Electronic Supplementary Material (ESI) for Molecular Systems Design & Engineering.
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Supporting information of

Direct Detection as a probe of Platinum Nanoparticles Encapsulated in MFI Zeolite Nanocrystallite Aggregates

1 The progress for Pt@ZSM-5 and the Characterization

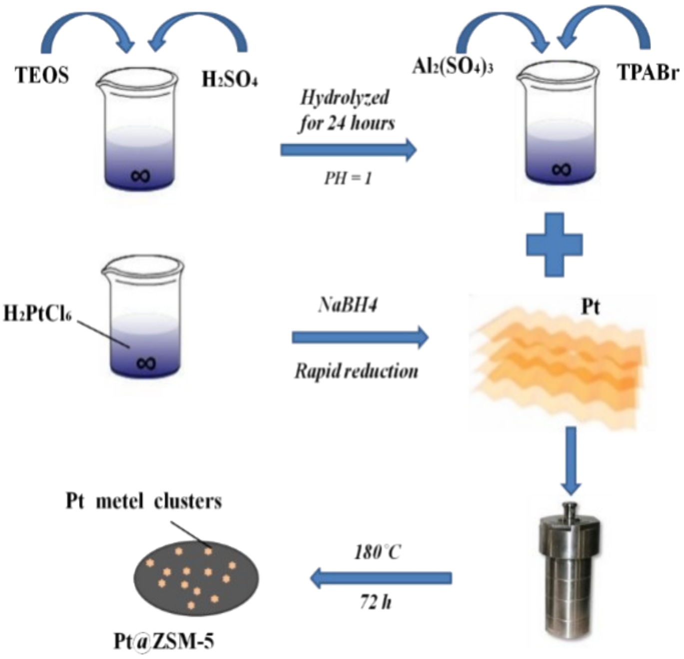

Fig. S1 Illustration of the formation process of Pt@ZSM-5

The crystal phase was determined by Bruker D8 CEVANCE using Cu-Kα radiation. The data were collected from in a 2θ range of 5 to 40° with a scanning speed of 5°/min.

SEM (Scanning electronic microscopy, including mapping) images were taken with Hitachi FESEM-4800. Transmission electron microscopy (TEM) images were obtained at room temperature on a Tecnai G2 F20 field-emission transmitting electron microscope (Philips) operating at 30 kV.

The instrument used in this article is a NU type X-ray fluorescence(XRF) spectrometer produced by Amptek Company. Before testing, grind the catalyst thoroughly in an agate mortar and place it in an oven for overnight drying treatment. After allowing to cool down to room temperature, the molten liquid solidified into a disc of 5 mm in thickness. This transparent disc is used for the XRF measurement.

The N_2 adsorption–desorption isotherms and BET surface areas were measured using a Micrometrics ASAP2020 analyzer at a liquid N_2 temperature of 77 K. Prior to the experiments, the samples were pre-treated at 573 K in a vacuum of 0.01 kPa for 2 h. Thermogravimetric (TG) analysis was carried out with a NETZSCH 449 F3 instrument in dry air at a heating rate of 10 K min^{-1} from 303 to 873 K.

Temperature-programmed desorption of ammonia (NH_3-TPD) were conducted using a Quantachrome Instruments to measure the distribution of acidic sites in catalysts. Firstly, the sample (0.2 g) pre-treatment at 823 K for 30 min was placed in a U-shaped tube reactor with He. Subsequently, the sample adsorbed 10 vol % NH_3/He at 323 K with saturation, then using He to eliminate the physisorbed ammonia. Finally, the NH_3-TPD analysis was carried out by heating the sample from 323 K at a heating rate of 10 K·min^{-1}. The evolved ammonia was analyzed by a TCD. TCD data were monitored by a computer equipped with the software Quanta Chrome Chem.

