**Supplementary Information**

# Catalytic Upcycling of Waste Polyethylene to Fuels over a Nanosized Beta Zeolite under Mild Conditions

Qing Liu,[1] Zhendong Liu[1,2]*

[1]State Key Laboratory of Chemical Engineering, Department of Chemical Engineering, Tsinghua University, Haidian District, Beijing 100084, China
[2]Ordos Laboratory, Ordos, 017010, China

Email: liuzd@tsinghua.edu.cn

**Experimental section**

*Materials*

LDPE (avg. $M_w$ ~ 4000 Da) was obtained from Sigma-Aldrich. HDPE (avg. $M_w$ ~ 90.6 KDa) was obtained from Sinopec Yanshan, the molecular weight of which was estimated by GPC. The nano-sized beta (CP814E), MOR-type zeolite (CBV-21A) and FAU-type (CBV-720) were all purchased from Zeolyst International, and calcined at 550 °C for 5 h prior to use. The *M*-beta was purchased from Nankai Catalyst. The *L*-beta was synthesized with a gel composition of 1.97 $Na_2O$ : 1.00 $K_2O$ : 12.5 $(TEA)_2O$ : $Al_2O_3$ : 50 $SiO_2$ : 750 $H_2O$ : 2.9 HCl, following the reported procedure.[1] The H-type zeolites and the metal-modified zeolites were made through ion-exchange followed by a calcination at 550 °C for 6 h. $NH_4NO_3$, $Cu(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ were used as precursors for the ion-exchange, and all of these chemicals were purchased from J&K Scientific and used without further purification. The dealuminated nanosized beta zeolites were prepared by acid treatment in 1.0 mmol/g $H_2SO_4$ aqueous solution under 80 °C. The ratio of zeolite to acid solution was 1 g to 20 ml; and the treatment was carried out for 2 h and 4 h to get the dealuminated beta with the Si/Al ratio of 51.0 and 80.1, respectively.

*Characterization*

Powder X-ray diffraction patterns (XRD). XRD patterns of the samples were collected on a Bruker D8 advance with Cu Kα radiation at a scanning rate of 5 °/min in the 2θ range of 5°−50°.

Inductively coupled plasma mass spectrometry (ICP). Elemental analysis of the zeolite catalysts was carried out using an inductively coupled plasma−atomic emission spectrometer (ICP-AES, iCAP-6300, Thermo) after dissolving the solid products in a hydrofluoric acid solution.

$N_2$ adsorption-desorption. Textural properties, including BET surface area, micropore volume and external surface area of the samples were measured by $N_2$ adsorption-desorption on Quantachrome Autosorb-iQ2-MP at -196 °C. Prior to measurements, all the samples were preheated at 300 °C for 8 h under vacuum.

Scanning electron microscopy (SEM). The crystal sizes and morphologies of the zeolite catalysts were observed by means of FE-SEM (JSM-7001F, JEOL Japan) operating at an acceleration voltage of 15 keV.

Ammonia temperature programmed desorption ($NH_3$-TPD). $NH_3$-TPD analysis was conducted using a Micromeritics ChemSorb 2720 instrument. Approximately 0.1 g of the obtained H-type zeolite was pretreated at 600 °C for 1 hour under argon flow. NH3 adsorption was performed at 100 °C for 30 minutes, followed by a 30-minute argon flow at 100 °C to remove physically adsorbed NH3. Subsequently, the temperature was

ramped up to 600 °C at a rate of 10 °C/min, and the chemisorbed NH3 TPD profile was recorded using a TCD detector.

Fourier-transform infrared spectroscopy using pyridine as probe (pyridine-FTIR). Pyridine-FTIR experiments were conducted using a Bruker INVENIO-S FTIR spectrometer equipped with an in-situ vacuum system featuring a secondary vacuum pump. Self-supporting wafers were prepared by pressing 10–15 mg of H-type samples obtained, which were pretreated at 400 °C for 1 hour. Subsequently, the samples were cooled to room temperature for pyridine adsorption for 0.5 hours, followed by an additional 0.5 hours of soaking to remove physically adsorbed pyridine. Thermal desorption was then carried out at 150 °C and 350 °C, followed by IR measurement of the samples.

