

Supporting Information for

**Insights into Support Wettability in Tuning Catalytic
Performance in the Oxidation of Aliphatic Alcohols to
Acids**

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Experimental section

Materials

Tetraethyl orthosilicate (TEOS, 99%), 1-butanol (99%), cyclohexane (99%), aqueous ammonia (25-28%), ethanol (99.5%) sodium borohydride (NaBH₄, 98%) chloroplatinic acid hexahydrate (H₂PtCl₆·H₂O, 99.9%), polyvinyl pyrrolidone (PVP, 98%), isobutyl alcohol (99%), 1-pentanol Isoamyl (99%), alcohol (99%), 1-hexanol (99%), 2-phenylethanol (99%), 1-octanol (99%), 2-octanol (99%), cyclohexanol (99%) and 1,2-propylene glycol (99%) were obtained from Tianjin Kermel Chemical Reagent Development Center, China. Poly (oxyethylene) nonylphenol ether (NP-7, Industrial Grade) was purchased from Dalian chemical ctl. Bis(trimethoxysilylpropyl)amine (BTSA, 99%) and phenyltriethoxysilane (PTES, 99%) were purchased from Nanjing Chemlin Chemical Industry Corporation and Aldrich, respectively. Deionized water used in all experiments was obtained from a Milli-Q system (Millipore).

Synthesis of superhydrophobic amine-bridged organic silicas

The phenyl-modified amine-bridged silicas (Ph-AOS) were prepared using a water-in-oil reverse microemulsion procedure according to our previous report. The microemulsion solution was prepared by mixing appropriate amounts of NP-7, n-butanol, cyclohexane, water, and aqueous ammonia. In a typical preparation of silica nanospheres, appropriate amounts of bis(trimethoxysilylpropyl)amine (BTSA) and phenyltriethoxysilane (PTES) were dripped slowly into the microemulsion. The molar ratio of the mixture was: 1(NP-7)/4.32(n-butanol)/15 (cyclohexane)/15.56(water)/1(NH₃)/0.8(BTSA)/0.2(PTES). The mixture was stirred for 12 h followed by addition of ethanol to break the microemulsion. The silica materials were washed a couple of times with ethanol to remove surfactants. The synthesis procedure of the hydrophilic amine-bridged silicas (AOS) is the same as above except without using PTES.

Synthesis of Pt/AOS and Pt/Ph-AOS

1 g of 1 wt% $\text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$ and 0.1 g PVPK10 was dissolved in 40 mL of water. Then 5 mL of 0.4 wt% NaBH_4 was added to the above solution under magnetic stirring. 0.2 g of the as-synthesized materials dispersed in 20 mL of ethanol was added to the solution and were stirred for 12 h. The solid was centrifuged and washed with water and dried at 80 °C.

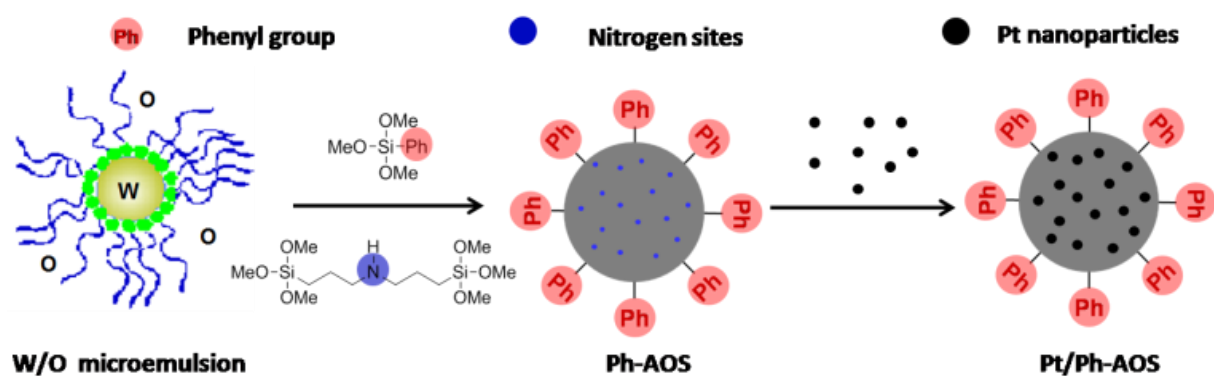
Oxidation of alcohols

0.2 mmol of alcohols, 0.05 mmol of mesitylene as internal standard, 2 mL of toluene and 10 mg of the catalyst were added to stainless steel autoclave. After heating to the desired temperature, the oxygen was charged into the reactor to 1 MPa and the reaction was performed for 24 h under magnetic stirring. The product was quantified by an Agilent 6890D GC equipped with hp-innowax (0.25 μm × 0.25 μm × 30m) column.

