

Supplementary Materials for *Catal. Sci. Technol.*

Homogenization of inorganic material-supported palladium catalysts in Suzuki coupling reaction at room temperature

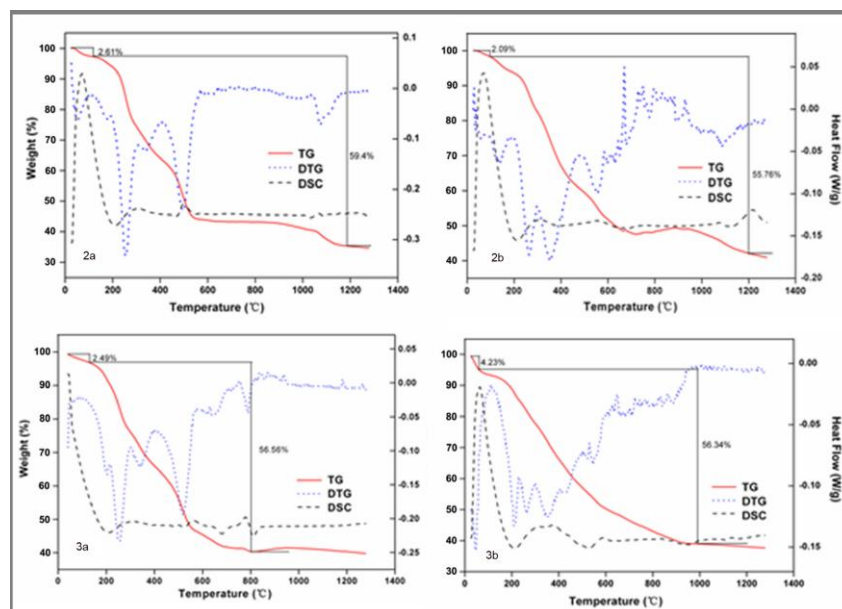
Yueyue Ma, Xuebing Ma,* Qiang Wang, Jinqin Zhou

College of Chemistry and Chemical Engineering, Southwest University, Chongqing, 400715, P. R. China

1. Sample characterization

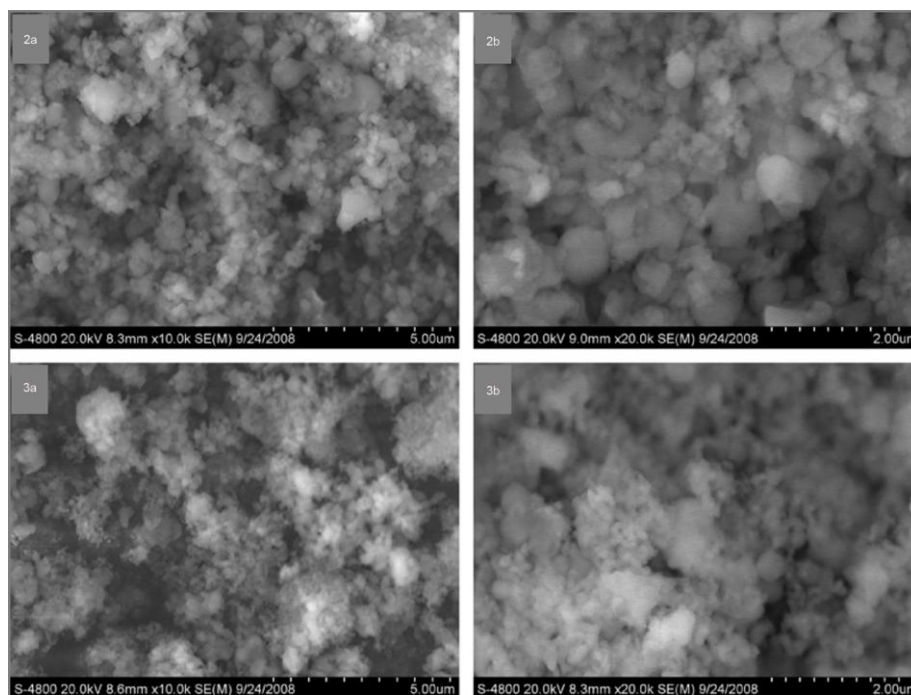
1.1. TGA

Thermogravimetric analysis (TGA) was performed on a SBTQ 600 Thermal Analyzer (USA) with a heating rate of 20 °C min⁻¹ over a temperature range of 40–800 °C under flowing compressed N₂ (100 mL min⁻¹).



