

1.1 Materials

Natural montmorillonite clay (MMT) with a cation exchange capacity (CEC) of 91 meq/100 g was obtained from Inner Mongolia and was used without any further purification or cationic-exchange process. Tetraethoxysilane (TEOS, A.R.) was purchased from West Long Chemical Co, Ltd., Guangdong, China. Dehydrated alcohol (A.R.), ammonia solution (25%), sodium hydroxide (NaOH, A.R.) and Nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, AR) were purchased from Beijing Chemical Plant, Beijing, China. Cetyltrimethylammonium bromide (CTAB, A.R.) and tetrabutylammonium bromide (TBAB, A.R.) were purchased from Jinke Tianjin Fine Chemical Research Institute, Tianjin, China. Commercial ZSM-5 (Si/Al=12) (model number: NZ-RZ5-012) was purchased from JCNANO limited company, Nanjing, China.

1.2 Synthesis of SPC

0.5 g of MMT was first dispersed in 20 mL of de-ionized water for 30 min. At the same time, 0.5 g of CTAB was dissolved in 2 mL of ethanol and 20 mL of de-ionized water, to which 3.5 mL of tetraethoxysilane (TEOS) was added and the mixture treated ultrasonically for 0.5 h to give an emulsion. The emulsion was dropped slowly into the clay dispersion and the mixture stirred vigorously for 1.5 h, and then stirred gently for 4.5 h. Subsequently, 2 mL of ammonia solution (25%) was added and stirring continued for 2 h. The resulting solid was filtered under vacuum and washed three times with de-ionized water. Finally the product was dried overnight at 110 °C. The organic part was entirely removed from the material by calcination in air flow in a tubular furnace at 600 °C for 6 h with a temperature ramp of 1 °C min⁻¹. The product is denoted SPC.

1.3 Synthesis of MPC

The zeolite was recrystallized by using an organic salt (TBAB, tetrabutylammonium bromide) as the template. In a typical synthesis, 0.3 g of fumed silica was first dissolved at 80 °C in 40 mL of a 0.0875 M NaOH solution. Then, 0.70 g of TBAB (TBAB, 98%) was added with stirring. After stirring for 20 min, 1.0 g of SPC was added, which was continue stirred for another 6 h. The suspension was then hydrothermally treated at 160 °C in a Teflon-lined stainless steel autoclave under autogeneous pressure for 72-120 h. After cooling the autoclave to room temperature, the solid was filtered under vacuum and washed three times with de-ionized water. Finally the product was dried overnight at 110 °C. The organic part was entirely removed from the material by calcination in air flow in a tubular furnace at 600 °C for 6 h with a temperature ramp of 1 °C min⁻¹. The product is denoted MPC.

1.4 Synthesis of catalysts with 6 wt. % nickel oxide

The precursors were impregnated with nickel nitrate solution with 6 wt. % nickel oxide loading (40 mL of nickel nitrate solution to 1 g of precursor). Then the catalysts were put into muffle furnace by calcination in air flow at 600 °C for 6 h with a temperature ramp of 1 °C min⁻¹. According to the precursors of MPC-3, MPC-4, MPC-5, SPC, ZSM-5 and (SPC&ZSM-5), the nickel oxide loading catalysts were named 6%NiO/MPC-3, 6%NiO/MPC-4, 6%NiO/MPC-5, 6%NiO/SPC, 6%NiO/ZSM-5 and 6%NiO/(SPC&ZSM-5), respectively.

2.1 Characterization

X-ray powder diffraction (XRD) patterns were recorded on a Philips X'Pert diffractometer equipped with a rotating anode, using Cu K α radiation ($\lambda = 0.1541$ nm). High-resolution transmission electron microscopy (HRTEM) images were obtained using a JEM-3010 microscope with an accelerating voltage of 200 kV. The crystal morphology was studied using a Hitachi S-4700 scanning electron microscope (SEM). Nitrogen adsorption-desorption isotherms were measured at liquid nitrogen temperature with a Quantachrome Autosorb-1

volumetric adsorption analyser. Prior to measurements, the samples were degassed at 300 °C for 16 h. The elemental contents in samples were measured by X-ray fluorescence analysis (XRF) on a Philips Magix-601 X-ray fluorescence spectrometer. The NH₃-TPD of samples was measured on an auto-catalytic adsorption system (AutoChem II 2920, Micromeritics, USA), using an on-line thermal conductivity detector (TCD), and quartz tubular reactor. Prior to measurements, the samples were degassed at 300 °C for 3 h.