Characterizations

Fourier transform infrared (FT-IR) spectra were collected on a Bruker Tensor 27 FT-IR spectrometer in KBr media. Samples were thoroughly dried before measured. The thermal gravity analysis (TGA) measurements were carried out under air flow on a NETZSCH STA 409 PC instrument. Samples were heated at a heating rate of 10 °C/min from 35 to 800 °C in an air flow of 30 mL/min. Microstructures of the materials were examined by transmission electron microscopy (TEM, JEOL JEM-2000EX). The nuclear magnetic resonance of ^{29}Si with magic-angle spinning (^{29}Si MAS NMR) were taken on a Bruker DRX-400 spectrometer at 79.5 MHz with a spinning frequency of 4 kHz. The X-ray photoelectron spectroscopy (XPS) measurements were carried out on a VG ESCALAB MK2 spectrometer equipped with an AlK α X-ray source ($h\nu = 1486.6$ eV) and operating at 12.5 kV and 220 W. The binding energy (BE) was calibrated with the C1s signal (285.0 eV) as a reference. CO- FT-IR was conducted on a Bruker 70 IR spectrometer. The sample was pressed into a self-supporting disk and placed in a homemade IR cell attached to a closed glass-circulation system. Prior to CO adsorption, the sample disk was pretreated by

heating at 150 °C for 1 h in vacuum and then cooled to room temperature. After a spectrum was collected, the sample disk was exposed to CO gas for 30 min. IR spectra of the chemisorbed CO were recorded after evacuation at room temperature to eliminate physically adsorbed CO. And the water droplets contact angles were measured with a 5 µL water droplet at ambient temperature on the materials deposited as a film on a glass substrate using a contact angle measuring system JC 2000C1. The sorption experiment was performed at 273 K on a Micromeritics ASAP 2020 system to measure the adsorbed quantity of hydrophilic water (V_{water}) and hydrophobic benzene (V_{benzene}), respectively. Prior to the measurement, the samples were outgassed at 80 °C for at least 10 h. Hydrophobicity index (HI) were obtained according to the formula: $HI = V_{\text{benzene}}/V_{\text{water}}$.