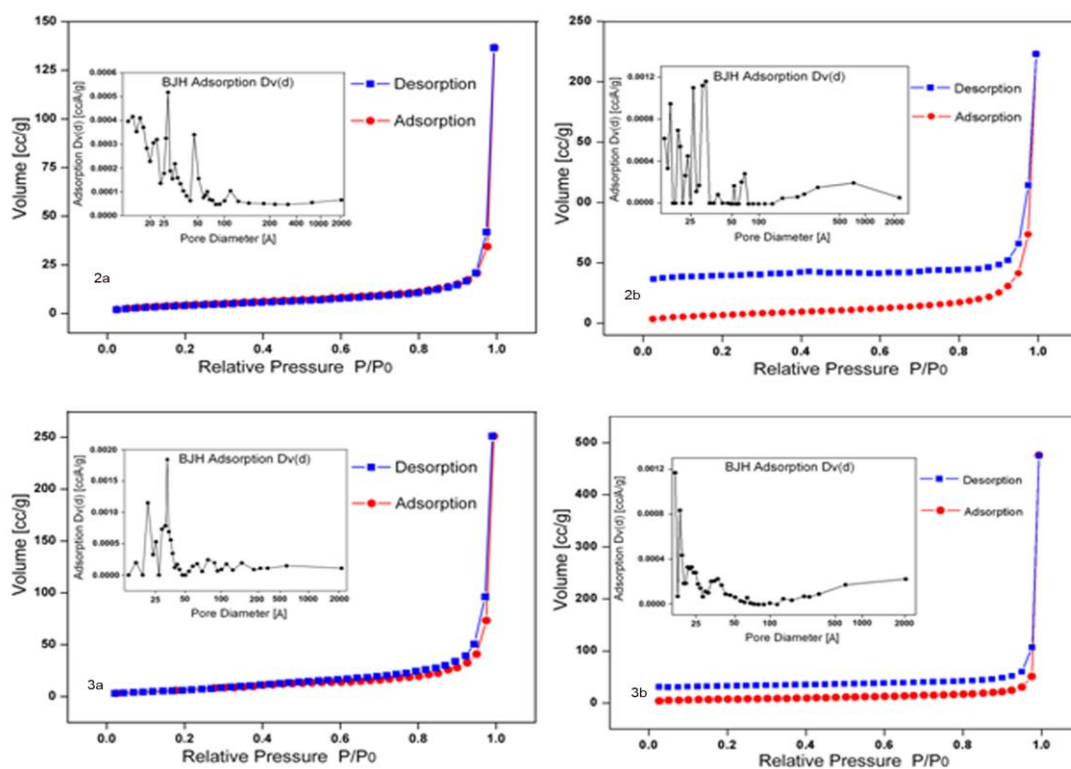
1.2. SEM images

InstructName=S-4800; DataSize=1280x960; PixelSize=9.921875; SignalName=SE(M);
Accelerating Voltage=20000 Volt; DecelerationVoltage=0 Volt; Magnification=10000; Working
Distance=8300 um; Emission Current=10100 nA; Lens Mode=Normal; Photo Size=1000;
Micron Marker=5000; Sub Magnification=0; SpecimenBias=0 V; Condencer1=5000;
ScanSpeed=Slow3; Calibration Scan Speed=25; Color Mode=Grayscale; Screen Mode=Small
Screen; Condition=Vacc=20kV; Mag=x10.0k, WD=8.3mm; Data Display Combine=1; Stage
Type=0; Stage PositionX=25000000; Stage Position Y=25000000; Stag ePosition R=0; Stage
Position Z=8000000; Stage PositionT=0.



