Synthesis of short b-axis nano Zn/ZSM-5

In a typical synthesis of short b-axis nano Zn/ZSM-5 (Pristine), 13.1 g TPAOH, 11.2 g TEOS, 2.0 g urea, 0.3 g $Al(NO_3)_3 \cdot 9H_2O$, 0.1 g NaOH and 0.1 g IPA were added into 18.4 g H_2O under stirring. After stirring at room temperature for 1-2 h, the resulting solution was transferred into an autoclave for further crystallization. The autoclave was placed into a temperature programming oven. The oven was heated from room temperature to 180 ^oC with a rate of 15 ^oC/h, and then hold on for 48 h. The crystallization reaction was subsequently quenched by cold water. The obtained crystals were separated by filtration and washed by deionized water for three times, subsequently dried at 90 ^oC in air, then calcined at 550 ^oC for 5 h to remove the template. The obtained Na-ZSM-5 was converted to the ammonium form by cation-exchange in a NH_4NO_3 solution. 10 g Na-ZSM-5 was dispersed in 100 mL NH_4NO_3 solution (1 M) and vigorously stirred for 6 h. The exchange process was performed repeatedly for 3 times to complete the exchange reaction, and NH_4-ZSM-5 was formed. The HZSM-5 was obtained by calcining the NH_4-ZSM-5 powder at 550 ^oC for 5 h.

The as-prepared HZSM-5 was hydrothermally treated at 760 ^oC in 100% water vapor for 4 h to obtain the aged HZSM-5 designated as 760 HZSM-5.

The corresponding Zn-modified HZSM-5 with mass loading of Zn of 3% was prepared by traditional incipient wetness impregnation of HZSM-5 using aqueous solutions of $Zn(NO_3) \cdot 6H_2O$. After drying and calcinating in air at 550 ^oC for 5 h, the resultant catalyst was designated as pristine. If using760 HZSM-5 as the starting materials, the resultant catalysts were designated as aging.

Synthesis of DETA-ZSM-5

To synthesize DETA-ZSM-5, diethylenetriamine was used instead of urea. And the crystallization temperature was lowered to 180 ^oC. Other processes were the same as the method of pristine sample.

Synthesis of rod-like ZSM-5

To synthesize rod-like ZSM-5, 0.1 g NaCl was added and the temperature was lowered to 180 ^oC during crystallization. Other processes were the same as the method of pristine sample.

Synthesis of sheet-like ZSM-5

To synthesize sheet-like ZSM-5, NaCl was not added compared with the method of rod-like ZSM-5. Other processes were the same as above.

Characterization

X-ray diffractions (XRD) were recorded on a Rigaku D/Max-RB diffractometer with Cu KαRadiation at 40 kV and 120 mA. Scanning electron microscope (SEM) images were obtained by a high-resolution scanning electron microscope (JEOL, JSM-7401) at 3.0 kV. TEM, EDX and STEM experiments were performed on high-resolution transmission electron microscopes (Titan Themis^3 300, exited at 300 kV and JEOL, JEM-2010, exited at 120 kV). Brunauer-Emmett-Teller (BET) surface area were recorded in a Quantachrome automated surface area and porosity analyzer with Ar as the adsorption gas. NH_3-TPD was recorded in a Quantachrome automated chemisorption analyzer from room temperature to 700 ^oC with a ramp of 10 ^oC/min. The Si/Al of the zeolite was obtained by an inductively coupled plasma optical emission spectrometer (ICP-OES, IRIS Intrepid II XSP). NMR spectra were obtained on a Bruker AVANCE III 600 spectrometer. Brønsted acid sites and Lewis acid sites were determined by pyridine adsorption. The samples were first dried, *in situ*, by heating to 420 ^oC under vacuum, and then were cooled to 100 ^oC. At this temperature, the samples were exposed to pyridine vapor using an equilibration time of 30 min. After the physically adsorbed pyridine molecules were removed by outgassing at 200 ^oC for 1 h, IR spectra were collected at 200 ^oC with 4 cm^{-1} resolution using a Bruker Tensor 27 FTIR spectrometer. After the

collection was done, the samples were heated to 350 ^{o}C to desorb pyridine molecules adsorbed at weak acid sites for 30 min. IR spectra were collected at 350 ^{o}C.