Scheme S1. Preparation of Pt/Ph-AOS catalyst

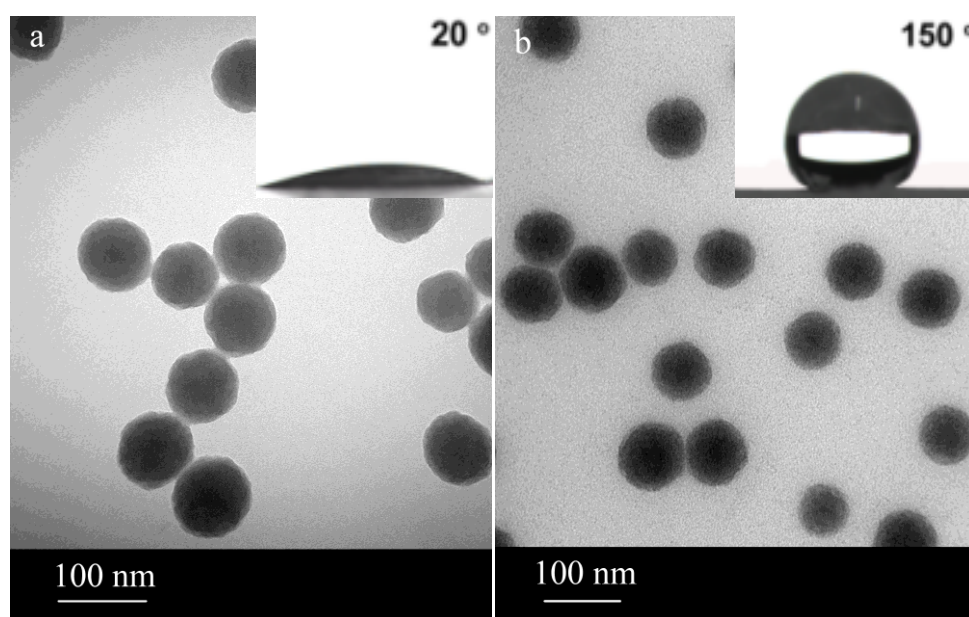


Fig. S1. TEM images of (a) AOS and (b) Ph-AOS. The insert is the photo of water contact angle.

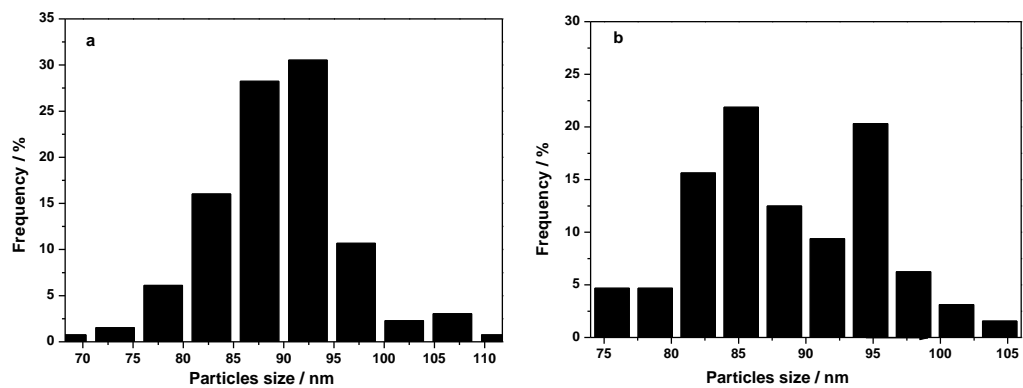


Fig. S2 Particle size distribution of (a) AOS and (b) Ph-AOS.

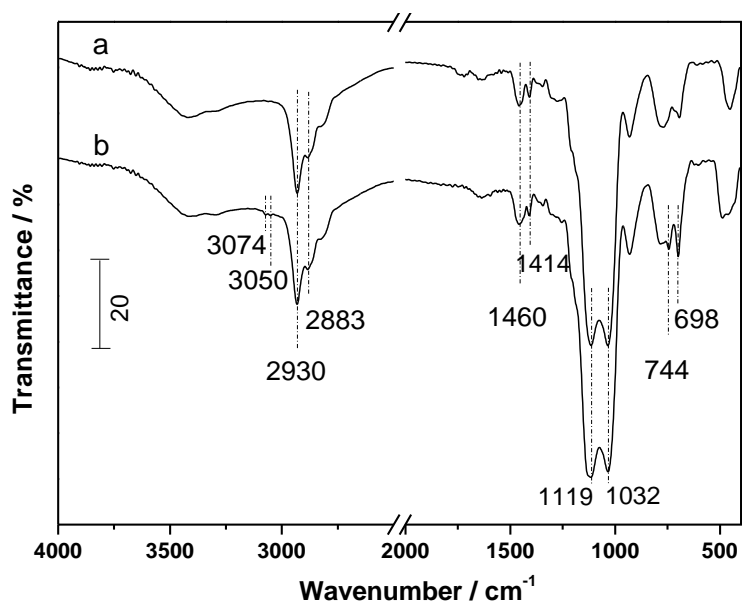


Fig S3. FT-IR spectra of (a) AOS and (b) Ph-AOS.