2.2 Catalytic isomerization of *m*-xylene to *p*-xylene

For catalytic reactions, all of the samples were NH₄⁺-ion exchanged with a 1 M NH₄NO₃ solution for 8 h (30 mL of NH₄NO₃ solution to 1 g of sample), and then converted to the H⁺ form by calcination in air at 600 °C for 6 h. These processes were repeated three times.

The catalytic isomerization of *m*-xylene to *p*-xylene was carried out in a fixed reactor. The samples were first activated in dry air at 450 °C for 2 h and then cooled to the reaction temperature (350 °C) in a flow of dry nitrogen. *m*-Xylene was fed (WHSV = 8 h⁻¹) by a metering pump, vaporized in a preheated assembly and then passed through the catalyst. High-performance liquid chromatography analysis was carried out on a Varian Prostar liquid chromatograph consisting of two quaternary pumps, a solvent degasser, manual injection, a column oven, and a wavelength UV detector.

The main product of the reaction is *p*-xylene. The conversion of *m*-xylene (*x*) and the yield of the main product (*p*-xylene) (*y*) are calculated as follows:

$$x_{m\text{-xylene}} = \frac{[m\text{-xylene}]_i - [m\text{-xylene}]_f}{[m\text{-xylene}]_i} \times 100\%, \quad (1)$$

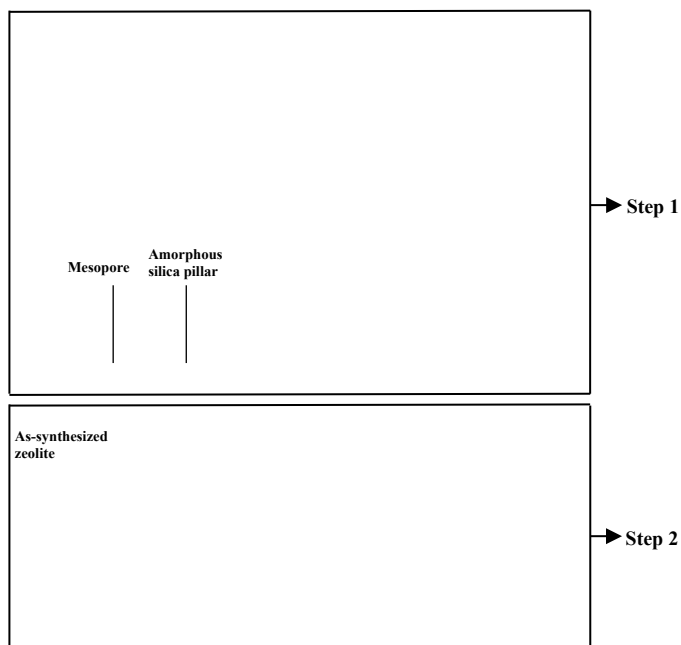
$$y_{p\text{-xylene}} = \frac{[p\text{-xylene}]}{[m\text{-xylene}]_i - [m\text{-xylene}]_f} \times 100\%, \quad (2)$$

where $[m\text{-xylene}]_i$ and $[m\text{-xylene}]_f$ are the concentration of *m*-xylene before and after reaction, respectively, and $[p\text{-xylene}]$ is the concentration of *p*-xylene.