*Catalytic tests*

The activity for PE catalytic cracking was evaluated in a stainless steel batch reactor equipped with magnetic stirring in the temperature range of 250−280 °C under autogenous pressure. The LDPE powder was used as received, and HDPE was cut to pieces approximately 2 mm in diameter before reaction. In a typical run, 0.1 g of catalyst and 1.0 g of PE powder were added into the reactor followed by gently grinding. The air inside autoclave was completely purged out by $N_2$. Thereafter, the reactor was heated to the reaction temperature over the course of 40 min with a temperature controller accurate to ±5 °C. After a specific reaction time (including the heating time of ~40 min), the reactor was naturally cooled down. The final pressure in the reactor was recorded. The headspace was sampled in a gas bag and analyzed with gas chromatography (GC) equipped with a flame ionization detector (FID) to quantify volatile C1−C6 hydrocarbons. Calibration curves of volatile products were obtained by flowing known ratios of standard species to the GC-FID. Liquid products (C7−C40) were dissolved in chloroform, first identified with GC−MS and also quantified with GC-FID using 1,3,5-tri-tertbutyl benzene as an external standard. Calibration of GC signals was conducted using normal alkanes standard mixtures, and alkane isomers were assumed to have the same calibration factor as the corresponding normal alkanes. Calibration factors of gases (C1−C6) were using commercial mixed standard gases (Air Liquid, China), factors of liquids (C7−C40) were using standards from Sigma Aldrich. The solids remaining mixed with the spent catalysts were estimated by thermogravimetric analysis coupled with differential thermal analysis (TG-DTA) (METTLER, Switzerland). The weight loss from 200 to 700 °C was assumed to be coke combustion or non-dissoluble PE fragments.

The conversion of PE is defined by:

$$C_{PE}[\text{mass \%}] = \frac{\Delta G\ (weight\ loss)\%}{1 - \Delta G} \times \frac{mass\ catalyst}{initial\ mass\ PE} \times 100\%$$
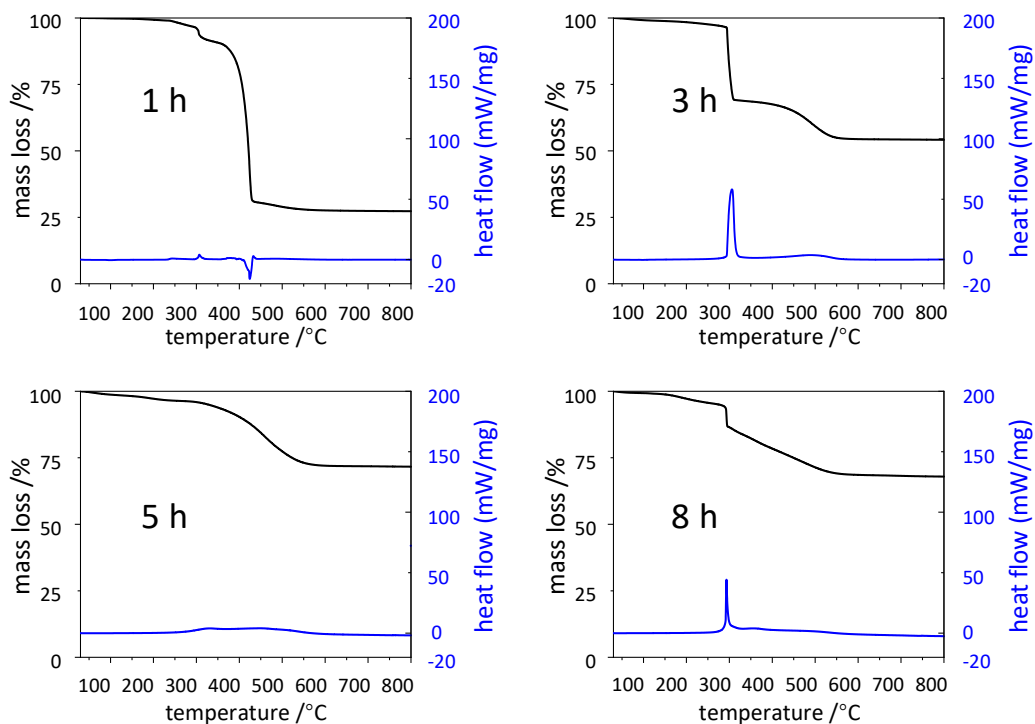
Liquid yield is defined by:

