

## **Electronic Supplementary Information (ESI)**

### **Simultaneous realization of high catalytic activity and stability for catalytic cracking of n-heptane on highly exposed (010) crystal planes of nanosheet ZSM-5 zeolite**

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## 1. Catalyst preparation

The nanosheet ZSM-5 zeolite was prepared according to the literature<sup>1</sup> except for static condition during hydrothermal crystallization of 13 days. Subsequently, all the samples were converted to the H<sup>+</sup> form through three times ion-exchanged in 1 M NH<sub>4</sub>NO<sub>3</sub> solution (80 °C, 4 h, weight ratio of zeolite to NH<sub>4</sub>NO<sub>3</sub> solution is 1:20) and calcination at 550 °C for 4h. Prior to catalytic evaluation, powder was pressed, crushed, and sorted into grains of 40-60 mesh. The conventional ZSM-5 zeolite was purchased from Nankai catalyst factory. Synthesis of nanosheet ZSM-5 zeolite was prepared according to the previously reported procedures.

## 2. Catalyst characterization

Powder X-ray diffraction (XRD) patterns were collected by a Bruker D8 Advance diffractometer, using Cu K $\alpha$  ( $\lambda=0.15406$  nm ) radiation with a Nickel filter operating at 40KV and 100 mA at a scanning rate of 2°/min from 5° to 50°.

The scanning electron microscopy (SEM) images of the samples were observed on an FEI Quanta 200F instruments using accelerating voltages of 5 KV. The samples were dusted on an adhesive conductive carbon belt attached to a copper disk and were coated with Au prior to measurement.

Transmission electron microscopy (TEM) was performed on a JEOL JEM-2100 equipped with a field emission source at an acceleration voltage of 200 kV. The powder samples were dispersed in ethanol by ultrasonication and then several drops of the suspended were planed on an ultrathin carbon films.

Nitrogen adsorption–desorption isotherms were measured on a Micromeritics TriStar II 3020 volumetric adsorption analyzer at 77 K. Prior to the adsorption measurement, all samples were degassed at 363 K under vacuum for 1 h then heating up to 623 K outgas for 4 h under  $1 \times 10^{-4}$  Pa. The specific surface area was calculated from the adsorption data obtained at P/P<sub>0</sub> between 0.05 and 0.20 using Brunauer–

Emmett–Teller (BET) equation. The total pore volume was derived from the nitrogen amount adsorbed at a relative pressure of 0.95. The external surface area and micropore volume was evaluated by t-plot method. The pore size distribution and mesopore volume was evaluated by Barrett-Joyner-Halenda (BJH) method following the adsorption branch of the isotherm.

The Si/Al molar ratios of all samples were confirmed by inductively coupled plasma optical emission spectroscopy (ICP-OES) using an Optima 7300V instrument (Perkin-Elmer).

<sup>27</sup>Al solid-state MAS NMR spectra were recorded on a Bruker AVANCE III 400 NMR spectrometer under one pulse condition. <sup>27</sup>Al MAS NMR spectra were recorded with a frequency of 104.1 MHz, a spinning rate of 12.0 kHz, and a recycling delay of 1 s. Hydrated Al(NO<sub>3</sub>)<sub>3</sub> powder was used as an external reference. The spectra are dominated by a signal at 54 ppm corresponding to tetrahedrally coordinated framework Al. A weaker band at 0 ppm relates to octahedral coordination extraframework Al. The tetrahedral and octahedral Al content in the catalysts was estimated from spectral deconvolution and peak areas.

Temperature-programmed desorption of ammonia (NH<sub>3</sub>-TPD) was carried out to detect the acidity of the samples. Prior to the measurements, about 100 mg of sample was outgassed at 873 K for 1 h. After cooling to 373 K, the sample was saturated in NH<sub>3</sub> stream for 30 min, followed by purging with nitrogen for 1 h to remove co-adsorbed NH<sub>3</sub>. The remaining strongly adsorbed NH<sub>3</sub> was then desorbed by heating the sample to 873 K at a constant rate of 10 K min<sup>-1</sup>, and the amount of desorbed NH<sub>3</sub> was monitored by thermal conductivity detector (TCD) simultaneously.

