

Supplementary Information

***In situ* synthesis of metal clusters encapsulated within small-pore zeolite via a dry gel conversion method**

Xiaoli Yang,<sup>ab</sup> Qinggang Liu,<sup>a</sup> Yaru Zhang,<sup>ab</sup> Xiong Su,<sup>\*a</sup> Yanqiang Huang<sup>\*ac</sup> and Tao Zhang<sup>ac</sup>

<sup>a</sup> State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, No. 457 Zhongshan Road, Dalian 116023, P. R. China.

<sup>b</sup> University of Chinese Academy of Sciences, Beijing 100049, P. R. China.

<sup>c</sup> iChEM (Collaborative Innovation Center of Chemistry for Energy Materials), Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, P. R. China.

\* Corresponding authors, E-mail: [suxiong@dicp.ac.cn](mailto:suxiong@dicp.ac.cn), [yqhuang@dicp.ac.cn](mailto:yqhuang@dicp.ac.cn).

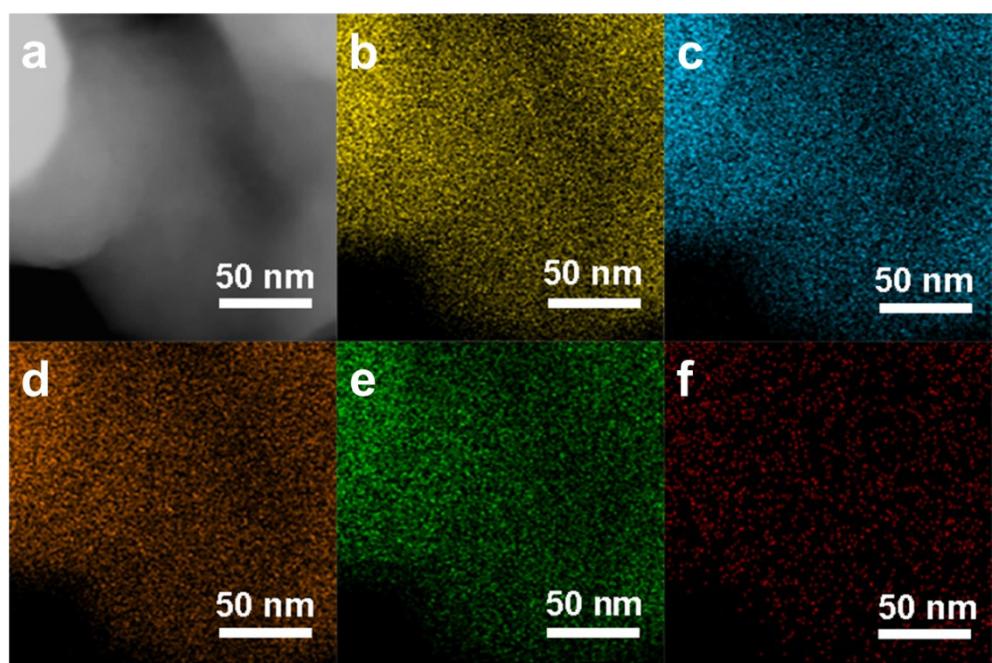


Fig. S1 Elemental maps for the Pt/Schiff-SiO<sub>2</sub> sample, (a) TEM image, (b) Si (yellow), (c) C (blue), (d) O (orange), (e) N (green), (f) Pt (red).

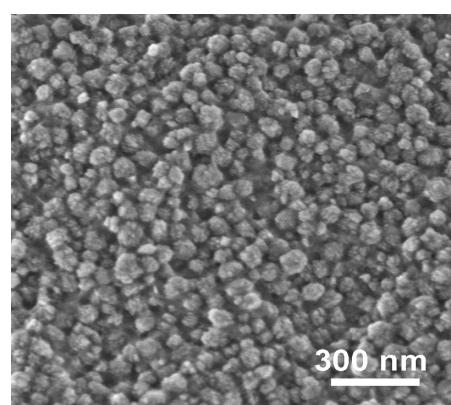


Fig. S2 SEM images of ZSM-5 seed.

