

SUPPORTING INFORMATION

**Supporting Information**

**Nanoparticles Sandwiched in Hollow Amorphous Metal–Organic-Frameworks with Enhanced Diffusion for Highly Selective Benzene Oxidation.**

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### Part S1. Chemicals and Reagents

Chloroplatinic acid ( $\text{H}_2\text{PtCl}_6$ , 37.5 wt% Pt), Ruthenium (III) chloride hydrate Reagent Plus ( $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ ), Iron (III) chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , 97wt%), 1,3,5-benzenetricarboxylic acid ( $\text{H}_3\text{BTC}$ , 95wt%), Polyvinyl pyrrolidone (PVP,  $M_w = 55000$ ) was purchased from Sigma-Aldrich (China). Rhodium (III) chloride anhydrous (48.7 wt% Rh), Aluminium (III) nitrate nonahydrate ( $\text{AlNO}_3 \cdot 9\text{H}_2\text{O}$ , 98wt%) by Alfa Assar. Chromium (III) nitrate nonahydrate ( $\text{CrNO}_3 \cdot 9\text{H}_2\text{O}$ ) by Adamas. scandium (III) nitrate hydrate ( $\text{ScNO}_3 \cdot \text{H}_2\text{O}$ ) by Accela chem-bio co.ltd, Benzene (99.7 %) by Aladdin. Oxidant  $\text{H}_2\text{O}_2$  (30wt% water) Beijing Chemical Reagent Company (China). The deionized water used in our experiments was obtained from the Milli-Q System. Other analytical grade solvents including DMF, Ethanol, Methanol were supplied by Beijing Chemical Reagent Company (China). All the chemicals were used without further purification.

### Part S2. General Characterization

Scanning electron microscopy (SEM) measurement was performed on a Hitachi SU8200 scanning electron microscope at 6.0 kV. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) imaging and High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) imaging were carried out using Tecnai G2 F20 S-TWIN at 200 kV. Powder X-ray diffraction (XRD) patterns were recorded on D/MAX-TTRIII (CBO) with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.542 \text{ \AA}$ ) operating at 40 kV and 300mA. X-ray photoelectron spectroscopy (XPS) spectra were performed by an ESCALAB 20 Xi XPS system. The specific surface area, pore volume and pore size of catalysts were measured using a BET (Brunauer-Emmett-Teller) instrument (ASAP 2420-4, Micromeritics). The average size and shell thickness were calculated using software Nano Measurer 1.2.

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**Synthesis of Pt nanoparticles (NPs).** Pt NPs were synthesized according to the literature with modification.<sup>1</sup> In a typical procedure, 16.6 mg PVP (Mw = 55000) was dissolved in 40 mL ethanol (2 mL H<sub>2</sub>O) then 3.0 mL H<sub>2</sub>PtCl<sub>6</sub> aqueous solution (10.0 mM) was added drop by drop to the solution then it was refluxed in a 100 mL flask at 90°C for 2 h under air to synthesize the PVP-stabilized Pt NPs. The concentration of as-synthesized Pt NPs was about 0.6 mM and used directly without further treatment.

**Synthesis of Rh nanoparticles (NPs).** Rh NPs were synthesized according to the literature with modification.<sup>2</sup> In a typical procedure, 16 mg of RhCl<sub>3</sub> and 16.6 mg PVP (Mw = 55000) was dissolved 6 mL H<sub>2</sub>O and 44 mL of EtOH. After stirring for about 2 min at room temperature, the solution was refluxed in a 100 mL flask at 80°C for 2 h under argon atmosphere to synthesize the PVP-stabilized Rh NPs. The concentration of as-synthesized Rh NPs was about 0.6 mM and used directly without further treatment.

**Synthesis of Ru NPs.** Ru NPs were synthesized according to the literature.<sup>3</sup> In a typical procedure, 13.05 mg RuCl<sub>3</sub>·3H<sub>2</sub>O and 55.5 mg PVP were added into 10 mL ethylene glycol at room temperature. The solution was refluxed in a 100 mL flask at 80°C for 30 min under argon atmosphere. After that, the solution was heated to 180 °C and kept at this temperature for 2 h. When the reaction was complete, acetone was added into the solution, and the resulting black suspension was subjected to centrifuge. The precipitated Ru NPs were then separated, collected, and redispersed in 80 mL ethanol (0.6 mM).

### **Synthesis of template nanospheres**

The monodisperse polystyrene (PS) nanospheres were synthesized via emulsifier-free emulsion polymerization. First, 100 mL of deionized water was added to a 250 mL three-necked flask equipped with a mechanical stirrer and condenser under nitrogen atmosphere. 7.5 mL of styrene was added into the above reactor. When the temperature was raised to 70 °C, 66 mg of potassium persulfate was added. The reaction mixture was reacted for 24 h under nitrogen protection and continuous stirring and the resulting product was separated by centrifugation and washed with deionized water and ethanol three times, respectively. Sulfonated PS spheres were prepared according to reported techniques. 0.4 g of freeze-dried PS nanospheres were immersed in 40 mL of concentrated sulfuric acid and stirred at 40 °C for 2 h. The sulfonated PS spheres were separated by centrifugation and washed with water and ethanol for further use.

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### **Preparation of Ps@aMIL-100(Fe)**

The freshly prepared sulfonated-PS spheres (0.25g) were dispersed alternately in an ethanolic solution of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (2mM, 10 ml) for 2h and then in an ethanolic solution of 1,3,5-benzenetricarboxylic acid ( $\text{H}_3\text{BTC}$ ) (2mM, 10 ml) for 2h at 30 °C. Between each step, the resulting products were collected by centrifugation and washed several times with ethanol. With repeated cyclic growth, PS@aMIL core-shell microspheres were fabricated and the expected shell thickness was achieved.

### **Synthesis of supported Ps@aMIL-100(Fe)@X (Pt, Rh, Ru).**

5mL as-synthesized X- (Pt, Rh, Ru) NP solution was added drop by drop into 5 mL ethanol of Ps@aMIL-100(Fe) under stirring, and then the mixed solution was further stirred at room temperature for 12h. Subsequently, Ps@aMIL-100(Fe)@X was collected by centrifugation at 4000 rpm for 3 min and washed twice with ethanol. Finally, the obtained Ps@aMIL-100(Fe)@X was redispersed in 10 mL ethanol, which was directly used as the catalyst for liquid-phase selective hydroxylation.