The concentrations of Lewis (c<sub>L</sub>) and Brønsted (c<sub>B</sub>) acidities were determined by Pyridine adsorption IR measurements (Py-IR). Prior to measurement, a sample was pressed into a pressed in ca 10 mg/cm<sup>2</sup> self-supporting wafers in the absence of any binder and evacuated in an in situ IR cell at 723 K for 2 h up to 10<sup>-2</sup> Pa. After the

sample was cooled to room temperature, the wafer was saturated with pyridine vapor (equilibrium vapor at 273 K) for 30 min, followed by outgas at 473 K or 623 K for 30 min. The IR spectrum was recorded after cooling to room temperature. The  $c_L$  and  $c_B$  were evaluated from the integral intensities of bands at  $1454\text{ cm}^{-1}$  ( $c_L$ ) (2.22  $\text{cm}/\mu\text{mol}$  as a molar extinction coefficient) and  $1545\text{ cm}^{-1}$  ( $c_B$ ) (1.67  $\text{cm}/\mu\text{mol}$  as a molar extinction coefficient).<sup>2</sup>

To determine the external acid sites in the nanosheet ZSM-5 zeolites, a relatively large probe molecule 2,6-di-methylpyridine (DMPy) was used.<sup>3</sup> The adsorption of DMPy took place at 423 K for 15 min at an equilibrium vapor pressure of the probe molecule. Desorption proceeded at the same temperature for 1 h followed by collection of spectra at room temperature.

### **3. Catalytic tests and carbon deposition analyses**

#### **3.1. Catalytic tests**

Catalytic cracking of n-heptane (purchased from Sinopharm Chemical Reagent Co, purity 99%, without any further purification), which is a typical acid-catalyzed reaction, was carried out in a fixed bed stainless steel continuous-flow reactor (10 mm i.d.), with a thermocouple in the center of the catalyst bed to measure the reaction temperature. In a typical run, the reaction was carried out under atmospheric pressure using  $\text{N}_2$  as a carrier gas. The catalyst loading and flow rate of  $\text{N}_2$  carrier were 0.75 g and  $400\text{ ml min}^{-1}$ , respectively. The feedstock was injected into the vaporization zone of reactor by using a syringe pump (KDS Scientific), the weight hourly space velocity of the n-heptane was kept at  $1.82\text{ h}^{-1}$ . The output reaction products were analyzed online by a gas chromatograph (SP-2100) equipped with an Agilent GC- $\text{Al}_2\text{O}_3$  capillary column ( $30\text{ m} \times 0.53\text{ mm}$ ) and a hydrogen flame ionization detector.

#### **3.2. Carbon deposition analyses**

The coke-deposited sample was obtained after the n-heptane cracking reaction at 873 K for time on stream (TOS) of 100 h. Subsequently, the reactor was purged with

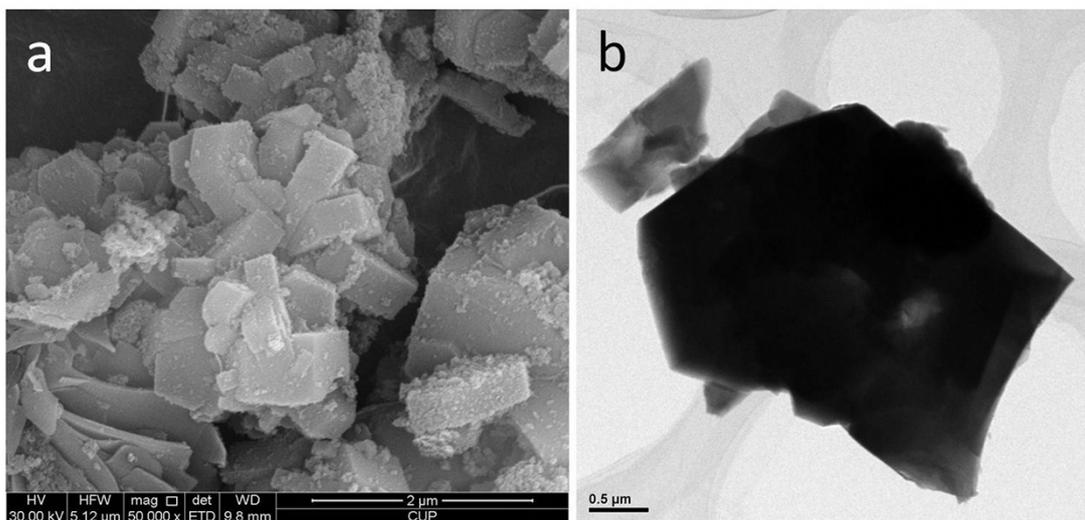
a high-purity N<sub>2</sub> gas flow (400 mL min<sup>-1</sup>) for 2 h at 873 K to remove organic volatiles. The amount, location and type of coke species deposited in the zeolite samples which were used in the n-heptane cracking reaction as catalysts are investigated in both quantitative and qualitative methods.

