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Supporting Information

Amorphous Aluminosilicate Nanosheets as Universal Precursors for the Synthesis of Diverse Zeolite Nanosheets for Polymer-Cracking Reactions

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Supporting Information
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Amorphous Aluminosilicate Nanosheets as Universal Precursors for the Synthesis of Diverse Zeolite Nanosheets for Polymer-Cracking Reactions

Koki Sasaki, Jose Andres Hernandez Gaitan, Tsuyoshi Okue, Shotaro Matoba, Yuki Tokuda, Koji Miyake, Yoshiaki Uchida,* and Norikazu Nishiyama

Abstract: Zeolites catalyze some reactions in their molecular-sized pores, but large molecules can react only on their external surface. Zeolite-nanosheets (NSs) have been developed as catalysts for large molecules. The previously reported methods to synthesize zeolite-NSs are specialized for each crystal. Here we propose a new method to synthesize various zeolite-NSs from the same amorphous aluminosilicate NSs (AAS-NSs) as a universal precursor. We successfully synthesized the unprecedented AAS-NSs in the hydrophilic space of the stable hyperswollen lyotropic lamellar (HL) phase. The four zeolite types could be obtained from the single-species AAS-NSs. These results imply that this method enables us to synthesize almost all types of zeolite-NSs. Moreover, the synthesized CHA-NSs have great potential for various applications because of their thickness and large external surface area.

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Experimental Procedures

Materials

Decane, 1-pentanol, ethanol, *p*-octylbenzenesulfonate (SOBS), tetraethyl orthosilicate (TEOS), sodium hydroxide (NaOH) and aluminum isopropoxide ($\text{Al}(\text{O-}i\text{-Pr})_3$) were purchased from Wako Pure Chemical Industries Co. 20 – 25 wt% tetrapropylammonium hydroxide (TPAOH) was purchased from Tokyo Chemical Industry Co., Ltd. Low density polyethylene powder (LDPE) (500 μm) was purchased from Alfa Aesar. 25 wt% N,N,N-trimethyl-1-adamantanammonium hydroxide (TMAdaOH) was donated from SACHEM, Inc. The water used was obtained from a water purifier (Direct-Q UV) with a resistivity of 18.2 M Ωcm .

Synthesis methods

Amorphous aluminosilicate nanosheets synthesis

Amorphous aluminosilicate nanosheets (AAS-NSs) were synthesized in the hyperswollen lyotropic lamellar (HL) phases of the decane solutions of SOBS (0.95 wt %), 1-pentanol (8.4 wt %), and deionized water (1.1 wt %). NaOH (9.4×10^{-3} wt%), TEOS (0.25 wt%), and $\text{Al}(\text{O-}i\text{-Pr})_3$ (1.2×10^{-2} wt%) was added to the decane solution and stirred at 60°C for 24 hours. After stirred, we added ethanol to this solution and did centrifugal separation. After drying at 90°C for 24 h, the white powder, mixture of AAS-NSs and SOBS, was collected.

CHA type zeolite nanosheets synthesis

TMAdaOH solution (1.4 g) was added to the AAS-NSs coated with SOBS (0.215 g) and mixed. After drying at 90°C for 24 h, the resulting gel was put in a Teflon-lined stainless steel autoclave with water separately where the reaction take place with the steam produced. Treatment was carried out at 160°C for 96 h. After the autoclave was cooled down at room temperature, the product was washed with deionized water and dried 90°C. The catalyst was calcined in air at 550°C for 5 h to eliminate the organic template.

PHI type zeolite nanosheets synthesis

TMAdaOH solution (1.4 g) was added to the AAS-NSs coated with SOBS (0.215 g) and mixed. After drying at 90°C for 24 h, the resulting gel was put in a Teflon-lined stainless steel autoclave with water separately where the reaction take place with the steam produced. Treatment was carried out at 160°C for 48 h. After the autoclave was cooled down at room temperature, the product was washed with deionized water and dried 90°C. The catalyst was calcined in air at 550°C for 5 h to eliminate the organic template.

SOD type zeolite nanosheets synthesis

NaOH (0.015 g) and water (0.2 g) were added to the AAS-NSs coated with SOBS (0.215 g) and put in a Teflon-lined stainless steel autoclave with water separately where the reaction take place with the steam produced. Treatment was carried out at 180°C for 48 h. After the autoclave was cooled down at room temperature, the product was washed with deionized water and dried 90°C.

MFI type zeolite nanosheets synthesis

TPAOH solution (1.2 g) was added to the mixture of AAS-NSs coated with SOBS (0.215 g) and mixed. After drying at 90°C for 24 h, the resulting gel was put in a Teflon-lined stainless steel autoclave with water separately where the reaction take place with the steam produced. Treatment was carried out at 180°C for 48 h. After the autoclave was cooled down at room temperature, the product was washed with deionized water and dried 90°C. The product was calcined in air at 550°C for 5 h to eliminate the organic template.

Catalytic test

LDPE was dissolved in the toluene at 70°C, and added the toluene dispersion of CHA-NSs. After drying the solution, we obtained the mixture of LDPE and CHA-NSs. The LDPE cracking test was carried out using a fixed-bed reactor made of quartz glass (id 4 mm) with a continuous-flow system under atmospheric pressure at 500°C. Helium gas was introduced at 10 mL min⁻¹. The products were analyzed online with a Shimadzu GC-2025 gas chromatograph equipped with a flame ionization detector.

Characterization methods

X-ray Diffraction (XRD) Measurements

The crystal structures were estimated from XRD patterns collected using a PANalytical X'Pert PRO diffractometer with Cu K α radiation, operated at 45 kV and 40 mA. The scan range was from 30° to 45° (2 θ) at 0.10°s⁻¹. The full width at half maximum was calculated using X'Pert Data Viewer.

Dynamic Light Scattering (DLS)

The distributions of samples were measured by DLS using ELSZ-2000 (Otsuka Electronics Co., Ltd.) at 25°C.

Atomic Force Microscopy (AFM)

AFM images were obtained using a Veeco Instruments MMAFM-2. The samples were deposited on freshly exfoliated mica sheets as substrates. We measured 15 samples and calculated the average and standard deviation of the size and thickness, respectively.

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Transmission Electron Microscopy (TEM)

TEM images were obtained using a Hitachi H-800 at 200 kV.

Field Emission Transmission Electron Microscopy (FE-TEM)

FE-TEM images were obtained using a Hitachi HF-2000 at 200 kV.

Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy (SEM-EDX)

SEM-EDX images were obtained using a JEOL JCM-7000 microscope at 15 kV.

Nitrogen adsorption isotherms

The porosity of the products was characterized by nitrogen adsorption measurements using a BELSORPmax (MicrotracBEL).