Catalytic conversion of methanol to aromatics

The MTA reactions were performed at the conditions of 1 atm, 475 ^{o}C and WHSV=0.8 h^{-1} (under N_2 flow (10 mL/min)) in a conventional fixed bed stainless steel reactor (13.0 mm i.d.) equipped with a thermocouple in the middle of the catalyst bed. 1.0 g catalyst was placed in the fixed bed reactor. The flow rate of the pure methanol and N_2 was controlled using a dual micro-plunger pump and the mass flow controllers, respectively. The products (hydrocarbons) were analyzed using two flame ionization detectors (FIDs). The conversion of methanol and the selectivity of the different products were calculated (carbon base) by considering the oxygenates (methanol and dimethylether) as the unconverted reactants.

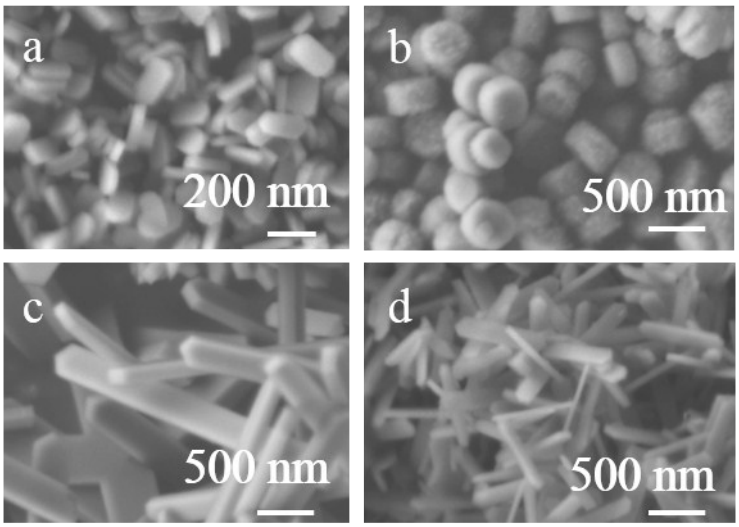

Figure S1 SEM images of a) pristine, b) DETA-ZSM-5, c) rod-like ZSM-5, d) sheet-like ZSM-5.

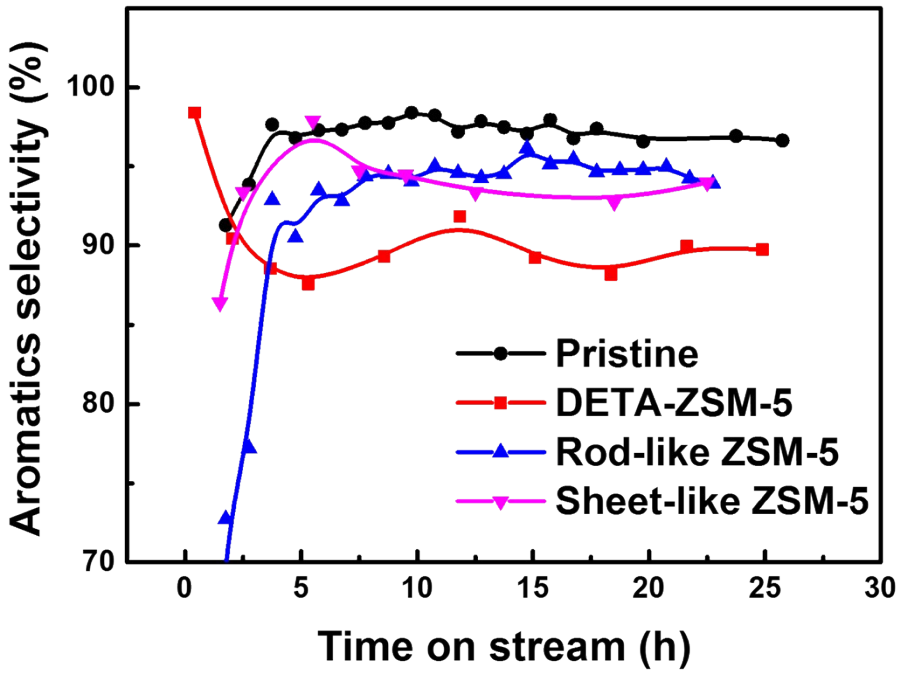

Figure S2 Methanol conversion and aromatic selectivity of Pristine, DETA-ZSM-5, rod-like ZSM-5 and sheet-like ZSM-5. Reaction temperature: 475 ^{o}C, reaction pressure: atmospheric pressure, WHSV: 0.8 h^{-1}.