The degree of metal dispersion in different samples was analyzed using H_2 pulse and CO pulse chemical adsorption experiments. The H_2 pulse adsorption was measured by America Conta Corporation instrument. the 0.2g sample was first reduced in flowing pure hydrogen gas (10 ml/min) at 500 ° C for 2 h, then purged in N_2 atmosphere at 540 ° C for 2 h and cooled to room temperature. Pulses of 0.69 ml H_2 with a mass fraction of 5% were performed in the N_2 mixture for 3 minutes at intervals until the chromatography-peak area remained stable. Calculated by assuming H:Pt =1:1, the metal dispersion using hydrogen pulse chemical adsorption is listed in Table S1. The CO pulse adsorption was measured by America Micromeritics AutoChem II 2920 instrument. The sample was heated to 200°C in a He flow and held at this temperature for 0.5 h. Then He was switched to H_2 flow and the sample was heated to 570°C under H_2 flow and kept for 0.5 h. Then reactor was cooled to 200°C under H_2 flow, flushed by He flow for 30 min, and cooled to measurement temperature in the He flow. CO pulses were injected at that temperature until the adsorption reached saturation. Calculated by assuming a CO to surface metal atom ratio of 1:1, the metal dispersion is listed in Table S1.

The data of inductively coupled plasma optical emission spectroscopy (ICP-OES) were analyzed on a Perkin-Elmer Optima 2000 spectrometer. The method is as follows: 0.1 g zeolite sample is added into the mixture of 2 g HF solution and 2 g aqua regia. After evaporation of acid, the mixture was diluted to 100ml for ICP analysis.

2 Preparation of DBT poisoned Pt-based catalysts

The Pt catalysts poisoned by DBT are prepared by simple impregnation of equal volumes. An appropriate amount of ethanol to fully stir the maceration solution ultrasound for 30 min, mixed well and put it into a 70 °C water bath to evaporate, dried in a 100 °C oven overnight, and finally calcined in a muffle furnace at 550 °C for 3 hours before cooling, and grind evenly with a mortar to obtain DBT poisoned Pt@ZSM-5 catalyst. Under the same conditions, a DBT poisoned Pt/ZSM-5 catalyst was prepared for comparison.

Scheme S1. The protection of ZSM-5 aggregates against DBT

3 Surface morphology and analysis of the catalysts

Fig.S2 (a) SEM and (b) TEM images of Pt/ZSM-5

Table S1. Physicochemical properties of the catalysts.

Catalyst	S_{BET}(m^2/g)	D (nm)	Si/Al_2	Pt dispersion [a] (%)	Pt dispersion [b] (%)
Pt@ZSM-5	340	3.8	38	39	26
Pt/ZSM-5	335	3.8	38	25	15
Pt/ZSM-5(p)	260	3.8	38	21	12.5

[a] Calculated from H_2 pulse adsorption experiment.

[b] Calculated from CO pulse adsorption experiment.

Table S2. Pt content of the catalyst samples detected by XRF with different incidence wavelength

Sample	0.9889 nm (Mg kα)/%	0.2291 nm (Cr kα) /%
Pt@ZSM-5	0.37	0.38
Pt/ZSM-5	0.38	0.38
Pt/ZSM-5(p)	0.39	0.38

Fig. S3 EDS elemental mapping images of Pt@ZSM-5: (a) Pt, Al and Si elements; (b)Al mapping image; (c) Si mapping image; (d) Pt mapping image;

Fig. S4 (a) SEM image of Pt@ZSM-5 and the red frame were characterized by EDS spectra; (b-d) EDS spectra corresponding to three selected areas of Pt@ZSM-5.

To investigate the distribution of various elements, EDS element mapping were carried out on selected Pt@ZSM-5 catalyst. It could be viewed from the elemental mapping images (Fig. S4(a-d)) that Al, Pt and Si elements were homogeneously dispersed according to the regular shape of the catalyst. In addition, Figure. S4(a) shows the SEM image of Pt@ZSM-5 and the red frame were characterized by EDS, of which results are listed in Figure. S4(b-d). It was clear that the signal intensity for both Si and O elements in all line scanning positions were significantly strong, but there was almost no the signal of Pt element, implying that the outermost layer was composed of Si and

O elements, and the most amounts of Pt element was distributed in the inner of ZSM-5.