Ammonia's Temperature-Programmed Deposition (NH₃-TPD)

The acidic properties of the samples were analyzed by NH₃-TPD measurement using a MicrotracBEL BELCAT II as follows. About 0.05 g of sample was pretreated under a He flow at 773 K for 1 h and then cooled to the adsorption temperature of 373 K. A gas mixture of NH₃ and He (1 vol% of NH₃) was introduced into the sample cell for 1 h. Subsequently, He (30 cm³ (STP) min⁻¹) was passed through the sample to remove weakly adsorbed NH₃ for 1 h. Then, the sample was heated up to 973 K at a rate of 10 K min⁻¹. The desorbed NH₃ signal was recorded on a quadrupole mass spectrometer (MicrotracBEL, BELMass).

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Results and Discussion

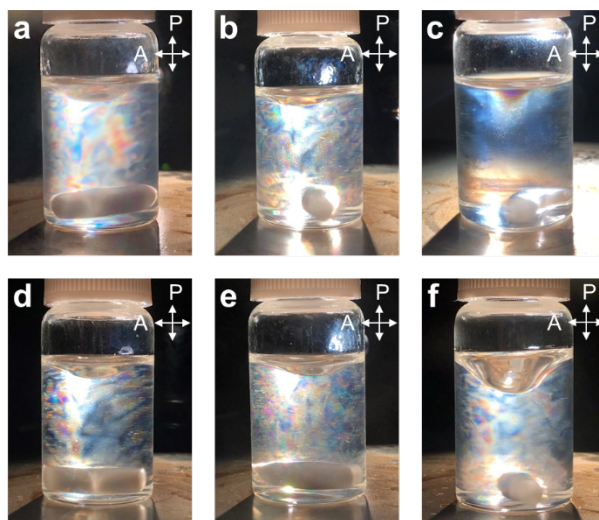


Figure S1. Liquid crystalline textures of hyperswollen lyotropic lamellar phases. These are decane solutions of SOBS (0.95 wt%), 1-pentanol (8.4 wt%), and water (1.1 wt%) with the following additives at 60°C: a) No additives, b) NaOH (9.4×10^{-3} wt%), c) NaOH (3.8×10^{-2} wt%), d) NaOH (9.4×10^{-3} wt%) and TEOS (0.25 wt%), e) NaOH (9.4×10^{-3} wt%) and Al(O-*i*-Pr)₃ (1.2×10^{-2} wt%), and f) NaOH (9.4×10^{-3} wt%), TEOS (0.25 wt%) and Al(O-*i*-Pr)₃ (1.2×10^{-2} wt%). Samples are placed between crossed polarizers.

Table S1. Specific surface area (S_{total}), external surface area (S_{ext}) and pore volume (V_{total}) of AAS bulk samples and AAS-NSs after filtration measured by nitrogen adsorption isotherms.

| | $S_{\text{total}}^{[a]} / \text{m}^2\text{g}^{-1}$ | $S_{\text{ext}}^{[b]} / \text{m}^2\text{g}^{-1}$ | $V_{\text{total}}^{[b]} / \text{cm}^3\text{g}^{-1}$ |
|------------------|--|--|---|
| AAS bulk samples | 35 | 1.3 | 0.07 |
| AAS-NSs | 63 | 63 | 0.75 |

[a] BET surface area calculated using the BET method applied to the nitrogen adsorption isotherm.

[b] S_{ext} , and V_{total} calculated using the α_s -plot method applied to the nitrogen adsorption isotherm.

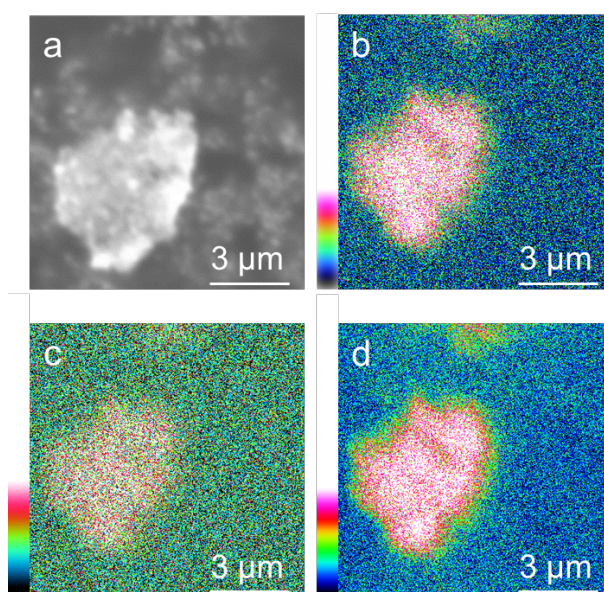


Figure S2. SEM-EDX photographs of one of the synthesized AAS-NSs. a) SEM photograph of one of the synthesized AAS-NSs. EDX mapping of b) silicon, c) aluminum, and d) oxygen elements in one of the synthesized AAS-NSs.

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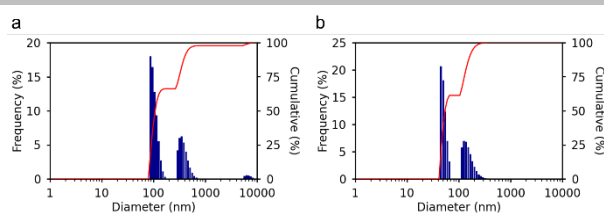


Figure S3. DLS analysis. a) AAS-NSs after centrifugal separation. b) AAS-NSs separated by filtration.

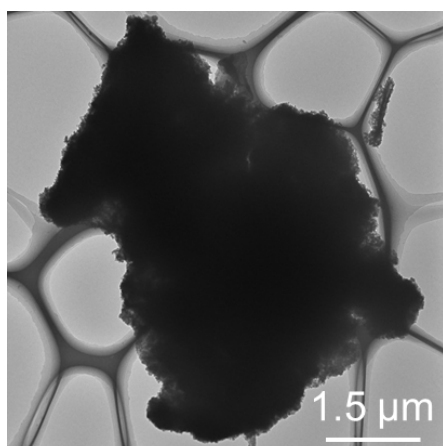


Figure S4. TEM photograph of a particle in the obtained white powder crystalizing after washing SOBS.

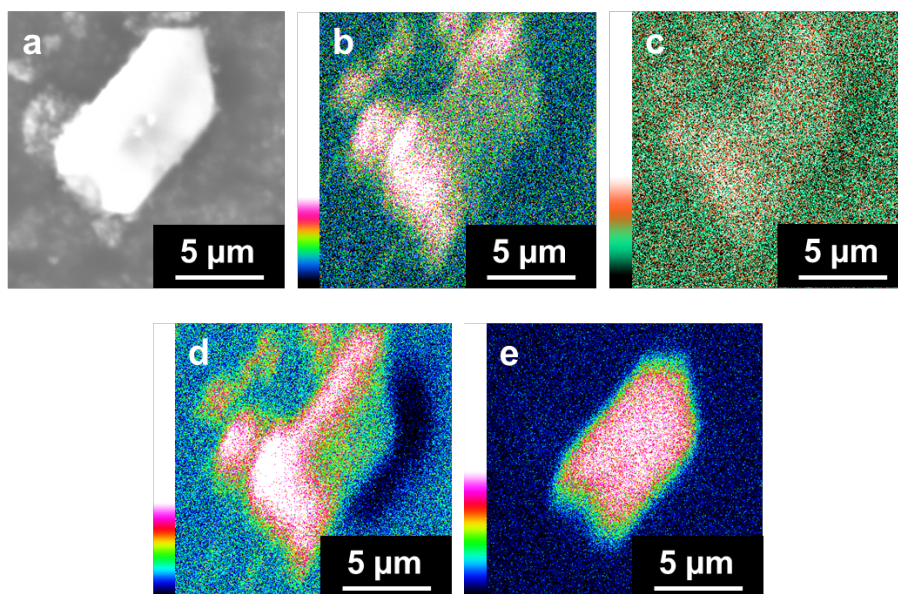


Figure S5. SEM-EDX photographs of one of the synthesized AAS-NSs coated with SOBS. a) SEM photograph of one of the synthesized AAS-NSs. EDX mapping of b) silicon, c) aluminum, d) oxygen, and e) sulfur elements in one of the synthesized AAS-NSs.