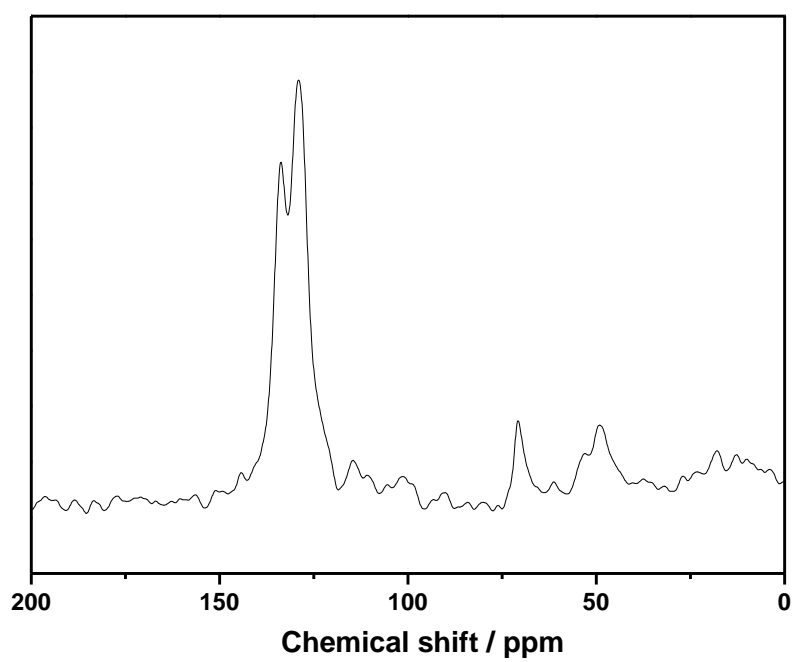


Fig. S4 ^{13}C CP/MAS NMR of Ph-AOS.

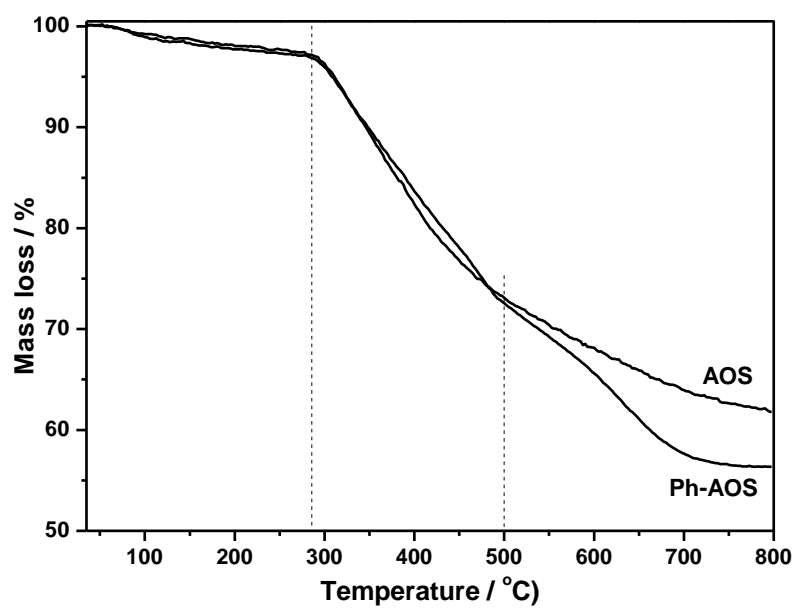


Fig. S5 TGA traces of (a) AOS and (b) Ph-AOS.

