

1 **Supplementary Material (ESI) for Journal of Materials Chemistry A**  
2 **This journal is (c) The Royal Society of Chemistry 2012**

3

4 **Supporting Information:**

5 **Direct synthesis of c-axis oriented ZSM-5 nanoneedles from acid-treated**  
6 **kaolin clay**

7

8 Kui Shen, Weizhong Qian, Ning Wang, Jingui Zhang, Fei Wei

9

## 10 **Experimental Section**

11

### 12 *1. Preparation of c-axis oriented ZSM-5 nanoneedles*

13 In a typical synthesis of c-axis oriented ZSM-5 nanoneedles sample (denoted as HZS-18; 18 was the Si/Al  
14 ratios), the precursor of Kaolin was firstly calcinated at 1073 K for 3 hrs and then treated with 3 M H<sub>2</sub>SO<sub>4</sub> (5 g  
15 H<sub>2</sub>SO<sub>4</sub>/1 g kaolin clay) for 2 hrs to get the suitable ratio of Si/Al for the ZSM-5 synthesis. Then 6 g acid-treated  
16 kaolin clay was mixed with 120 g deionized water, 0.6 g NaOH and 3 g ethylene diamine (EDA). The suspension  
17 was aged with stirring for 12-24 hr at room temperature. Then the mixture was transferred into the stainless-steel  
18 autoclave lined with polytetrafluoroethylene (PTFE) and was heated to 453 K for 3 days with continuous  
19 stirring. After cooling to room temperature, the products were filtrated and washed thoroughly with deionized  
20 water. Then the samples were dried at 383 K overnight and subsequently calcined in air at 823 K for 6 h to  
21 remove the template (EDA). Using 3 g acid-treated kaolin clay instead of 6 g as the alumina source and silica  
22 source, 100 nm i.d monodispersed ZSM-5 nanoneedles were also synthesized under the same conditions. For  
23 comparison, the conventional ZSM-5 zeolites with Si/Al ratio of 19, in H<sup>+</sup> ion-exchanged form, was purchased  
24 from Nankai university catalyst factory (designated as CZS-19; 19 is the Si/Al ratios).

### 25 *2. Preparations of Zn-modified ZSM-5*

26 The Zn-modified HZSM-5 with mass loading of Zn of 3% was prepared by traditional incipient wetness  
27 impregnation of HZS-18 using aqueous solutions of Zn (NO<sub>3</sub>)<sub>2</sub> · 6H<sub>2</sub>O. After drying overnight and calcinating in  
28 air at 823 K for 5 h, the resultant catalyst was designated as Zn/HZS-18. To compare catalytic performances,  
29 CZS-19 was also impregnated with the same Zn content and manner (designated as Zn/CZS-19).

### 30 *3. Characterization*

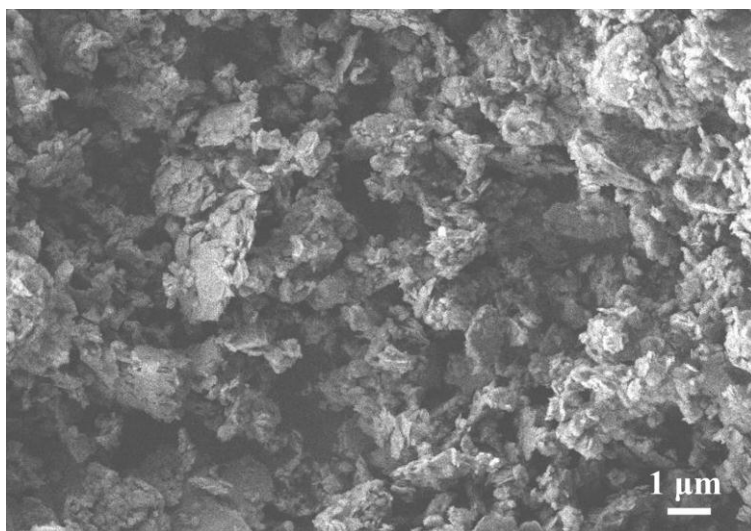
31 X-ray diffractions (XRD) were recorded on a Rigaku D/Max-RB diffractometer with Cu K $\alpha$  Radiation at 40