2.3 The hydrocracking of residual oil

Before the hydrocracking performance, the catalysts were loaded with Ni(NO₃)₂·6H₂O with nickel oxide content of 6 wt.%. The extra part was entirely removed from the material by calcination in air flow in a tubular furnace at 600 °C for 6 h with a temperature ramp of 1 °C min⁻¹. The samples were denoted as 6%NiO/MPC-3, 6%NiO/MPC-4, 6%NiO/MPC-5, 6%NiO/SPC, 6%NiO/ZSM-5 and 6%NiO/(SPC&ZSM-5). The catalytic hydrocracking performance assessment of the samples was conducted in a fixed-bed reactor (200 mm*10 mm ID) at hydrogen atmosphere, using the residual oil as feedstock, by the pulse method. The reactor was heated to the requisite temperature with the help of a tubular furnace inserted with a thermocouple. About 0.3g catalyst was homogeneously mixed with granular quartz which placed in the middle of reactor and supported on both side with a thin layer of quartz wool and ceramic beads in order to maintain constant flow of the reactants into the catalyst. Before entering the reactor, the feedstock was preheated to 50 °C to improve its flow ability. Reaction conditions were as follows: temperature, 400 °C; hydrogen pressure, 5MPa; weight hourly space velocity (WHSV) of residual oil, 7 h⁻¹. The reaction product was cooled and separated into gaseous and liquid products, using a gas-collector and a glass liquid collector, respectively. The different distillation range oil was obtained by distillation of the liquid products. According to the boiling range of petroleum products, the composition of petroleum distillates was defined to gasoline fraction (70-120 °C), which is the middle distillates, and kerosene fraction (120-150 °C). The residue after the distillation was washed with acetone prior to the coke analysis. To analysis the coke yield, the

catalyst with coke was dissolved in a HF solution at room temperature. After the catalyst solved, the coke was filtered, washed with deionized water and dried in an oven at 100 °C and then weighed to calculate rate of the residual carbon.



Scheme 1 Synthesis procedure for MPC.

The synthesis procedure of MPC can be divided into two steps. The SPC material was synthesized following the procedure of Step 1. More details can be found in Section 1.2 above. In Step 2, MPC was synthesized using SPC as the precursor material. The details can be seen in Section 1.3 above.

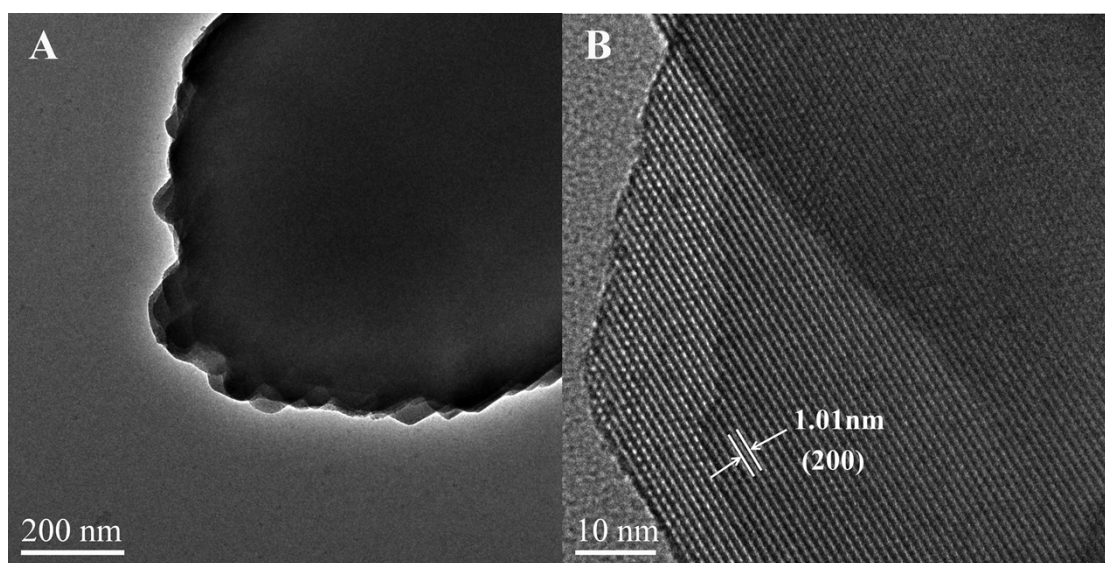


Fig. 1S HRTEM images of ZSM-5.

