Supplementary Information

Seed-directed Synthesis of Zeolites with Enhanced Performance in the Absence of Organic Templates

Bin Xie,[b] Haiyan Zhang,[b] Chengguang Yang,[b] Siyu Liu,[b] Lin Zhang,[b] Limin Ren,[b] Xiangju Meng,[a] Bilge Yilmaz,[c] Ulrich Müeller,[c] and Feng-Shou Xiao[a],*

[a] Department of Chemistry, Zhejiang University, Hangzhou 310028, China.

[b] State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun 130012, China.

[c] BASF SE, Ludwigshafen 67056, Germany.

To whom correspondence should be addressed. E-mail: fsxiao@mail.jlu.edu.cn

Synthesis

Beta-SDS. Seed-directed synthesis of Beta zeolite (Beta-SDS) was carried out from a starting aluminosilicate gel at temperature of 120-140°C in the presence of calcined Beta zeolite seeds from the use of fumed silica (Shenyang Chemical Co.), sodium aluminate ($Al_2O_3 \geq 41.0$ %, Sinopharm Chemical Reagent Co.), and sodium hydroxide ($NaOH \geq 96$ %, Tianjin Yongda Chemical Reagent Development Center). As a typical run for synthesis of Beta-SDS at 120°C, (1) 0.07 g of $NaAlO_2$ and 0.312 g of NaOH were dissolved in 7.56 ml of H_2O, followed by addition of 0.72 g of fumed silica; (2) After stirring for 10 min, 0.036 g of Beta zeolite seeds (Si/Al=11.6, 4.6%), was introduced into the gel; (3) The gel mixture with molar ratio of SiO_2:1/40Al_2O_3:0.36Na_2O:35.3H_2O was transferred into an autoclave to crystallize at 120°C for 120 h; (4) After filtrating at room temperature and drying at about 80°C, crystalline products were obtained. As a typical run for synthesis of Beta-SDS at 140°C, (1) 0.07 g of $NaAlO_2$ and 0.312 g of NaOH were dissolved in 8.64 ml of H_2O, followed by addition of 0.72 g of fumed silica; (2) After stirring for 10 min, 0.086 g of Beta zeolite seeds (Si/Al=10.2, 10.3%), was introduced into the gel; (3) The gel mixture with molar ratio of SiO_2:1/40Al_2O_3:0.36Na_2O:40.3H_2O was transferred into an autoclave to crystallize at 140°C for 18.5 h; (4) After filtration at room temperature and drying at about 80°C, crystalline products were obtained. Beta-SDS synthesized at 140 °C for 18.5 h in the presence of 10.3 % Beta seeds (Si/Al=10.2) was designated as 100 % crystallinity.

In comparison, the synthesis of Beta zeolite (Beta-TEA) was carried out in aluminosilicate gel with molar ratio of $62.85SiO_2/1.00Al_2O_3/10.09TEA_2O/2.96Na_2O/794.44H_2O$ at temperature of 140 °C for 96 h. The removal of TEA^+ cations was done by calcination at 550 °C for 4 h with increasing rate of 1 °C/min from room temperature to 550 °C.

We have used two Beta zeolite seeds in this work, one was supplied from Sinopec Company (Si/Al=10.2) and another (Si/Al=11.6) was synthesized in our lab.

HEU-SDS. As a typical run for seed-directed synthesis of HEU zeolite (HEU-SDS), (1) 0.07 g of $NaAlO_2$ and 0.312 g of NaOH were dissolved in 7.56 ml of H_2O, followed by addition of 0.72 g of fumed silica; (2) After stirring for 10 min, 0.036 g of HEU zeolite seeds (4.6%), was introduced into the gel; (3) The gel mixture with molar ratio of SiO_2:1/40Al_2O_3:0.36Na_2O:35.3H_2O, was transferred into an autoclave to crystallize at 120°C for 120 h; (4) After filtration at room temperature and drying at about 80°C, crystalline products were obtained.

LEV-SDS. As a typical run for seed-directed synthesis of LEV zeolite (LEV-SDS), (1) 0.064 g of $NaAlO_2$ and 0.312 g of NaOH were dissolved in the mixture of 7.56 ml H_2O and 0.552 g ethanol, followed by addition of 0.72 g of fumed silica; (2) After stirring for 10 min, 0.036 g of RUB-50 zeolite seeds (Si/Al=9.7, 4.6%) supplied from BASF SE (Ludwigshafen, Germany)., was introduced into the gel; (3) The gel mixture with molar ratio of SiO_2:1/44Al_2O_3:0.357Na_2O:35.3H_2O:C_2H_5OH was transferred into an autoclave to crystallize at 120°C for 96 h; (4) After filtration at room temperature and drying at about 80°C, crystalline products were obtained.

Characterization

X-ray diffraction (XRD) patterns were obtained with a Rigaku D/MAX 2550 diffractometer with Cu Kα radiation. Scanning electron microscopy (SEM) images were collected by JEOL electron microscopes (FE-JSM 6700, Japan), Hitachi S-4800 and S-5200 microscope, respectively. Energy dispersive X-ray (EDX) analysis was obtained on Bruker Quantax 200 attached to the SEM microscope. Transmission electron microscopy (TEM) images were recorded on a JEM 3010 electron microscope (JEOL, Japan) with an acceleration voltage of 300 kV. Energy dispersive X-ray spectrometer (EDS) was obtained on Phoenix 30T (EDAX Co.) attached to the TEM microscope. The nitrogen isotherms at -196 °C were measured using a Micromeritics ASAP 2020M system. The samples were outgassed for 10 h at 200 °C before the measurements. The pore-size distribution for micropores was calculated using HK model. NMR spectra were recorded on a Varian Infinityplus-400 spectrometer. The sample composition was determined by inductively coupled plasma (ICP) with a Perkin-Elmer plasma 40 emission spectrometer. XPS spectra of the samples were recorded at room temperature using an ESCALAB Mark II system with Al-Kα X-ray radiation. The C(1s) line at 284.6 eV was taken as a reference for binding energy (BE) calibration. Temperature programmed desorption of ammonia (NH_3-TPD) experiments were performed using a Micromeritics AutoChem II 2920 automated chemisorption analysis unit with a thermal conductivity detector (TCD) under helium flow. The NH_3-TPD setup was also equipped with an on-line mass spectroscopy (MS) system, which allowed continuous analysis of the desorbed species. Deconvolution and integration of the TPD profiles were performed by utilizing the Peak Editor (Micromeritics) software.