1 kV and 120 mA. Scanning electron microscope (SEM) images were obtained by a high-resolution scanning  
2 electron microscope (JEOL, JSM-7401) at 3.0 kV. Energy-dispersive X-ray (EDX) analysis was performed  
3 using a JSM-7401F apparatus at 15.0 kV with the analytical software INCA. TEM experiments were performed  
4 on a high-resolution transmission electron microscope (JEOL, JEM-2010, exited at 120kV) equipped with  
5 selected area electron diffraction (SAED). Brunauer–Emmett–Teller (BET) surface area were recorded in a  
6 Quantachrome automated surface area and porosity analyzer with N<sub>2</sub> as the adsorption gas. Thermogravimetric  
7 analysis (TGA) was carried out using a thermo gravimetric analyzer (TGA/DSC-1) from 30-900 °C at a heating  
8 rate of 10 °C min<sup>-1</sup> in air. NH<sub>3</sub>-TPD analysis was completed in a Quantachrome automated chemisorption  
9 analyzer from room temperature to 850°C with a ramp of 10°C/min. Brønsted acid sites and Lewis acid sites  
10 were determined by pyridine adsorption. The samples were first dried, in situ, by heating to 723 K under  
11 vacuum, and then were cooled to 323 K. At this temperature, the samples were exposed to pyridine vapour using  
12 an equilibration time of 30 min. After physically adsorbed pyridine molecules were removed by outgassing at  
13 423 K for 1 h, IR spectra were collected at 423 K with 4 cm<sup>-1</sup> resolution using a Nicolet FTIR spectrometer.

#### 14 *4. Catalytic Activity Testing*

15 The MTA reaction were performed at the conditions of 1 atm, 748 K and WHSV = 0.79 h<sup>-1</sup>(under N<sub>2</sub> flow  
16 (10 mL min<sup>-1</sup>) in a conventional fixed bed stainless steel reactor (13.0 mm i.d) equipped with a thermocouple in  
17 the middle of the catalyst bed. 1 g of catalyst was placed in the fixed bed reactor. The flow rate of pure methanol  
18 and N<sub>2</sub> were controlled using a dual micro-plunger pump and the mass flow controllers, respectively. The  
19 product (hydrocarbons) was analyzed using two flame ionization detector (FID). The conversion of methanol  
20 and the selectivity of different products were calculated (carbon base) accordingly.

21



1

2

Fig.S1 SEM image of the kaolin clay, showing that the Kaolin clay had a nano-sized laminated structure.

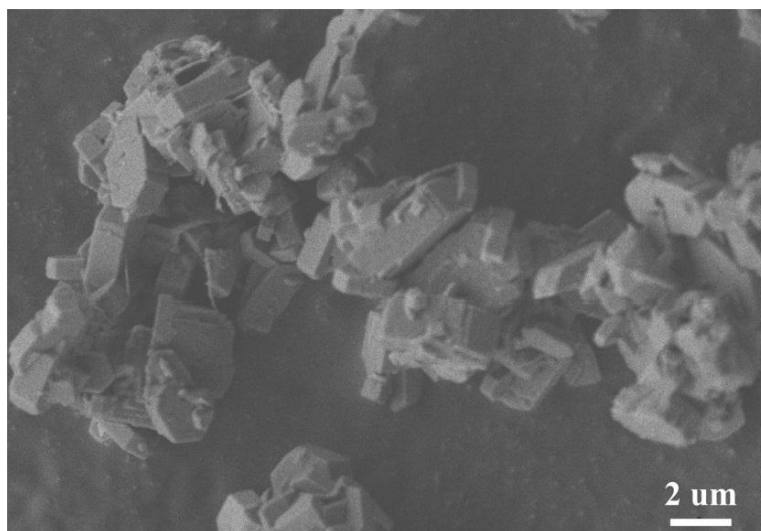
3

4

5

6

7



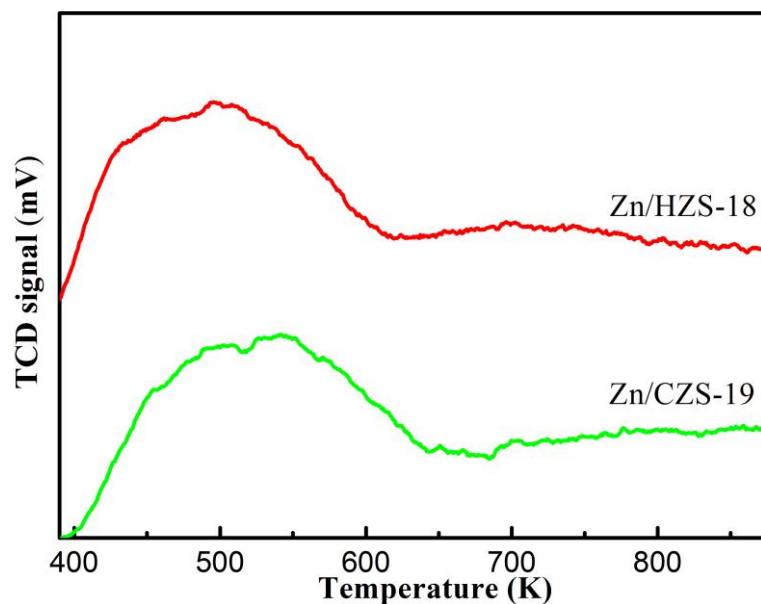
8

9

Fig.S2 SEM image of the CZS-19. The particle sizes of the coffin-shaped or inter grown CZS-19 was about 3μm.

