

Electronic Supplementary Information for Nanoscale

**Mercaptosilane-assisted synthesis of sub-nanosized Pt particles within hierarchically porous ZSM-5/SBA-15 material and enhanced hydrogenation property**

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**Supplementary information**

**Experimental**

*Synthesis of Pt@ZSBA:* First, a zeolite seed Pt@ZSM-5 solution was prepared by hydrothermal crystallization in the presence of (3-mercaptopropyl)-trimethoxysilane. In a typical synthesis of Pt@ZSM-5 seed, 0.34 g of (3-mercaptopropyl)-trimethoxysilane and 0.3 g of NaOH were dissolved in 4.0 g of deionized H<sub>2</sub>O. A solution of 0.143 g of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O in 3.0 g of H<sub>2</sub>O was added dropwise into the previous solution with vigorous stirring to form solution I. To prepare the solution II, 0.6 g of NaOH, 0.25 g of NaAlO<sub>2</sub>, 2.71 g of tetrapropyl- ammonium bromide (TPABr) and 15.0 g of colloidal silica were dissolved in 20.0 g of deionized H<sub>2</sub>O. Solution I was then poured into the solution II, and the resulting synthesized mixture was vigorously mixed for 4 h at ambient temperature. The resultant gel was then crystallized hydrothermally at 443 K without stirring for 4 h in polypropylene bottle to obtain a zeolite Pt@ZSM-5 seed solution. Second, Pt@ZSBA material was prepared by using tetraethylorthosilicate (TEOS) and zeolite Pt@ZSM-5 seed as silicon sources. An amount of 2 g of EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub> (Pluronic P123) was dissolved in

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65 g of 2 M hydrochloric acid at 40 °C for more than 4h. 4.28 g of TEOS and 4.85 g of zeolite Pt@ZSM-5 seed solution (containing 10.1mmol of SiO<sub>2</sub>) were mixed with the P123 solution and further stirred for 24 h at 40 °C. The gel solutions were transferred into a teflon bottle and heated at 100 °C for 24h without stirring. After cooling to the room temperature, Pt@ZSBA was recovered by filtering and drying at room temperature in air. The template Pluronic P123 was removed by extractor using acidic EtOH for 24h. The removal of the (3-mercaptopropyl)trimethoxysilane was carried out by heating the samples from ambient temperature to 623K and held for 3 h in dry air.

*Synthesis of Pt@ZSM-5:* The synthesis process of Pt@ZSM-5 was the same as the zeolite seed Pt@ZSM-5 during the synthesis of Pt@ZSBA. The resultant gel was crystallized hydrothermally at 443 K without stirring for 4 h in a polypropylene bottle.

*Synthesis of Pt/SBA-15:* In a typical experiment, SBA-15 was synthesized using a triblock copolymer (P123) as the structure-directing agent. 2 g of P123 was dissolved in 65 g of 2 mol/L HCl at 40 °C. Then, 4.28 g of TEOS was added in P123 solution under confined stirring rate for 3 min and further maintained at static condition for 24 h. The gel solutions were transferred into a teflon bottle and heated at 100 °C for 24 h without stirring. After cooling to the room temperature, the solid product was recovered by filtering and drying at room temperature in air. Then, the sample was calcined at 550 °C for 6 h to remove the copolymer template. Pt/SBA-15 was

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prepared by one-step incipient-wetness impregnation of  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  solution. Then the obtained Pt/SBA-15 was calcined at 350 °C for 3 h.

*Synthesis of Pt/ZSBA-M:* A physical mixture of Pt@ZSM-5 and SBA-15 (Pt/ZSBA-M) was prepared by adding 1 g of Pt@ZSM-5 and 2 g of SBA-15 into 30 g of  $\text{H}_2\text{O}$ . The mixture was stirred for 4 h at room temperature and dried at 60 °C for 20 h.

*Synthesis of SBA-15 with the filtrate of Pt@ZSM-5 after treatment with hydrochloric acid:* First, a zeolite seed Pt@ZSM-5 solution was prepared by hydrothermal crystallization in the presence of (3-mercaptopropyl)-trimethoxysilane. And 4.85g of zeolite seed Pt@ZSM-5 solution was treated with hydrochloric acid (2M) for 24h at 40 °C. Second, SBA-15 was synthesized using the filtrate of Pt@ZSM-5 after treatment with hydrochloric acid. 2 g of P123 was dissolved in the above filtrate at 40 °C with stirring. Then, 4.28 g of TEOS was added in P123 solution and further maintained at static condition for 24 h. The gel solutions were transferred into a teflon bottle and heated at 100 °C for 24 h. The solid product was recovered by filtering and drying at room temperature in air. Then, the sample was calcined at 550 °C for 6 h to remove the copolymer template.