### **Synthesis of HMIL-100(Fe)@X (Pt, Rh, Ru) @aMIL-100(Fe).**

Synthesis of sandwich HMIL-100(Fe)@X (Pt, Rh, Ru) @aMIL-100(Fe). 50mg of Ps@aMIL-100(Fe)@X in 5ml of ethanol were dispersed alternately in an ethanolic solution of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (2mM, 10 ml) for 6h and then in an ethanolic solution of 1,3,5-benzenetricarboxylic acid ( $\text{H}_3\text{BTC}$ ) (2mM, 10 ml) for 12h at 30 °C. Between each step, the resulting products were collected by centrifugation and washed several times with ethanol. With repeated cyclic growth, achieved sandwich Ps@aMIL-100(Fe)@X (Pt, Rh, Ru) @aMIL-100(Fe). Then, through immersing the as-prepared Ps@aMIL-100(Fe)@X (Pt, Rh, Ru) @aMIL-100(Fe) into N, N-dimethylformamide (DMF) to remove the polystyrene cores, hollow sandwich HMIL-100(Fe)@X (Pt, Rh, Ru) @aMIL-100(Fe). were successfully prepared.

### **Preparation of Ps@aMIL-100 (M- Cr, Al, Sc)**

The freshly prepared sulfonated-PS spheres (0.25g) were dispersed alternately in an ethanolic solution of (M-Cr, Al, Sc) metal precursors (2mM, 10 ml) for 2h and then in an ethanolic solution of 1,3,5-benzenetricarboxylic acid ( $\text{H}_3\text{BTC}$ ) (2mM, 10 ml) for 2h at 30 °C. Between each step, the

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resulting products were collected by centrifugation and washed several times with ethanol. With repeated cyclic growth, Ps@MIL-100 (X-Cr, Al, Sc) core-shell was fabricated and the expected shell thickness was achieved.

### **Synthesis of supported Ps@aMIL-100 (M-Cr, Al, Sc) @Pt**

5mL as-synthesized Pt NP solution was added drop by drop into 5 mL ethanol of Ps@MIL-100 (X-Cr, Al, Sc) under stirring, and then the mixed solution was further stirred at room temperature for 2h. Subsequently, Ps@MIL-100 (M-Cr, Al, Sc) @Pt was collected by centrifugation at 4000 rpm for 3 min and washed twice with ethanol. Finally, the obtained Ps@MIL-100 (M-Cr, Al, Sc) @Pt was redispersed in 10 mL ethanol, which was directly used as the catalyst for liquid-phase selective hydroxylation.

### **Synthesis of HMIL-100 (M-Cr, Al, Sc) @Pt@ aMIL-100 (M-Cr, Al, Sc)**

synthesis of sandwich HMIL-100 (X-Cr, Al, Sc) @Pt@ MIL-100 (X-Cr, Al, Sc). 50mg of Ps@MIL-100 (X-Cr, Al, Sc) @Pt in 5ml of ethanol were dispersed alternately in an ethanolic (X-Cr, Al, Sc) metal precursors (2mM, 10 ml) for 2h and then in an ethanolic solution of 1,3,5-benzenetricarboxylic acid (H<sub>3</sub>BTC) (2mM, 10 ml) for 2h at 30 °C. Between each step, the resulting products were collected by centrifugation and washed several times with ethanol. With repeated cyclic growth, achieved sandwich Ps@MIL-100 (X-Cr, Al, Sc) @Pt@ MIL-100 (X-Cr, Al, Sc) Then, through immersing the as-prepared Ps@MIL-100 (X-Cr, Al, Sc) @Pt@ MIL-100 (X-Cr, Al, Sc) into N,N-dimethylformamide (DMF) to remove the polystyrene cores, hollow sandwich HMIL-100 (X-Cr, Al, Sc) @Pt@ MIL-100 (X-Cr, Al, Sc) were successfully prepared.

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### Catalytic benzene oxidation

The benzene oxidation reaction was carried out in a 15-ml glass tube with 0.4 ml of benzene, 6 ml of H<sub>2</sub>O<sub>2</sub> (30%), and 3 ml of H<sub>2</sub>O, 1ml EtOH at room temperature. After the reaction the catalysts were separated by centrifugation, and washed with EtOH for reusing, while the obtained reaction solution was filtered through a filter membrane (0.22 μm), and then was analyzed by gas chromatography-mass spectrometry (GC-MS, Thermo DSQ, column: TR-5MS) and gas chromatography (GC, Shimadzu, GC-2014C, column: Rtx-5, 30 m × 0.25 mm × 0.25 μm).

**Table S1** Summary of oxidation of benzene to phenol based on solvents.

No	Catalyst	Time/h	Solvent	Selectivity	Conversion
1	HMIL@Pt	24	Ethanol	61	10
2	HMIL@Pt	24	Acetonitrile	94	15
3	HMIL@Pt	24	Water	90	55
4	HMIL@Pt	24	Water+Ethanol	90	64

#### Experiment condition

Benzene (0.40 mL,) 6ml H<sub>2</sub>O<sub>2</sub>, RT

**Table S2** Summary of oxidation of benzene to phenol based on time.

No	Catalyst	Time/h	selectivity	Conversion
1	HMIL(Fe)@Pt@MIL(Fe)	12	99.5	52
2	HMIL(Fe)@Pt@MIL(Fe)	24	61	88
3	HMIL(Fe)@Pt@MIL(Fe)	30	48	99

#### Experiment condition

Benzene (0.40 mL,) 6ml H<sub>2</sub>O<sub>2</sub>, catalyst, 1ml Ethanol + 3ml water at RT.

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**Table S3** Summary of oxidation of benzene to phenol based on Fe-contained catalyst and H<sub>2</sub>O<sub>2</sub> as an oxidant recent published works.

No	catalyst	conversion	Selectivity	Publication
1	SA-Fe/CN	45%	94%	J. Am. Chem. Soc. 2017, 139, 10976–10979
2	FeN <sub>4</sub> /GN	23.4%	91%	Deng et al. Sci. Adv. 2015;1:e1500462
3	Fe/SBA-16	12.1%	96.4%	Ind. Eng. Chem. Res. 2016,55, 3900–3908
4	Fe–NHC complex	12.1%	97%	<i>Microporous and Mesoporous Materials</i> , 2020, <b>294</b> , 109891.
5	Fe <sub>3</sub> O <sub>4</sub> @C	8%	100%	<i>Reac Kinet Mech Cat</i> <b>126</b> , 1055–1065(2019).
6	NH <sub>2</sub> -MIL-88B(Fe)-SA-V	20%	98.2%	<i>ChemistrySelect</i> <b>2020</b> , 5, 6818.
7	Fe@Cu-BDC	37%	62%	<i>Appl Organometal Chem.</i> 2019; 33:e4662.
8	MIL-100(Fe)	16.9%	66.9%	Journal of Materials Science and Chemical Engineering, 8, 55-64(2020)
9	Fe/GO	15.9%	94.1%	Catal. Commun. 2015, 68, 1.
10	HMIL@Pt@MIL-100(Fe)	52%	99.5%	This work