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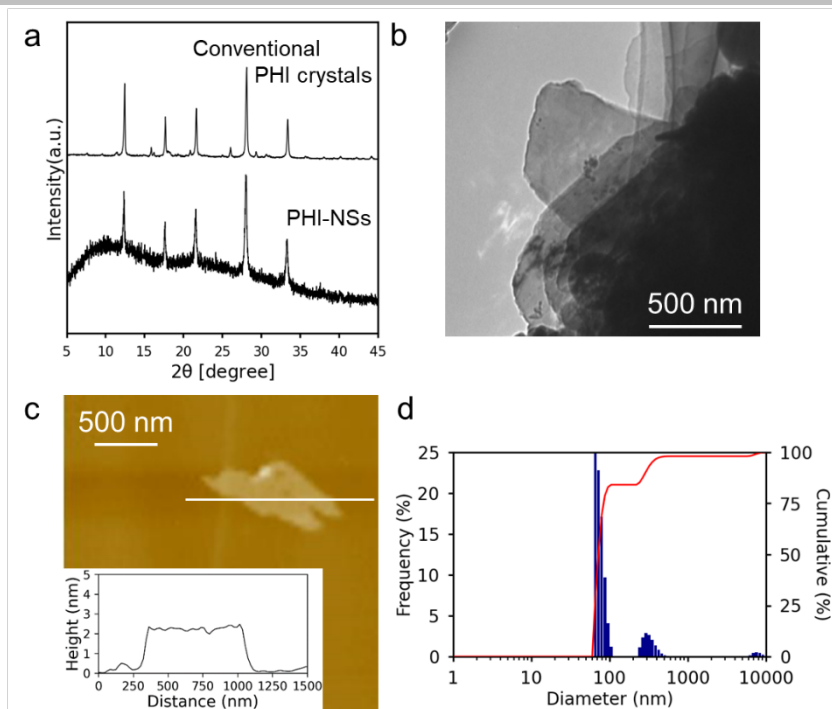


Figure S6. Characterization of synthesized PHI-NSs. a) XRD pattern of PHI-NSs. b) TEM photograph of one of the synthesized PHI-NSs. c) AFM photograph and cross section of one of the synthesized PHI-NSs. d) DLS analysis of PHI-NSs.

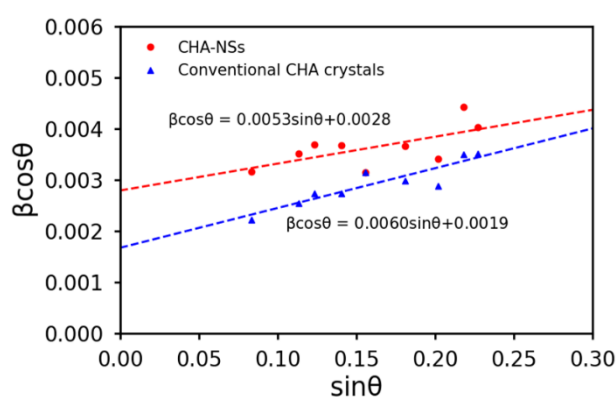
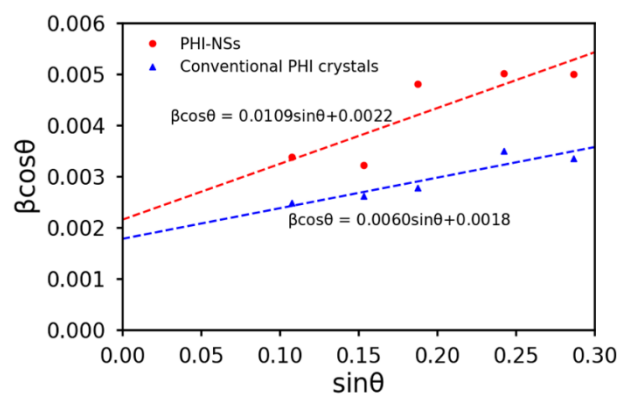
Table S2. XRD peak positions and full widths at half maximum for CHA-NSs and conventional CHA crystals.

| Peak (2θ) | Full width at half maximum (°) | |
|-----------|--------------------------------|---------------------------|
| | CHA-NSs | Conventional CHA crystals |
| 9.6 | 0.182 | 0.128 |
| 13.0 | 0.203 | 0.147 |
| 14.1 | 0.213 | 0.158 |
| 16.2 | 0.213 | 0.158 |
| 17.9 | 0.183 | 0.183 |
| 20.8 | 0.213 | 0.174 |
| 23.3 | 0.200 | 0.169 |
| 25.2 | 0.260 | 0.206 |
| 26.2 | 0.237 | 0.207 |
| 28.0 | 0.311 | 0.195 |
| 28.4 | 0.134 | 0.179 |

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Table S3. XRD peak positions and full widths at half maximum for PHI-NSs and conventional PHI crystals.

| Peak (2 θ) | Full width at half maximum (°) | |
|--------------------|--------------------------------|---------------------------|
| | PHI-NSs | Conventional PHI crystals |
| 12.4 | 0.195 | 0.143 |
| 17.7 | 0.187 | 0.152 |
| 21.6 | 0.281 | 0.162 |
| 28.1 | 0.296 | 0.207 |
| 33.3 | 0.299 | 0.201 |

**Figure S7.** Williamson-Hall plots of CHA-NSs (red) and conventional CHA crystals (blue). In the equations, β is full width at half maximum, η is internal strain, K is Scherrer constant, λ is the X-ray wavelength, and D is crystallite size. The Scherrer constant used was 0.94. The estimated D s for CHA-NSs and conventional CHA crystals are 51 nm and 76 nm, respectively.**Figure S8.** Williamson-Hall plots of PHI-NSs (red) and conventional PHI crystals (blue). In the equations, β is full width at half maximum, η is internal strain, K is Scherrer constant, λ is the X-ray wavelength, and D is crystallite size. The Scherrer constant used was 0.94. The estimated D s for PHI-NSs and conventional PHI crystals are 66 nm and 81 nm, respectively.