For the quantitative analysis, thermogravimetric analysis (TGA) was conducted on TGA/DSC 1 STAR system of Mettler Toledo. In a typical TGA measurement, the temperature was increased from ambient temperature to 1073 K at a constant ramping rate of 10 K min<sup>-1</sup> under flowing oxygen (50 mL min<sup>-1</sup>). The sample weight loss between 473 and 950 K was taken as the total coke content.

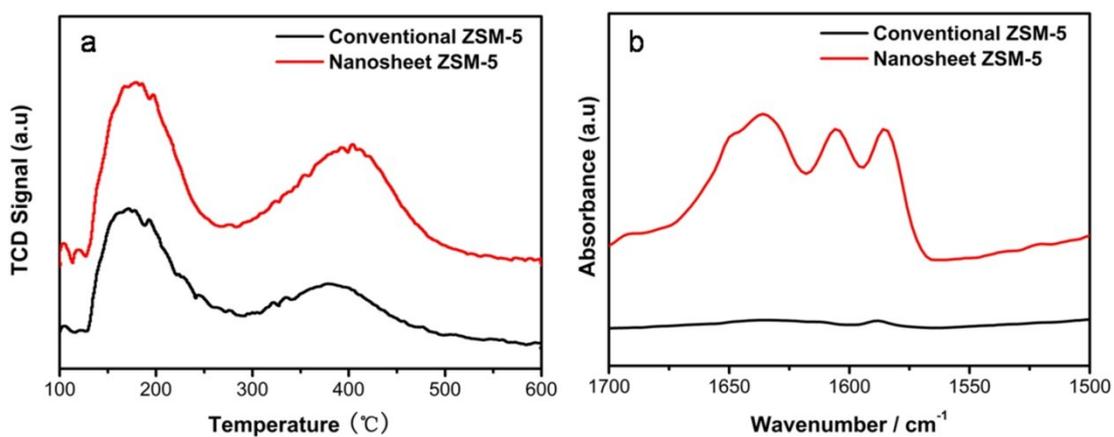
The location of coke deposited on the catalysts was determined by N<sub>2</sub> adsorption isotherm. Adsorption was measured at 77 K using the procedure described above. The amount of internal coke in the zeolite micropores was calculated from the decrease in the micropore volume of the spent catalysts, as compared with the pristine sample. The amount of external coke (coke deposition on the external surface or mesopores) was calculated by subtracting the internal coke content from the total coke content. The calculated methods of internal coke content were based on the assumption that the remaining micropore volume in the spent catalysts is fully accessible to N<sub>2</sub> molecules through the three dimensionally interconnected zeolite channels. The internal coke content was calculated with the assumption that the coke density was 1.22 g cm<sup>-3</sup>. The coke analysis method was reported by Ryoo et al.<sup>4</sup>

For the qualitative analysis of the coke species in the zeolites, the Raman spectra of spent catalysts were performed on an in Via Raman microscope (Renishaw) using an excitation source of 532 nm, and subtracting the fluorescence caused by coke. The laser spot size was approximately 1–2 mm with a power of 10 mW.

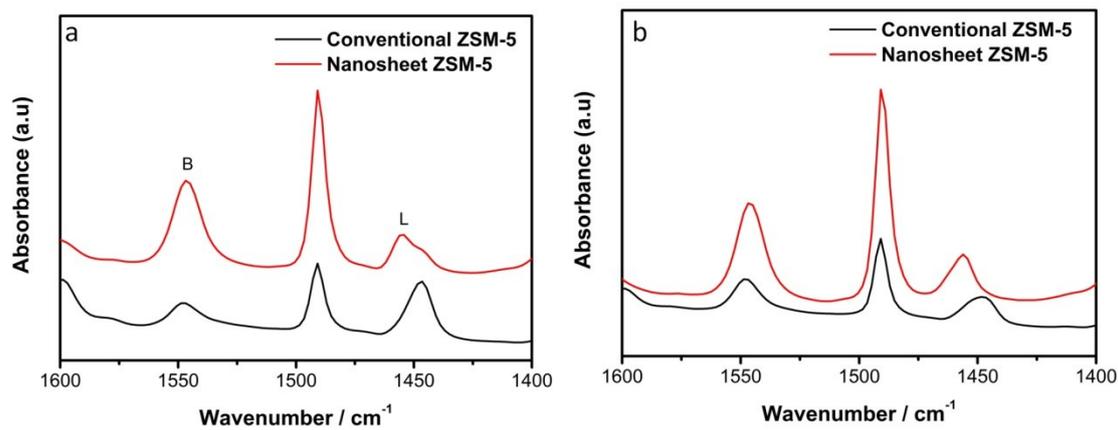
#### **4. Supplementary Figures and Tables**