10

11

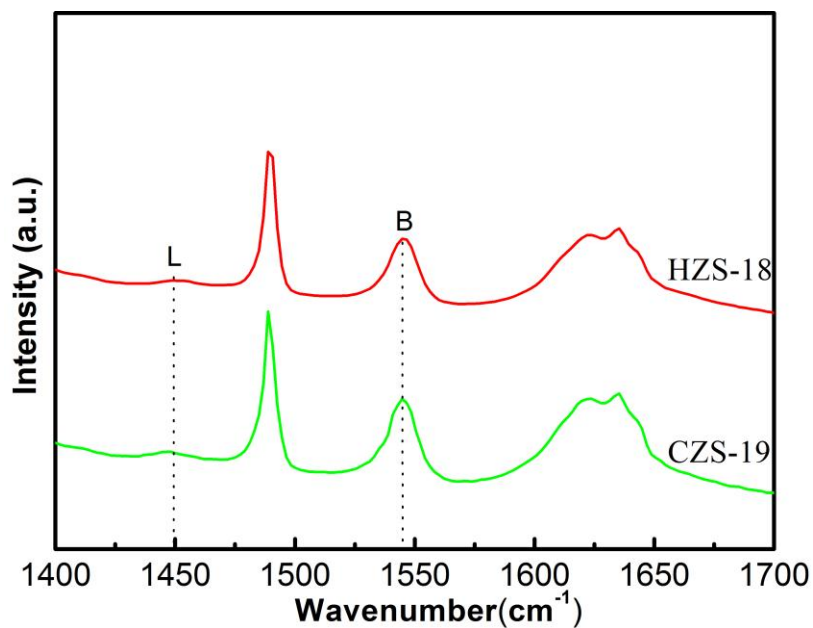


1

2 Fig. S3 NH<sub>3</sub>-TPD adsorption of Zn/HZS-18 and Zn/CZS-19. The low temperature desorption peak (400-650 K)  
3 indicates weak adsorption sites and the high temperature peak (650-800 K) was interpreted to be caused by ammonia  
4 desorption from strong Brønsted acid sites and strong Lewis acid sites.

5

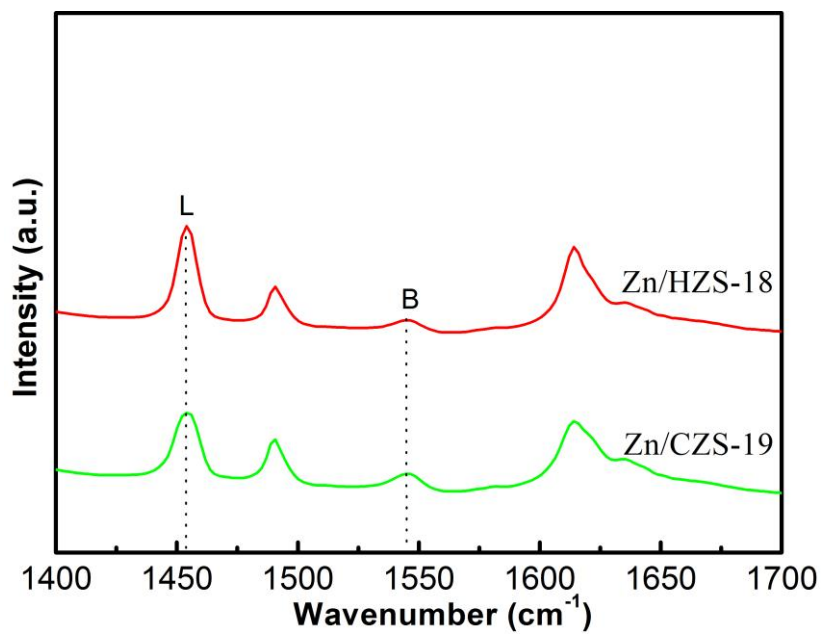
6



7

8 Fig. S4 FTIR spectra of HZS-18 and CZS-19 samples after desorption of pyridine at 423 K; B=Brønsted acid sites,  
9 L=Lewis acid sites.