Catalytic tests

All samples used in catalytic tests were H-form. As a typical run, the sample was ion-exchanged with 1M NH_4NO_3 at 80 °C, followed by calcination at 500 °C for 3 h. This procedure was repeated.

Cumene cracking was performed at 300 °C by pulse injections. In each run, 50 mg of catalyst was used, the pulse injection of the reactant was 1.5 μml, and the reaction flow rate was 53.7 ml/min.

The cracking of industrial feed-Fushun vacuum gas oil (VGO) was carried out in a microreactor unit based on ASTM D-3907-80, and the feedstock parameters are presented in Table S1. The mass of feedstock was 1 g and the oil was injected for 104s. The products were quenched using ice bath and separated into liquid and gas products. The gases were analyzed by Varian 3800 GC, and liquids were examined using a simulated distillation gas chromatogram with the ASTM D2887 standard to obtain the percentage weight of gasoline, diesel, and heavy oil. The amount of coke deposited on the catalysts was determined by the amount of CO_2 formed from burning of coke *in situ* using the chromatogram. For preparation of the catalysts, pseudoboehmite was mixed with an aqueous solution of HCl (HCl mass concentration of 1 %, pH value at

3-4) at 60 °C for 1 h, followed by addition of Kaolin. After stirring at room temperature for 3 h, the zeolite was added into the slurry. After stirring at room temperature for 1 h, the slurry was pelletized with the spray-drying unit at 450 °C. The catalysts contain 30 wt.% zeolite, 35 wt.% Kaolin, and 35 wt.% Al_2O_3, and their sizes were ranged from 80 to 180 μm.

Supporting Figures

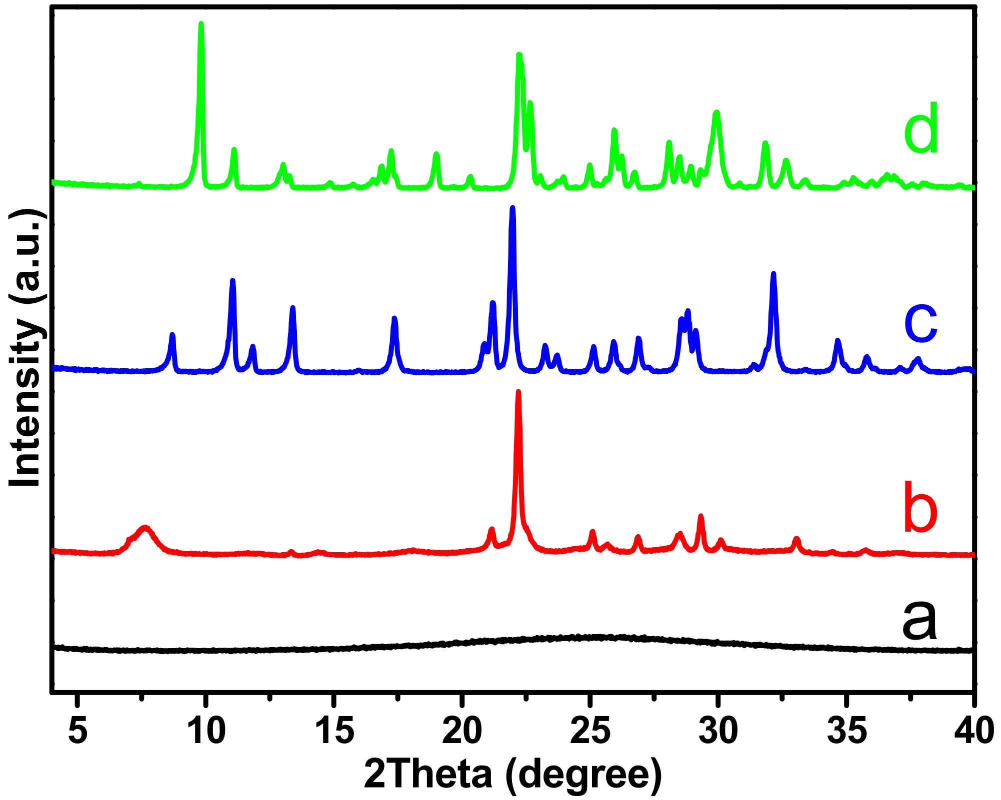


Figure S1. XRD patterns of the samples synthesized in the aluminosilicate gel (a) without, with zeolite seeds of (b) Beta, (c) RUB-50, and (d) Heulandite in the absence of organic templates.

