

Supporting Information for PCCP

The Control of Pt and Ru Nanoparticle Size on High Surface Area Supports

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Experimental procedure:

Synthesis of Catalysts:

SiO₂ (Aerosil-380) was obtained from Evonik industries and SBA-15 was prepared as per the main article. Ruthenium hexamine chloride ([Ru(NH₃)₆]Cl₃, 99.9%) and platinum tetraamine chloride ([Pt(NH₃)₄]Cl₂, 99.9%) obtained from Aldrich which are designated as RuHA and PTA respectively were used as ruthenium and platinum precursors. Stock solutions of 200ppm Ru or Pt were prepared.

1) PZC determination

Deionized water was added to incipient wetness of 2g SBA-15 or Aerosil 380 in a 50 mL centrifuge tube. A spear-tip pH meter was used to measure the pH of the thick slurry. Results are shown in Table S1.

Table S1 Single point determination of different SiO₂ supports.

Support	SBA-15	Aerosil-380
PZC	4.4	4.5

2) Uptake survey and catalysts synthesis

Metal uptake-pH surveys were carried out in 60-mL polypropylene bottles containing 55 mL of 200 ppm RuHA or PTA, with initial pH adjusted in the range of 5 to 13 by HCl and NaOH. 5 ml solution was taken out for later ICP analysis ($C_{\text{metal,initial}}$). The amounts of supports were added to achieve surface loadings of 1000 m²/L. Taking as received SBA-15 (SA=710 m²/g) as an example,

$$m (g) = \frac{1000 \frac{m^2}{L} \times \frac{50 L}{1000}}{710 \frac{m^2}{g}} = 0.0704g$$

After adding supports into metal precursor solutions they were placed on an orbital shaker for 1 h to ensure adsorption equilibrium. Final pH values were recorded and 5 mL solution was filtered for ICP analysis ($C_{\text{metal,final}}$). The metal surface density, Γ , is calculated as

$$\Gamma \left(\frac{\mu\text{mol}}{L} \right) = \frac{(C_{\text{metal,initial}} - C_{\text{metal,final}}) \left(\frac{\mu\text{mol}}{L} \right)}{SL \frac{m^2}{L}}$$

3) Steaming- Reduction procedure

All RuHA/SBA-15 and PTA/SBA-15 samples were dried at 100 °C overnight to remove moisture. 25% H₂/He (200 cm³/min) was passed through a bubbler filled with water and connected to a quartz tube in a horizontal furnace. Steaming reduction temperature was ramped from room temperature to 900 °C for Ru and 800 °C for Pt with rate of 10 °C per min.

4) Oxidation-Reduction procedure

After removal of moisture by overnight drying, samples were placed in muffle

furnace for oxidation (static air) and taken out after cooling down to room temperature. The reduction cycle was followed with ramp rate of 2.5 °C/min from room temperature to 180 °C for 1 hr (Ru and Pt). 50% H₂/He (200 cm³/min) in He was used as reducing gas to ensure all metal oxides could be completely reduced.

Characterization

Powder X-ray diffraction (XRD) analysis was performed using a Siemens D5000 diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) operated at 30 kV and 40 mA, operating in Bragg–Brentano geometry. Scans were made in the 10°–80° 2 θ range, with step size of 0.02°, and 2 s exposure at each step. Z-contrast STEM imaging for particle size determination in the materials was conducted with a JEOL JEM-2010F FasTEM with a probe size of 0.14–0.2 nm. The catalyst samples were sonicated in isopropanol for 15 min, and the slurry was deposited onto a carbon-coated copper grid (200 mesh, Cu PK/100), supplied by SPI, U.S.A. The applied voltage was 200 kV and extracting voltage of 4500 V. Approximately 500 particles were counted for size distribution. After removal of moisture at 100 °C for overnight, Temperature programmed reduction analysis was used to determine the reduction temperature of dried sample in an AutoChem II 2920 automated catalyst characterization system. Approximately 0.15 g of dried sample was loaded in a U-shaped pyrex glass cell (10 cm long x 3.76 mm i.d.). Then 50 cm³/min argon gas was passed over the sample for 20 min to desorb moisture in the pores of silica. After this treatment sample was reduced in 10% H₂/Ar (50 cm³/min) to certain temperature under temperature-programmed control with ramp rate of 5 °C/min.