10



1

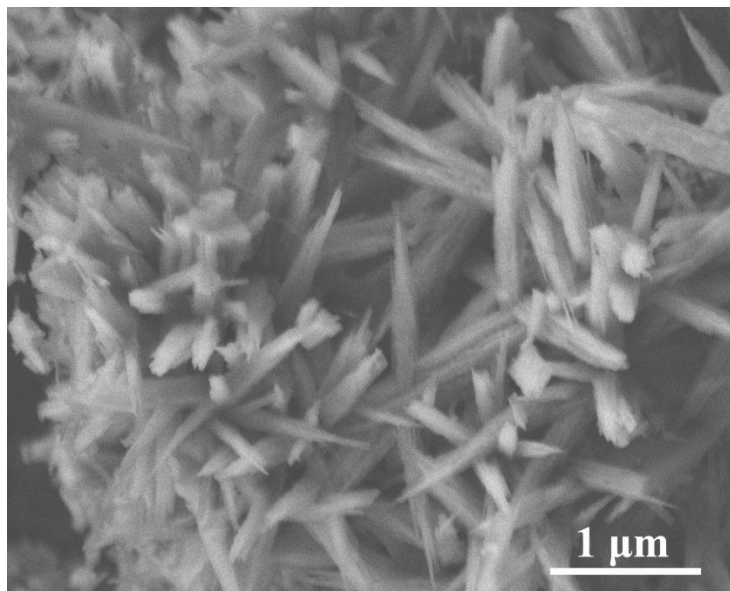
2 Fig. S5 FTIR spectra of Zn/HZS-18 and Zn/CZS-19 samples after desorption of pyridine at 423 K; B=Brønsted acid  
3 sites, L=Lewis acid sites.

3

4

5

6



7

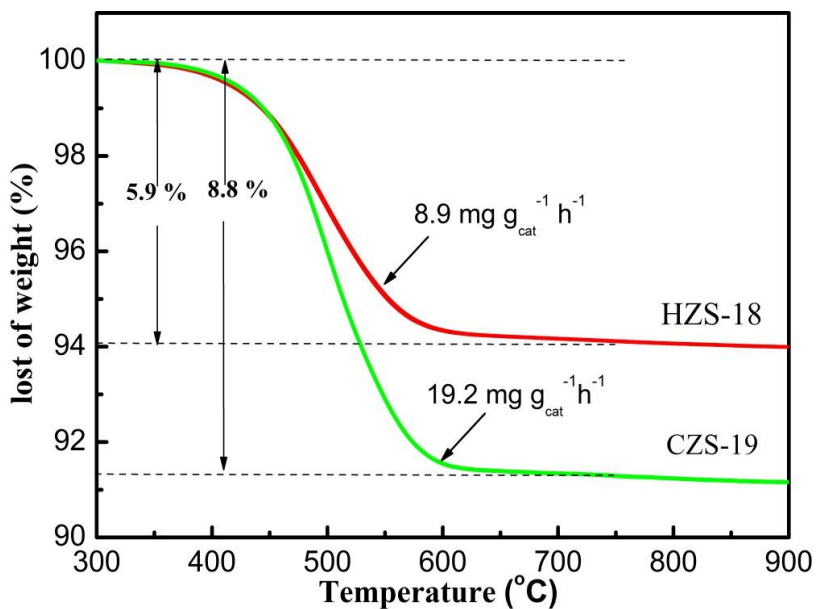
8

9 Fig.S6 SEM image of the needle-like ZSM-5 polycrystalline obtained by regulating synthetic conditions.  
10

11

12

1



2  
3

Fig. S7 TG curves of Zn/HZS-18 and Zn/CZS-19 after MTA reaction tested at 748 K ( $W_{cat} = 1\text{g}$ ;  $GHSV = 0.79\text{ h}^{-1}$ ).

4  
5  
6  
7  
8  
9  
10  
11  
12

**Table S1** Physical properties of the HZS-18 and the CZS-19 and product selectivities of MTA reactions over the Zn/HZS-18 and the Zn/CZS-19 after 50 minutes reaction <sup>a</sup>.

Catalyst	Si/Al atomic ratio <sup>b</sup>	BET surface area ( $\text{m}^2\text{g}^{-1}$ )	Total pore volume ( $\text{cm}^3\text{g}^{-1}$ )	Micropore volume ( $\text{cm}^3\text{g}^{-1}$ ) <sup>c</sup>	Mesopore volume ( $\text{cm}^3\text{g}^{-1}$ ) <sup>d</sup>	Average pore diameter (nm) <sup>e</sup>	Selectivity (%)			
							C <sub>1</sub> -C <sub>4</sub> alkanes	C <sub>2</sub> -C <sub>4</sub> olefins	C <sub>5+</sub> etc	Total aromatics
HZS-18	18.3	374	0.39	0.12	0.27	3	27.8	11.9	3.8	56.5
CZS-19	19.8	345	0.18	0.14	0.04	-	26.1	17.5	6.3	50.1

<sup>a</sup>Reaction conditions: Reaction temperature, 748K;  $W_{cat} = 1\text{g}$ ;  $GHSV = 0.79\text{ h}^{-1}$ .  
<sup>b</sup> Determined by Energy-dispersive X-ray (EDX) analysis.  
<sup>c</sup>T-plot method; <sup>d</sup> $V_{meso} = V_{tot} - V_{micro}$ ; <sup>e</sup>BJH method.

13