Fig. S5 NH_3-TPD profiles of the Pt catalysts (a)Pt/ZSM-5(p), (b) Pt/ZSM-5, (c)Pt@ZSM-5

Table S3. Total acidity of the Pt catalysts

Catalyst	Acid Amount			
	Weak	Moderate	Strong	Total
Pt@ZSM-5	4.8	36.6	59.3	100
Pt/ZSM-5	4.7	35.5	59	99
Pt/ZSM-5(p)	6.1	36.8	59.3	102.2

4 Effect of sulfur poisoning for the catalytic dehydrogenation performance over Pt catalysts

The two poisoned catalysts were evaluated on a propane dehydrogenation fixed-bed reactor in the laboratory. Catalyst dosage: 0.5 g, reaction temperature: 550 °C, propane mass airspeed: 3 h^{-1}, particle size: 40~60 mesh, reaction pressure: 0.03 MPa, reaction time: 1 hour. The sample was quantitatively analyzed by gas chromatography, and the conversion rate of propane and the selectivity of propylene were calculated according to the principle of conservation of carbon atoms, and the conversion rate of propane and the selectivity of propylene were shown in Fig. S6.

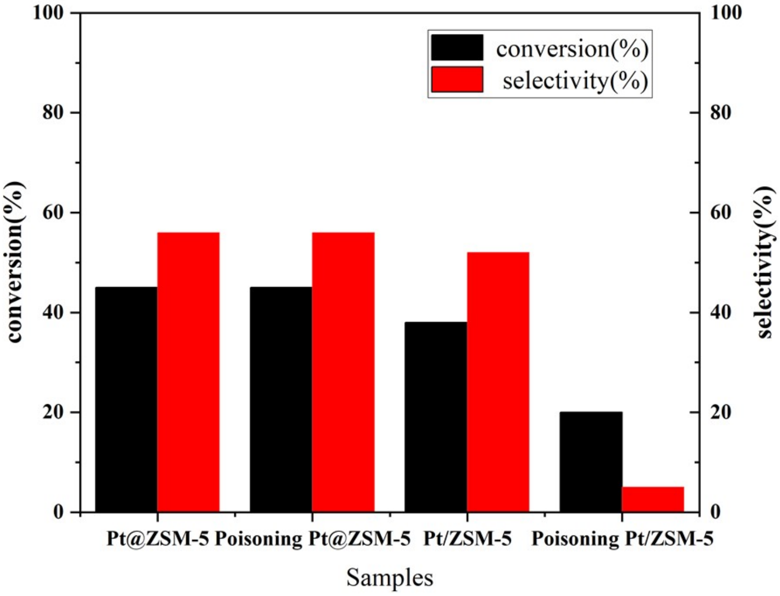

Fig. S6 Effect of DBT poisoning over Pt catalysts for propane dehydrogenation to propylene. Experiment conditions: temperature of 550 °C, WHSV=3 h^{-1}, catalyst dosage= 0.5 g, H_2/C3=1, time on stream=1 h

5 Effect of coking for the catalytic dehydrogenation performance over Pt catalysts

In order to study the carbon deposition of three Pt based catalysts after the reaction, thermogravimetric tests were conducted on the three catalysts. In the third stage, the mass loss of Pt/ZSM-5 (p), Pt/ZSM-5, and Pt@ZSM-5 was 0.9%, 1.2% and 0.5%, respectively. The total mass loss in the three stages was 7.9%, 5.8%, and 4.3%, respectively. The mass loss of encapsulated catalysts was significantly smaller than that of catalysts prepared by simple impregnation.