$$Y_{liquid}[\text{mass \%}] = \frac{mass\ hydrocarbons\ C_7 - C_{40}}{initial\ mass\ PE} \times 100\%$$

Gas yield is defined by:

$$Y_{gas}[\text{mass \%}] = \frac{mass\ hydrocarbons\ C_1 - C_6}{initial\ mass\ PE} \times 100\%$$

The yield of product alkanes with $i$ carbon numbers ($C_i$) was calculated using the following equation:

$$S_i[\text{mass \%}] = \frac{Y_i}{Y_{liquid} + Y_{gas}} \times 100\%$$

**Figure S1. A typical evolution of LDPE cracking over the nanosized beta zeolite for different reaction times.** The weight losses in the temperature range of 200 to 700 °C after reaction times for 1 h, 3 h, 5 h and 8 h were 70.2%, 44.5%, 23.2% and 27.6%, respectively. This tendency shows how LDPE cracks on the zeolite catalyst over different periods of reaction time. Note that all the TG-DTA curves exhibit similar patterns, making it impossible to distinguish between coke and residual PE fragments. Given the relatively low temperature used for cracking in this work, we assume that the weight loss was primarily due to non-dissoluble polymers, that is, unconverted LDPE.
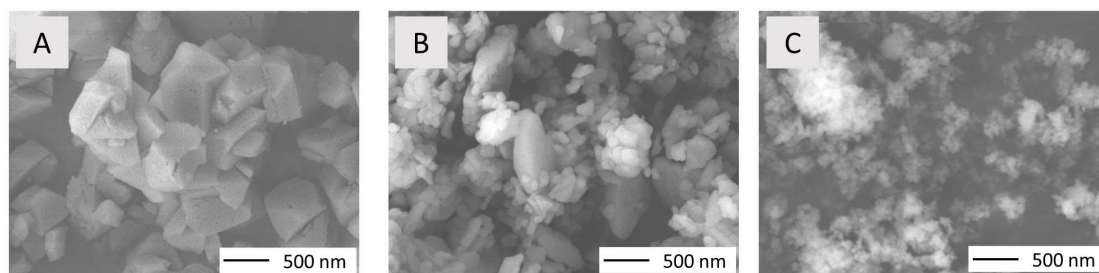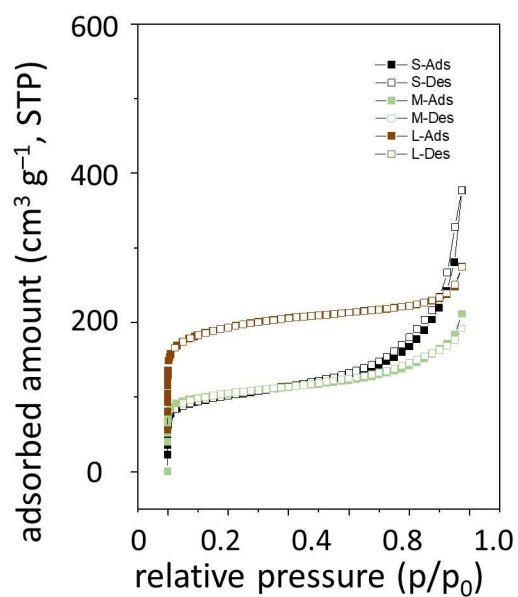
| Si/Al | acidity (mmol/g) |
|---|---|
| H-Y (15) | 0.842 |
| H-MOR (10) | 1.033 |
| H-beta (12.5) | 0.945 |