Catalytic HDO of *p*-cresol

The catalytic HDO reaction with *p*-cresol was performed in a 100 mL Autoclave Engineers stirred batch reactor. In a typical experiment, 0.1 mol of *p*-cresol, 55 mL of water and 0.2 g catalyst were charged into the reactor. Then the reactor was sealed and purged 3 times with N₂. The reactor was heated to 300 °C with gentle stirring (300 rpm). As soon as temperature is reached 300 °C H₂ was charged (H₂ partial pressure 300 PSIG) and stirring speed was increased to 1000 rpm. Throughout the reaction H₂ partial pressure was maintained by keeping the reactor inlet valve open and setting the H₂ cylinder outlet pressure equal to reactor pressure. After 2 h the products were recovered and analyzed. Two liquid phases obtained after the reaction were separated and organics from the water phase were recovered by adding dichloromethane. The organic and dichloromethane washed phases were mixed together and analyzed by an HP 5189 series II GC with Suplowax-10 column (30 m x 0.2 mm x 0.2 μ m) and a flame ionized detector (FID). The *p*-cresol conversion is defined as the ratio of the moles of *p*-cresol consumed during the reaction to the moles of *p*-cresol charged initially into reactor. Selectivity is defined as the ratio of the moles of carbon in a specific product to the total number of carbon in all products. In all runs, the analysis of reactants and products accounts for >80 wt% of the starting *p*-cresol. The turn over frequency was calculated using particle size dispersion data based on XRD assuming Pt particles spherical.

Supplementary Figures

Temperature programmed reduction study

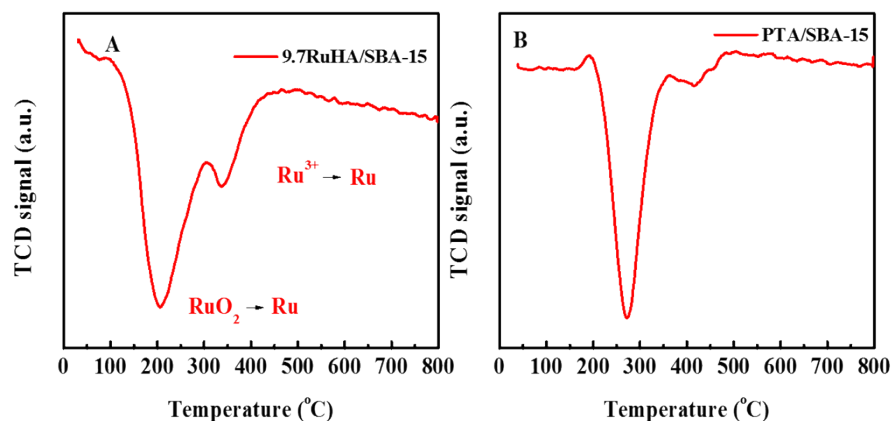


Fig S1. TPR profiles of dried RuHA/SBA-15 (A) and PTA/SBA-15 (B)

Typical TPR profiles of RuHA/SBA-15 and PTA/SBA-15 are shown in Fig S1. Two peaks can be observed in both. Those in RuHA pattern are taken as reduction of RuO_2 to Ru and Ru^{3+} to Ru respectively, and they are confirmed by the control experiment in Fig S2, using physical mixtures of RuO_2 and SBA-15 and RuHA and SBA-15. It appears RuHA is partially oxidized to RuO_2 during overnight drying at 100 °C.

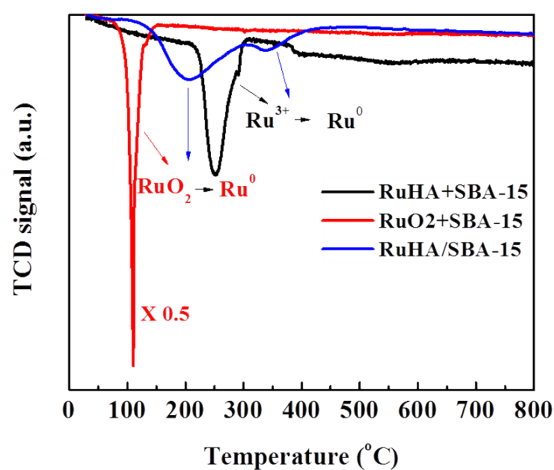


Fig S2. Control experiment shows RuHA was oxidized during preparation.