1.3. The nitrogen adsorption–desorption isotherms

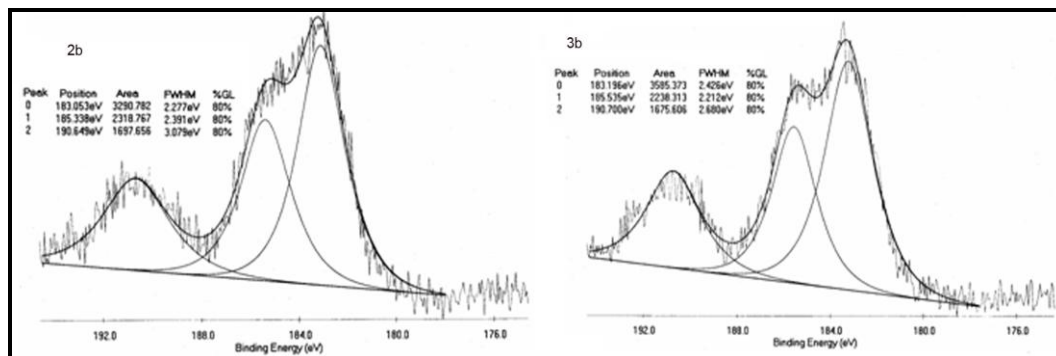
N₂ adsorption–desorption analysis was carried out at 77 K on an Autosorb-1 apparatus (Quantachrome), and specific surface area was determined by using the BET equation and pore diameter was estimated according to the BJH model. The samples were degassed at 100 °C for 5 h.



1.4. XPS

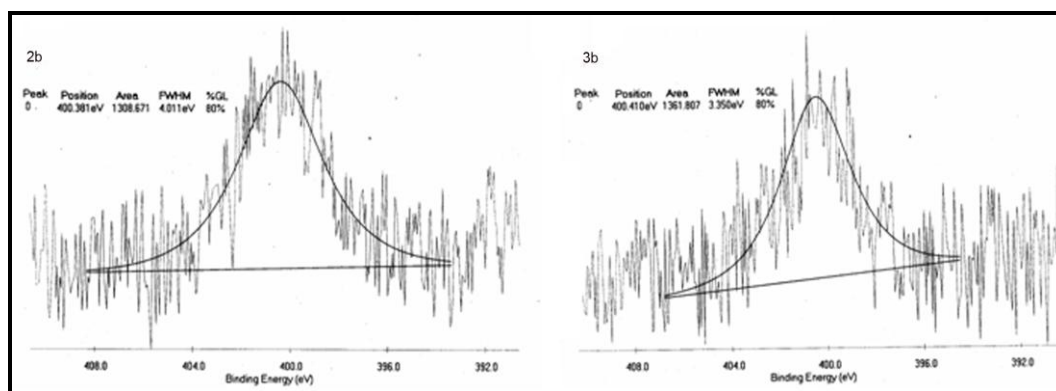
(1) The XPS spectra of P_{2s}

Technology: XPS; Analyser Mode: FAT; Magnification: Low; Energy Range: X 1; Exciting Source: Mg; Region 03: P2p. B.E. 146.00-126.00eV; ChargeShift:2.300eV, 200mS per 0.05eV; Across Scan for 5 times.



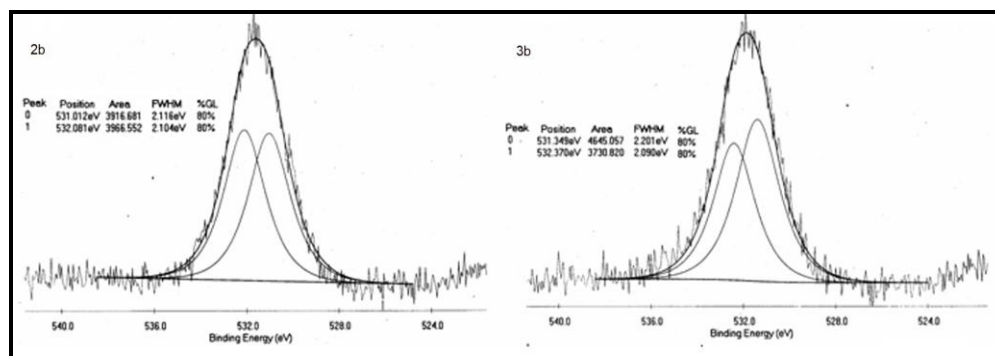
(2) The XPS spectra of N_{1s}

Technology: XPS; Analyser Mode: FAT; Magnification: Low; Energy Range: X 1; Exciting Source: Mg; Region 04: N1s, B.E. 414.00-394.00eV; ChargeShift:2.300eV, 200mS per 0.05eV; Across Scan for 5 times.