**Figure S2.** SEM images of the proton-type zeolites. A, H-Y. B, H-MOR. C, H-beta. The amounts of acidic sites for these three zeolites were calculated from $NH_3$-TPD to be 0.842, 1.033, and 0.945 mmol/g, respectively (shown in the table).
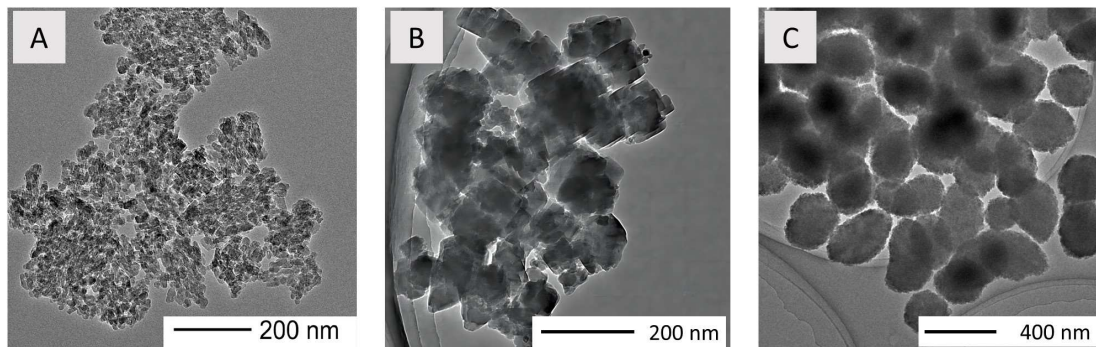
**Figure S3.** TEM images of S-beta (A), M-beta (B) and L-beta (C).

| sample | Si/Al ratio[a] | external surface area[b] $(m^2\ g^{-1})$ | micropore volume[b] $(cm^3\ g^{-1})$ |
|---|---|---|---|
| *S*-beta | 12.5 | 146.609 | 0.093 |
| *M*-beta | 12.5 | 86.897 | 0.126 |
| *L*-beta | 13.0 | 63.553 | 0.283 |

[a]Estimated by ICP-AES.