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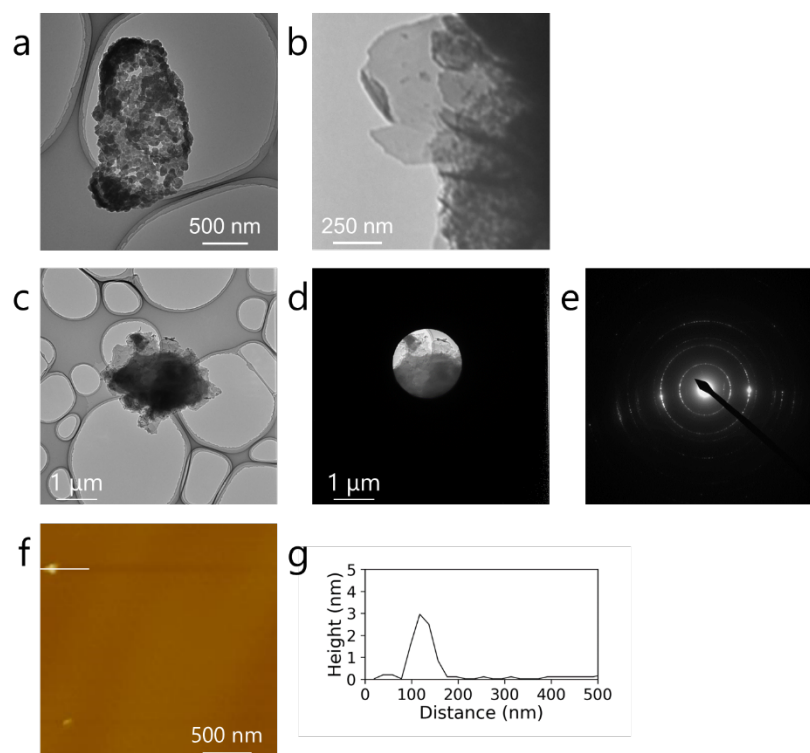


Figure S9. TEM and AFM photographs of PHI-NSs. TEM photographs of a) small PHI-NSs and b) large PHI-NSs. TEM photographs c) without and d) with selected area diffraction aperture. e) SAED pattern. f) AFM photograph and g) cross section of one of the synthesized PHI-NSs.

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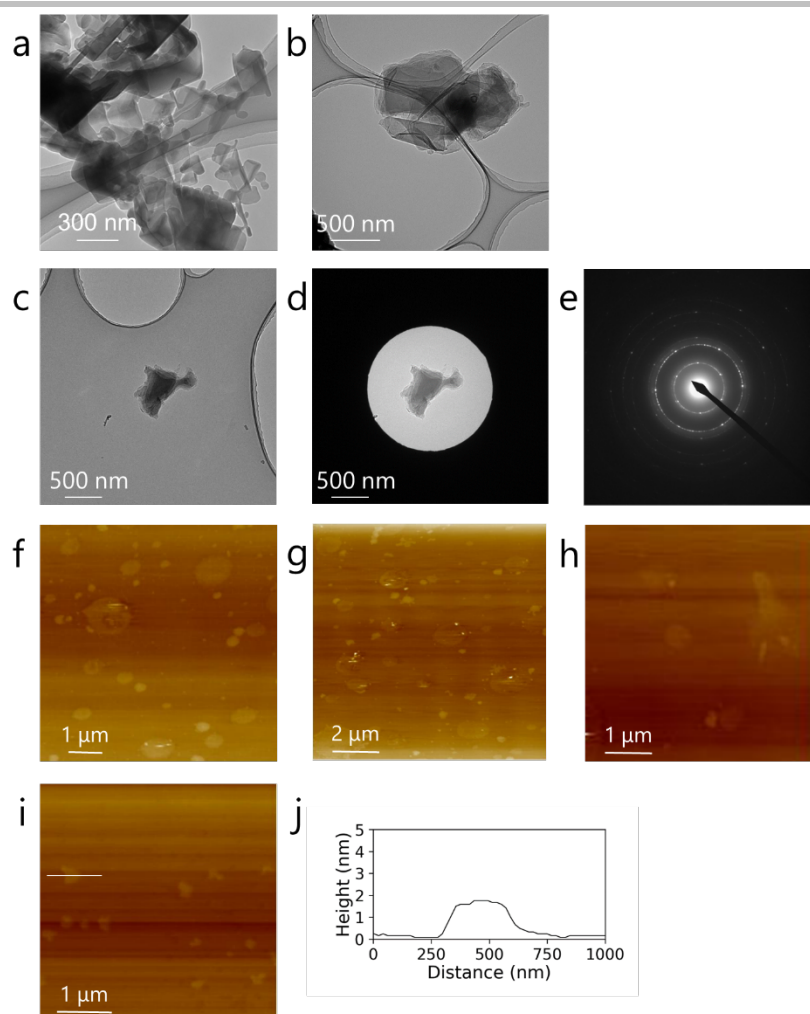


Figure S10. TEM and AFM photographs of CHA-NSs. TEM photographs of a) small CHA-NSs and b) large CHA-NSs. TEM photographs c) without and d) with selected area diffraction aperture. e) SAED pattern. f)-i) AFM photograph and j) cross section of one of the synthesized CHA-NSs.

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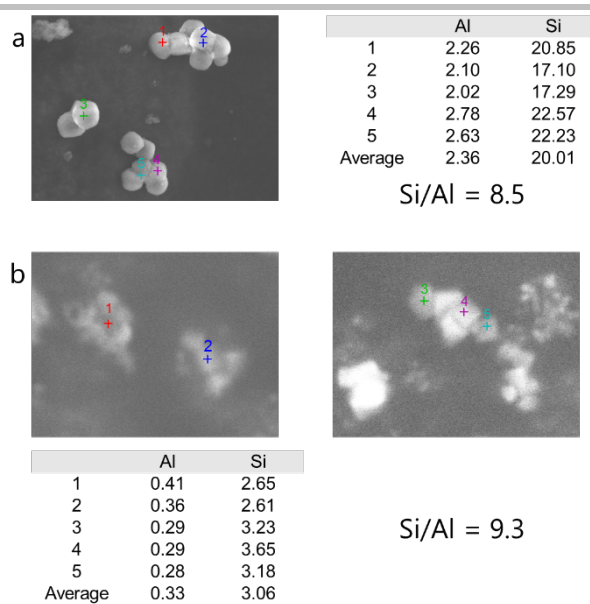


Figure S11. SEM-EDX spectra and Si/Al ratio for CHA zeolites. a) Conventional CHA crystals. b) CHA-NSs.