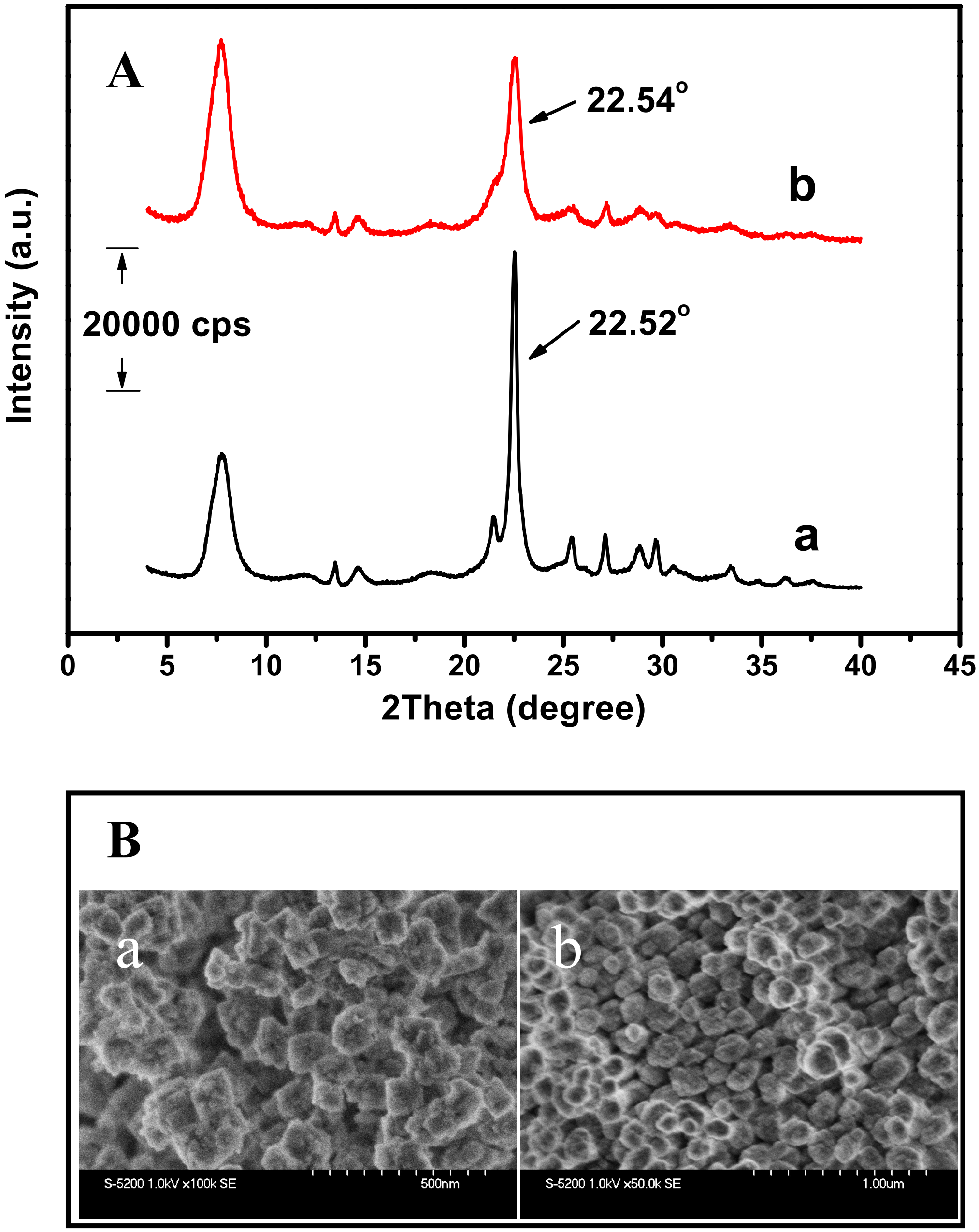


Figure S2. (A) XRD patterns and (B) SEM images of Beta seeds at Si/Al ratio of (a) 10.2 and (b) 11.6.

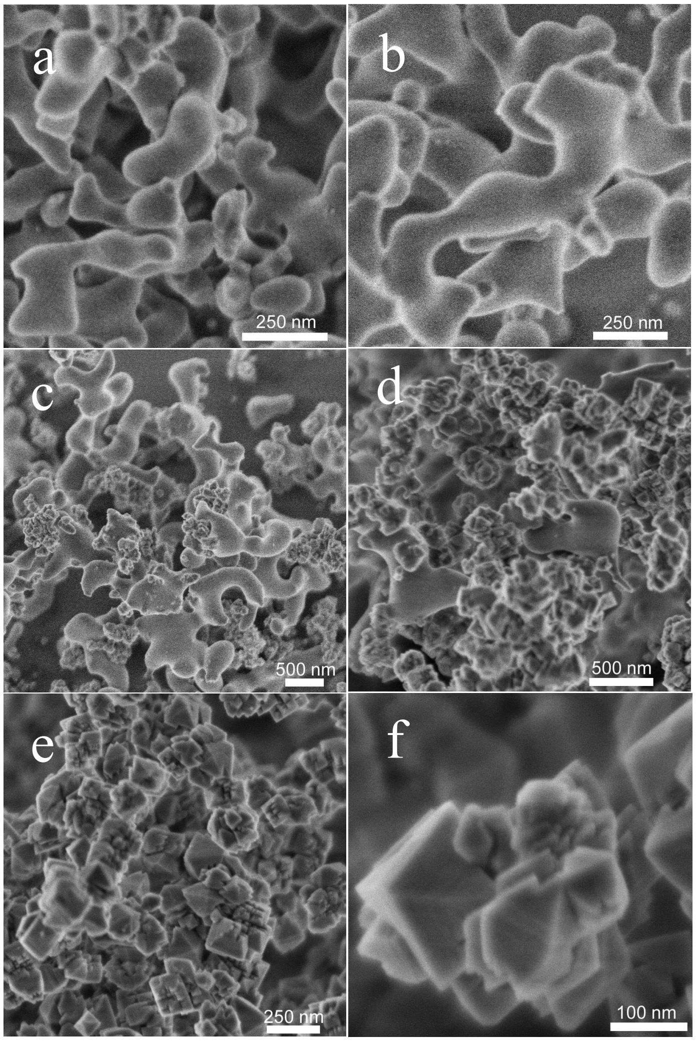


Figure S3. SEM images of Beta-SDS samples crystallized for (a) 2, (b) 4, (c) 10, (d) 15, and (e & f) 18.5 h at the temperature of 140 °C by addition of 10.3 % Beta seeds (Si/Al=10.2) in the starting aluminosilicate gels.