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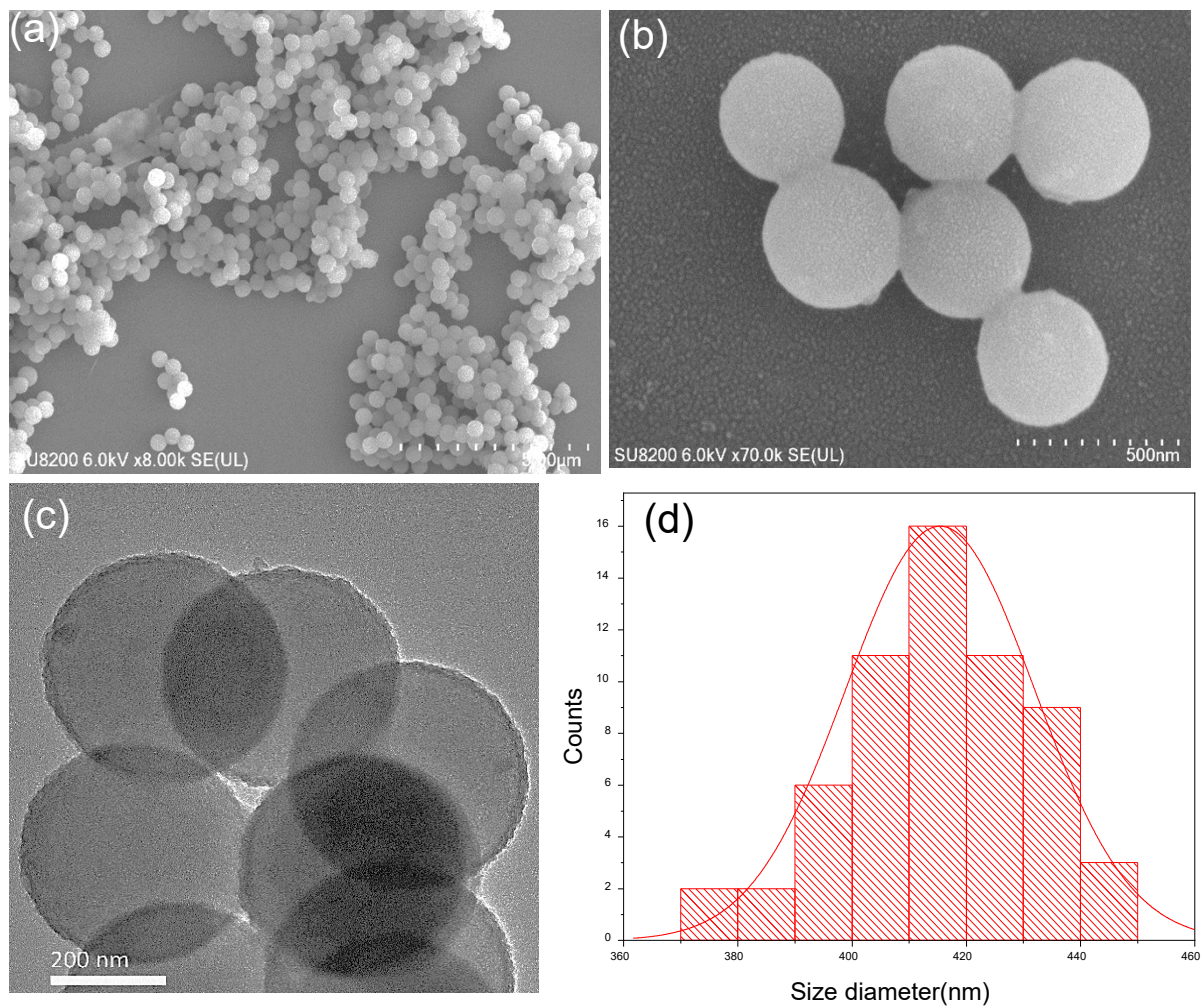


Fig. S1 Ps@aMIL-100(Fe) SEM images (a) small magnifications (b) large magnifications (c) TEM images (d) corresponding size histogram with average diameter of 416 nm.



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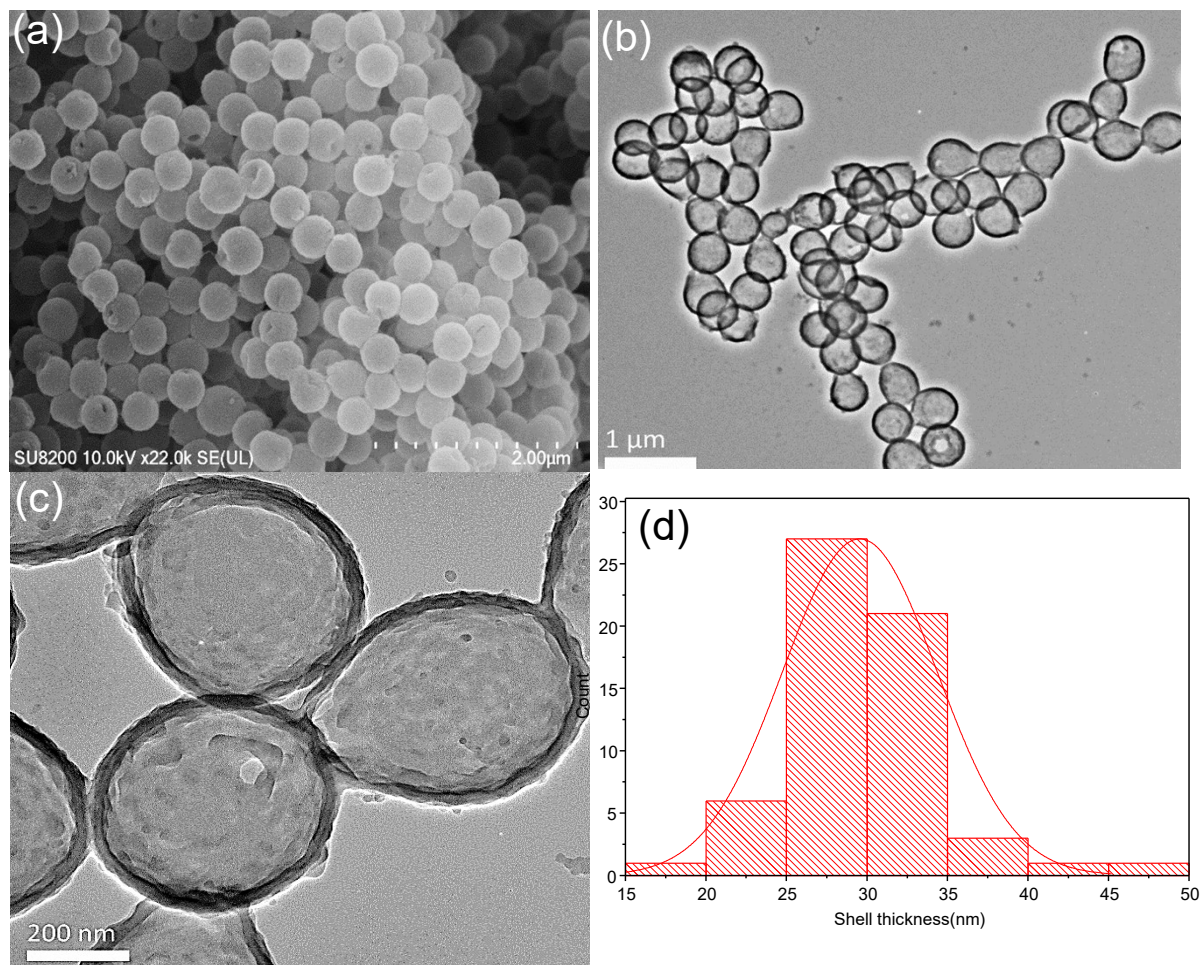