After oxidation in oven at 200 °C for 3 hrs, RuHA was fully oxidized to RuO_2 , and the same is the case with PTA, oxidized at 300 °C for 1 hrs, they were reduced at 180 °C for 1 hr.

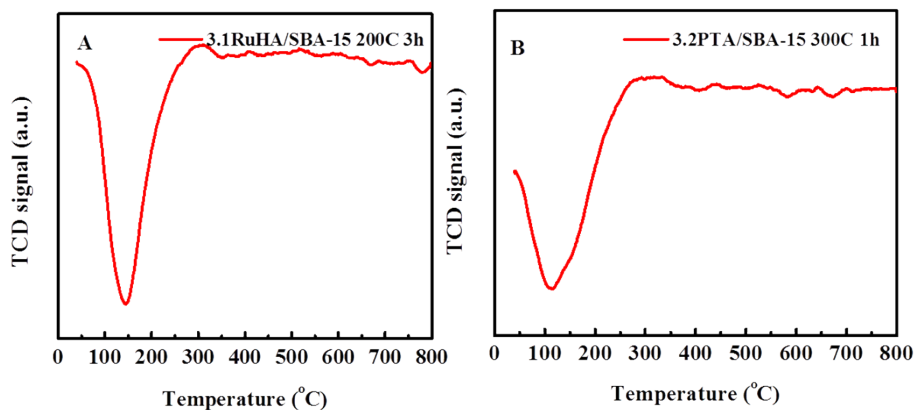


Fig S3. TPR profiles of calcined catalysts, both Ru oxides (A) and Pt oxides (B) can be reduced at lower temperature as synthesized.

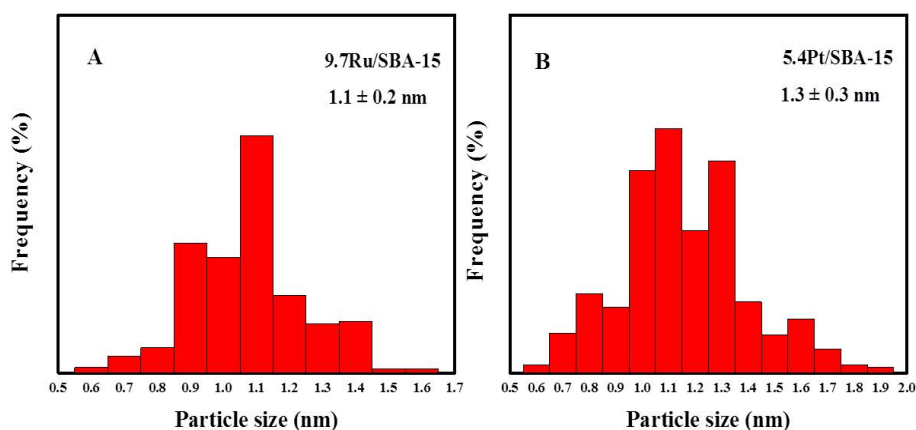


Fig S4. After reduction at 350 °C and 300 °C, highly dispersed Ru (A) and Pt (B) particles deposit on support. Approximately 1000 particles of each images were considered. The corresponding statistical data on particle size distribution was obtained using Particule2 software.

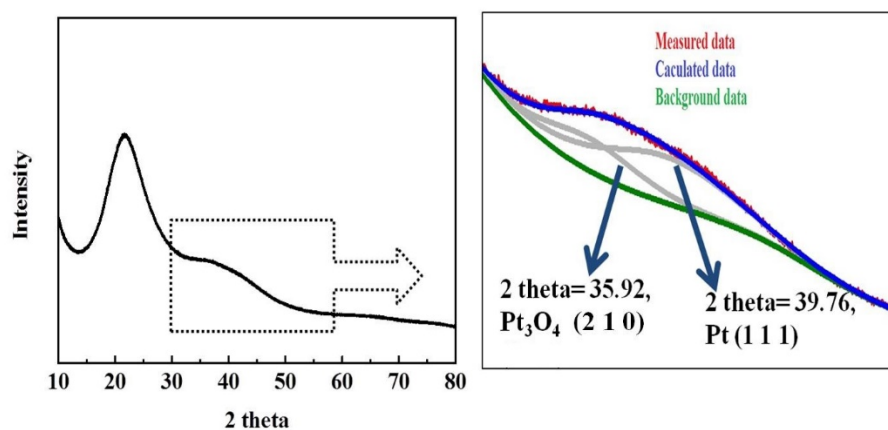


Fig S5. XRD of 5.4Pt/SBA-15 SR at 700 °C for 2 hrs, 1.0 nm Pt particles formed and partially oxidized to Pt_3O_4 .