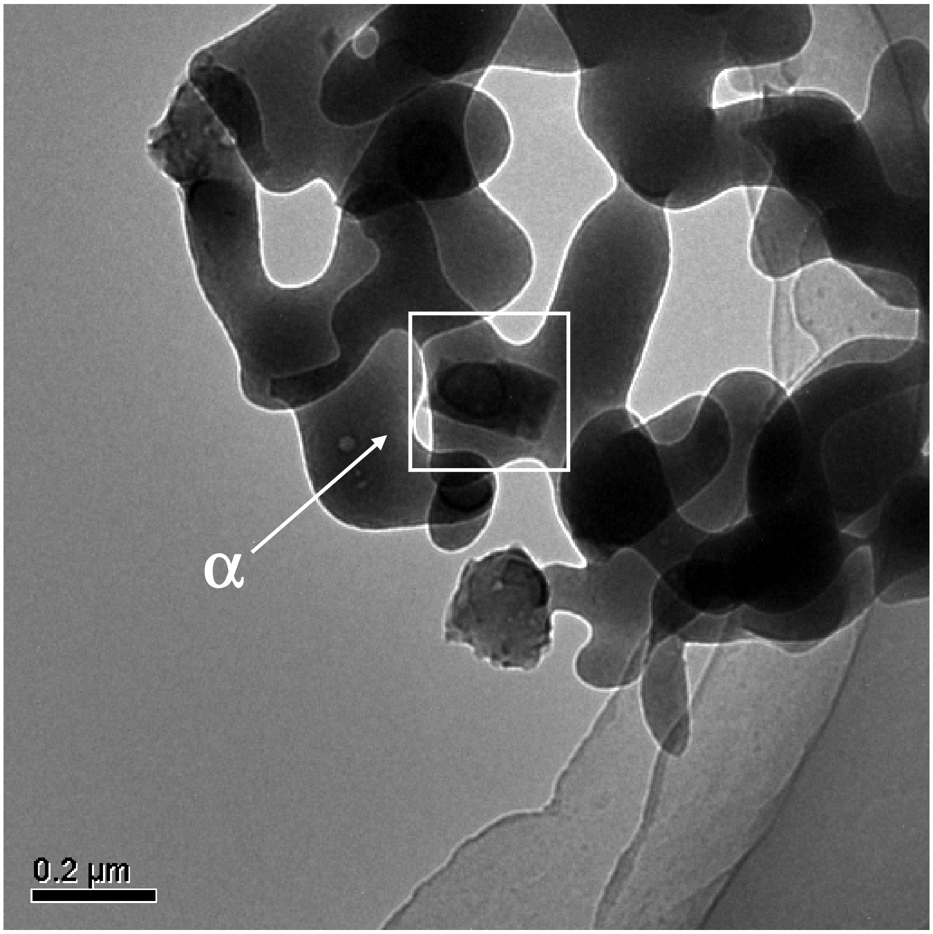


Figure S4A. TEM image of Beta-SDS sample crystallized for 4 h at the temperature of 140 °C by addition of 10.3 % Beta seeds in the starting aluminosilicate gel. This image indicates that a crystal exists in amorphous aluminosilicate gel.

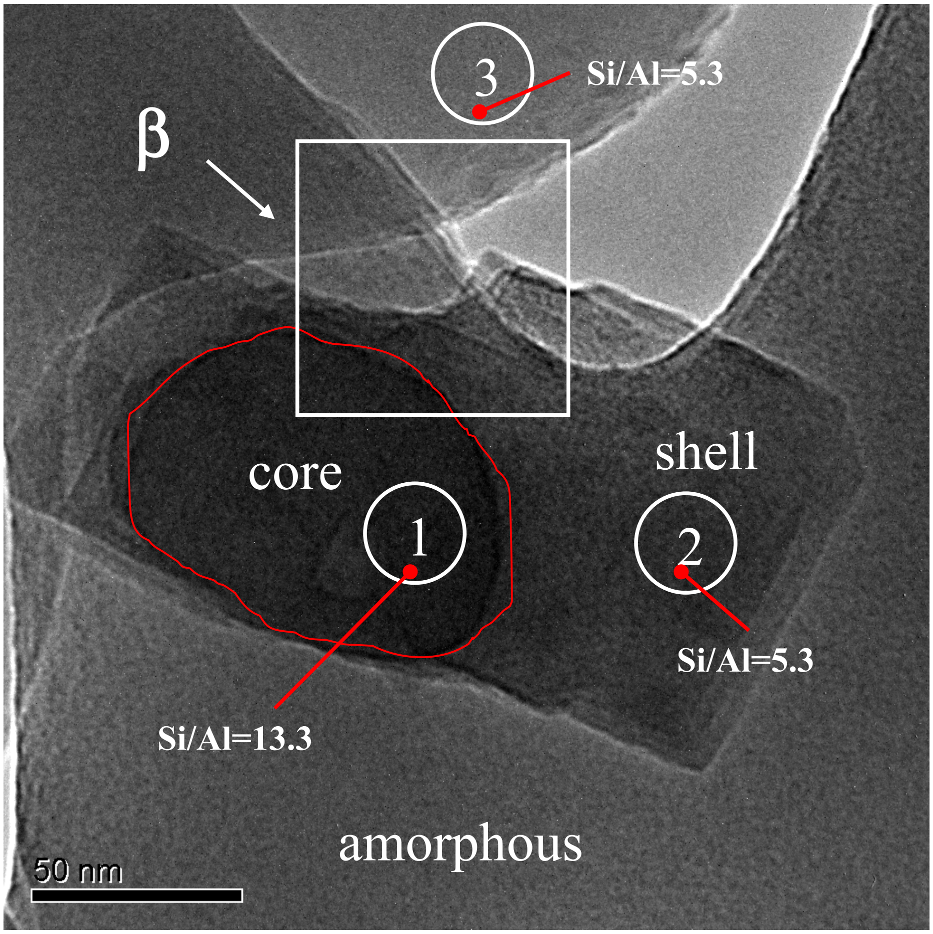


Figure S4B. HR TEM image of Area α in Figure 2b. This image confirms that there is a core (marked by red circle) in the crystal. EDS analysis shows that Si/Al ratio of the core and shell is 13.3 and 5.3, respectively. The value of the shell is the same as that of amorphous aluminosiliate gel.