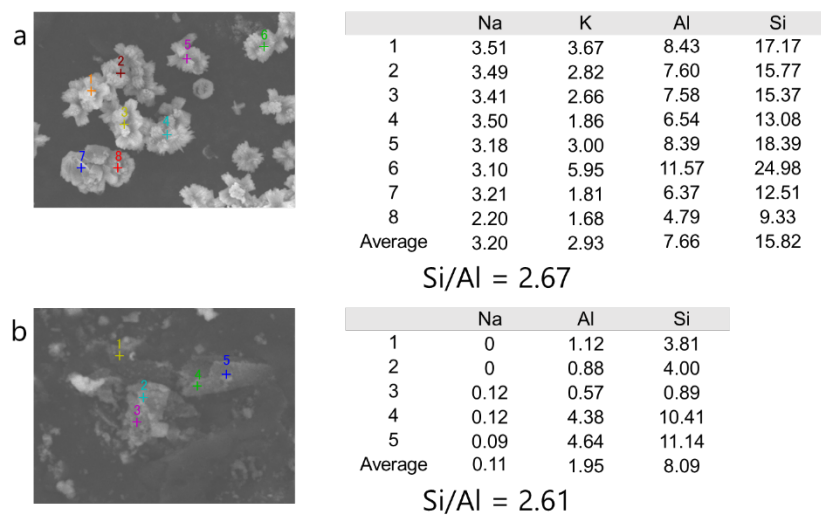


Figure S12. SEM-EDX spectra and Si/Al ratio for PHI zeolites. a) Conventional PHI crystals. b) PHI-NSs.

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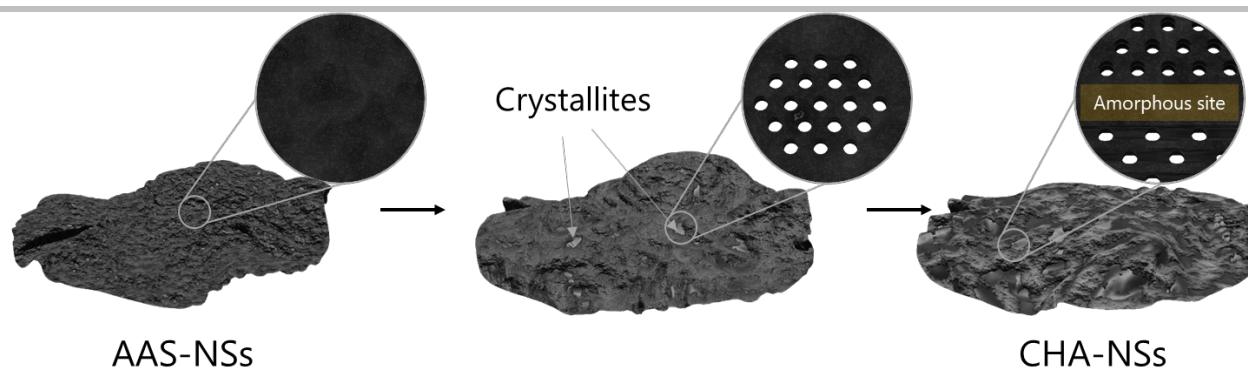


Figure S13. Schematic illustration of the crystallization process of the CHA-NSs. Crystallization begins at many points, and each crystallite grows individually, resulting in the residual amorphous sites at the boundaries between the crystallites due to inconsistency.

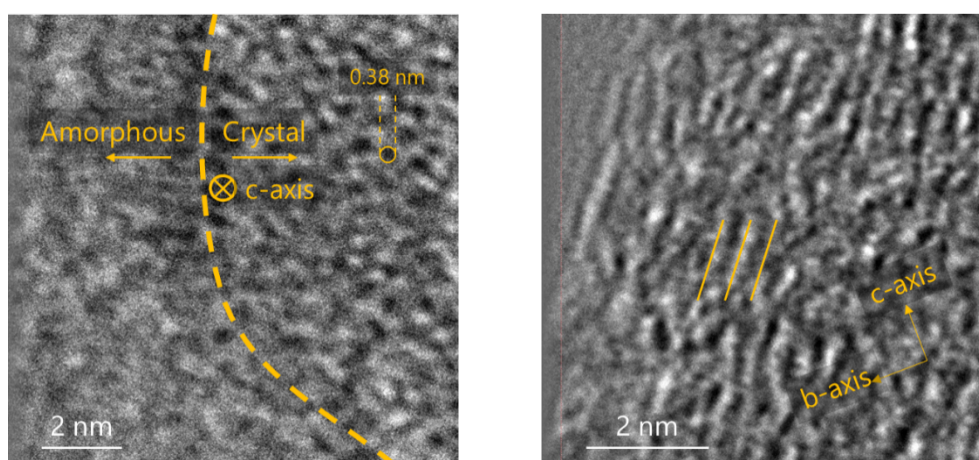


Figure S14. FE-TEM photographs for CHA-NSs.

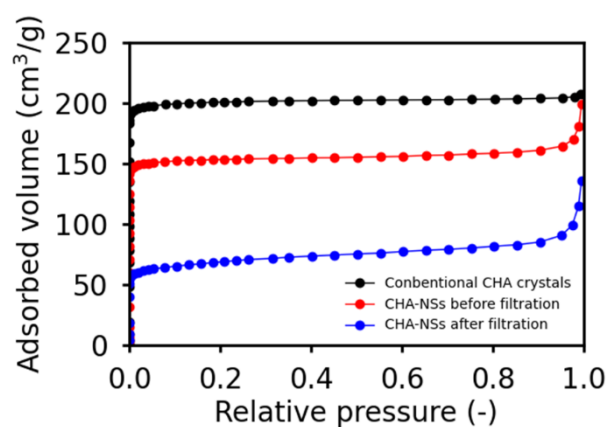


Figure S15. Nitrogen adsorption isotherms of CHA-NSs before (red) and after (blue) filtration and conventional CHA crystals (black).

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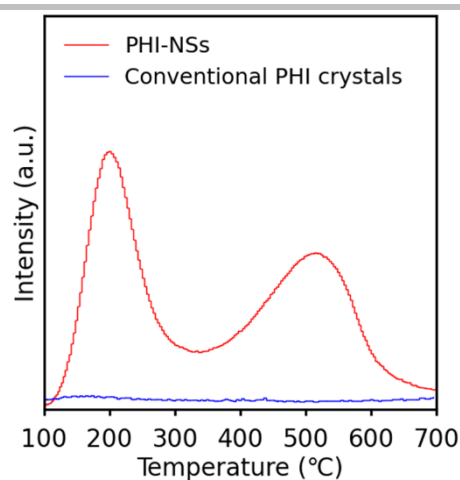


Figure S16. NH_3 -TPD profiles of PHI-NSs (red) and conventional PHI crystals (blue).

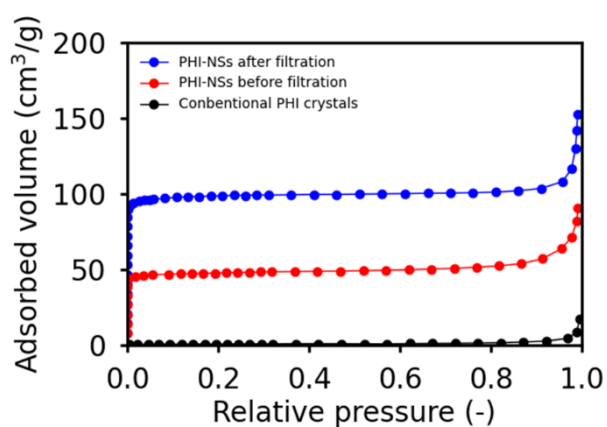


Figure S17. Nitrogen adsorption isotherms for PHI-NSs before (red) and after (blue) filtration and conventional PHI crystals (black).