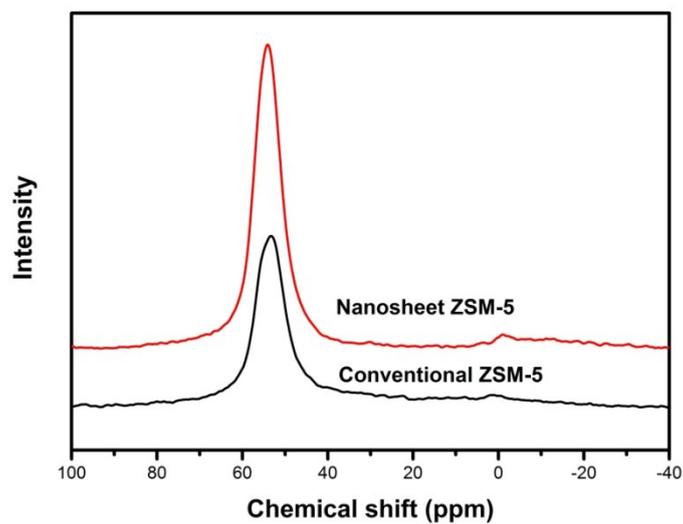
**Figure S1.** The SEM (a) and TEM (b) image of conventional ZSM-5 zeolite catalyst



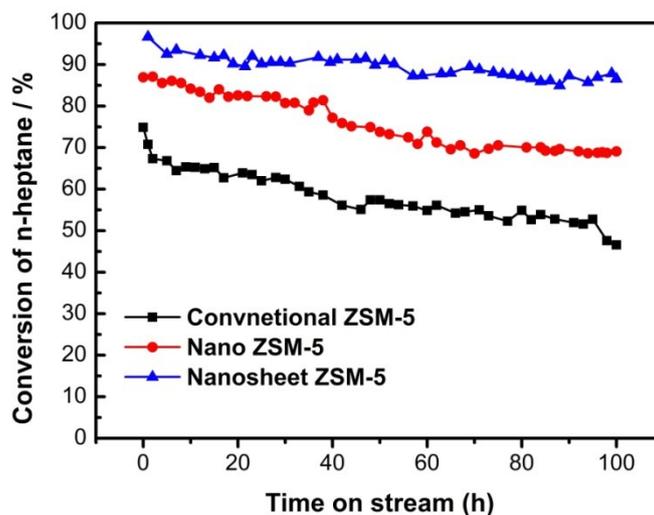
**Figure S2.** NH<sub>3</sub>-TPD profiles of the protonic form ZSM-5 zeolite catalyst (a) and FTIR spectra of ZSM-5 zeolites after adsorption of 2,6-dimethylpyridine (b).



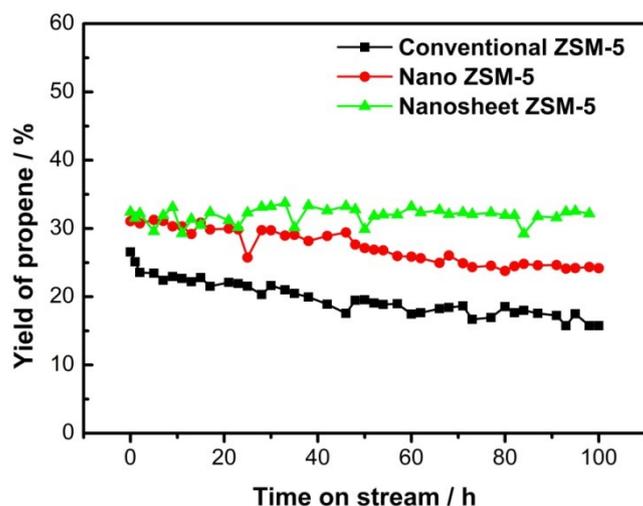
**Figure S3.** The FTIR spectra of ZSM-5 zeolite catalysts after degassing of pyridine at 473K (a) and 623K (b)