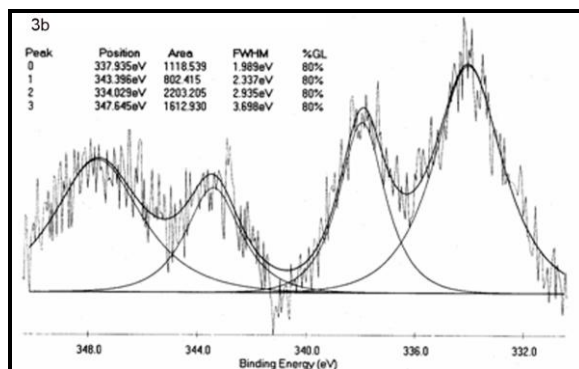


(3) The XPS spectra of O_{1s}

Technology: XPS; Analyser Mode: FAT; Magnification: Low; Energy Range: X 1; Exciting Source: Mg; Region 05: O1s, B.E. 547.00-527.00eV; ChargeShift:2.300eV, 200mS per 0.05eV; Across Scan for 5 times.



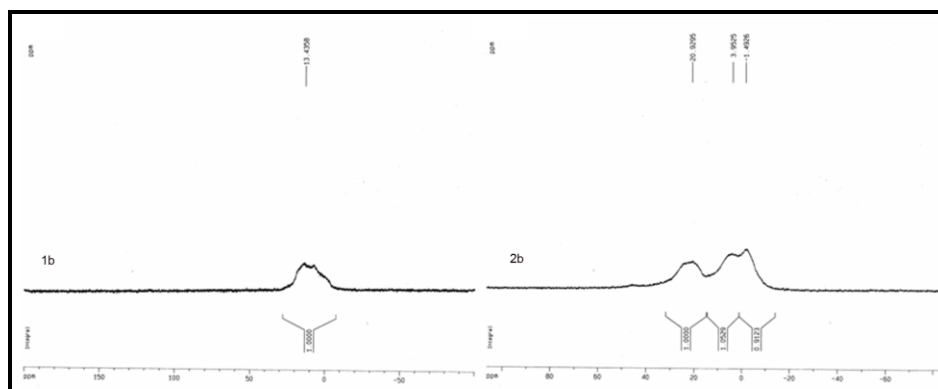
Technology: XPS; Analyser Mode: FAT; Magnification: Low; Energy Range: X 1; Exciting Source: Mg; Region 06: Pd3d, B.E. 353.00-333.00eV; ChargeShift:2.300eV, 200mS per 0.05eV; Across Scan for 5 times.