*The hydrothermal treatment of Pt@ZSBA:* The hydrothermal stability of Pt@ZSBA was tested by treatment of Pt@ZSBA refluxing in boiling water for 168 h. The above solid materials were then filtered, washed with deionized water and dried at 60 °C in

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air.

*Characterization of Pt@ZSBA:* The surface morphology of the supports was observed by field emission scanning electron microscopy (FESEM) on a Quanta 200F instruments using accelerating voltages of 20 kV. The silica-based samples were coated with gold before the SEM measurement. TEM images were taken from thin edges of particles supported on a porous carbon grid using a JEOL JEM 2100 electron microscope operated at 120 kV. The HAADF-STEM and EDX elemental mapping images were taken by Tecnai F20 instrument at 200 kV. The low-angle ( $2\theta = 0.5\text{--}5^\circ$ ) X-ray diffraction patterns of the supports and catalysts were measured on a Bruker D8 Advance Powder diffractometer using Cu K $\alpha$  radiation and the scattering slits of  $0.05^\circ$ . The wide-angle ( $2\theta = 5\text{--}80^\circ$ ) XRD patterns were performed on a powder X-ray diffractometer (Shimadzu XRD6000) using CuK $\alpha$  ( $\lambda = 0.15406$  nm) radiation and with a scanning rate of  $4^\circ/\text{min}$ . The Raman spectra were obtained using a Renishaw Raman InVia Microscope (Spectra-Physics model 163), operated at the argon ion laser operating at wavelength of 325 nm. The laser spot size was approximately  $1\text{--}2\mu\text{m}$  with a power of 3.6 mW. The laser-hyperpolarized (HP)  $^{129}\text{Xe}$  NMR experiments were carried out at 110.6 MHz on the Varian Infinity-plus 400 spectrometer using a 7.5 mm probe. The average diameter of sub-nanosized Pt NPs was obtained through statistical analyses based on about 10 representative micrographs involving 100-150 Pt NPs by Nano Measurer Statistic Software.

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*Catalytic 1,3-butadiene hydrogenation:* Hydrogenation of 1,3-butadiene was performed in a fixed-bed flow stainless reactor (i.d. 6 mm) under atmospheric pressure. 5 mg of the catalyst used in a powder form (>100 mesh) was mixed with quartz sand as a diluent (quartz sand/catalyst = 90/1, weight ratio). The reactants of H<sub>2</sub> and 1.02 vol% 1,3-butadiene N<sub>2</sub> passed through the catalyst bed at the rate of 18.0 and 22.9 ml min<sup>-1</sup>, respectively, which corresponds to the space velocities of 490,800 ml h<sup>-1</sup> (g-cat.)<sup>-1</sup>. Before it was switched to the reaction feed gas, the catalyst was pretreated in flowing N<sub>2</sub> (19.3 ml min<sup>-1</sup>) at 323 K for 0.5 h. The reactor effluent was analyzed on line using a GC-8A gas chromatograph equipped with a GDX-501 column and a FID detector.

*Catalytic cyclooctadiene (COD) hydrogenation:* The liquid-phase hydrogenation of COD was carried out in a glass batch reactor (Supelco) closed with Teflon septum and equipped with a pressure gauge and a side arm with an on-off lock. A micro-syringe can be allowed to inject and withdraw liquid or gas through the lock. Typical procedure for this reaction follows: a mixture of catalyst (60mg), cyclooctadiene (0.46mmol, 50mg), isopropanol (2ml) were put into a closed glass batch reactor (5ml) under the condition of H<sub>2</sub> (5 bar) and were stirred (ca. 500 rpm) at 25 °C for 2 h. Recycle experiment was performed by removing the used reactant, and then washing the catalyst with isopropanol for 4 times. The reactor was refilled with the washed catalyst and the fresh COD, then, the recycle test restarted. The products were analyzed using a SP-6890 gas chromatography with FID detector (FFAP).