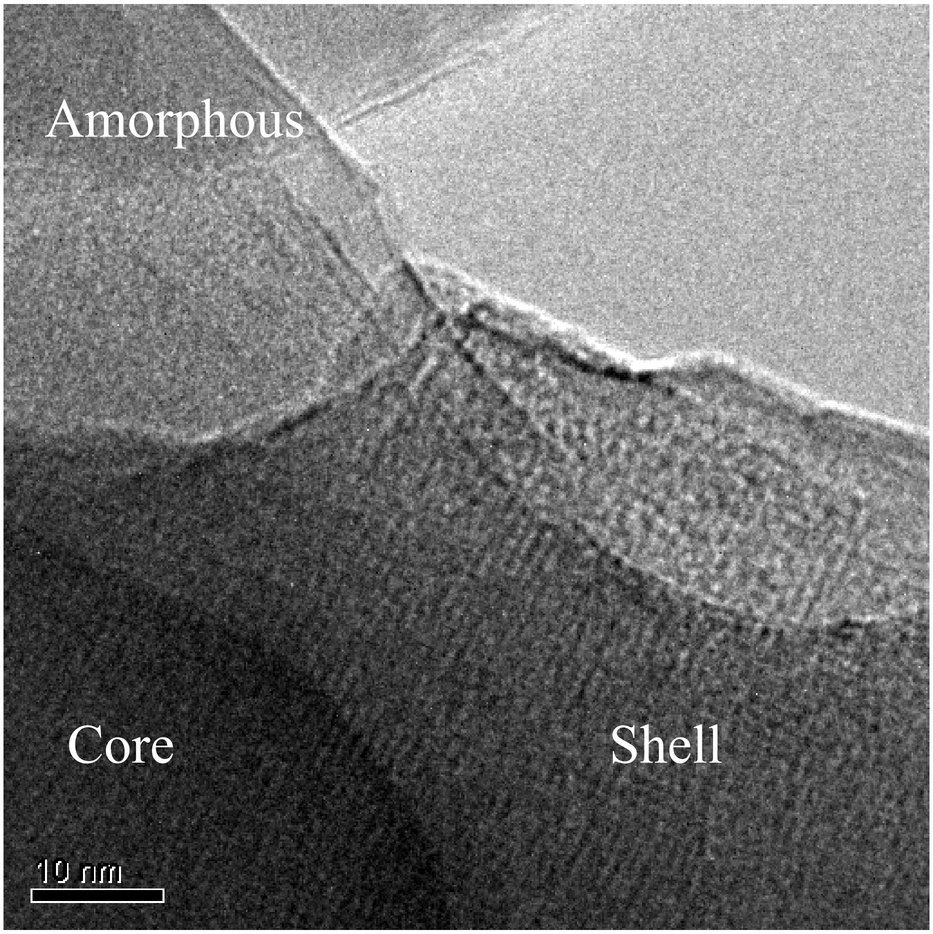


Figure S4C. HR TEM image of Area β in Fig. 2c. This image confirms the crystal with core-shell structure.

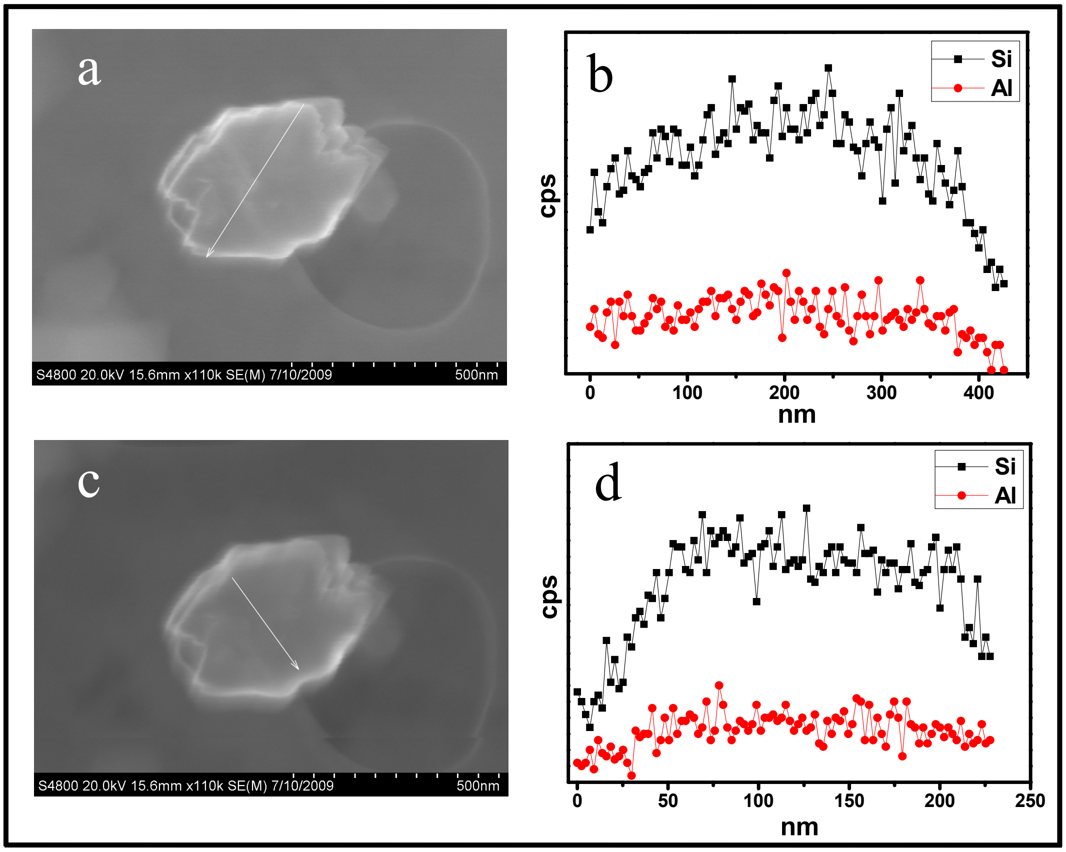


Figure S5. EDX analysis of a Beta-SDS crystal synthesized at 120 °C for 120 h in the presence of 4.6 % Beta seeds (Si/Al=11.6).