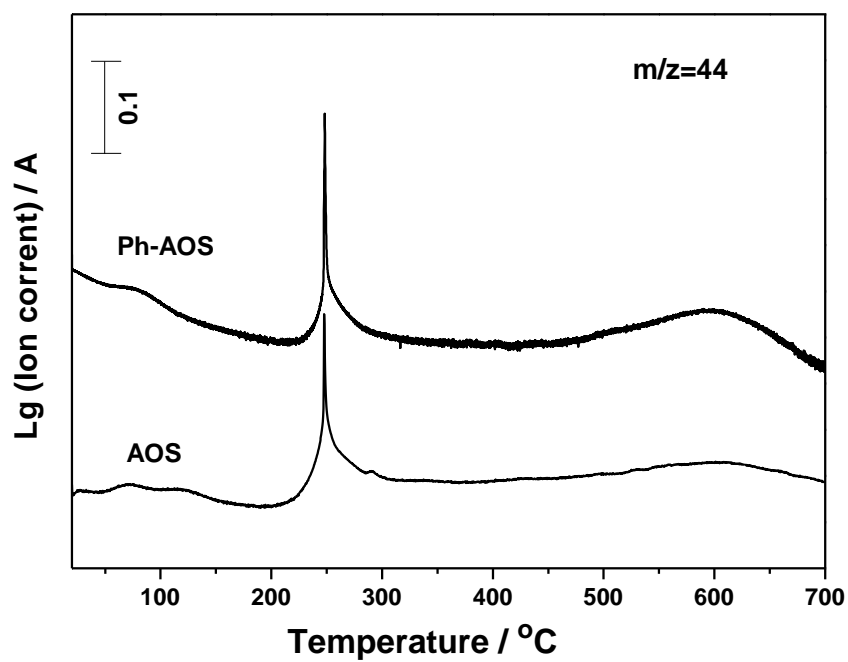


Fig. S6 TPO-MS patterns of AOS and Ph-AOS

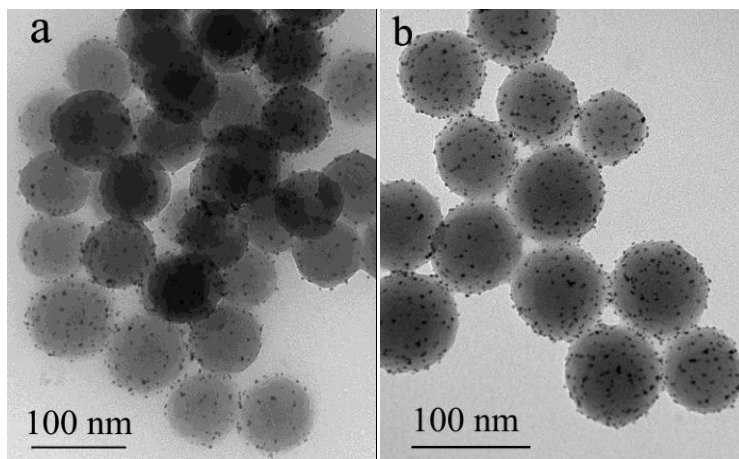


Fig. S7. TEM images of (a) Pt/AOS and (b) Pt/Ph-AOS.

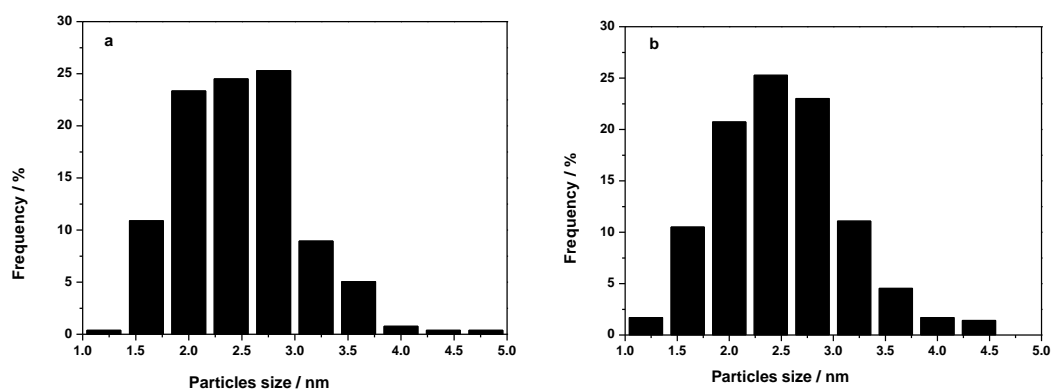


Fig. S8 Pt particle size distribution of (a) Pt/AOS and (b) Pt/Ph-AOS.

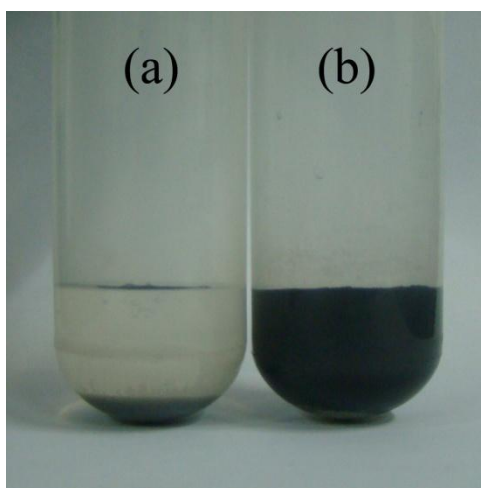


Fig. S9 The adsorption of Pt nanoparticles by AOS (a) and SiO₂ (b) after centrifugation.