Deconvoluting the 5.4 wt%Pt/SBA-15 sample from pattern a in Fig 4B, two peaks are

seen at 39.76° to 35.92°, which are indexed as Pt₃O₄ (210) and Pt (111). From the Scherrer formula, Pt particle size is 1.3 nm, while Pt₃O₄ is 1.5 nm.

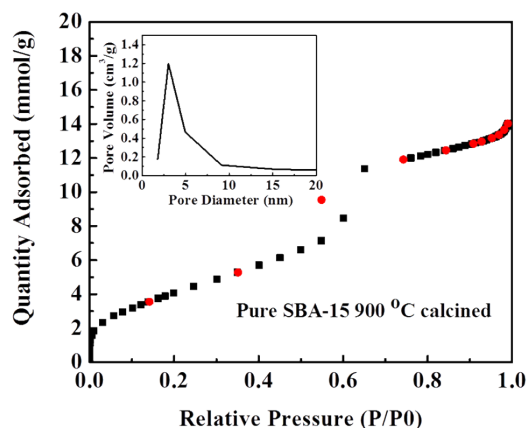


Fig S6. N₂ adsorption-desorption isotherm of pure SBA-15 calcined at 900 °C for 6 hrs, inset is BJH pore size distribution. Average pore size is 5.7 nm. BET surface area is 468 m²/g (used in Ru steaming reduction series) and 340 m²/g (used in Pt steaming reduction series).

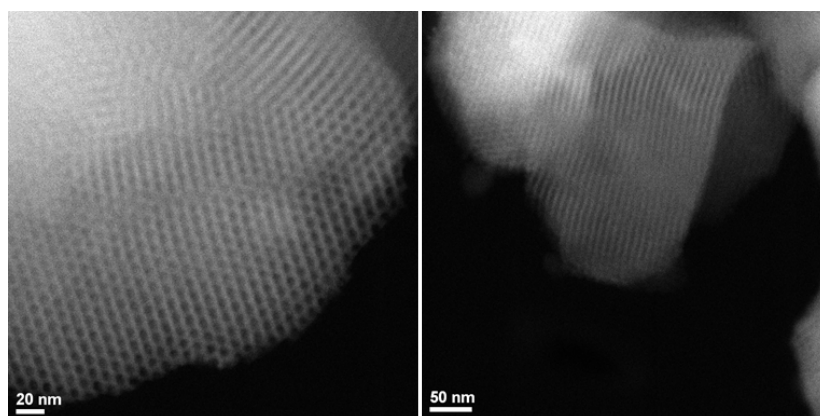


Fig S7. STEM images of pure SBA-15 calcined at 900 °C for 6h. The pore structure is intact.

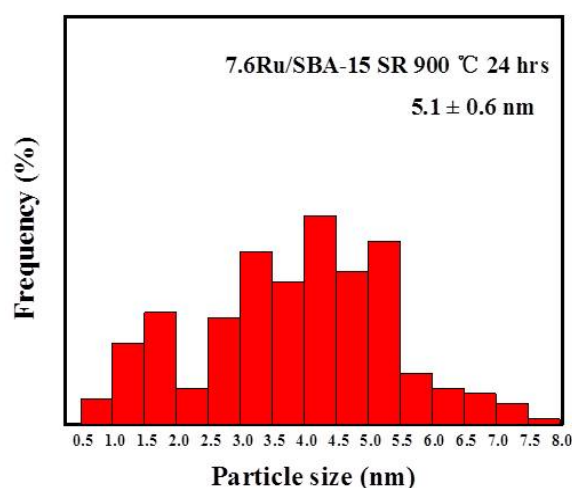


Fig S8. A Ru particle size distribution after steaming reduction treatment.