Table S4. Specific surface area (S_{total}), external surface area (S_{ext}) and pore volume (V_{total}) of conventional PHI crystals, PHI-NSs before filtration, and PHI-NSs after filtration measured by nitrogen adsorption isotherms.

| | $S_{\text{total}}^{[a]} / \text{m}^2\text{g}^{-1}$ | $S_{\text{ext}}^{[b]} / \text{m}^2\text{g}^{-1}$ | $V_{\text{total}}^{[b]} / \text{cm}^3\text{g}^{-1}$ |
|---------------------------|--|--|---|
| Conventional PHI crystals | 3 | 3 | 0 |
| PHI-NSs before filtration | 153 | 11 | 0.07 |
| PHI-NSs after filtration | 319 | 16 | 0.14 |

[a] Surface area calculated using BET method (BET surface area) applied to the nitrogen adsorption isotherm.

[b] S_{ext} and V_{total} calculated using the t -plot method applied to the nitrogen adsorption isotherm.

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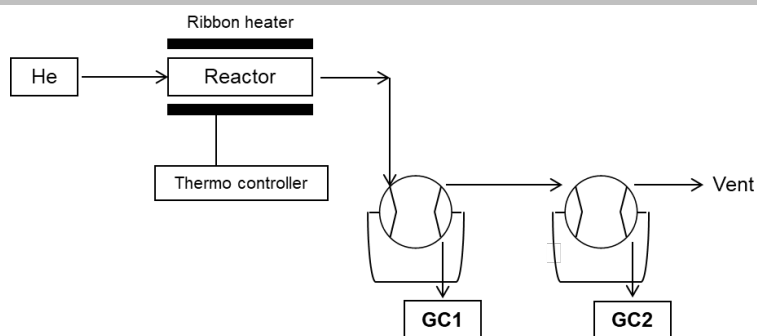


Figure S18. Experimental setup for the LDPE cracking reaction test.

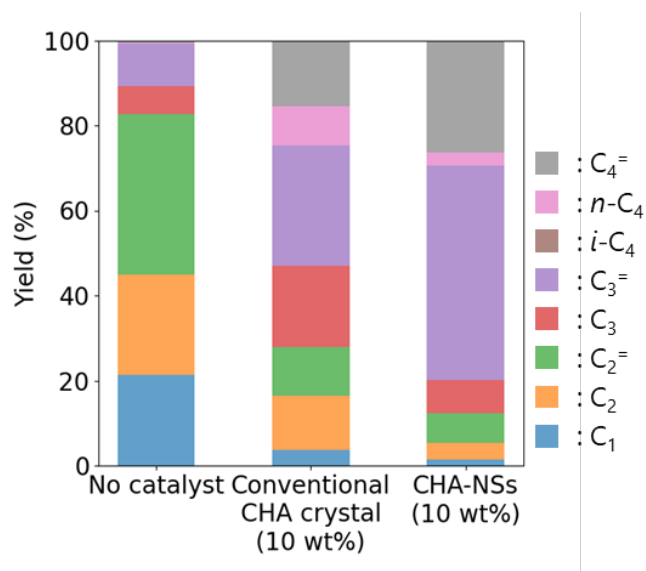
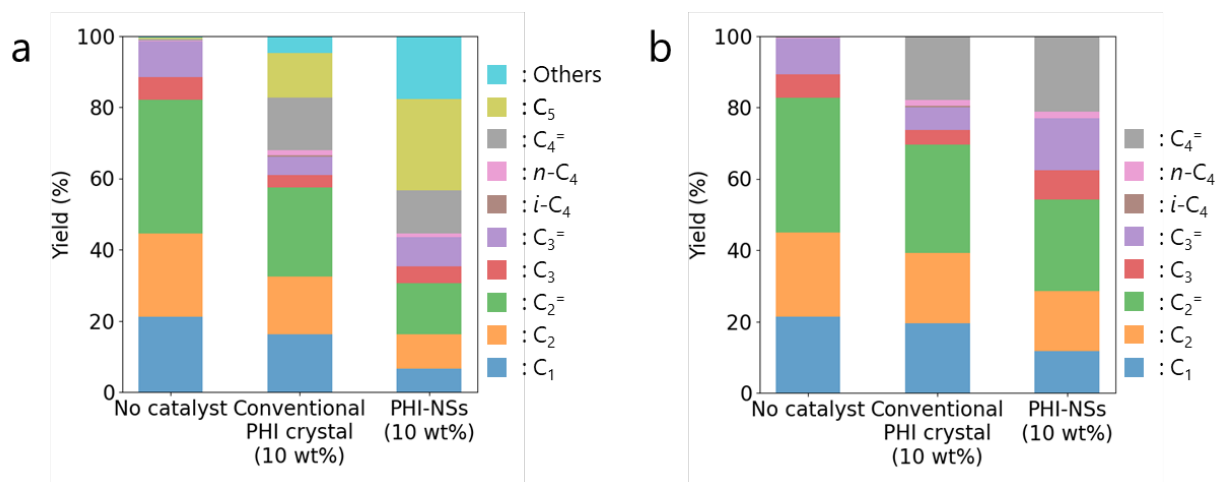


Figure S19. Distribution of the products smaller than pentene in LDPE cracking reactions without catalysts and with conventional CHA crystals (10 wt%) or CHA-NSs (10 wt%).

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Table S5. Product distribution in LDPE cracking reactions without catalysts and with conventional CHA crystals (10 wt%) or CHA-NSs (10 wt%). Product distribution with (left side) and without (right side) large molecules.

| | No catalyst | Conventional CHA crystals (10 wt%) | CHA-NSs (10 wt%) | No catalyst | Conventional CHA crystals (10 wt%) | CHA-NSs (10 wt%) |
|-----------------------------|-------------|--|---------------------|-------------|--|---------------------|
| C ₁ | 21.2 | 1.69 | 0.91 | 21.4 | 3.71 | 1.40 |
| C ₂ | 23.4 | 5.75 | 2.59 | 23.6 | 12.6 | 3.98 |
| C ₂ ⁼ | 37.4 | 5.23 | 4.57 | 37.8 | 11.5 | 7.01 |
| C ₃ | 6.42 | 8.66 | 5.09 | 6.48 | 19.1 | 7.81 |
| C ₃ ⁼ | 10.0 | 12.9 | 32.9 | 10.1 | 28.3 | 50.4 |
| <i>i</i> -C ₄ | 0 | 0 | 0 | 0 | 0 | 0 |
| <i>n</i> -C ₄ | 0.174 | 4.19 | 1.93 | 0.176 | 9.22 | 2.95 |
| C ₄ ⁼ | 0.453 | 7.04 | 17.2 | 0.457 | 15.5 | 26.4 |
| C ₅ | 0.316 | 9.34 | 7.83 | | | |
| Others | 0.601 | 45.2 | 27.0 | | | |
| Sum | 100 | 100 | 100 | 100 | 100 | 100 |

**Figure S20.** Product distribution in LDPE cracking reactions without and with conventional PHI crystals (10 wt%) or PHI-NSs (10 wt%). Product distribution a) with and b) without large molecules.