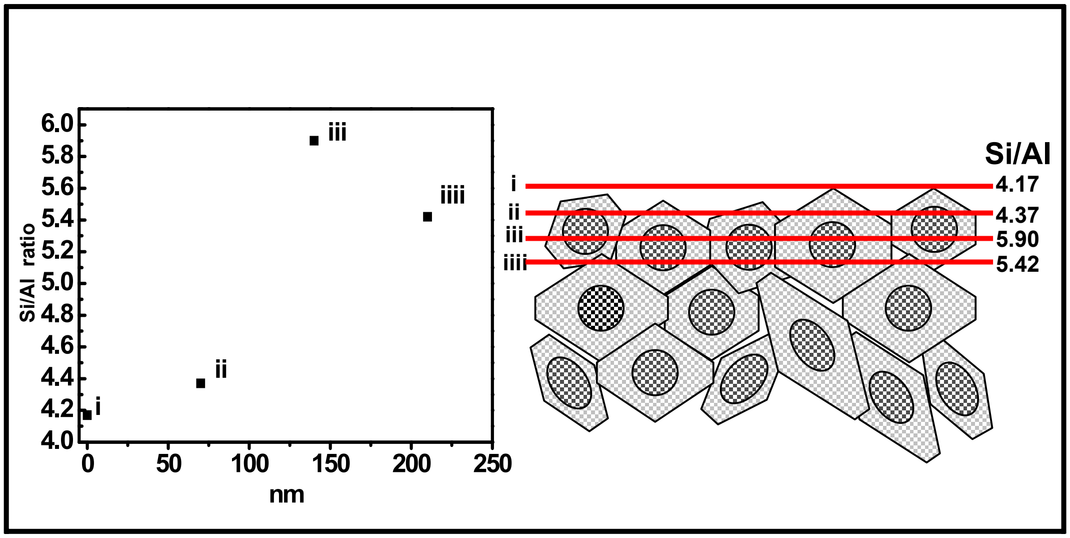


Figure S6. XPS analysis of Si/Al ratios on etching depth of Beta-SDS disk performed by Argon ion bombardment. Each of etching depth was about 70 nm.