Fig. S2 HMIL-100(Fe) SEM images (a) small magnifications and TEM images (b) small magnifications (c) large magnifications (d) corresponding size histogram with an average shell thickness of 30 nm.

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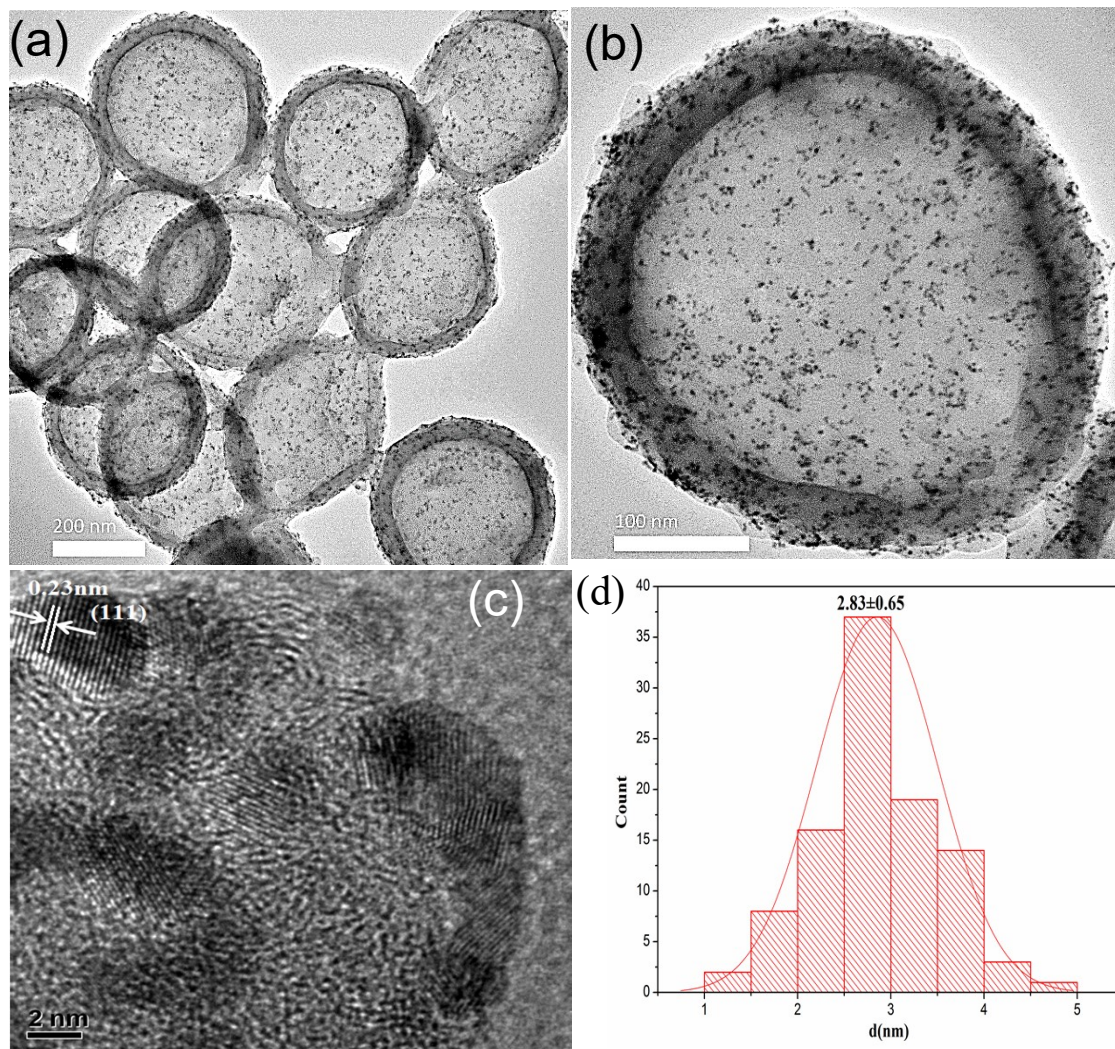


Fig. S3 TEM images of HMIL-100(Fe)@Pt (a) small magnifications (b) large magnifications (c) HR-TEM (d) corresponding size histogram of Pt NPs with an average size of 2.8 nm.