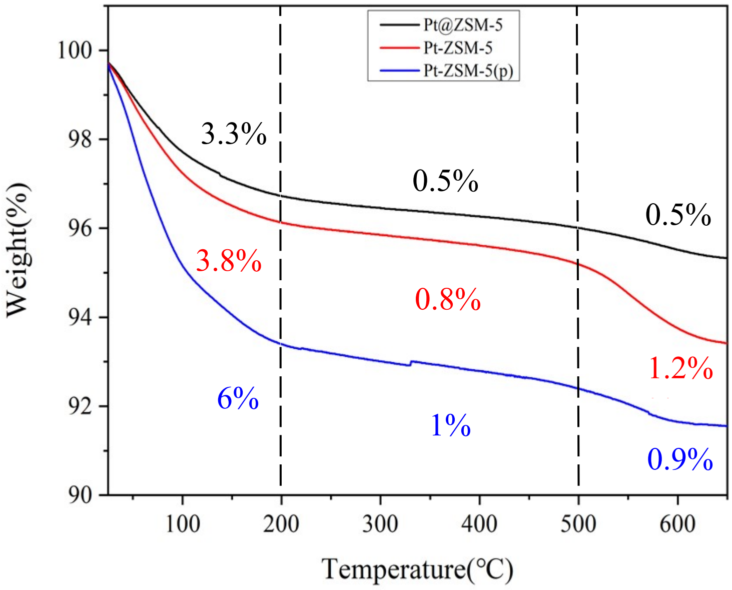

Fig. S7 TGA curves of the Pt catalysts.

6 The catalytic performance in long time over Pt catalysts for PDH

In order to study the anti-carbon deposition ability of three catalysts, air was added to the reaction system during the regeneration process to burn off the carbon deposition, and the burning temperature was recorded to measure the amount of carbon deposition. The carbon burning temperature of catalyst is shown in the figure. The bar chart from left to right is Pt/ZSM-5 (p), Pt/ZSM-5, Pt@ZSM-5.

From Figure. S8, it can be seen that the catalyst prepared by the simple impregnation method has a maximum carbonization temperature of 900 °C, indicating that a significant amount of carbon deposition was generated during the propane dehydrogenation reaction. The carbon burning temperature of encapsulated catalyst is always low and stable at about 700 °C, which is because the metal platinum encapsulation is limited to the inside of the skeleton, which plays a good role in protecting the metal active site, making it have more excellent carbon deposition resistance.

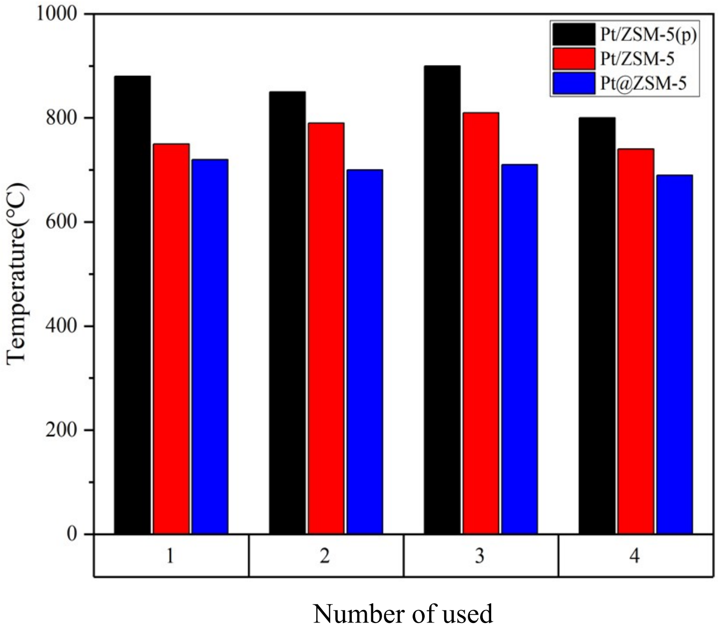

Fig. S8 Coke burning temperature of various catalysts

In order to study the stability of the catalyst Pt@ZSM-5, the catalyst with the best loading amount and reaction conditions was selected for catalytic performance evaluation. The catalyst dosage was 0.5 g, reaction temperature was 550 °C, propane mass space velocity was 3h^{-1}, particle size was 40-60 mesh, reaction pressure was 0.03 MPa, and reaction time was 600 minutes.

Fig. S9 Catalytic performance of Pt@ZSM-5 catalyst

Within 600 minutes of the reaction, the conversion rate of propane was maintained at 45%, and the selectivity of propylene was maintained at 60%. When the reaction continued for about 400 minutes, the conversion rate of propane slightly decreased. When the reaction reached 600 minutes, the conversion rate of propane decreased to 35%, and the selectivity decreased to 56%. This also indicates that carbon deposition covers the active center, which leads to a decrease in catalyst activity and a decrease in the generated by-products, resulting in a stable state of propylene selectivity.