The XPS spectra of Pd_{3d}

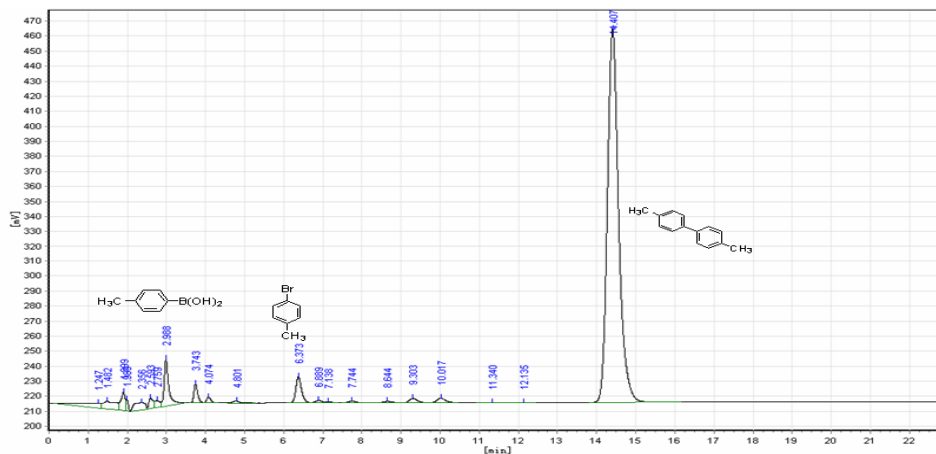
1.5. ³¹P NMR

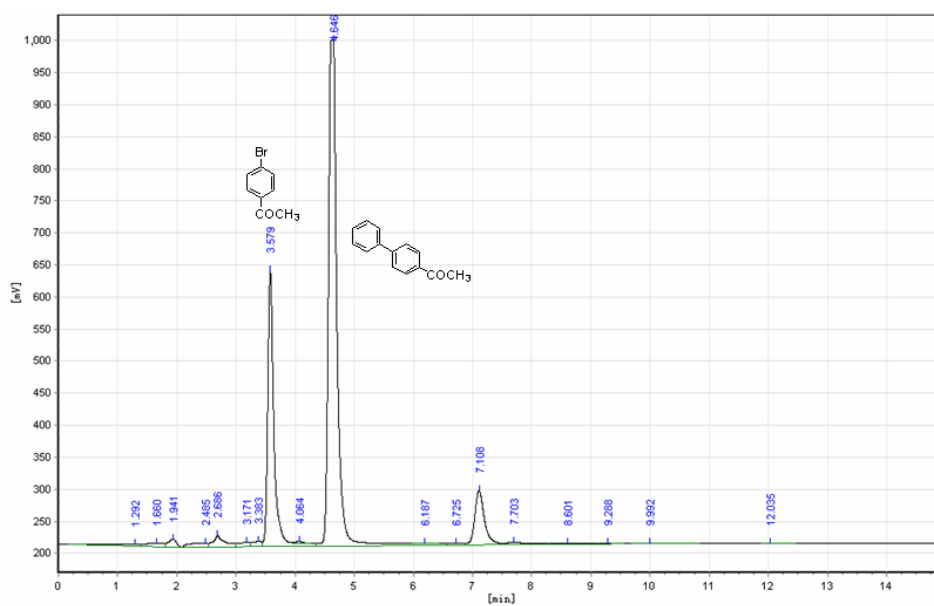
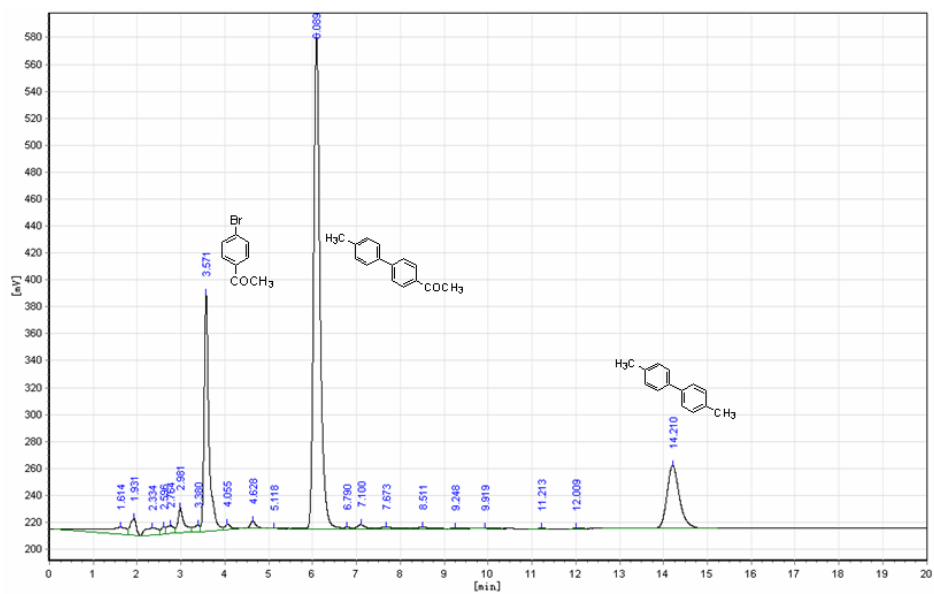
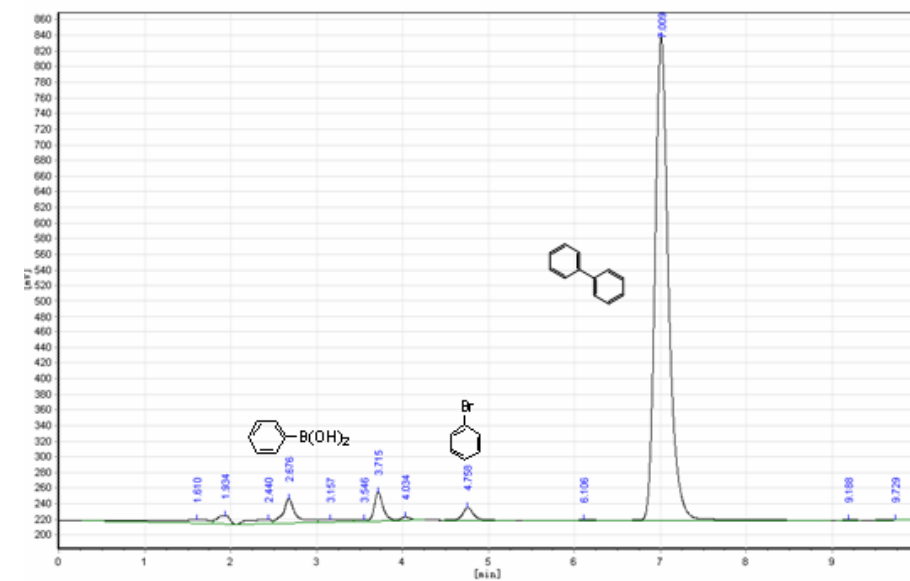
³¹P NMR were performed on a Bruker AV-300 NMR instrument at 121 MHz, in which chemical shifts were reported downfield in ppm relative to the phosphorus resonance of H₃PO₄ (85 %).