[b]Estimated by $N_2$ adsorption

**Figure S4.** $N_2$ adsorption-desorption isotherms of S-beta, M-beta, and L-beta and the textural properties calculated for the zeolites.
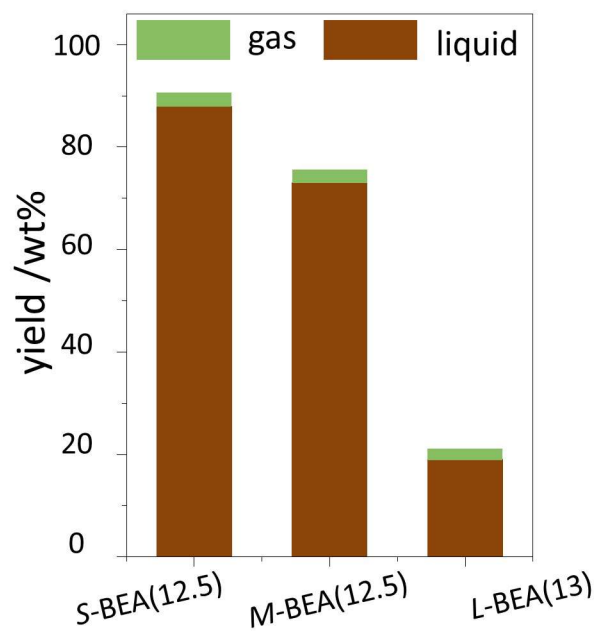
**Figure S5.** Comparison of yields for the catalytic cracking of LDPE over the beta zeolites of different particle sizes. reaction results using beta with various particle sizes. (Reaction condition: the catalytic cracking was done at 250 °C for 3 h; the amounts of LDPE and catalyst were 1.0 g and 0.1 g.)
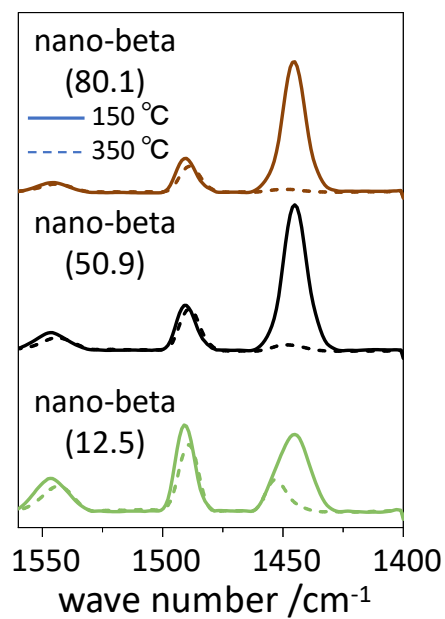
**Figure S6.** Pyridine-FTIR profiles for the nanosized beta zeolites before and after dealumination.
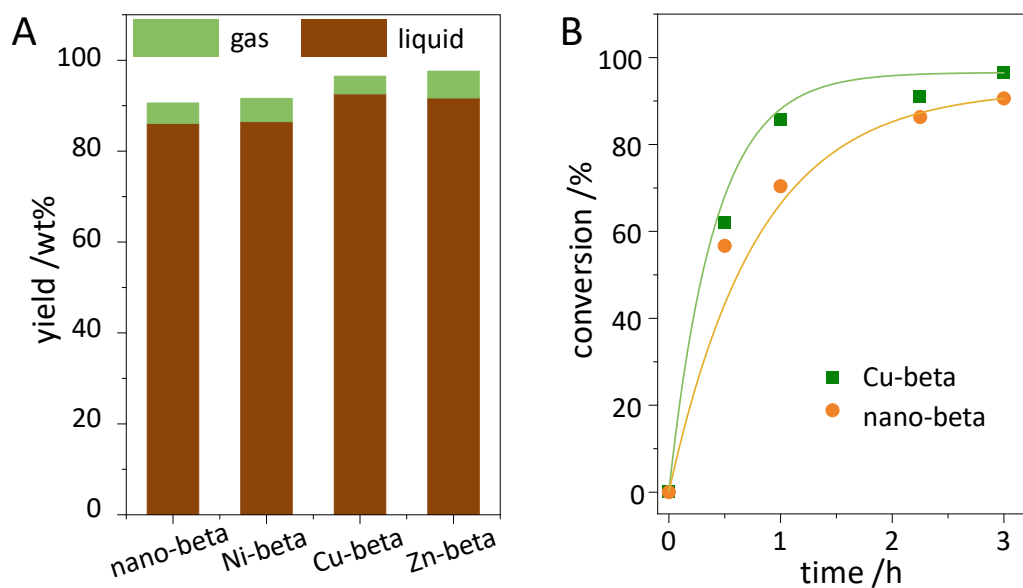