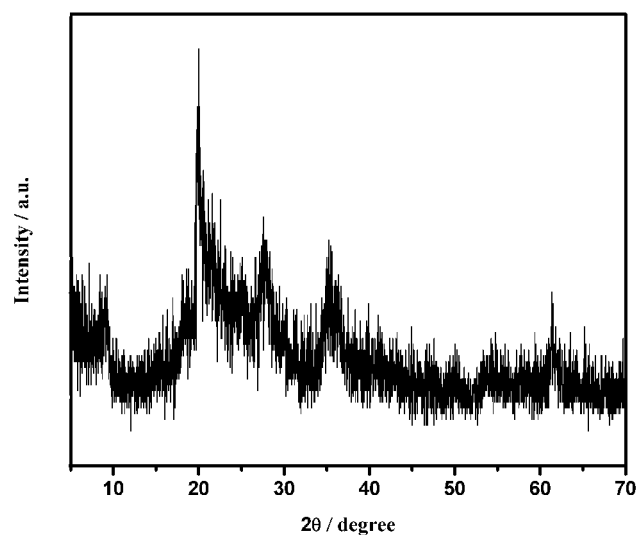


Fig. 2S High-angle XRD pattern of MMT after recrystallization.

Table 1S Textural properties of the samples.

Samples	BET (m ² g ⁻¹)	Total pore volume (cm ³ g ⁻¹)	Micropore diameter (nm)	Mesopore diameter (nm)
MPC-5	734	1.21	0.53	2.54/3.80
SPC	511	1.65	-	2.54
ZSM-5	396	0.20	0.51	-
MMT	54	0.12	-	3.76

Table 2S Element contents of the samples analyzed by XRF.

Samples	Si (wt. %)	Al (wt. %)	O (wt. %)	Mg (wt. %)	Ca (wt. %)
MPC-5	44.41	3.62	50.52	0.86	0.59
SPC	43.94	3.68	50.97	0.79	0.62
ZSM-5(Si/Al=12)	43.60	3.41	52.99	-	-

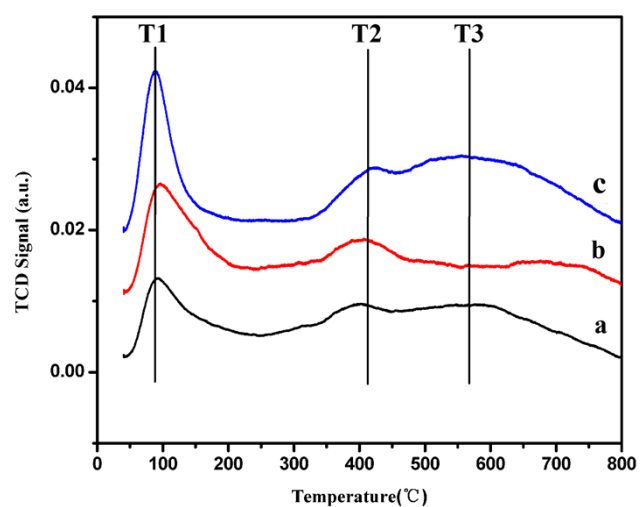


Fig. 3S NH₃-TPD profiles of the samples: (a) ZSM-5(Si/Al=12), (b) SPC, (c) MPC-5.

NH₃-TPD profiles of MPC-5, SPC and ZSM-5 are shown in Fig. 3S. Three NH₃ desorption peaks were detected

at about 50-300°C (T_1), 300-450°C (T_2) and 450-800°C (T_3). According to the published data³¹⁻³², the first peak (T_1) should be assigned to desorption of NH_3 on weak acid sites, the second peak (T_2) is desorption of NH_3 on middle strength acid sites, and the third peak (T_3) is desorption of NH_3 on strong acid sites. These peaks were deconvoluted, and the acidity of each peak was calculated according to the desorbed amount of NH_3 and summarized in Table 3S.