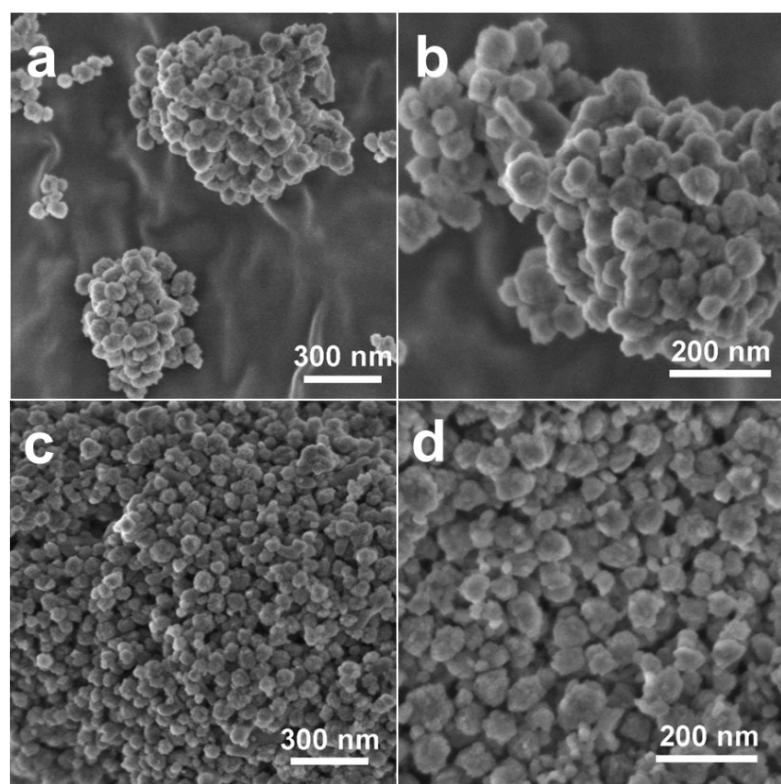


Fig. S3 SEM images of Pt@MFI-a (a-b) and Pt@MFI-b (c-d).

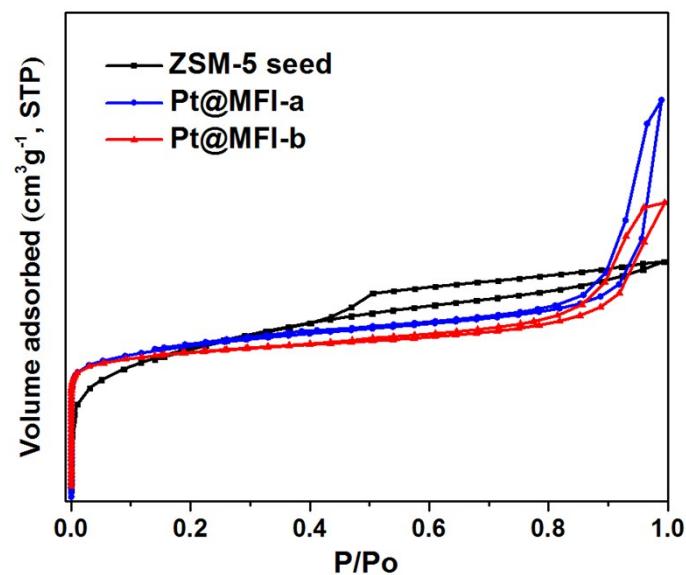


Fig. S4 N<sub>2</sub> adsorption-desorption isotherms of the samples.

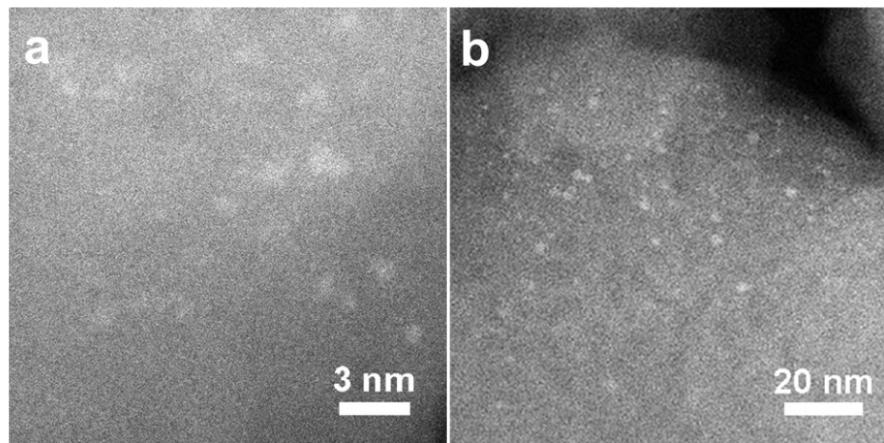


Fig. S5 STEM images of Pt@MFI-b after calcination at 500 °C with the scale bar of (a) 3 nm, (b) 20 nm.

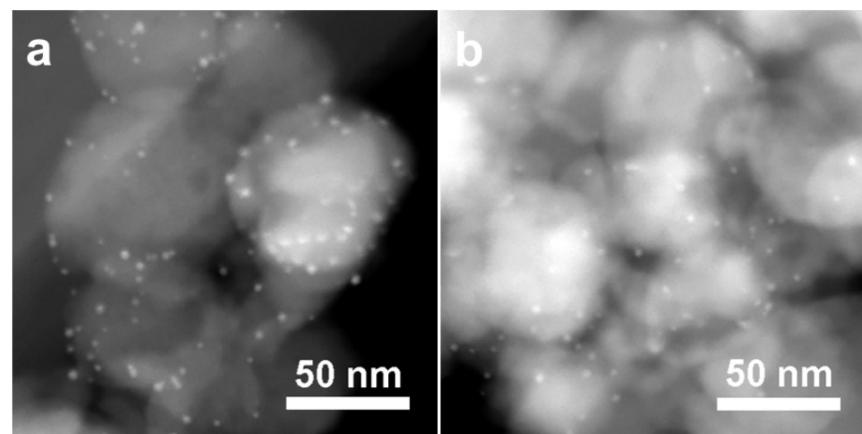


Fig. S6 STEM images of Pt@MFI-b after calcination at 800 °C.