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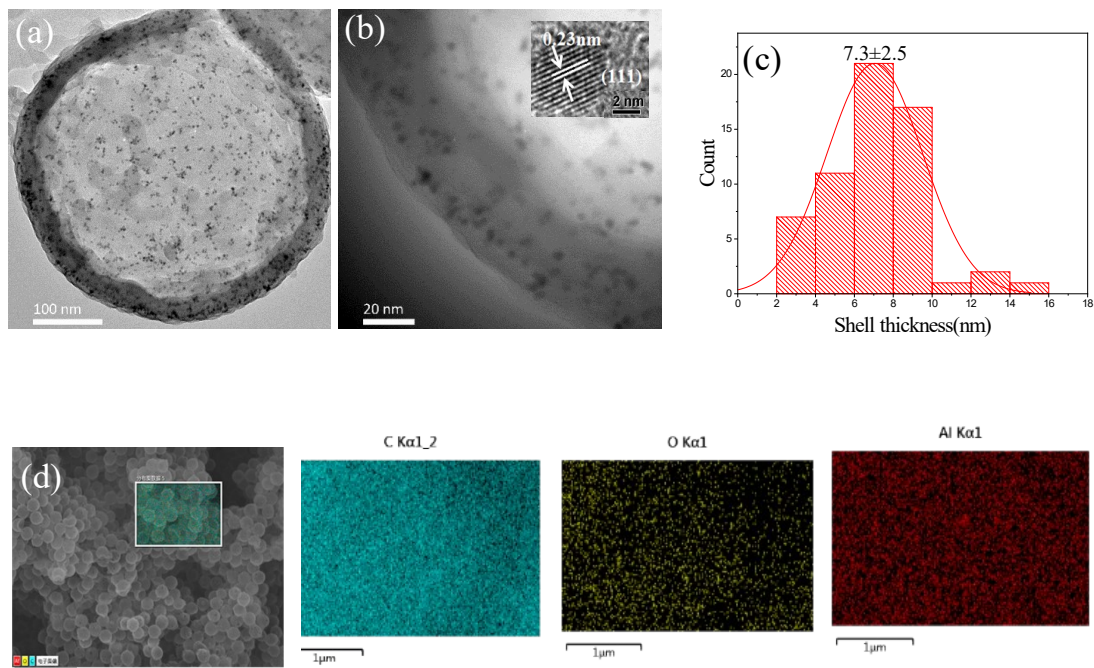


Fig. S4 TEM images of HMIL-100(Al)@Pt@HMIL-100(Al) (a) small magnifications (b) large magnifications, Inset: HRTEM image of Pt NP (c) corresponding outer shell thickness (d) SEM-EDS elemental mapping.

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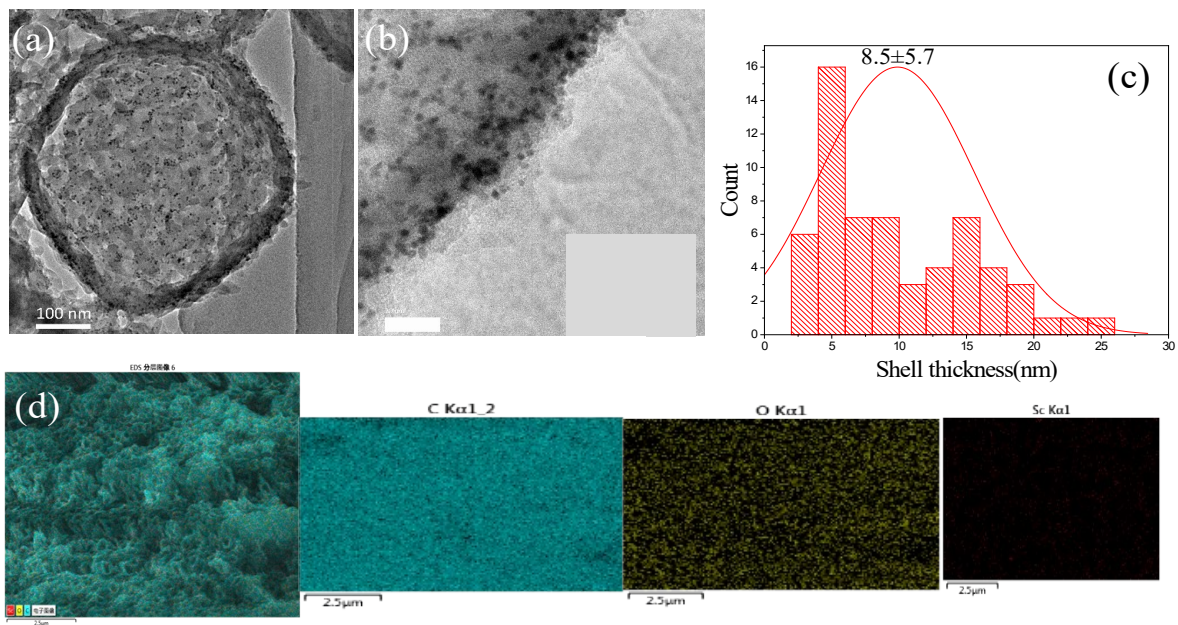


Fig. S5 HML-100(Sc)@Pt@HML-100(Sc) TEM images (a) small magnifications (b) large magnifications, Inset: HRTEM image of Pt NP (c) corresponding outer shell thickness (e) SEM-EDS elemental mapping.

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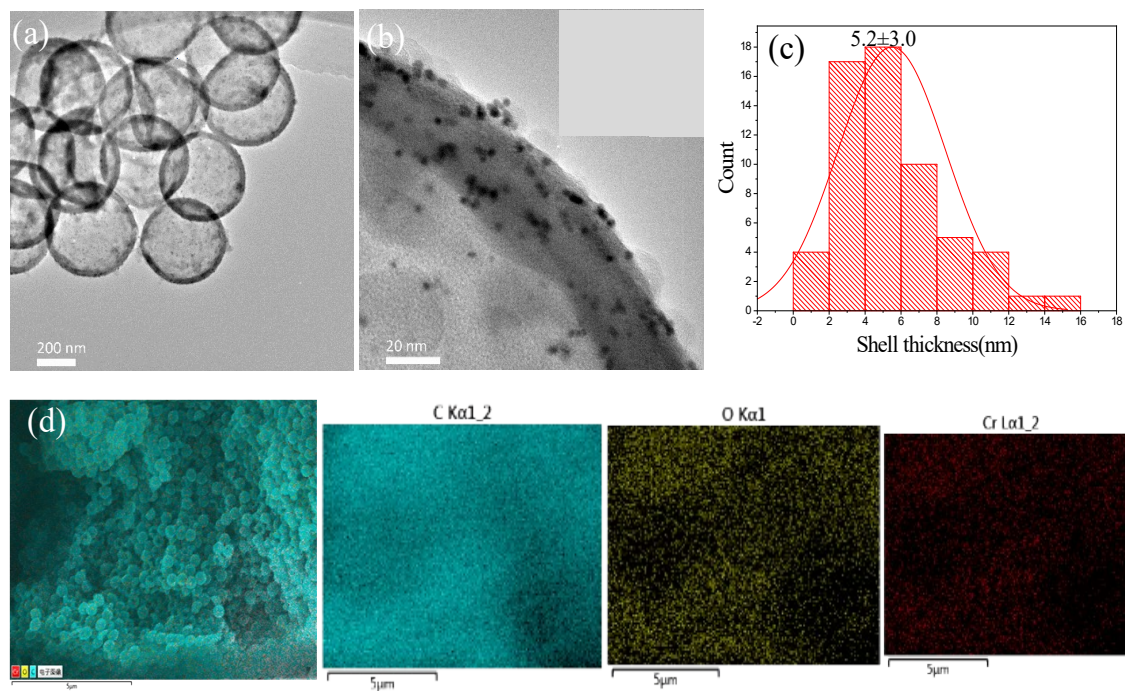


Fig. S6 HML-100(Cr)@Pt@HML-100(Cr) TEM images (a) small magnifications (b) large magnifications, Inset: HRTEM image of Pt NP (c) corresponding outer shell thickness (d) SEM-EDS elemental mapping.