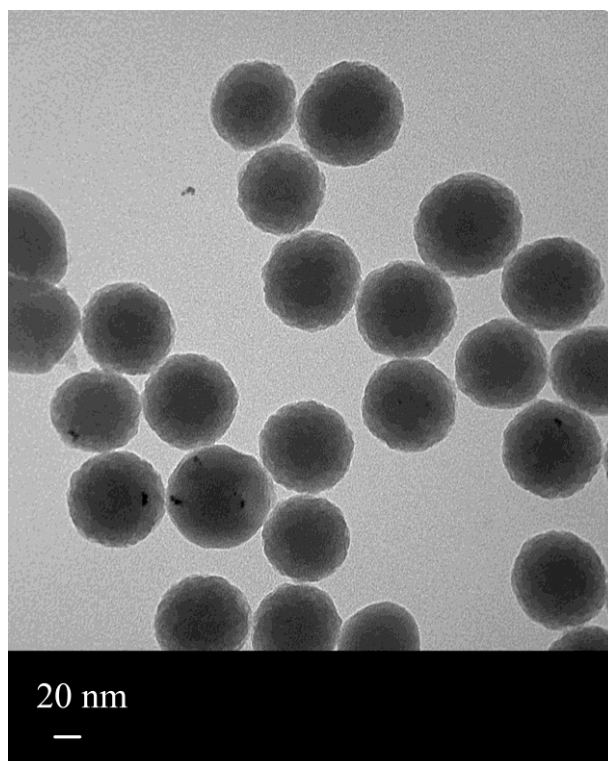


Fig. S10 TEM image of the adsorption of Pt nanoparticles on the SiO₂.

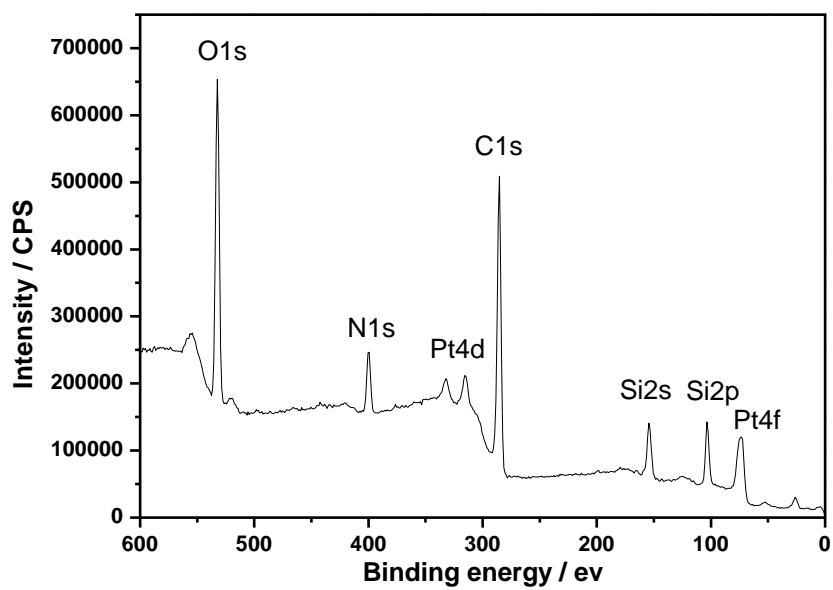


Fig. S11. XPS spectrum of Pt/Ph-AOS.