**Figure S7.** (A) Catalytic cracking of LDPE over different metal-modified nanosized beta zeolites. (Reaction condition: the catalytic cracking was done at 250 °C for 3 h; the amounts of LDPE and catalyst were 1.0 g and 0.1 g). (B) Comparison of LDPE conversion over time for the nano-beta and Cu-beta catalysts. (Reaction condition: the catalytic cracking was done at 250 °C for 0.5, 1.0, 2.3, 3 h; the amounts of LDPE and catalyst were 1.0 g and 0.1 g).
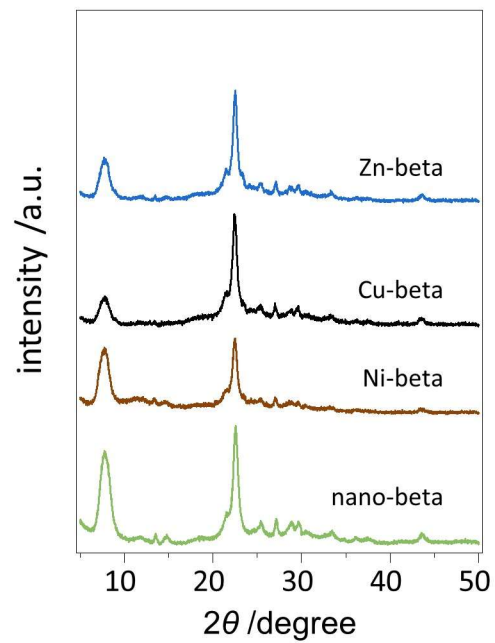
**Figure S8.** XRD patterns of the metal-modified nanosized beta zeolites.
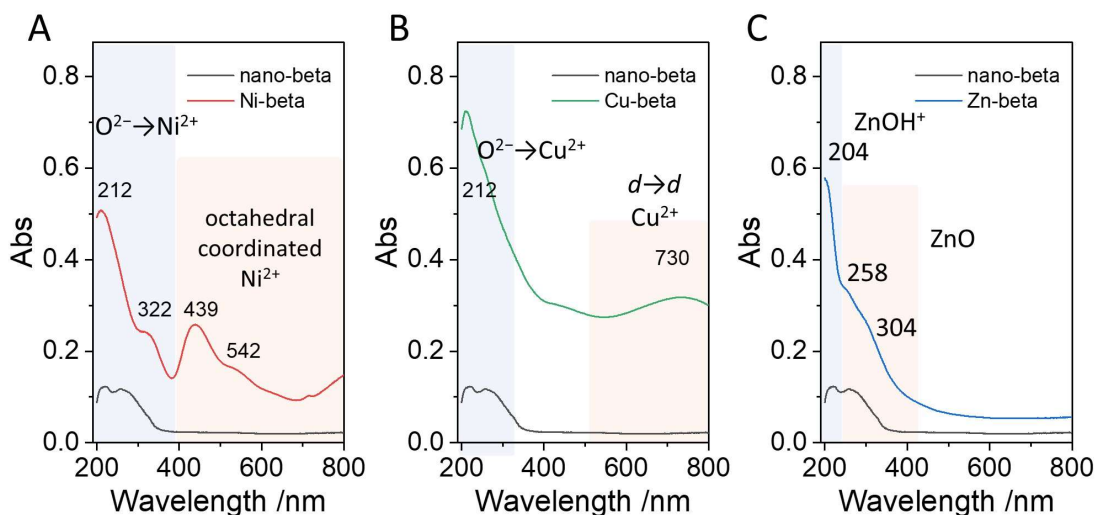
**Figure S9.** UV-vis diffuse reflectance spectra of the metal-modified nanosized beta zeolites. (A) Ni-beta; (B) Cu-beta and (C) Zn-beta.