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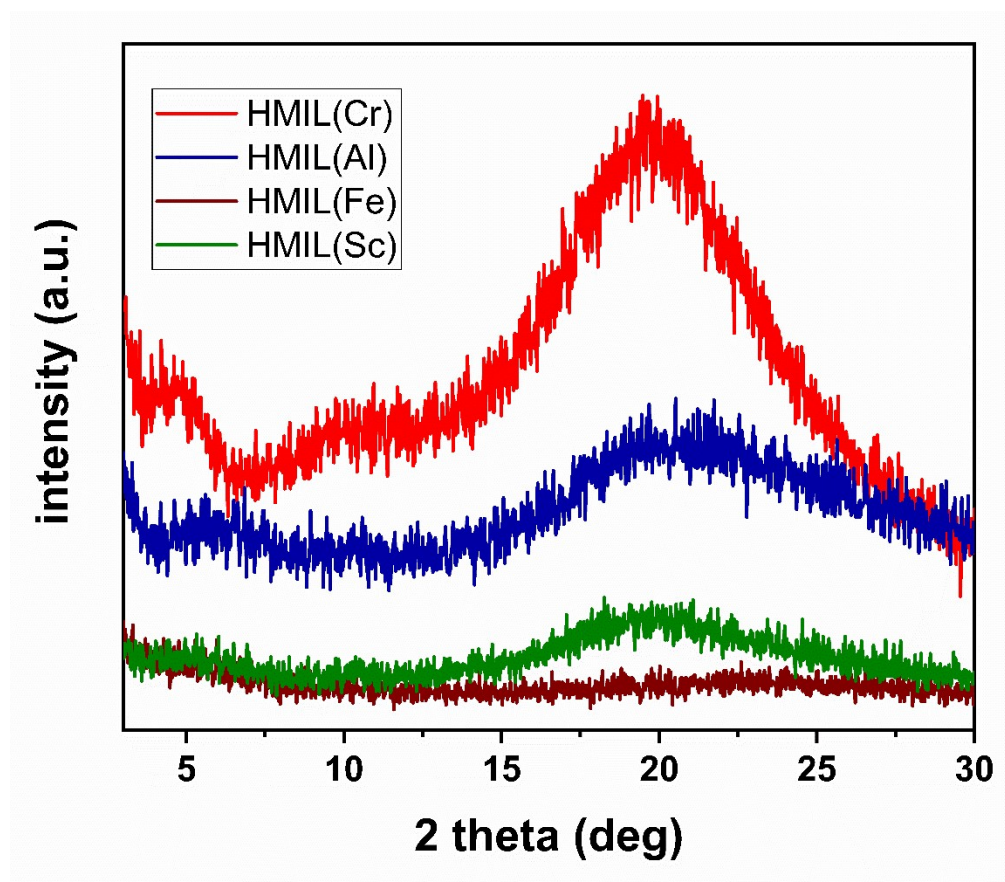


Fig. S7 The powder X-ray diffraction (PXRD) pattern for HMIL-100 series.



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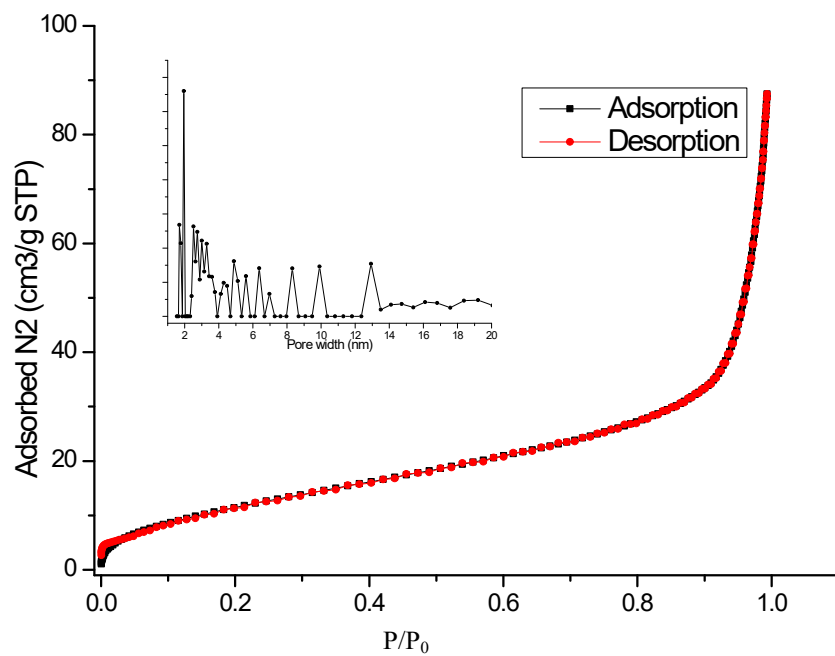


Fig. S8 N<sub>2</sub> adsorption-desorption isotherms of HMIL-100(Fe).

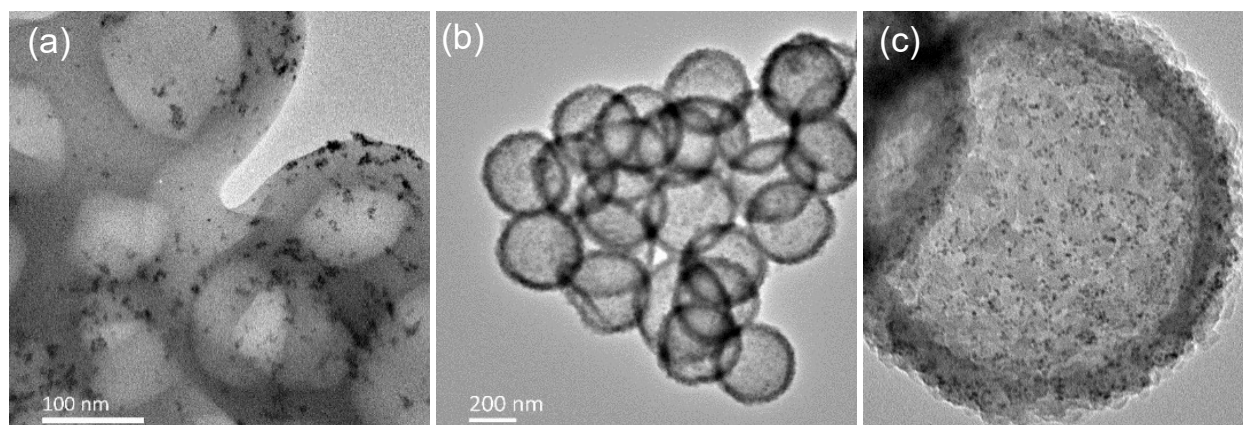


Fig. S9 Recovered catalyst TEM images (a) small magnifications HMIL-100(Fe)@Pt and HMIL-100(Fe)@Pt@HMIL-100(Fe) (b) small magnifications and (c) large magnifications.