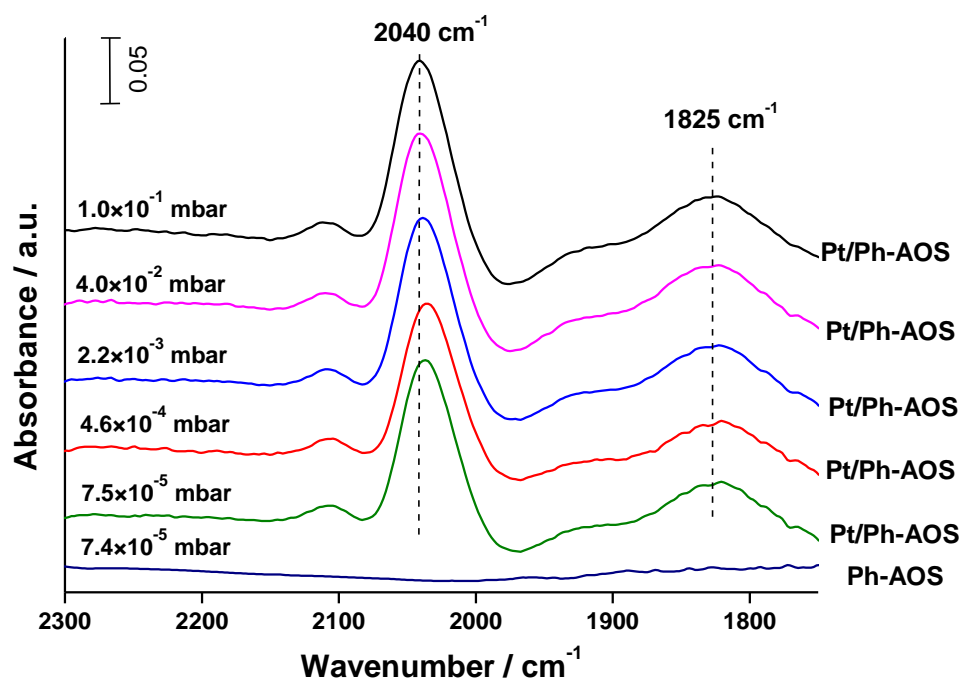


Fig. S12. In situ FT-IR spectra of Pt/Ph-AOS and Ph-AOS.

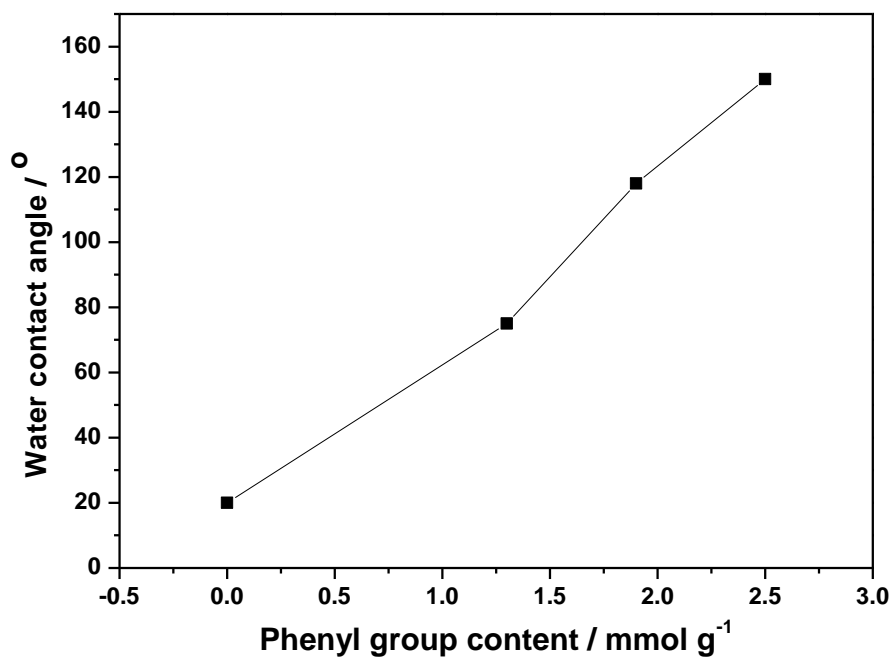


Fig. S13 The influence of phenyl group content on the water contact angle.