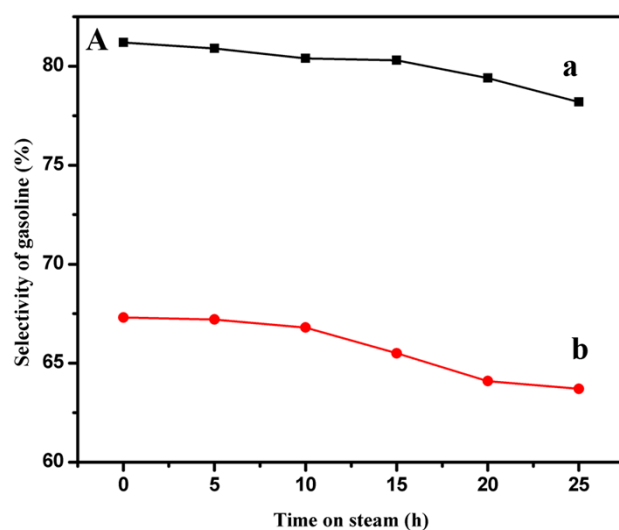
Table 3S The acid strength distribution of the catalysts calculated by the results of NH_3 -TPD.

Sample	Total acidity (mmol g ⁻¹) 1)	Acidity (mmol g ⁻¹)		
		Weak (T_1)	Strong (T_2 & T_3)	
		T_1 (50-300°C)	T_2 (300-450°C)	T_3 (450-800°C)
MPC-5	1.34	0.40	0.22	0.72
SPC	1.36	0.60	0.31	0.45
ZSM-5(Si/Al=12)	1.28	0.42	0.29	0.57

Table 4S Catalytic performance for isomerization of *m*-xylene to *p*-xylene.

Sample	Conversion (%)	Selectivity (%)	
		<i>p</i> -xylene	Coke and other products
MPC-5	17.6	82	18
SPC	7.6	0	100
ZSM-5(Si/Al=12)	14.3	84	16

Table 4S gives a comparison of the performance of MPC-5 in the catalytic isomerization of *m*-xylene to *p*-xylene with those of SPC and a commercial ZSM-5 zeolite. SPC affords no xylene because no micropores exist in this material. Compared with ZSM-5, MPC-5 exhibits better conversion of *m*-xylene with a comparable selectivity for *p*-xylene. It is known that the selectivity of this reaction is better within the micropores of zeolite crystals than on the outside of the crystals³³. The significantly enhanced catalytic activity of MPC-5 can be attributed to the acid sites afforded by the clay layers. This shows that the micropores in the pillars are intimately associated with the surface of the host clay layers.



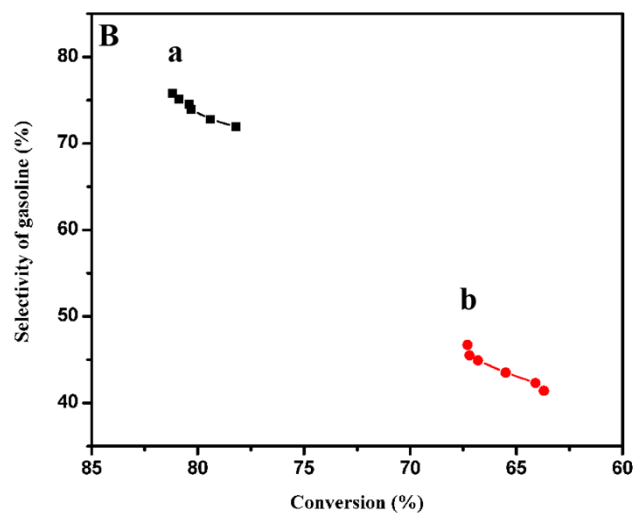


Fig 4S The hydrocracking of residual oil over (a) 6%NiO/MPC-5 and (b) 6%NiO/SPC; (A) the conversion of residual oil vs. time on stream and (B) the selectivity of gasoline vs. conversion.

It can be observed that after 25h of catalytic reaction, the conversion of residual oil with 6%NiO/MPC-5 as catalyst was still 78.2%, which is only 3.0% lower corresponding with the beginning. However, the catalytic performance of 6%NiO/SPC had decrease after 25h, and the conversion of residual oil was 63.7% in the 25th hour.