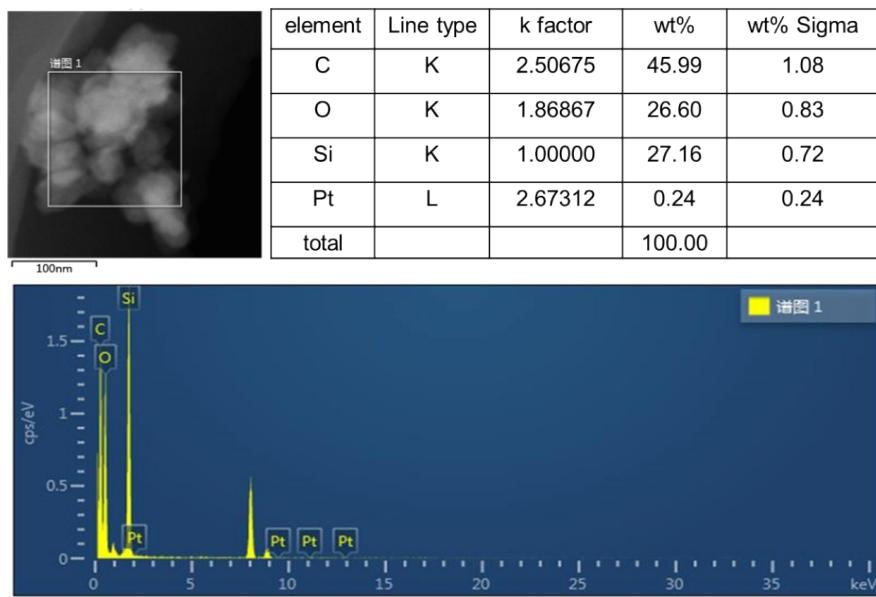


Fig. S7 EDS analysis of Pt@MFI-a without calcination.

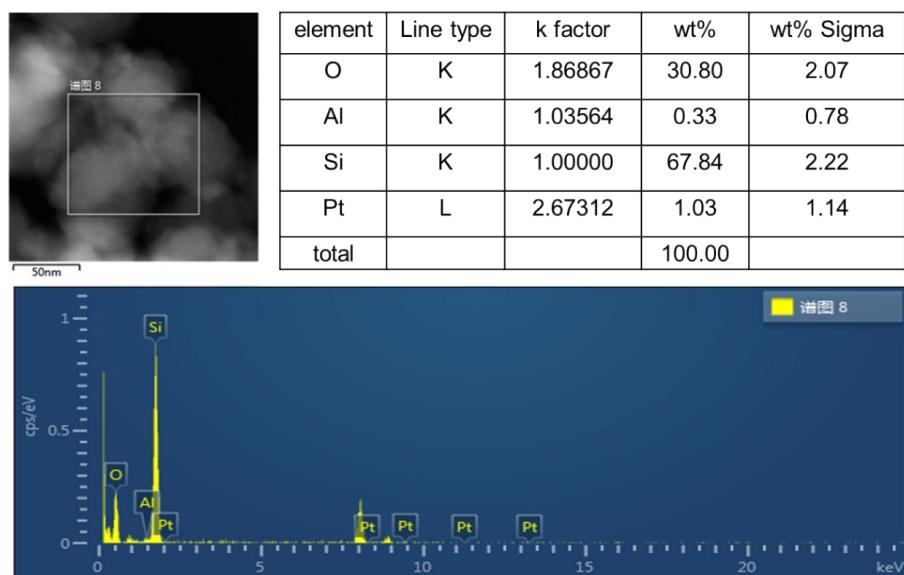


Fig. S8 EDS analysis of Pt@MFI-b without calcination.

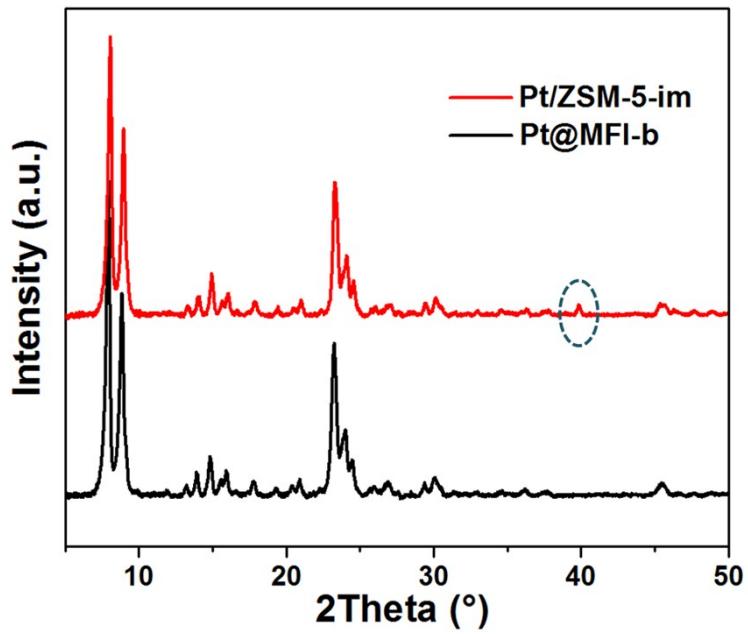


Fig. S9 XRD patterns of Pt/ZSM-5-im and Pt@MFI-b after calcination at 500 °C.