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Table S1. The catalytic activities of Pt supported catalysts in the hydrogenation of cyclooctadiene at 25 °C.

catalysts	Pt loading (wt %)	Tem. (°C)	Time (min)	Conversion (%)	Reaction rate(mmol min <sup>-1</sup> g-Pt <sup>-1</sup> )	TON <sup>a</sup>
Pt/SBA-15	0.25	25	120	16.8	4.3	101
Pt/ZSBA-M	0.16	25	120	9.0	3.6	84
Pt@ZSM-5	0.22	25	120	7.2	2.1	49
Pt@ZSBA	0.20	25	120	84.3	27.1	633

<sup>a</sup> Calculated on the basis of total weight of Pt.

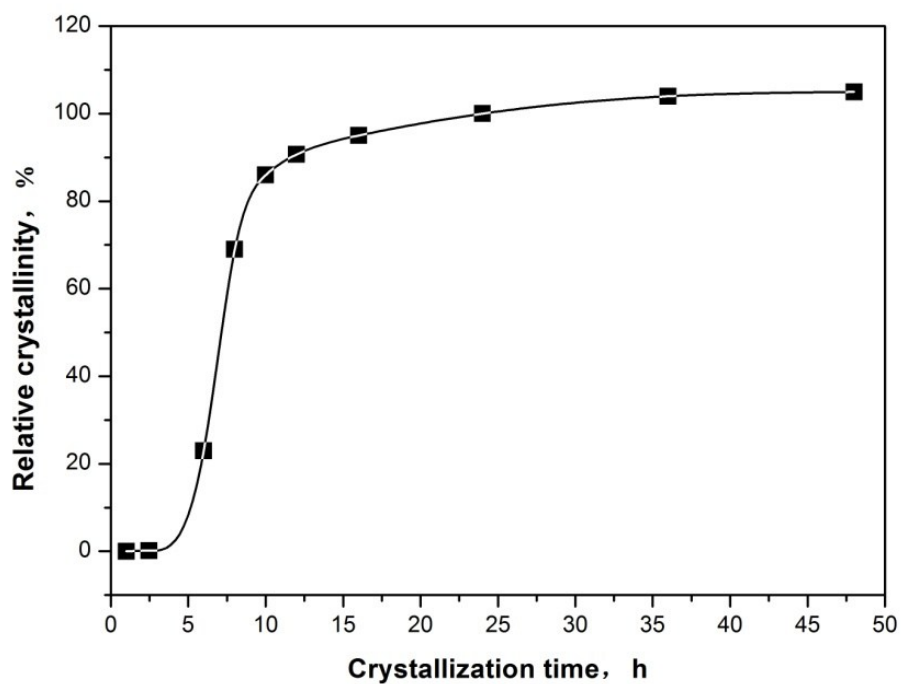


Fig. S1: The relative crystallinity of Pt@ZSM-5 as a function of the crystallization time at 170 °C.

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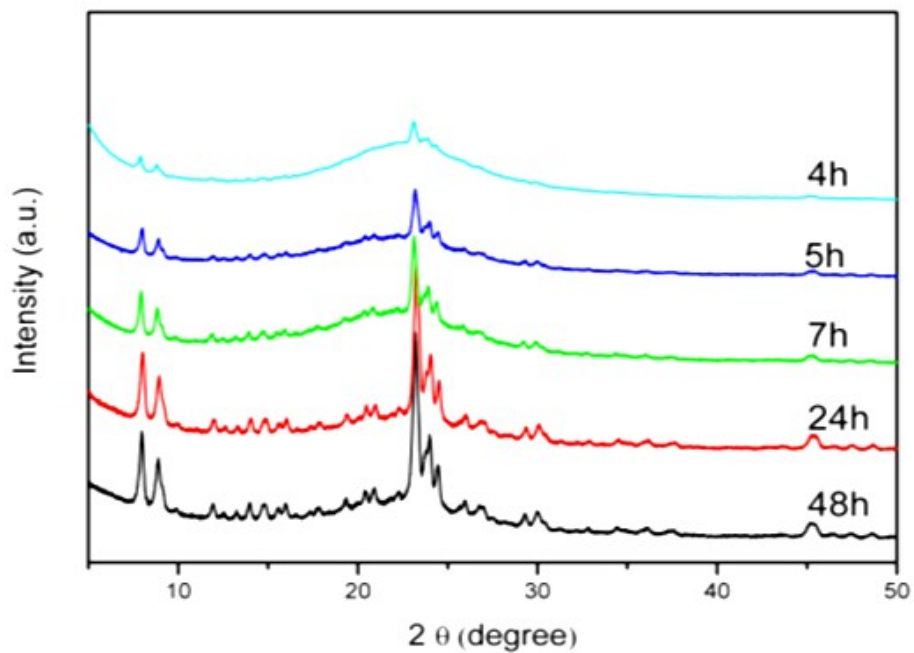