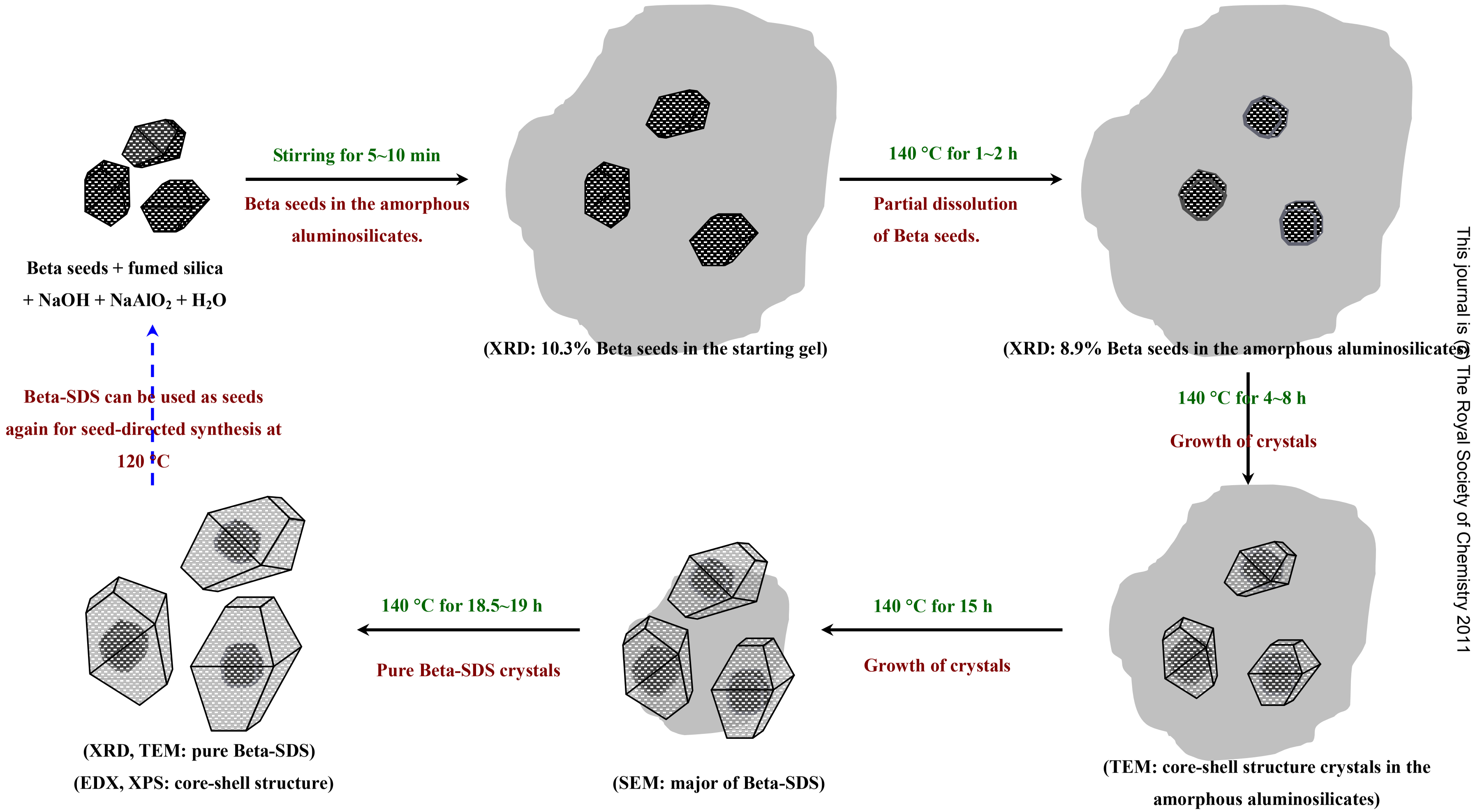


Figure S7. Proposed mechanism for the formation of Beta-SDS crystals

When Beta seeds are added in the starting aluminosilicate gels, the Beta seeds could be dispersed into amorphous aluminosilicates. Because the synthesis was carried out in strongly alkaline conditions, the crystals of Beta seeds could be partially dissolved, but most of solid Beta crystals are still remained in the amorphous phase. The undissolved solid seeds gradually grow in the amorphous aluminosilicates. Finally, pure phase of Beta-SDS would be obtained. In the final product, the Beta seed is actually the “core”, while growing part is the “shell”. It was also shown that it is possible to use the “shell” as the “core” again for further seeded growth in amorphous aluminosilicate gels. We have used Beta-SDS as seeds (core) to successfully synthesize Beta-SDS-2nd product. This phenomenon offers a route to completely avoid the use of organic templates in the synthesis of Beta zeolite. Recently, Tatsumi *et al.* reported an organotemplate-free synthesis of RTH-type zeolite (T. Yokoi, M. Yoshioka, H. Imai, T. Tatsumi, *Angew. Chem. Int. Ed.* 2009, **48**, 9884-9887), suggesting that the seed-directed approach is also suitable to the other zeolitic structures.

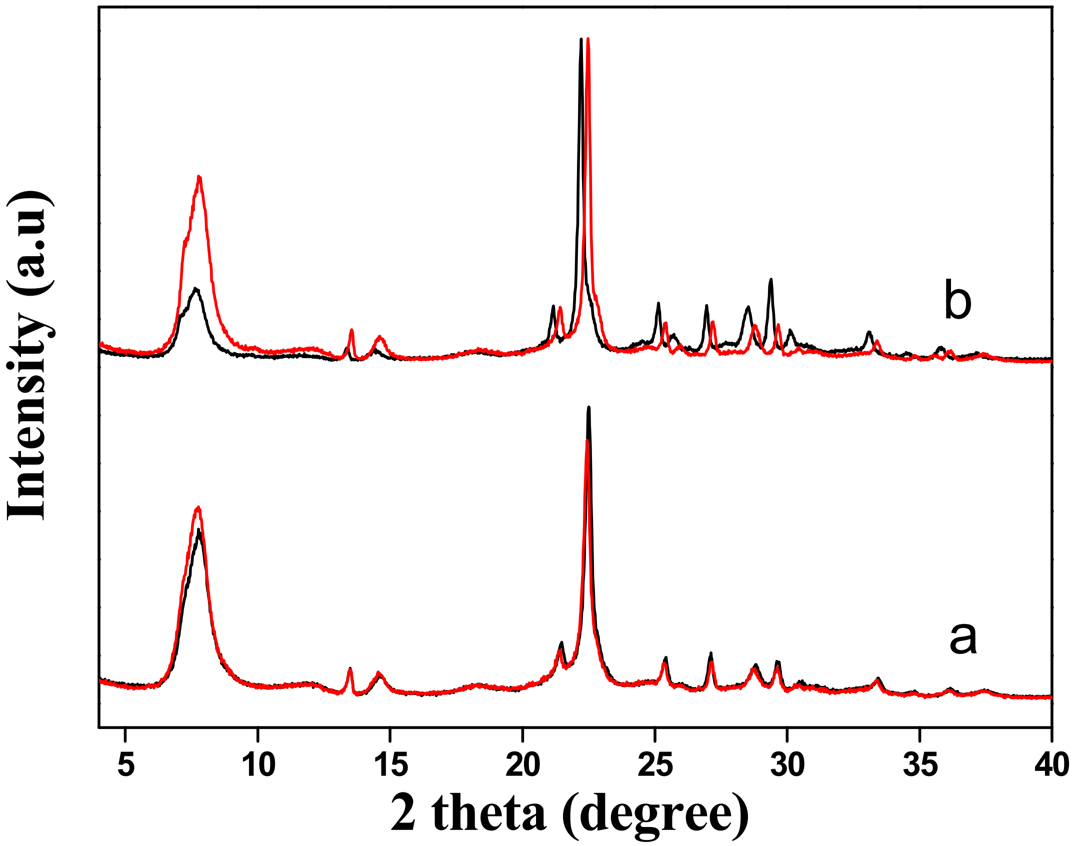
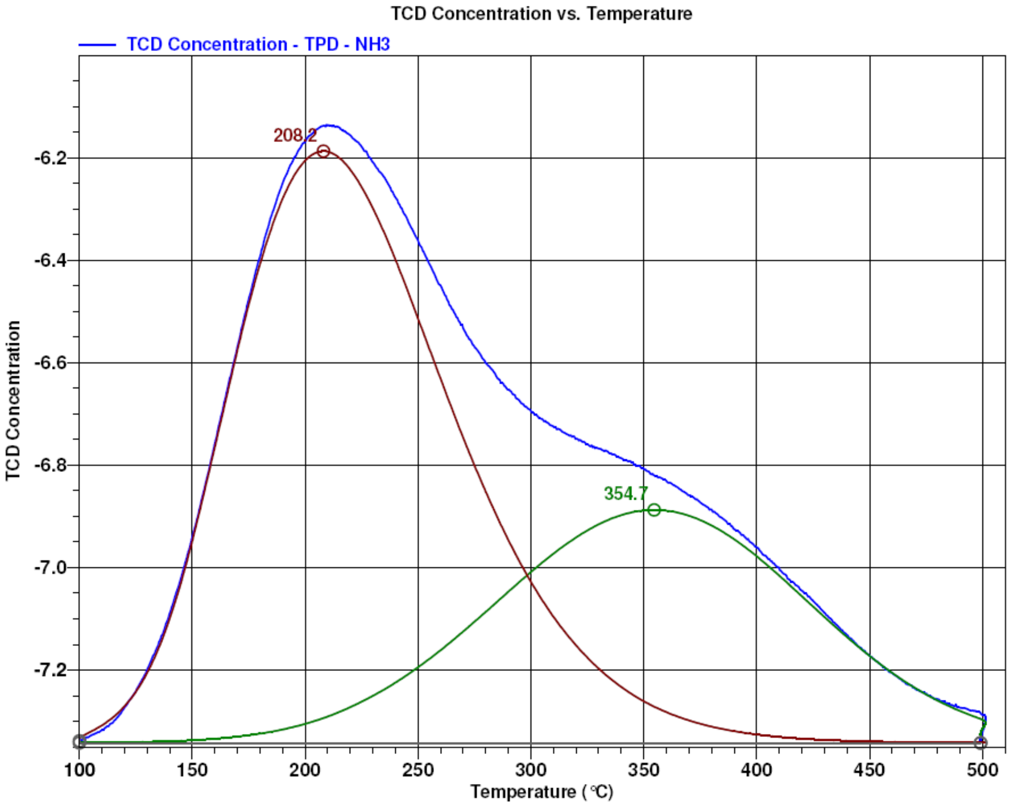