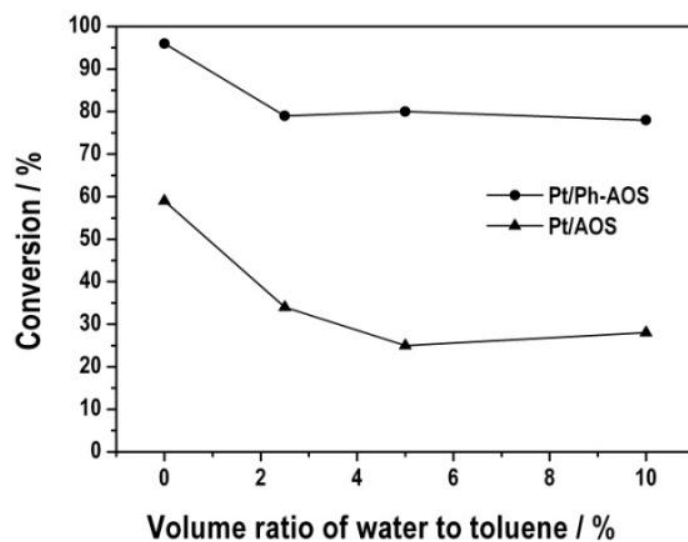


Fig. S14. The influence of water on the activity in 1-butanol oxidation. Reaction conditions: 0.2 mmol alcohol, 0.05 mmol mesitylene, 10 mg catalyst, 2 mL toluene, 1.0 MPa oxygen, 90 °C, 24 h. A calculated amount of water was added before reaction.

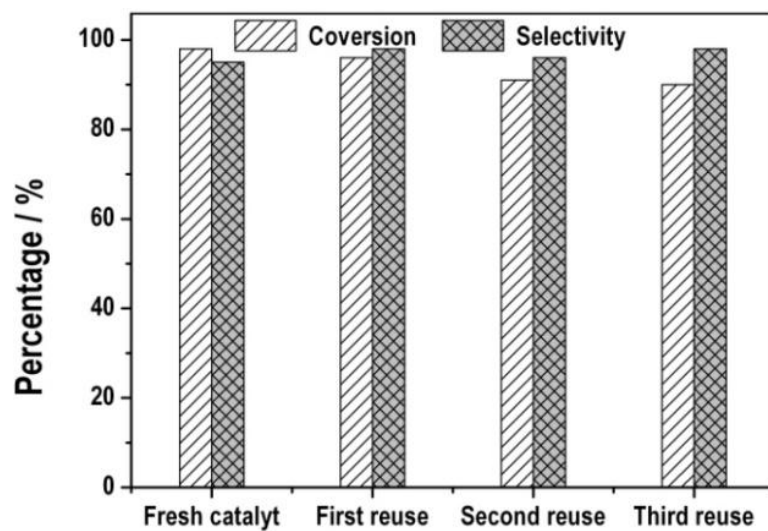


Fig. S15 Conversion and selectivity of fresh and reused Pt/Ph-AOS in the oxidation of 1-butanol to butanic acid at 100 °C for 24 h under 1.0 MPa oxygen.

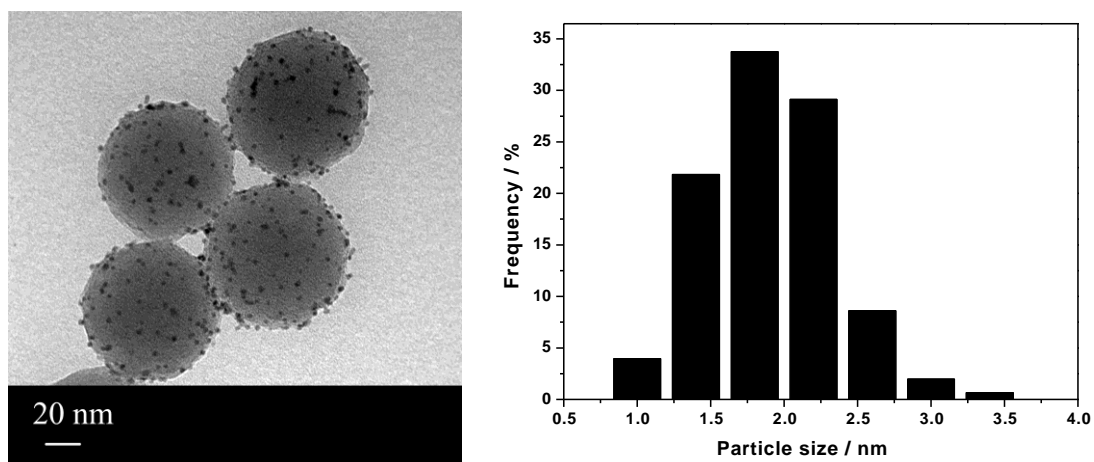


Fig. S16 TEM image and Pt particles size distribution of used Pt/Ph-AOS.