Fig. S2: The large angle XRD patterns of Pt@ZSBA material obtained from Pt@ZSM-5 nanocrystals with different crystallization time.



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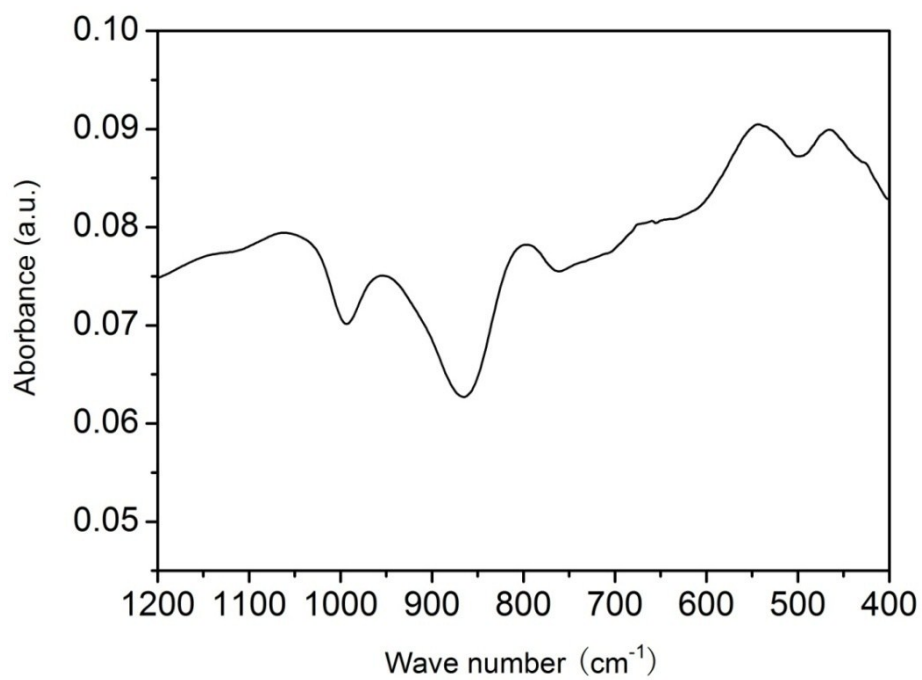


Fig. S3: The FT-IR spectrum of the Pt@ZSBA material.

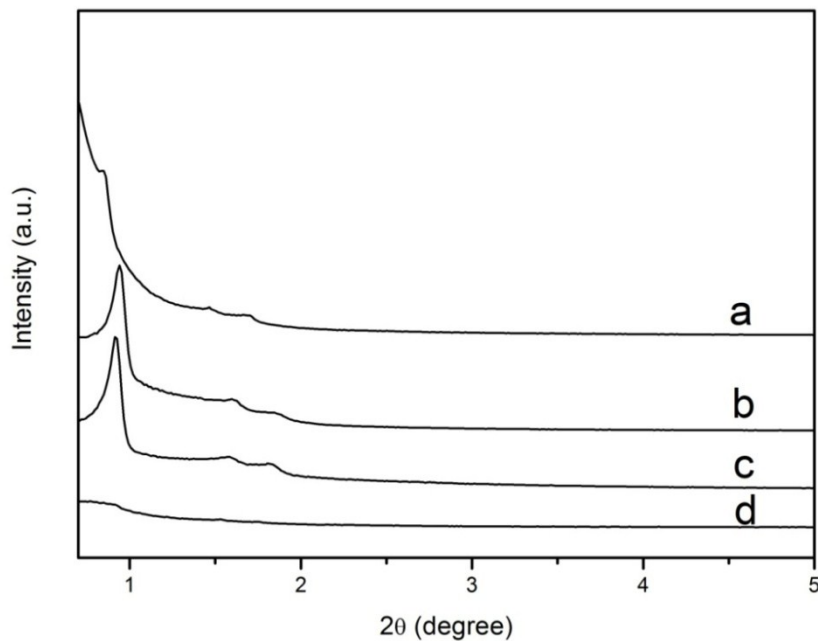


Fig. S4: The low angle XRD patterns of the calcined samples before and after treatment in boiling water for 168 h: (a) Pt@ZSBA after treatment, (b) calcined Pt@ZSBA, (c) calcined SBA-15, (d) SBA-15 after treatment.