All the metal-modified samples exhibited a distinct absorption band in the UV region ($\lambda < 350$ nm), indicating ligand-to-metal charge transfer (LMCT) from $O^{2-}$ to metal cations (Appl. Catal. A Gen. *2004*, 262, 155). This suggests that some metal species acted as charge-compensating cations, contributing to a reduction in the number of Brønsted acidic sites. Beyond cations at the ion-exchange sites, a significant portion of the metal species existed in oxidized forms. In the case of Ni-beta, absorption bands around 439 and 542 nm indicate octahedrally coordinated $Ni^{2+}$ within the NiO lattice (RSC Advances 2016, 6, 34600). For Cu-beta, absorption below 400 nm reflects monomeric $Cu^{2+}$ ions interacting with the zeolite framework oxygen (with a maximum around 212 nm) and oligomeric $[Cu^{2+}-O^{2-}-Cu^{2+}]$ species (around 280 nm) (Microporous Mesoporous Mater. 2015, 209, 54; Stud. Surf. Sci. Catal. 2004, 154, 2475). Additionally, a broad absorption band between 500 and 800 nm in Cu-beta corresponds to the d–d transition of $Cu^{2+}$ (Appl. Catal. B Environ. 2011, 102, 44; Catalysts 2020, 10, 506; Appl. Catal. B Environ. 1998, 16, 359). Zn-beta exhibits a high-intensity absorption band around 220 nm, indicating the presence of $ZnOH^+$ species formed by the interaction of $Zn^{2+}$ cations with framework aluminum, while bands around 258 nm correspond to small ZnO species (Microporous Mesoporous Mater. 2011, 143, 435; Mater. Lett. 2007, 61, 1675).
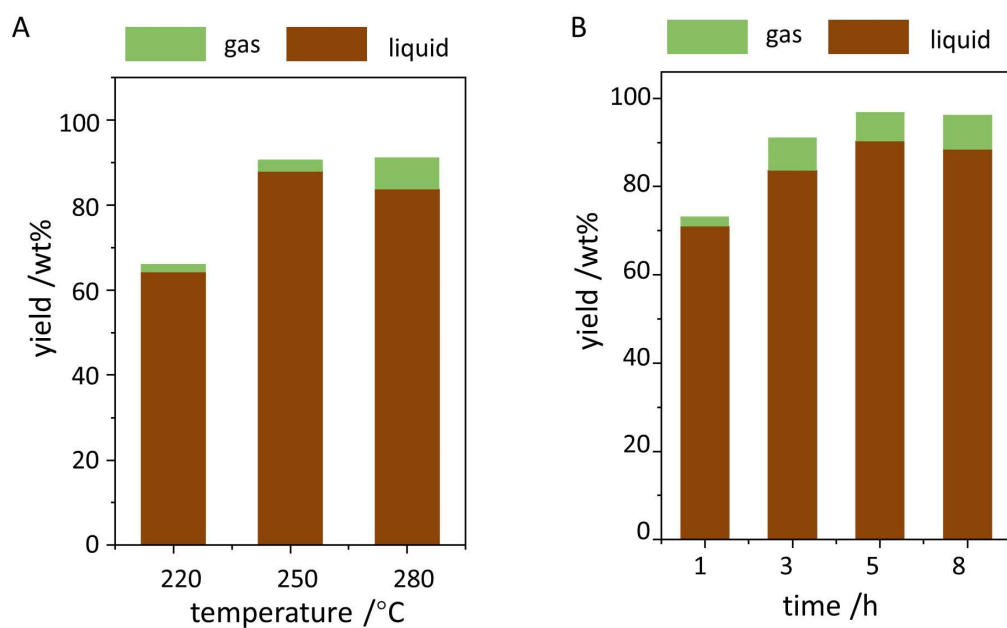
**Figure S10.** Activities of the nanosized beta in the catalytic cracking of LDPE. (A) Comparison of the yields obtained in cracking for 3 h under different temperatures. (B) Comparison of the yields obtained for cracking over different periods of time under 280 °C. (The amounts of LDPE and catalyst were 1.0 g and 0.1 g. in all the experiments.)
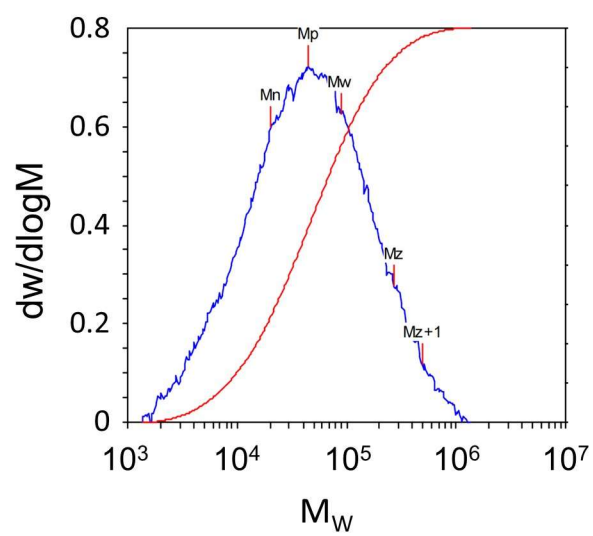
**Figure S11.** GPC analysis of HDPE (solvent: (1,2,4-trichlorobenzene stabilized with 0.0125% butylated hydroxytoluene).