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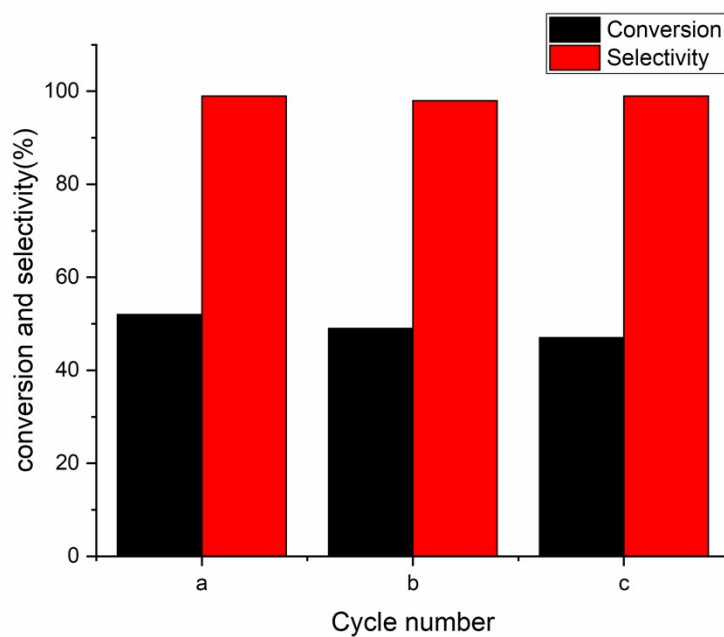


Fig. S10 Stability test of HMIL(Fe)@Pt@MIL(Fe)

It is observed that exhibit high stability with ~52% conversion of benzene and ~99.0% selectivity of phenol over three successive cycles.



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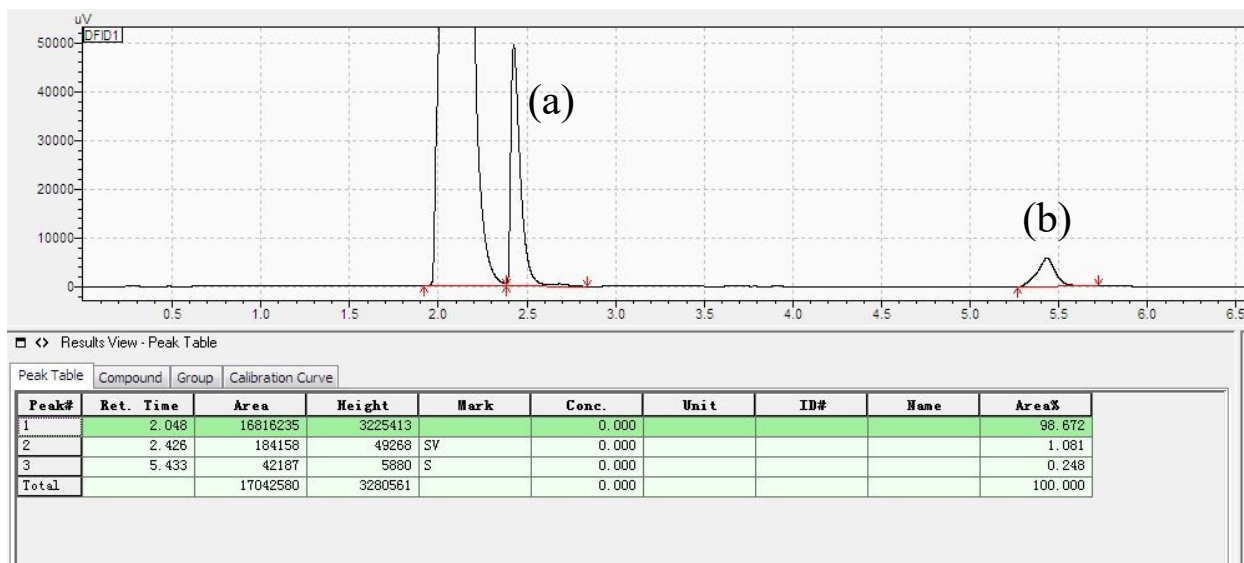


Figure S11 | Raw GC data for oxidation of Benzene (a) by HMIL-100(Fe)@Pt@MIL-100(Fe). (b) stands for Phenol.

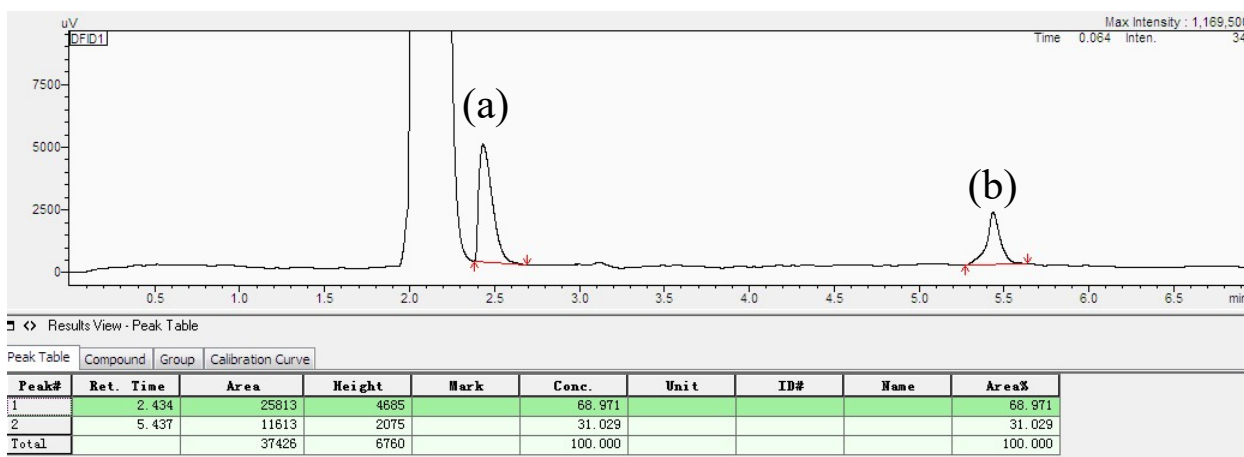


Figure S12 | Raw GC data for oxidation of Benzene (a) by HMIL-100(Fe)@Pt. (b) stands for Phenol.