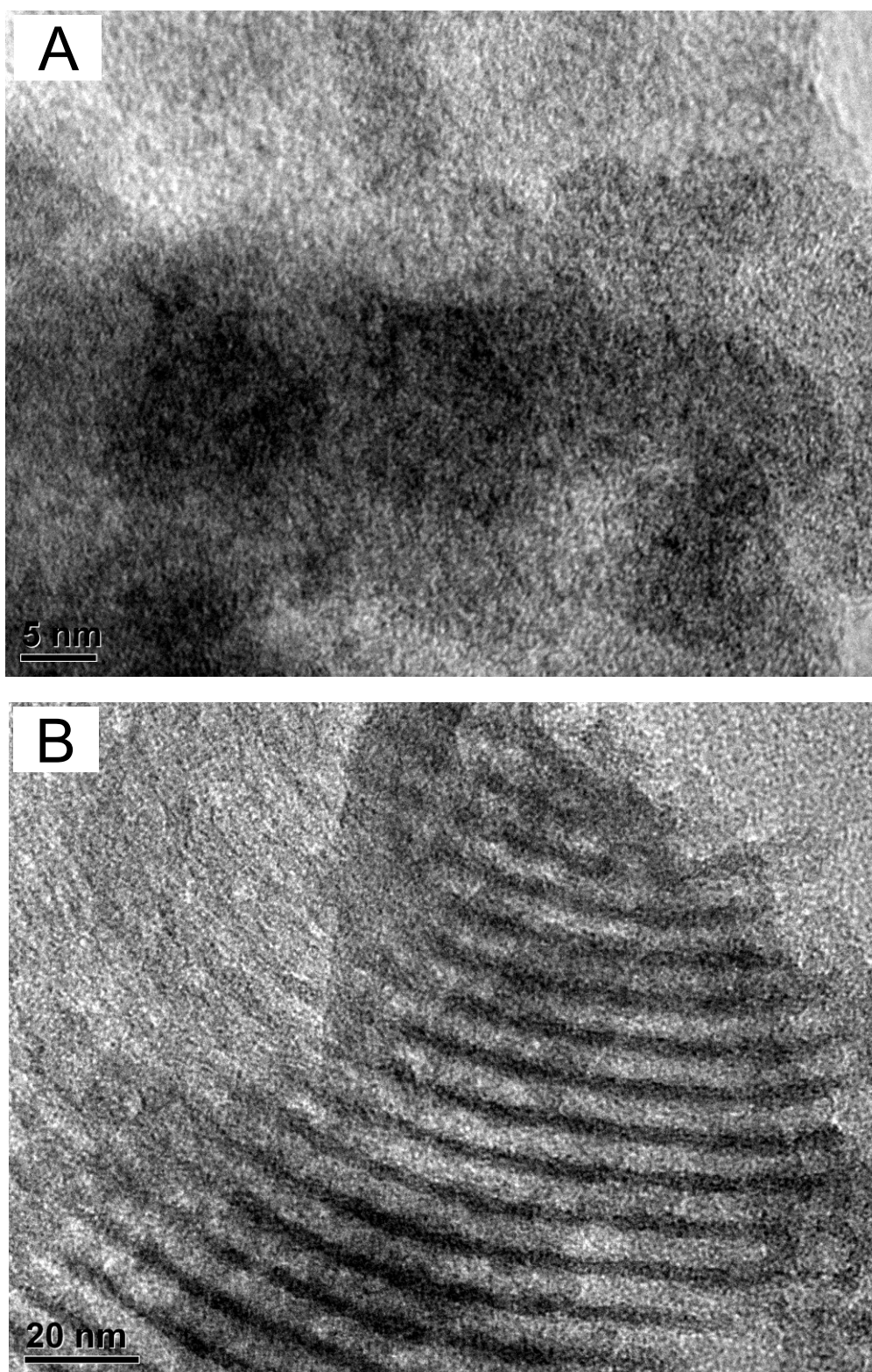


Fig. S5: TEM images of the as-synthesized materials. (A) Pt@ZSM-5 and (B) Pt@ZSBA without calcined.