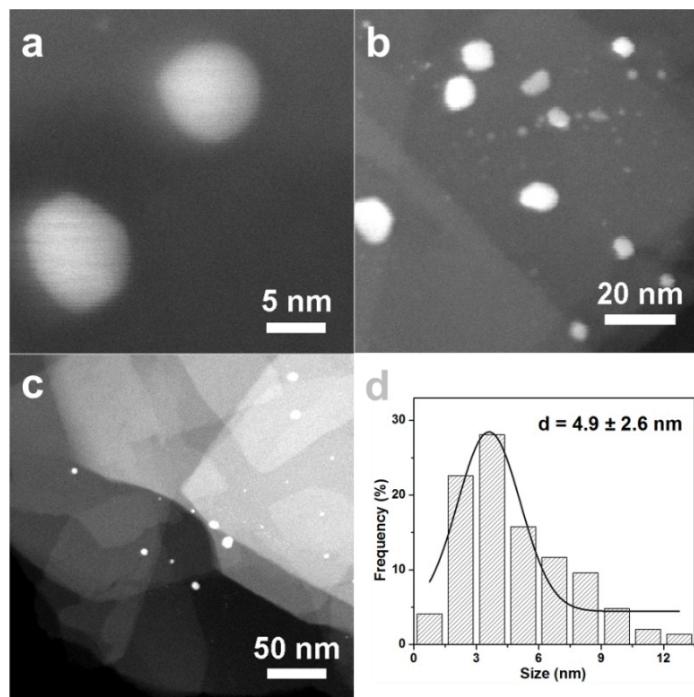


Fig. S10 STEM images of Pt/ZSM-5-im after calcination at 500 °C under the scale bar of (a) 5 nm, (b) 20 nm, (c) 50 nm, (d) the particle size distribution.

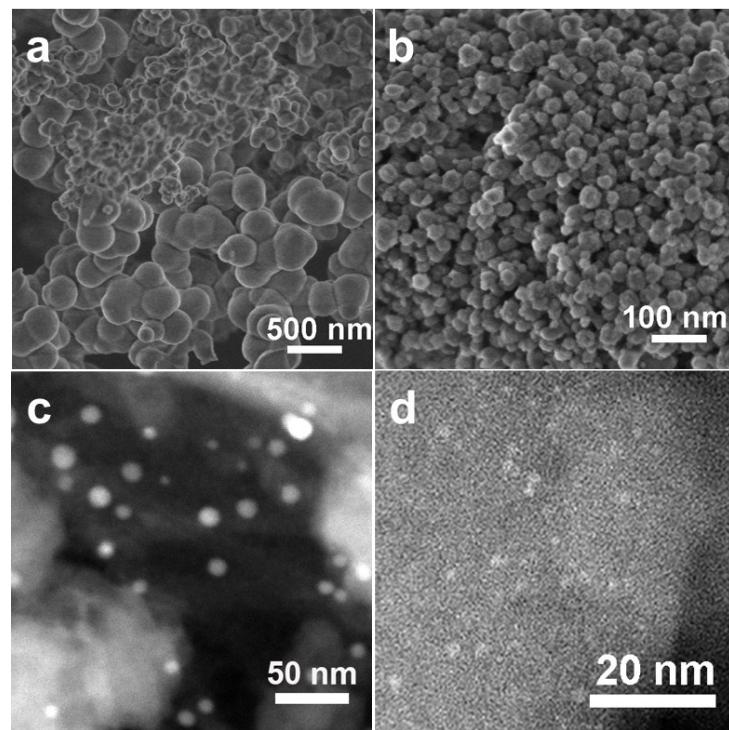


Fig. S11 SEM images of (a) Pt/Schiff-SiO<sub>2</sub>&MFI-b and (b) Pt@MFI-b, the corresponding TEM images of (c) Pt/Schiff-SiO<sub>2</sub>&MFI-b and (d) Pt@MFI-b after calcination at 500 °C.

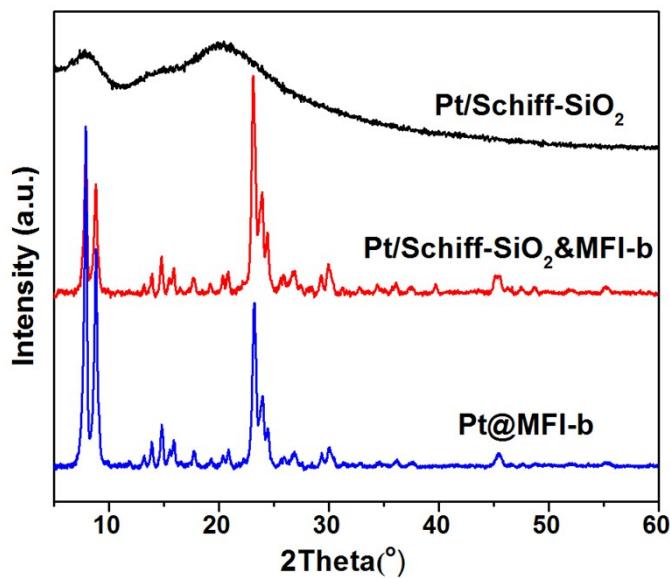


Fig. S12 XRD patterns of Pt/Schiff-SiO<sub>2</sub> before calcination, Pt/Schiff-SiO<sub>2</sub>&MFI-b and Pt@MFI-b after calcination at 500 °C.