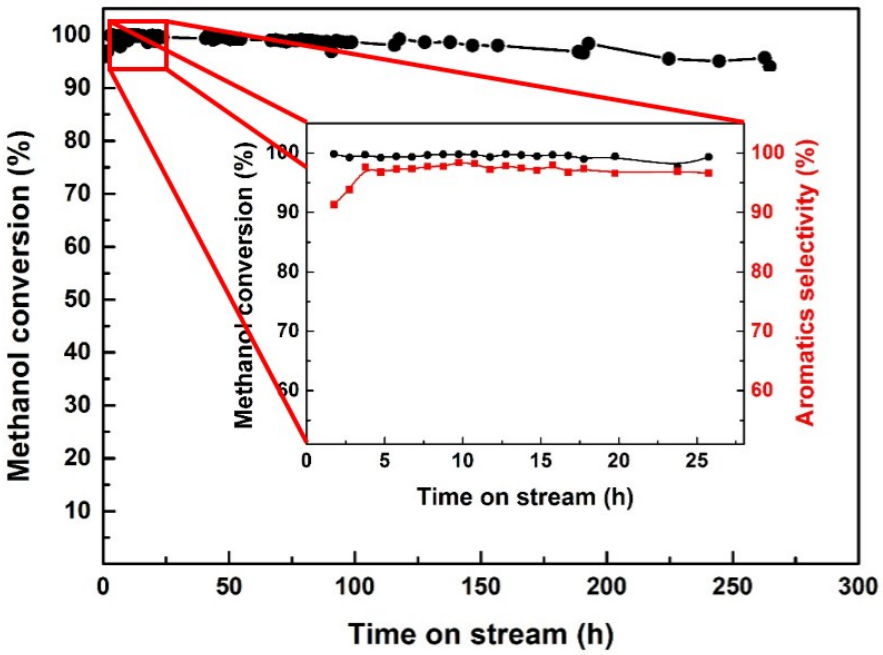

Figure S3 Long time methanol conversion and aromatic selectivity performance of pristine. Reaction temperature: 475 ^{o}C, reaction pressure: atmospheric pressure, WHSV: 0.8 h^{-1}.