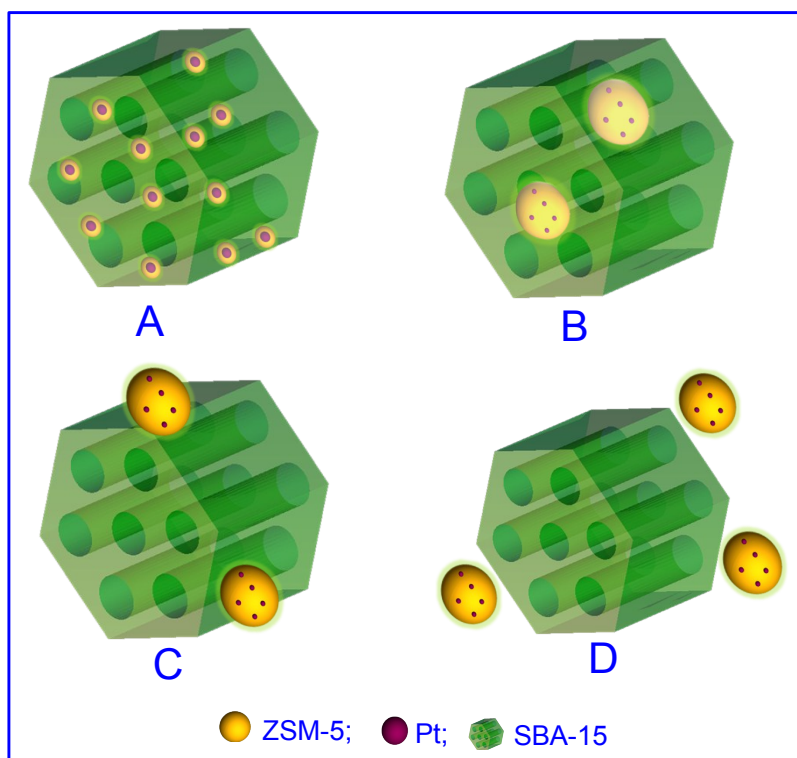


Fig. S6: Possible structures of the as-synthesized Pt@ZSBA. (A) Pt@ZSM-5 seeds embed in the pore walls of SBA-15, (B) sub-nanosized Pt particles are encapsulated in the large ZSM-5 zeolite, and the large Pt@ZSM-5 particles are wrapped by mesoporous SBA-15, (C) Pt@ZSM-5 particles adhere to the surface of SBA-15, (D) the mechanical mixture of Pt@ZSM-5 and SBA-15.

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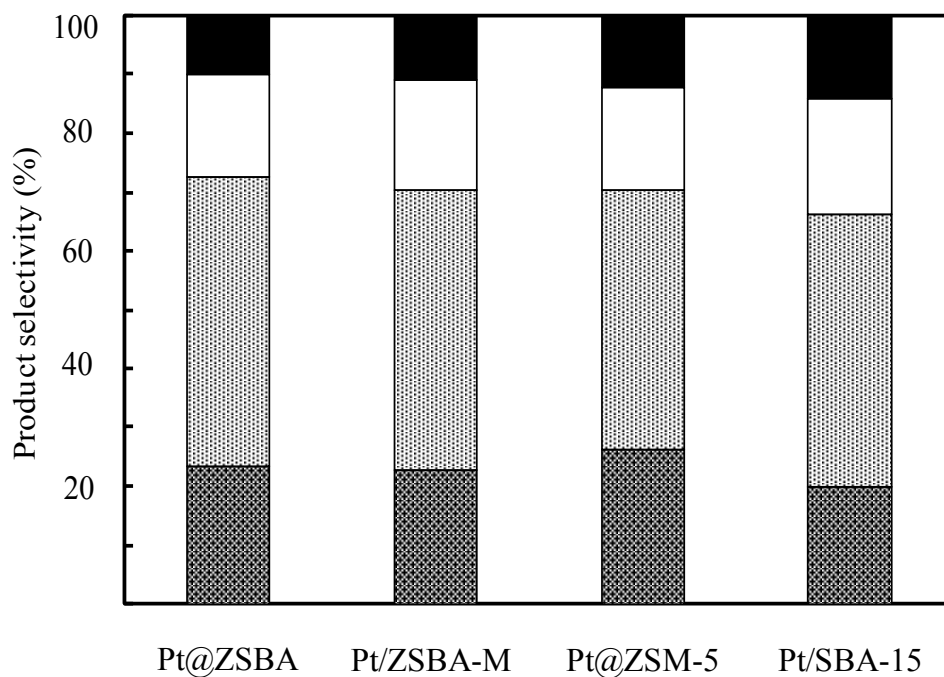