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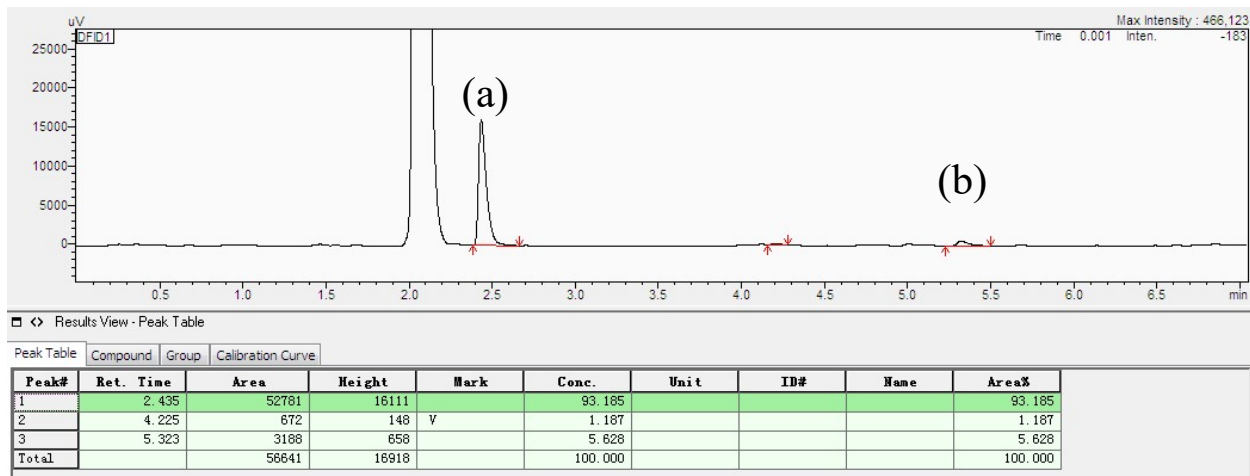


Figure S13 | Raw GC data for oxidation of Benzene (a) by HMIL-100(Fe). (b) stands for Phenol.

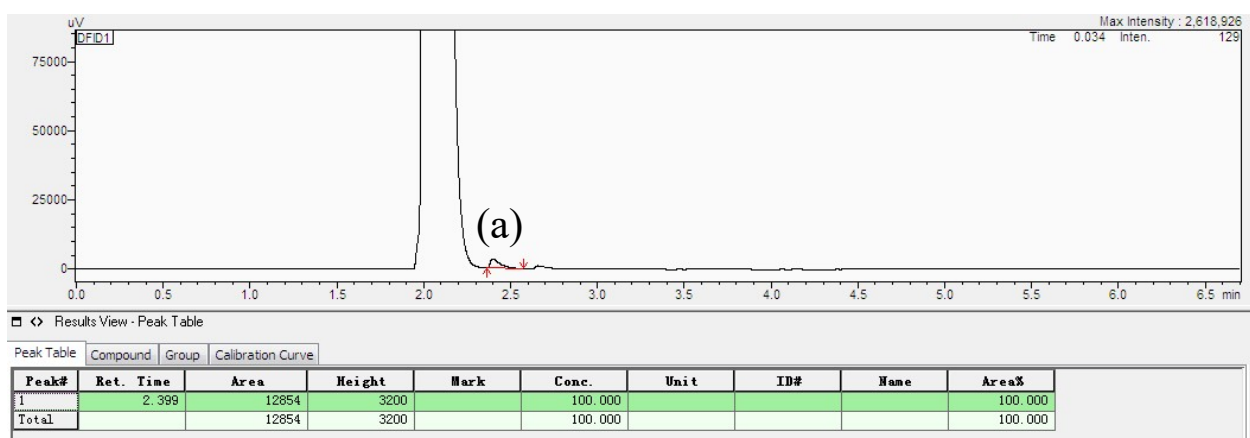


Figure S14 | Raw GC data for oxidation of Benzene (a) by Pt NPs. (b) stands for Phenol.

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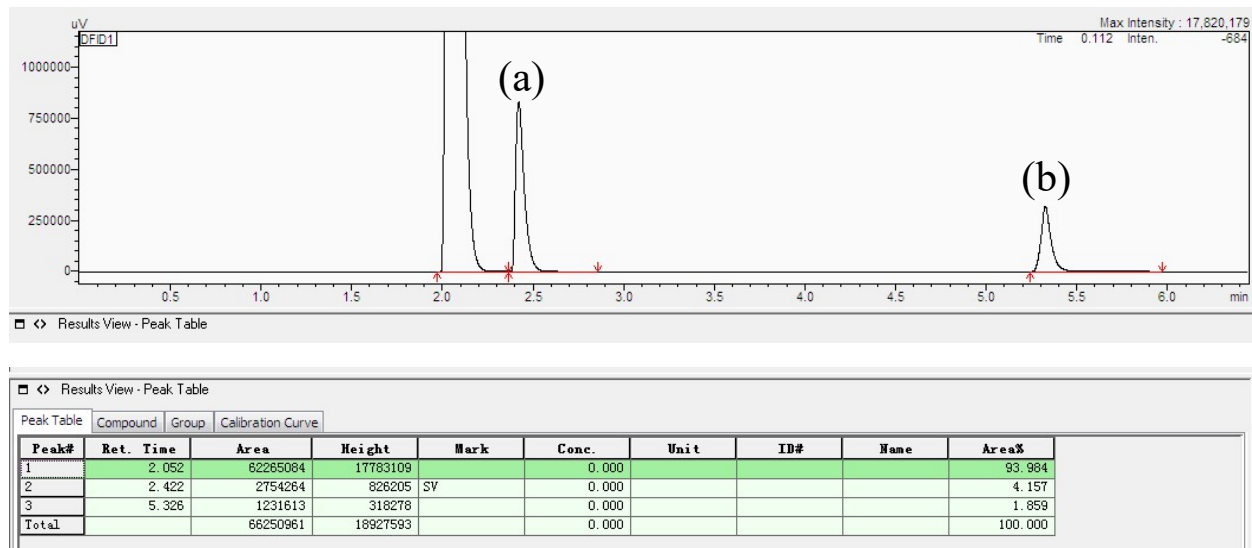


Figure S15| Raw GC data for Benzene (a) and for Phenol (b).

## S References

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3. L. Wang, J. Chen, L. Ge, V. Rudolph and Z. Zhu, *The Journal of Physical Chemistry C*, 2013, **117**, 4141-4151.