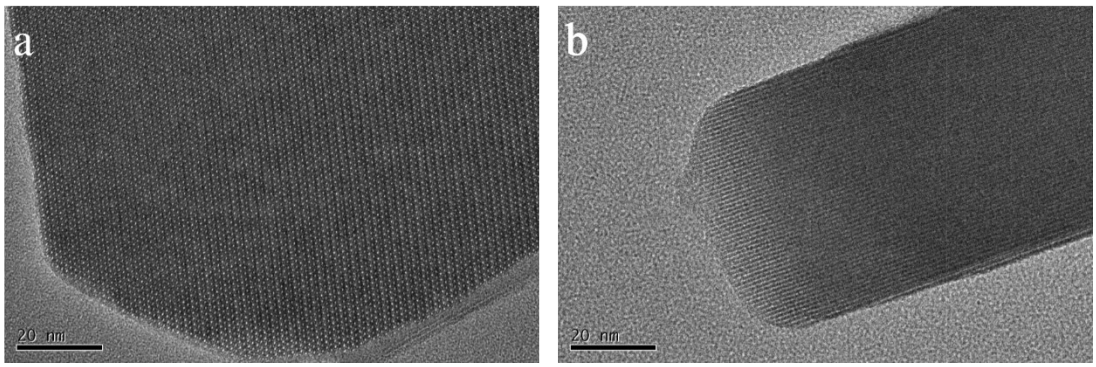

Figure S4 TEM images of pristine along a) b-axis and b) a-axis

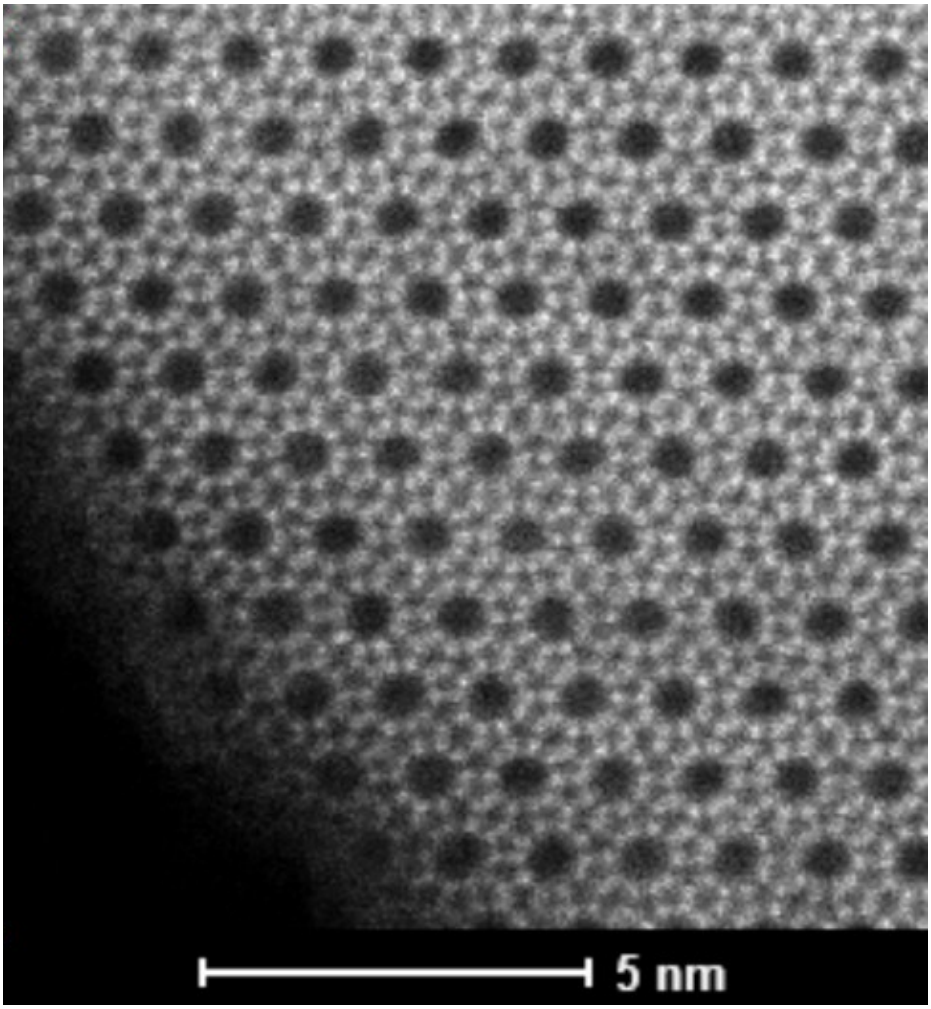

Figure S5 Cs-corrected STEM image of pristine

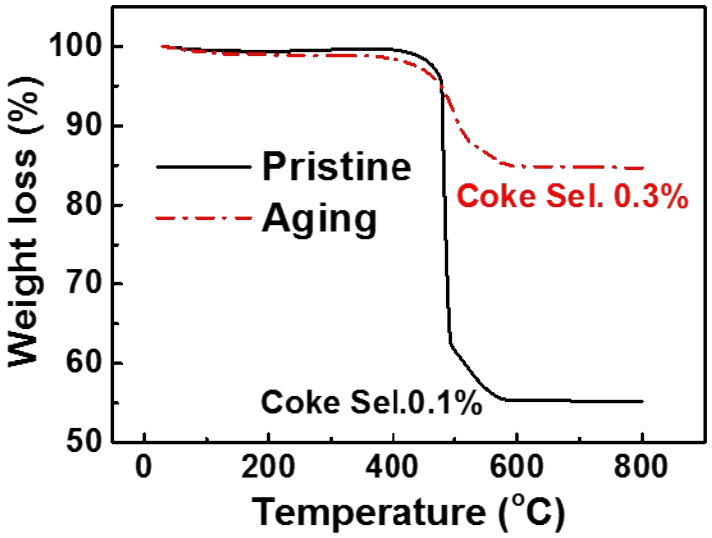

Figure S6 Thermo gravimeter (TG), coke selectivity & inset DSC profiles of coked pristine and aging samples. Oxidation gas: 20% O_2/N_2, heating rate 10 ^oC/min