Fig. S7: The product selectivity over the corresponding catalysts at the total BD conversion of 50% by changing the reaction temperature, (■) n-butane, (▨) 1-butene, (□) trans-2-butene, (■) cis-2-butene.

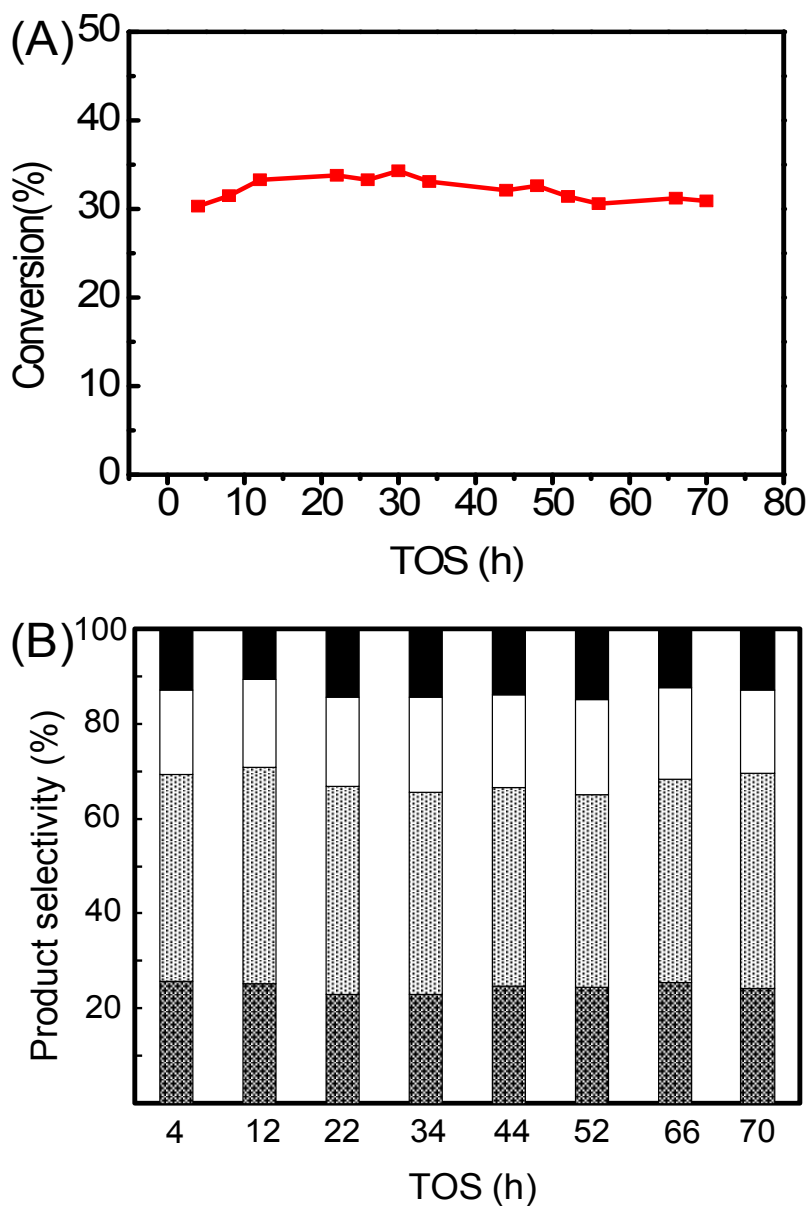


Fig. S8: (A) BD conversion with time on stream over Pt@ZSBA at 25 °C; (B) the product selectivity over Pt@ZSBA with time on stream, (▨) n-butane, (▩) 1-butene, (□) trans-2-butene, (■) cis-2-butene.