Figure S8. XRD patterns of (a) Beta-TEA and (b) Beta-SDS before (black line) and after (red line) 100% steaming treatment at 750 °C for 8 h.

(a)


TCD Concentration vs. Temperature
TCD Concentration - TPD - NH3
208.2
354.7
TCD Concentration
-6.2
-6.4
-6.6
-6.8
-7.0
-7.2
100
150
200
250
300
350
400
450
500
Temperature (℃)

(b)

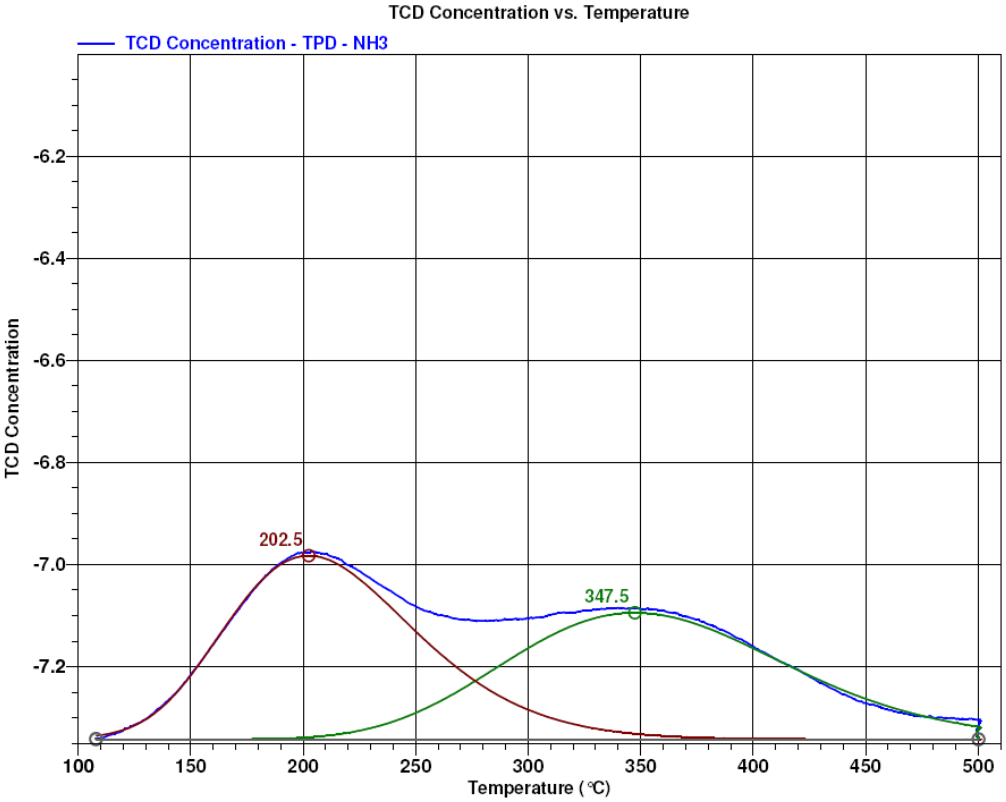


Figure S9. NH_3-TPD plots of (a) Beta-SDS and (b) Beta-TEA samples (plotted with identical scale for comparison). Integration of the data shows that the amount of desorbed NH_3 is 3.3 mmol/g for Beta-SDS and 0.9 mmol/g for Beta-TEA, suggesting substantially higher density of acid sites (active centers) for the Beta-SDS sample compared to the conventional Beta-TEA sample.

Table S1. Properties of Fushun vacuum gas oil (VGO)

Density (20°C, g/cm^3)		0.8607
Carbon Residue, wt.%		0.0032
Group composition, wt.%	Saturates	85.82
	Aromatics	11.54
	Resin	2.64
	Asphaltenes	0
Element analysis, wt.%	C	85.62
	H	13.69
	S	0.12
	N	0.18
Heavy metal content, wt.%	Ni	0.0083
	V	0.00084

Table S2. Gas-oil cracking activity and selectivities

Sample	Zeolite		
	HY	HBeta-TEA	HBeta-SDS
Gas-oil cracking conversion,[a] wt.%	79.60	92.27	95.20
Gasoline yield, wt.%	36.58	38.84	34.14
Diesel yield, wt.%	22.86	9.21	6.85
Coke yield, wt.%	2.65	7.42	9.63
Heavy oil, wt.%	20.41	7.73	4.80
Dry gas, wt.%	3.47	3.69	5.29
Liquid petroleum gas (LPG), wt.%	14.03	33.11	39.28
H_2, wt.%	0.47	0.41	0.63
Ethylene, wt.%	1.01	1.56	2.38
Propylene, wt.%	5.63	10.50	10.85
Propylane, wt.%	0.79	3.24	6.23
Butenes, wt.%	6.54	9.53	8.64
Butanes	1.11	9.89	12.65

[a] Cracking conditions: temperature at 540°C, catalyst-to-oil ratio of 5, mass of feedstock for 1 g, time on stream for 104 s.