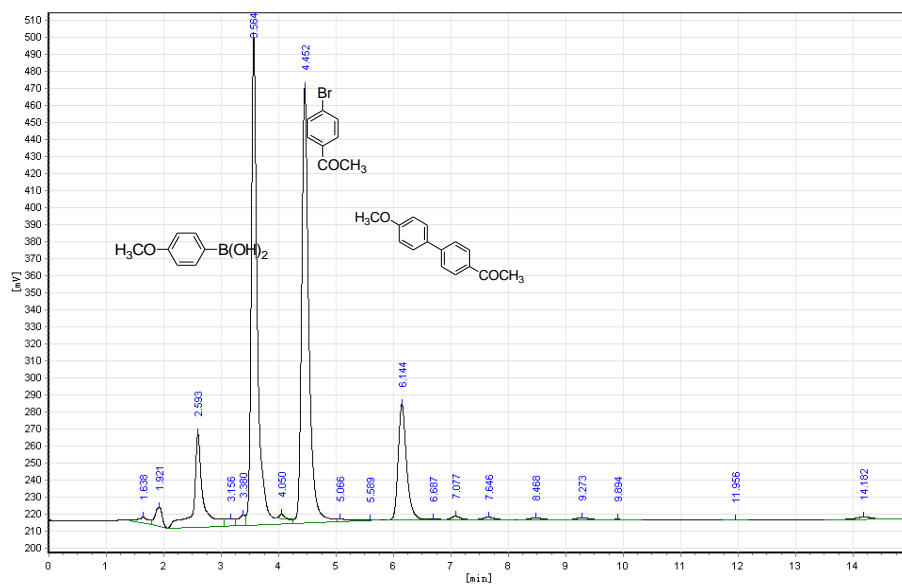
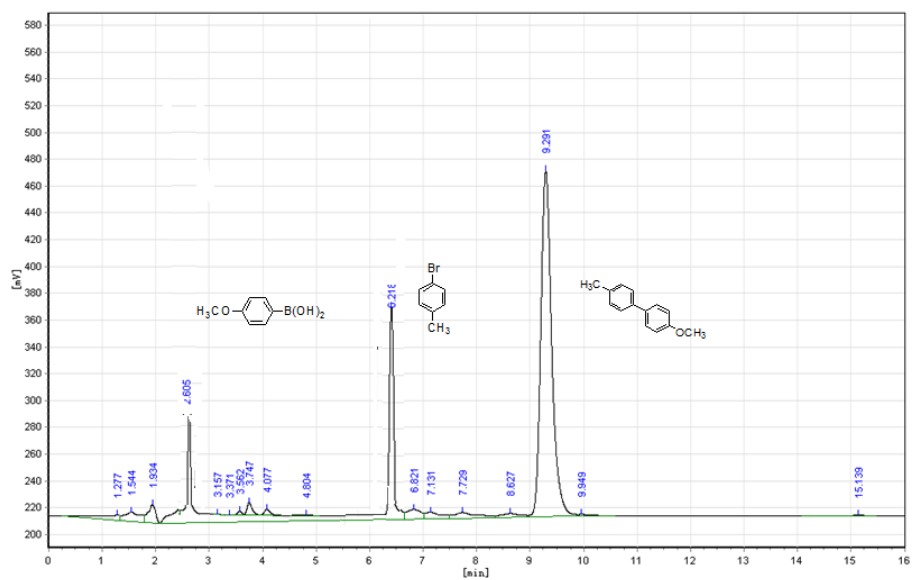
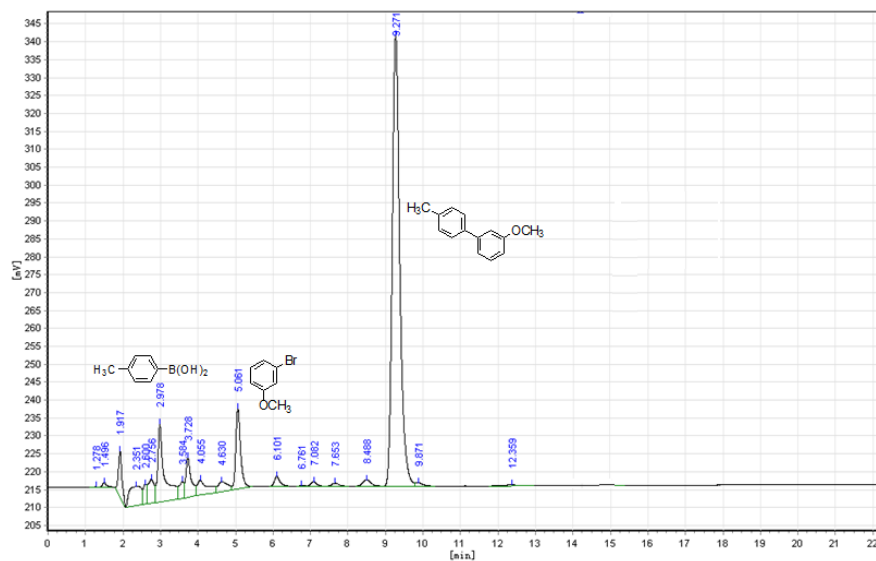