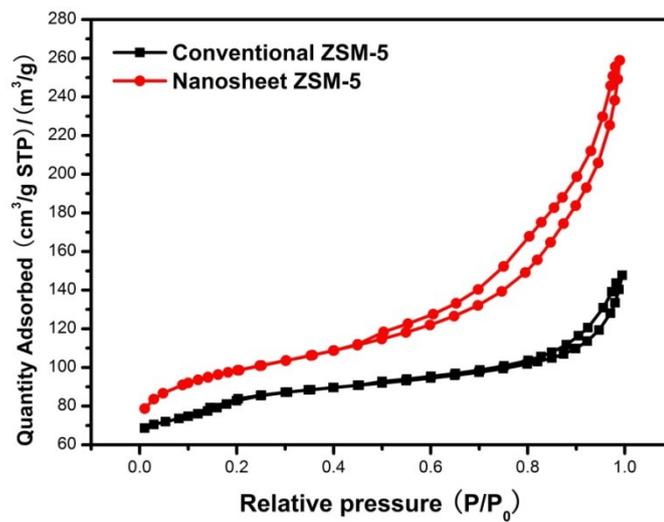
**Figure S4.** <sup>27</sup>Al MAS NMR spectra of the conventional and nanosheet ZSM-5 zeolite



**Figure S5.** The conversion of n-heptane on ZSM-5 catalysts plotted as a function of time on stream ( reaction conditions: WHSV = 1.82 h<sup>-1</sup>, reaction temperature at 873K, catalyst loading 0.75 g, and atmospheric pressure operation)



**Figure S6.** The yield of propene on ZSM-5 catalysts plotted as a function of time on stream ( reaction conditions: WHSV = 1.82 h<sup>-1</sup>, reaction temperature at 873K, catalyst loading 0.75 g, and atmospheric pressure operation)



**Figure S7.** Nitrogen adsorption-desorption isotherms of the coke deposited conventional and nanosheet ZSM-5 zeolite catalysts.

Table S1. Chemical composition and textural properties of ZSM-5 catalysts.

Sample	Si/Al <sup>a</sup>	Al <sub>EFAl</sub> /Al <sub>Total</sub> <sup>b</sup> (%)	S <sub>BET</sub> <sup>c</sup> (m <sup>2</sup> /g)	S <sub>ext</sub> <sup>d</sup> (m <sup>2</sup> /g)	V <sub>tol</sub> <sup>e</sup> (cm <sup>3</sup> /g)	V <sub>micro</sub> <sup>f</sup> (cm <sup>3</sup> /g)	Pore size <sup>g</sup> (nm)
Conventional ZSM-5	49	13.0	307	57	0.2	0.096	-
Nanosheet ZSM-5	54	8.3	515	260	0.4	0.091	4.5

<sup>a</sup> Si/Al molar ratio was obtained from ICP-OES analysis; <sup>b</sup> Al<sub>EFAl</sub>/Al<sub>Total</sub> is estimated from spectral deconvolution and peak areas; <sup>c</sup> S<sub>BET</sub> is the BET surface area obtained from N<sub>2</sub> adsorption in relative pressure range (P/P<sub>0</sub>) of 0.05-0.20; <sup>d</sup> S<sub>ext</sub> is the external surface area determined according to the t-plot method; <sup>e</sup> V<sub>tol</sub> is the total pore volume obtained at P/P<sub>0</sub>=0.95. <sup>f</sup> V<sub>micro</sub> is the micropore volume obtained evaluated from the t-plot method. <sup>g</sup> Average diameter distribution has calculated using the adsorption branch of BJH.

**Table S2.** Representative parameters of the Raman bands, corresponding to the coke deposited on the catalysts

Catalyst	Gp (cm <sup>-1</sup> )	D/G	La (nm)
Conventional ZSM-5	1591.3	1.45	1.62
Nanosheet ZSM-5	1598.6	2.11	1.96

There exists a potential correlation between D/G and the in-plane correlation length La (in nm), which also quantifies the coke particle size

$$D/G = 0.55 La^2 \quad (\text{Equation 1})$$

## References

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- [2] C. A. Emeis, *J. Catal.* 1993, **141**, 347–354.
- [3] K. Gora-Marek, K. Tarach and M. Choi, *J. Phys. Chem. C*. 2014, **118**, 12266–12274.
- [4] V. N. Shetti, J. Kim, R. Srivastava, M. Choi and R. Ryoo, *J. Catal.* 2008, **254**, 296–303.