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Table S6. Product distribution in LDPE cracking reactions without catalysts and with conventional PHI crystals (10 wt%) or PHI-NSs (10 wt%). Product distribution with (left side) and without (right side) large molecules.

| | No catalyst | Conventional PHI crystals (10 wt%) | PHI-NSs (10 wt%) | No catalyst | Conventional PHI crystals (10 wt%) | PHI-NSs (10 wt%) |
|-----------------------------|-------------|--|---------------------|-------------|--|---------------------|
| C ₁ | 21.2 | 16.1 | 6.61 | 21.4 | 19.5 | 11.7 |
| C ₂ | 23.4 | 16.2 | 9.53 | 23.6 | 19.7 | 16.9 |
| C ₂ ⁼ | 37.4 | 25.1 | 14.4 | 37.8 | 30.4 | 25.5 |
| C ₃ | 6.42 | 3.47 | 4.70 | 6.48 | 4.19 | 8.31 |
| C ₃ ⁼ | 10.0 | 5.16 | 8.16 | 10.1 | 6.24 | 14.4 |
| <i>i</i> -C ₄ | 0 | 0.407 | 0 | 0 | 0.491 | 0 |
| <i>n</i> -C ₄ | 0.174 | 1.36 | 1.14 | 0.176 | 1.64 | 2.03 |
| C ₄ ⁼ | 0.453 | 14.8 | 11.9 | 0.457 | 17.9 | 21.1 |
| C ₅ | 0.316 | 12.4 | 25.7 | | | |
| Others | 0.601 | 4.88 | 17.8 | | | |
| Sum | 100 | 100 | 100 | 100 | 100 | 100 |

Table S7. XRD peak positions and full widths at half maximum for SOD-NSs and conventional SOD crystals.

| Peak (2θ) | Full width at half maximum (°) | |
|-----------|--------------------------------|------------------------------|
| | SOD-NSs | Conventional SOD crystals |
| 14.1 | 0.239 | 0.218 |
| 24.3 | 0.266 | 0.321 |
| 32.8 | 0.355 | 0.391 |
| 34.5 | 0.391 | 0.412 |
| 42.7 | 0.386 | 0.482 |

SUPPORTING INFORMATION

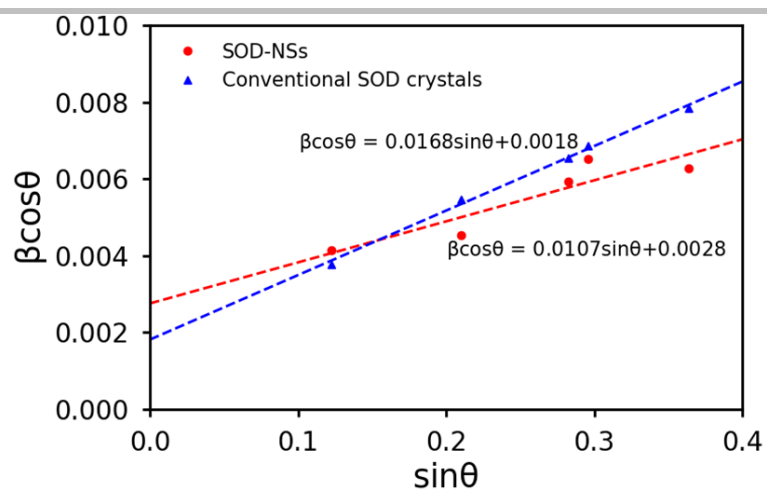


Figure S21. Williamson-Hall plots of SOD-NSs (red) and conventional SOD crystals (blue). In the equations, β is full width at half maximum, η is internal strain, K is Scherrer constant, λ is the X-ray wavelength, and D is crystallite size. The Scherrer constant used was 0.94. The estimated D s for SOD-NSs and conventional SOD crystals are 52 nm and 76 nm, respectively.

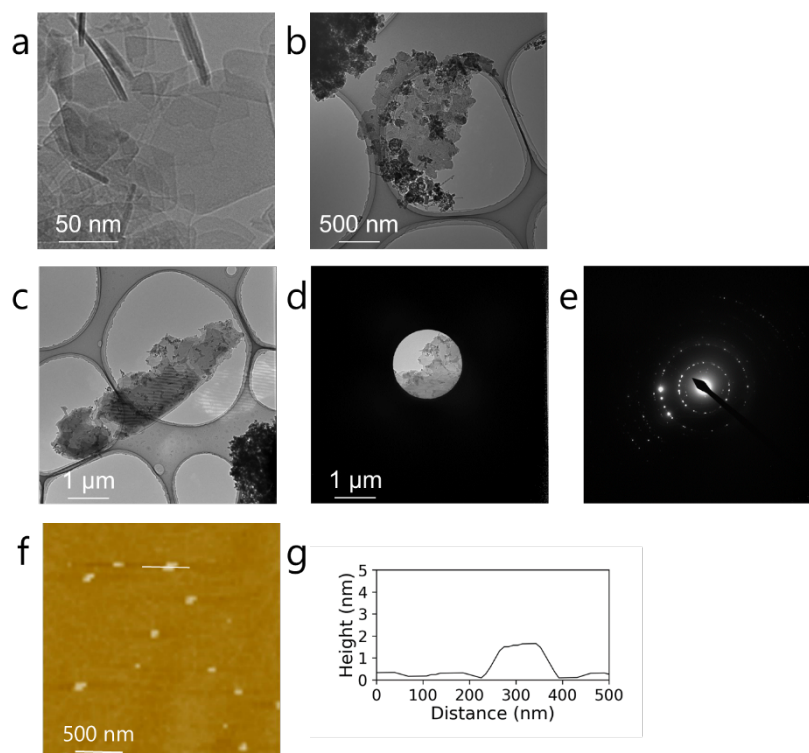


Figure S22. TEM and AFM photographs of SOD-NSs. TEM photographs of a) small SOD-NSs and b) large SOD-NSs. TEM photographs c) without and d) with selected area diffraction aperture. e) SAED patterns. f) AFM photograph and g) cross section of one of the synthesized SOD-NSs.