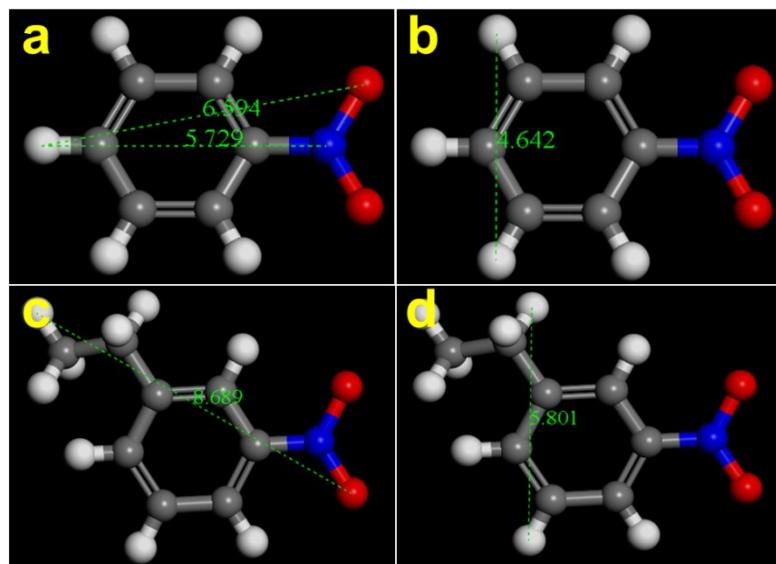


Fig. S13 The dynamic diameter of (a-b) nitrobenzene and (c-d) 3-nitrotoluene.

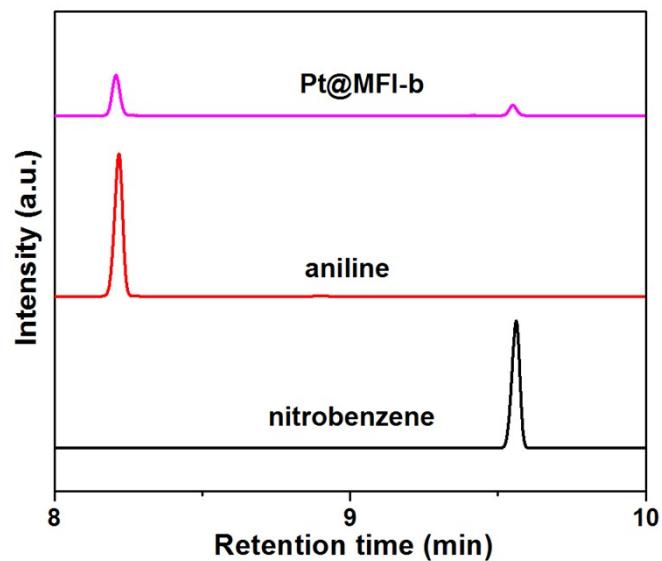


Fig. S14 Gas chromatogram of products after reduction of nitrobenzene over Pt@MFI-b catalysts and the corresponding standard samples.

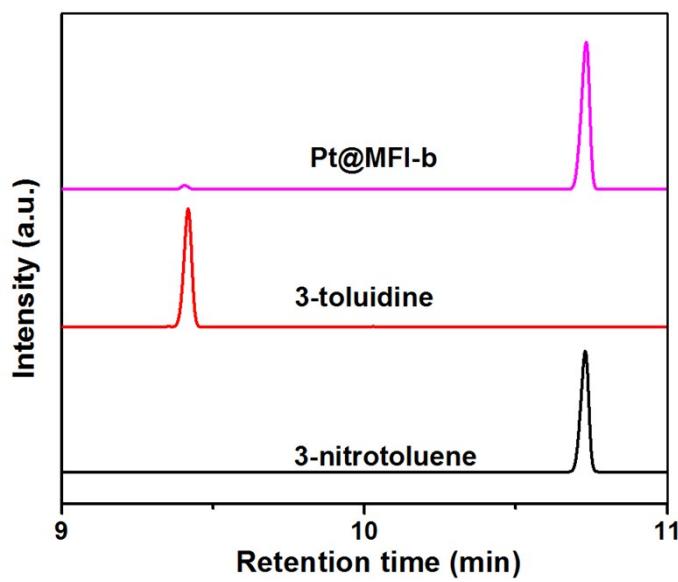


Fig. S15 Gas chromatogram of products after reduction of 3-nitrotoluene over Pt@MFI-b catalysts and the corresponding standard samples.

