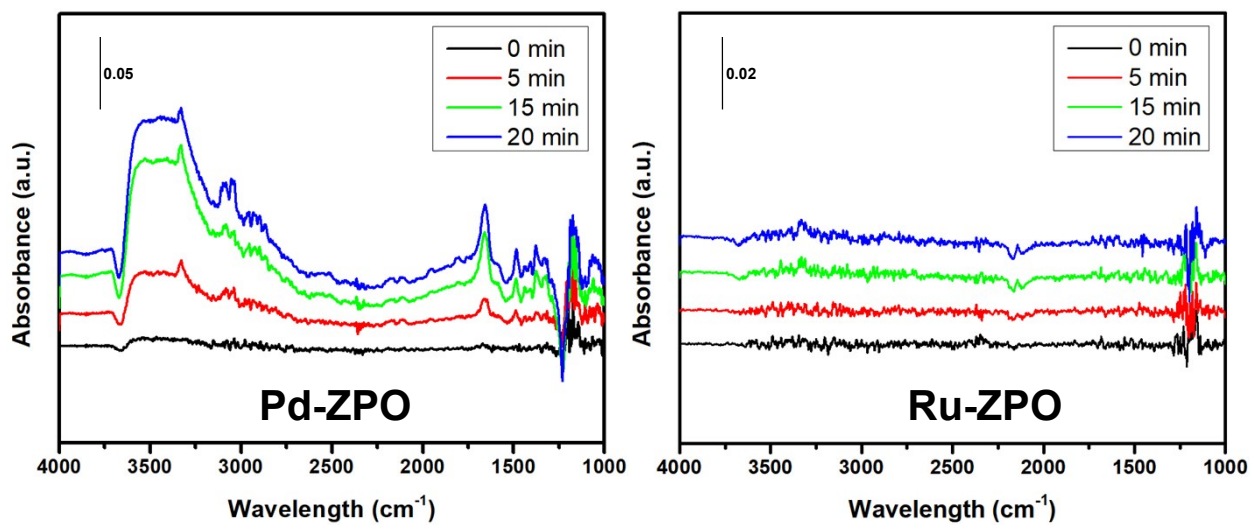


Figure S7. In situ FT-IR performed with Pd-ZPO and Ru-ZPO.

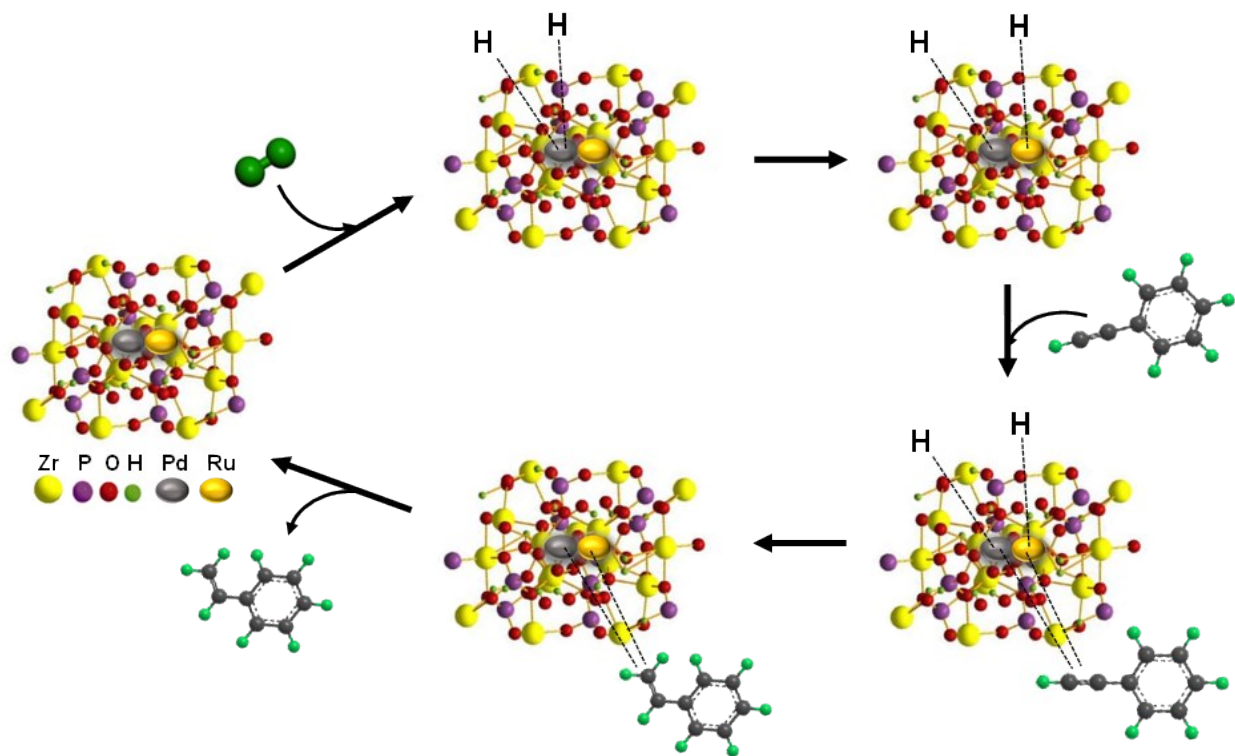


Figure S8 Possible reaction pathways for the semi-hydrogenation of phenylacetylene over atomically dispersed Pd and Ru dual sites in ZPO.