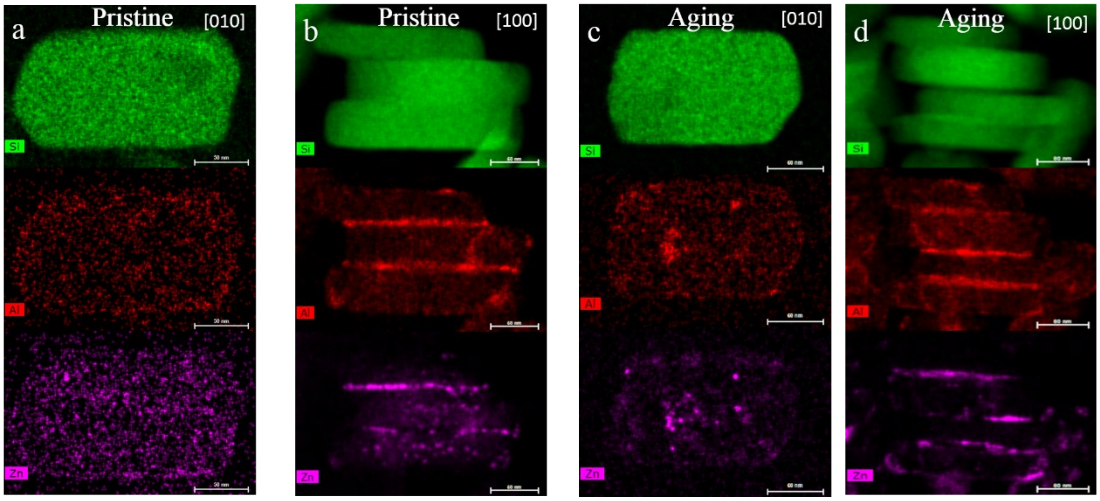

Figure S7 EDX analysis of pristine and aging samples

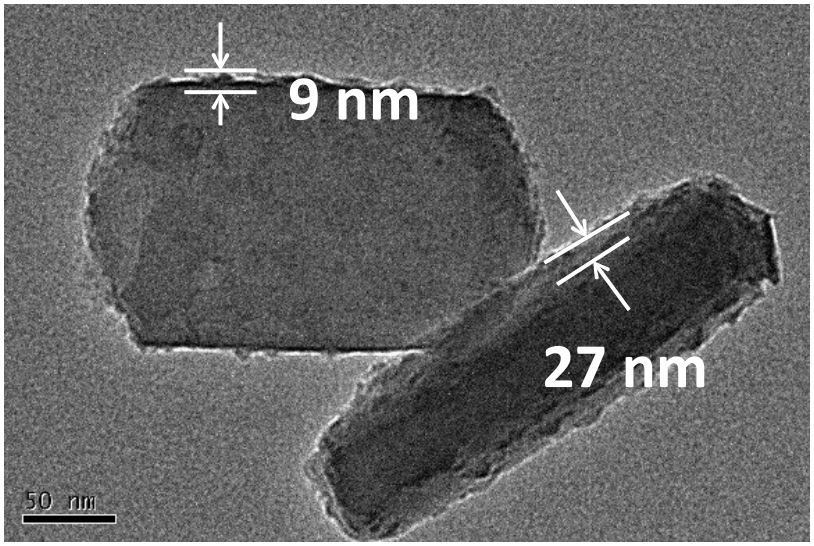

Figure S8 TEM image of used aging sample

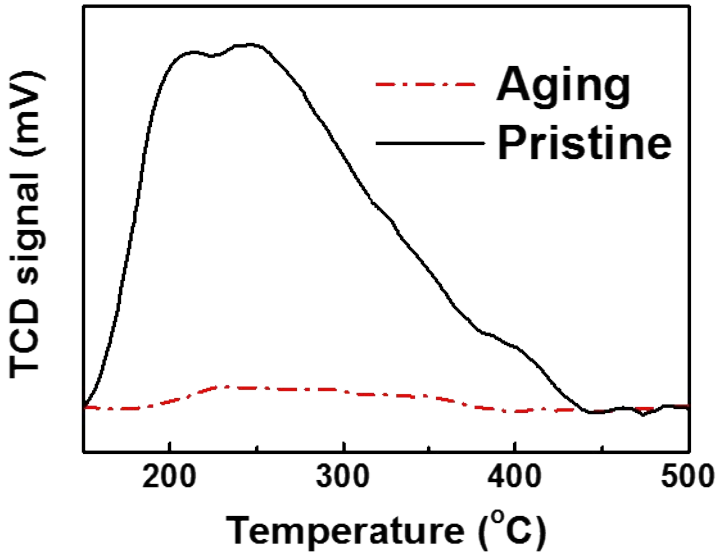

Figure S9 NH_3-TPD adsorption spectra of pristine and aging samples

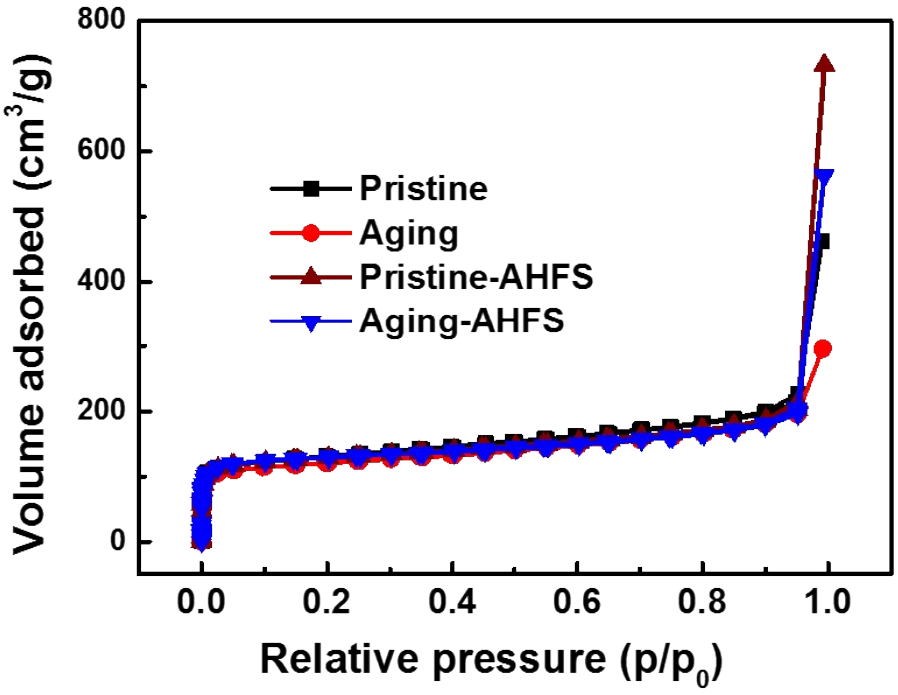

Figure S10 Ar adsorption/desorption isotherms of pristine, aging, pristine-AHFS, and aging-AHFS