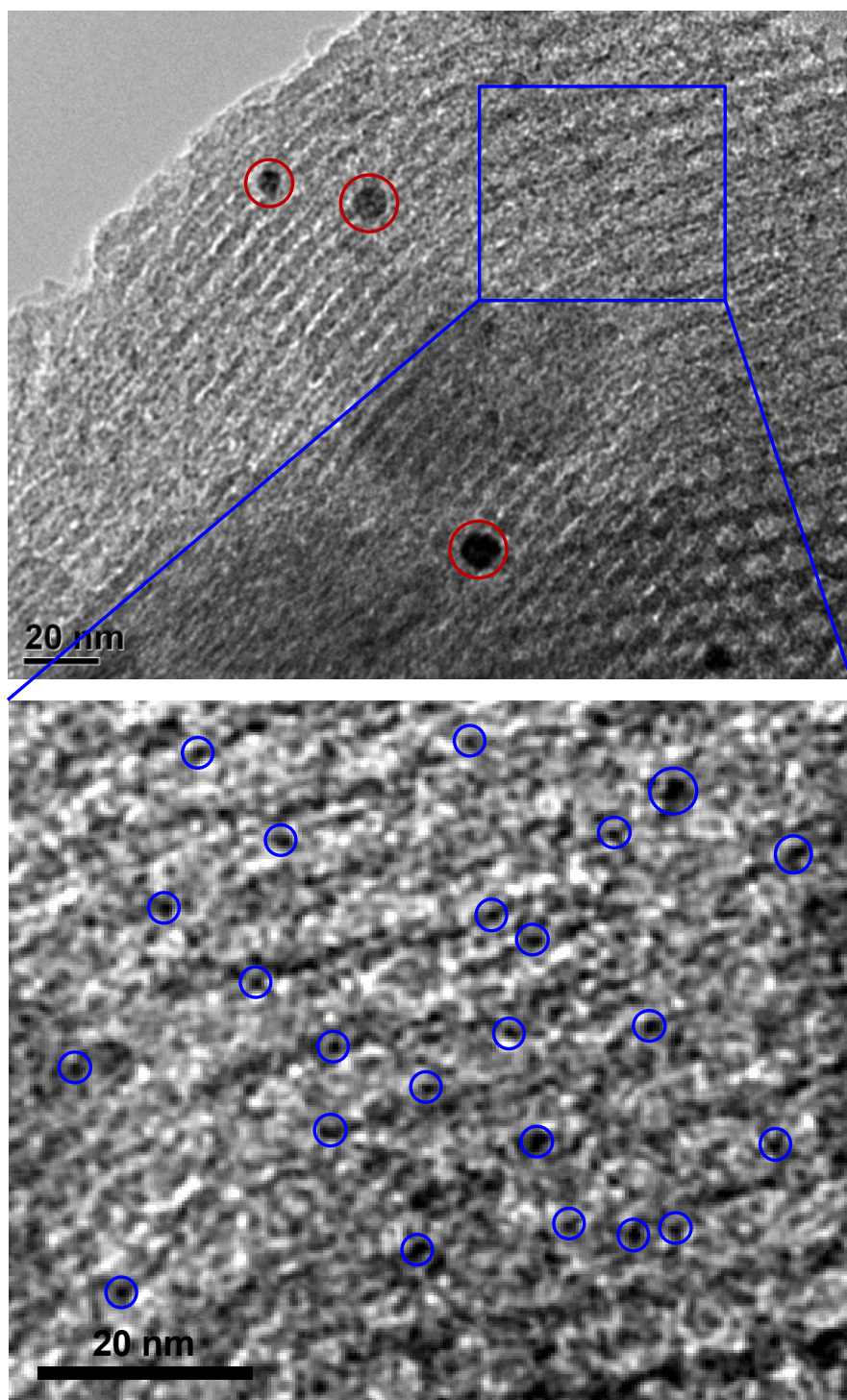


Fig. S9: TEM images of the as-synthesized Pt@ZSBA

TEM images show that more than 98% Pt nanoparticles (denoted with the blue circle) are very small size with diameter of ca. 0.8 nm, and very small fraction of Pt nanoparticles (denoted with the red circle) are big size up to 4.9 nm.