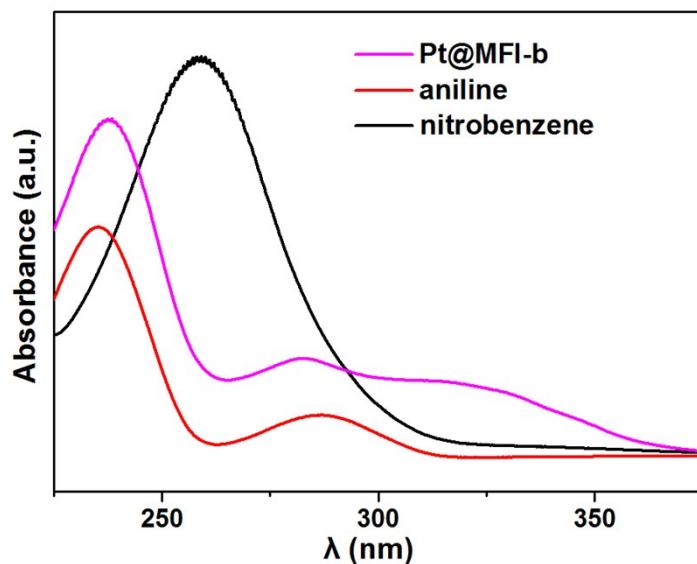


Fig. S16 UV-vis absorption spectra of products after reduction of nitrobenzene over Pt@MFI-b and the corresponding standard substances.

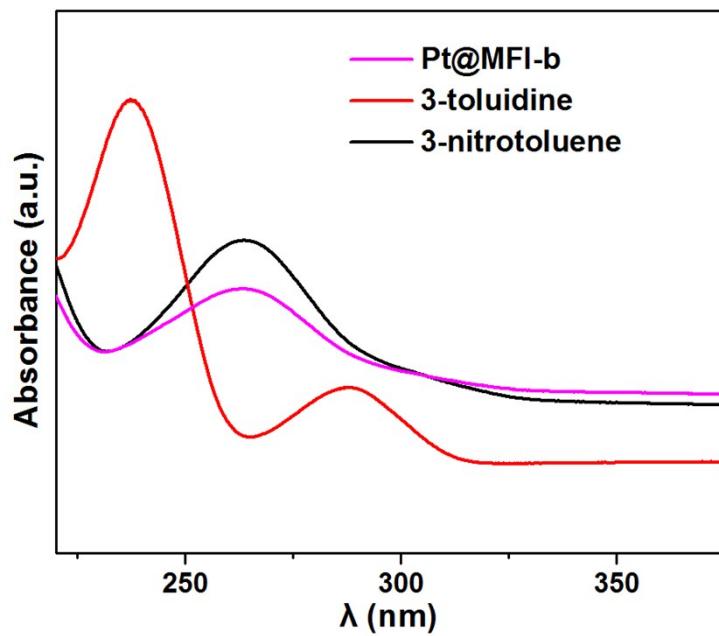


Fig. S17 UV-vis absorption spectra of products after reduction of 3-nitrotoluene over Pt@MFI-b and the corresponding standard substances.

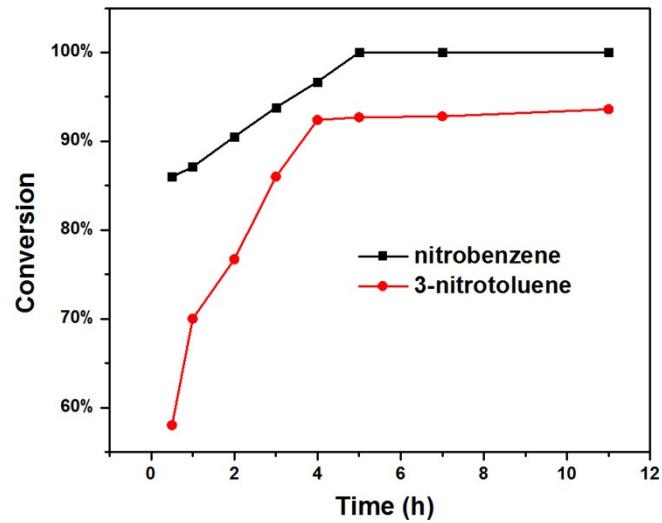


Fig. S18 The hydrogenation of nitrobenzene and 3-nitrotoluene over Pt@MFI-b catalyst.

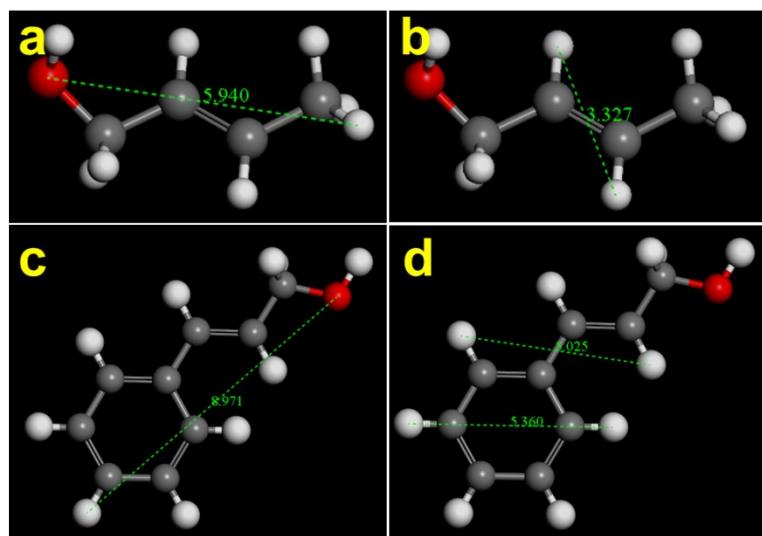


Fig. S19 The dynamic diameter of (a-b) croton alcohol and (c-d) cinnamyl alcohol.