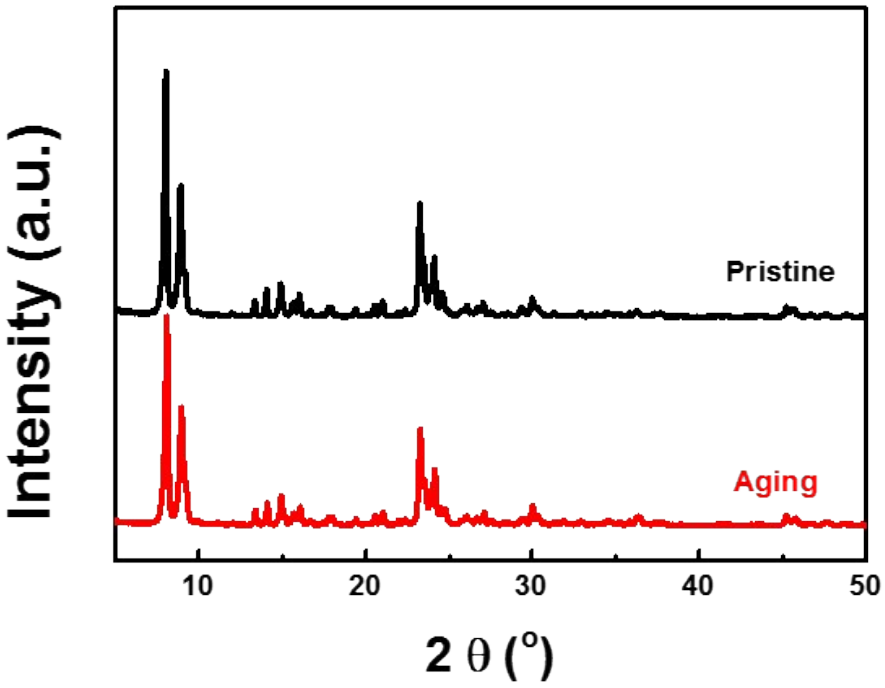

Figure S11 XRD patterns of pristine, aging samples

Table S1 Physical and chemical characters of pristine, aging, pristine-AHFS and aging-AHFS samples

Samples	Si/Al ratio[a]	BET Specific Area (m^2/g)	B/L molar ratio
H-pristine	---	---	0.690
Pristine	64.5	427	0.001
Aging	58.2	403	0
Pristine-AHFS	287	433	---
Aging -AHFS	667	442	----

[a] Determined by ICP.