2. HPLC analysis of the products

The conversions of bromobenzene and its derivatives in Suzuki-Miyaura coupling reactions were detected by HPLC: column C18, column temperature 30 °C, detection wavelength λ=254 nm, 0.8 mL/min, methanol/water=20/80. Some examples were shown as follows.

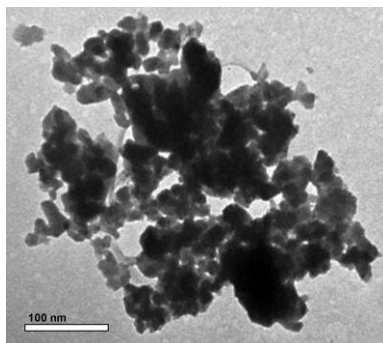






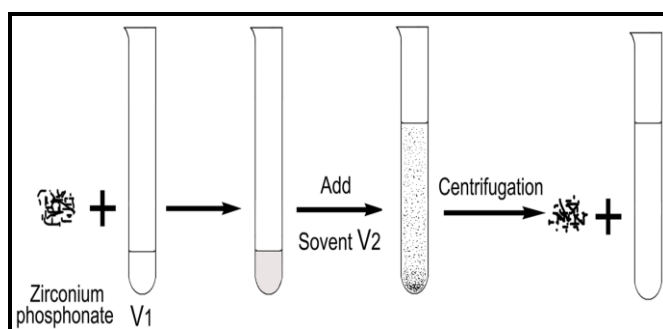
3. The recycling experiment

The recovered catalyst **3b** in centrifuge tube was dissolved in dried THF (2 mL), added petroleum ether (10 mL), and then the catalyst precipitated out. The centrifugated catalyst was dissolved in dried THF (2 mL) again and added to a 50-mL three-necked round-bottomed flask by injection syringe for the recycling experiment according to the catalytic procedure of Suzuki-Miyaura coupling reaction mentioned above.

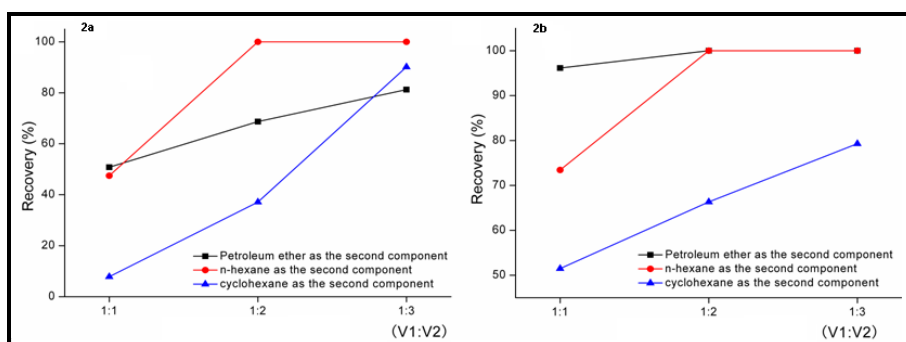


The TEM image of recovered Pd catalyst **3b** after the 10th cycle of the reaction