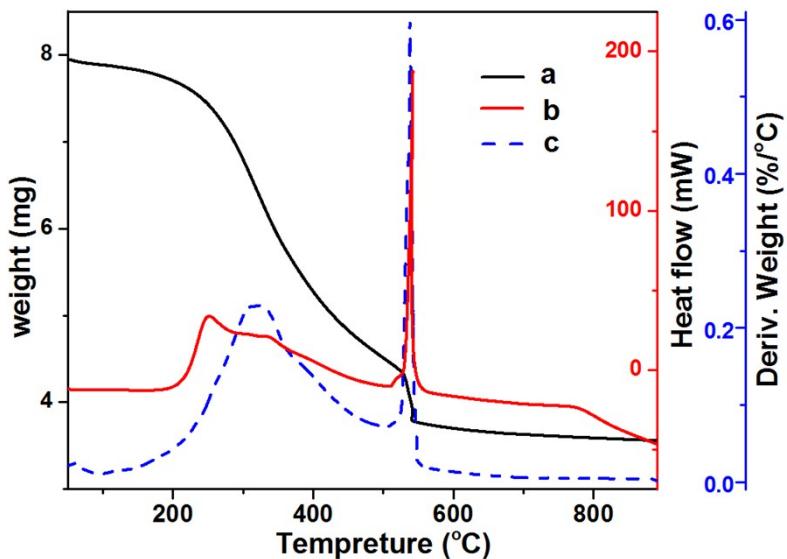


Fig. S20 (a) TG, (b) DTA and (c) DTG curves of Pt/Schiff-SiO<sub>2</sub>.

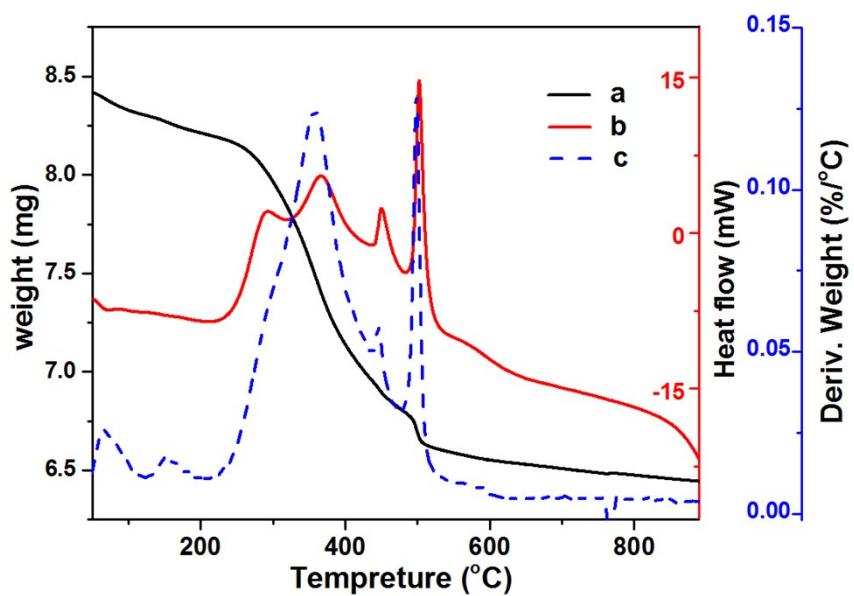


Fig. S21 (a) TG, (b) DTA and (c) DTG curves of Pt@MFI-a.

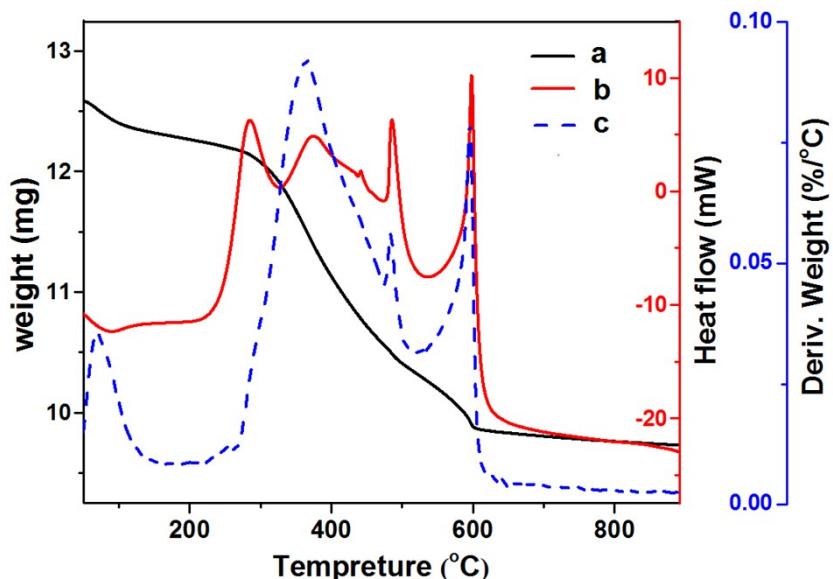


Fig. S22 (a) TG, (b) DTA and (c) DTG curves of Pt@MFI-b.