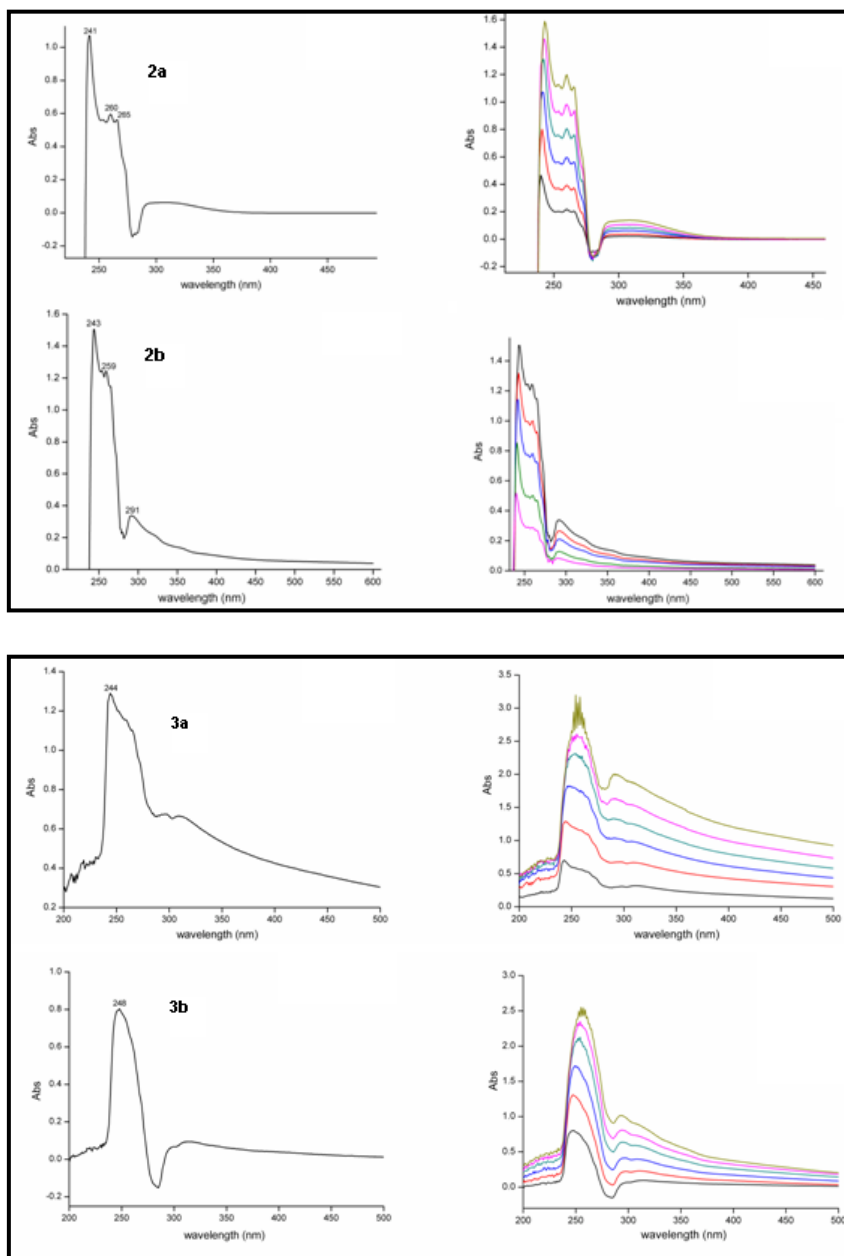
4. The recycled yield of the supports **2a, b** and their supported Pd catalysts **3a, b**



As an example, the sample **3a** (1.0000 g) were exactly charged and dissolved in 25.00 mL of the first solvent (v1). 1.0 mL of above solution was then added the second solvent (v2) in a volume ratio (v2/v1) between 10:1 and 1:1. The sample **3a** precipitated out as a solid and separated from the mixture centrifugally. 0.4 mL of the centrifugate was diluted to 25.00 mL, and then the content of the sample **3a** was determined by UV spectroscopy and calculated according to standard curve.



The recovery of the supports **2a, b** in various solvents



UV spectroscopy of the supports **2a**, **2b** and their supported Pd catalysts **3a**, **3b**