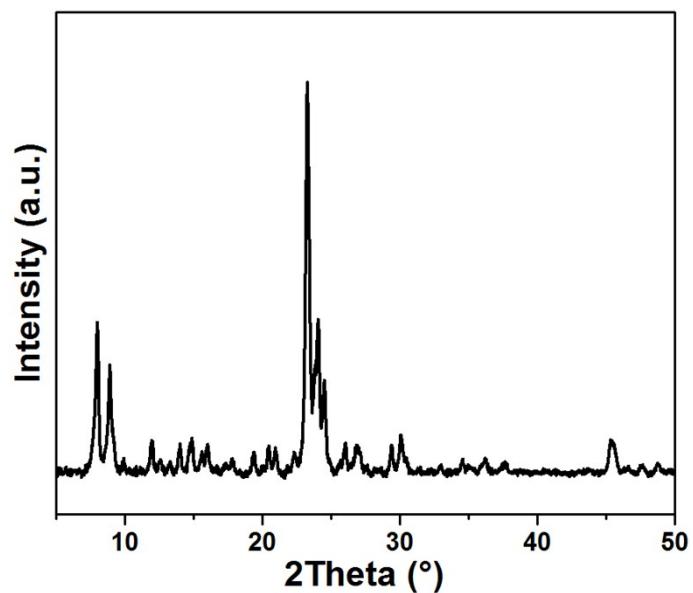


Fig. S23 XRD patterns of Ru@MFI after calcination at 500 °C.

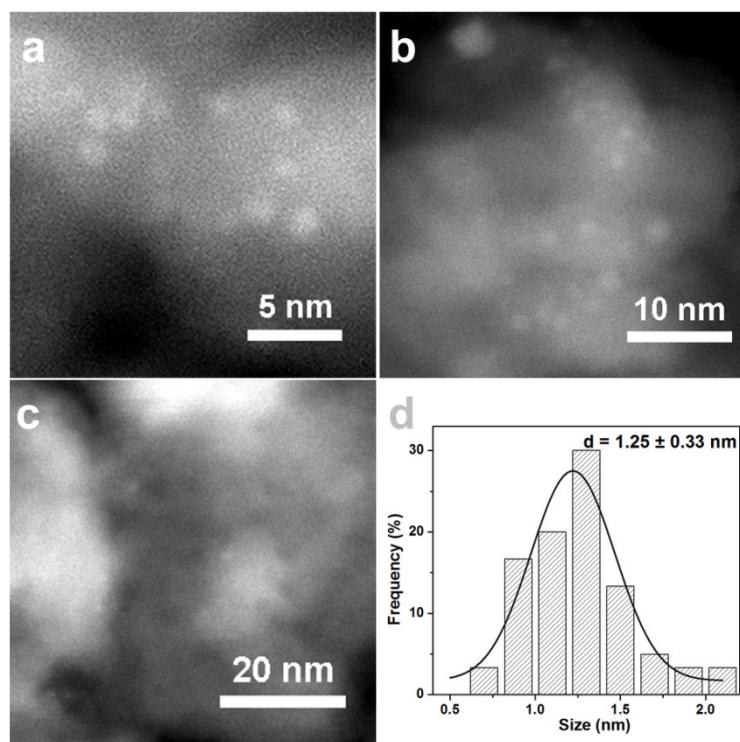


Fig. S24 STEM images of Ru@MFI after calcination at 500 °C under the scale bar of (a) 5 nm, (b) 10 nm, (c) 20 nm, (d) the particle size distribution.

**Table S1** The ICP measurement results of the samples

| Samples  | Pt<br>/wt.% | Al<br>/wt.% |
|----------|-------------|-------------|
| Pt@MFI-a | 0.25        | - ND        |
| Pt@MFI-b | 0.23        | 4.8         |

ND Not determined.

**Table S2** BET surface areas and pore volumes of the samples

| Samples    | S <sub>BET</sub><br>/m <sup>2</sup> g <sup>-1</sup> | S <sub>micro</sub><br>/m <sup>2</sup> g <sup>-1</sup> | S <sub>meso</sub><br>/m <sup>2</sup> g <sup>-1</sup> | V <sub>micro</sub><br>/cm <sup>3</sup> g <sup>-1</sup> | V <sub>macro</sub><br>/cm <sup>3</sup> g <sup>-1</sup> | Medium pore width<br>/nm |
|------------|---|---|--|--|--|--------------------------|
| ZSM-5 seed | 357   | 10  | 348  | 0.05   | 0.32   | 0.97                     |
| Pt@MFI-a   | 517   | 346   | 171  | 0.15   | 0.34   | 0.62                     |
| Pt@MFI-b   | 483   | 371   | 112  | 0.15   | 0.33   | 0.59                     |

**Table S3** The conversion of hydrogenation reactions over different catalysts

| samples     | C <sub>3</sub> -nitrotoluene/% |
|-------------|--------------------------------|
| Pt@MFI-b    | 58                             |
| Pt/ZSM-5-im | 100                            |