SUPPORTING INFORMATION

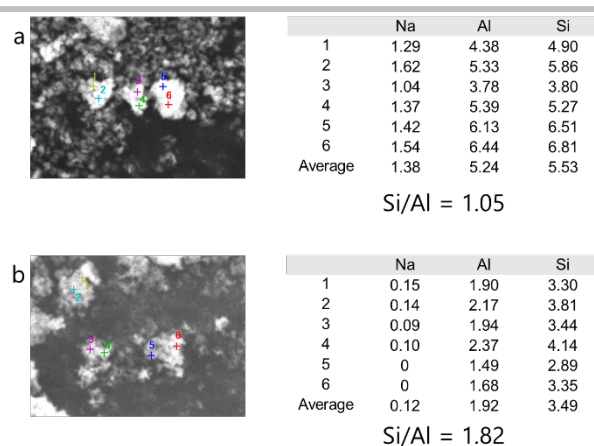


Figure S23. SEM-EDX spectra and Si/Al ratio for SOD zeolites. a) conventional SOD particles. b) SOD-NSs.

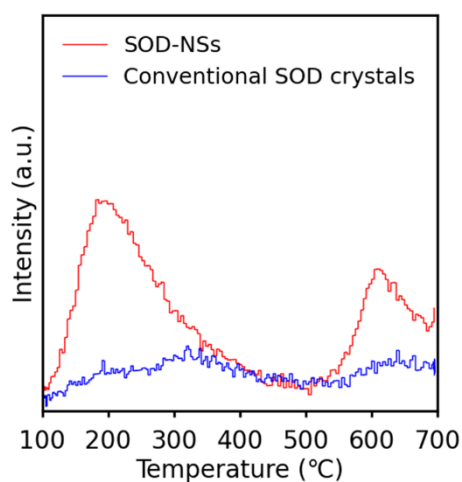


Figure S24. NH_3 -TPD profiles of SOD-NSs (red) and conventional SOD crystals (blue).

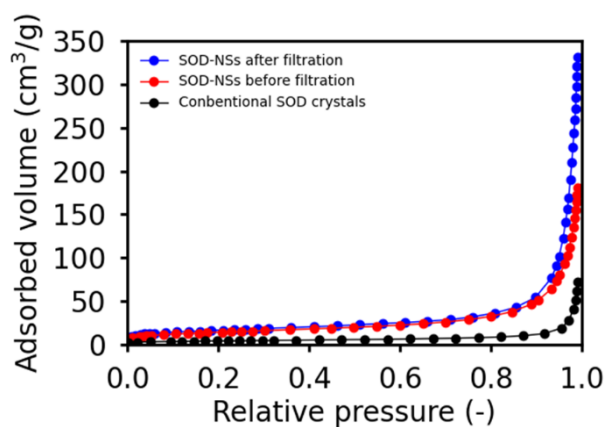


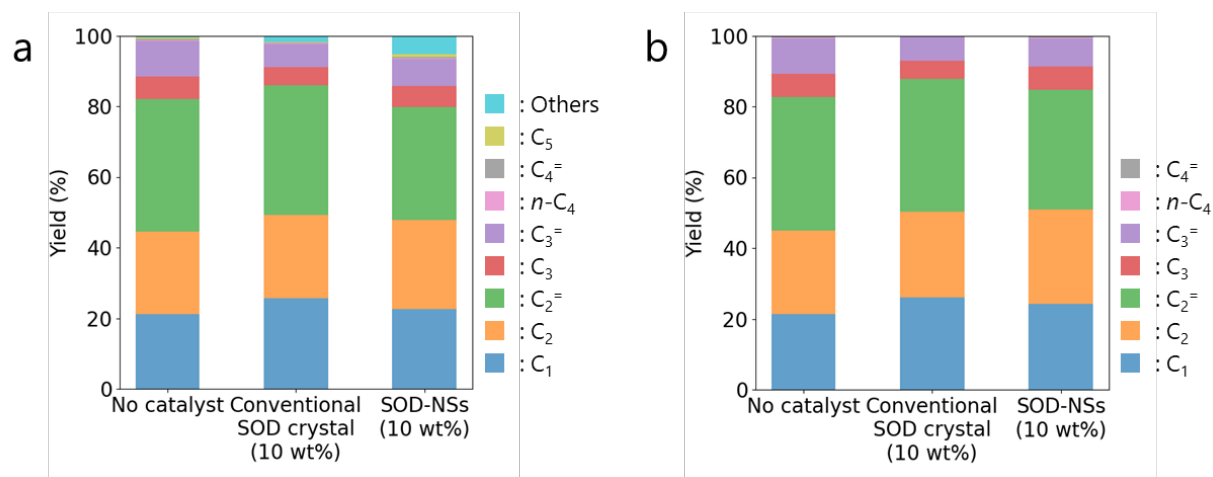
Figure S25. Nitrogen adsorption isotherms for SOD-NSs before (red) and after (blue) filtration and conventional SOD crystals (black).

SUPPORTING INFORMATION

Table S8. Specific surface area (S_{total}), external surface area (S_{ext}) and pore volume (V_{total}) of conventional SOD crystals, SOD-NSs before filtration, and SOD-NSs after filtration measured by nitrogen adsorption isotherms.

| | $S_{\text{total}}^{[a]} / \text{m}^2\text{g}^{-1}$ | $S_{\text{ext}}^{[b]} / \text{m}^2\text{g}^{-1}$ | $V_{\text{total}}^{[b]} / \text{cm}^3\text{g}^{-1}$ |
|---------------------------|--|--|---|
| Conventional SOD crystals | 15 | 14 | 0 |
| SOD-NSs before filtration | 50 | 48 | 0 |
| SOD-NSs after filtration | 59 | 54 | 0 |

[a] Surface area calculated using BET method (BET surface area) applied to the nitrogen adsorption isotherm.

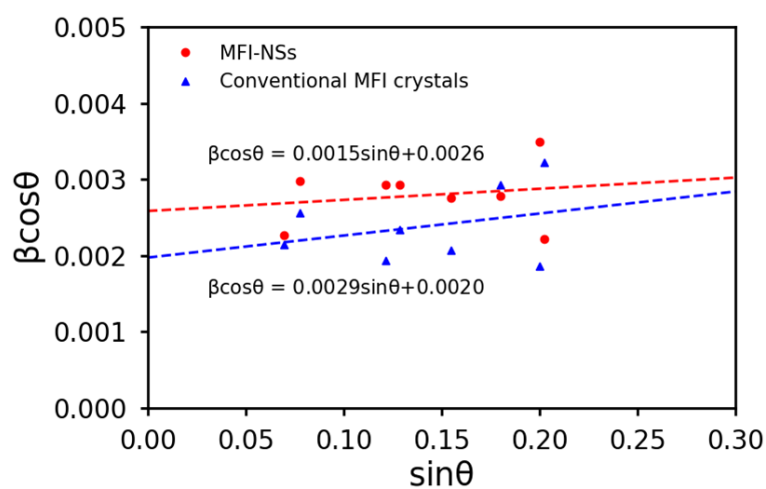
[b] S_{ext} and V_{total} calculated using the t -plot method applied to the nitrogen adsorption isotherm.**Figure S26.** Product distribution in LDPE cracking reactions without and with conventional SOD crystals (10 wt%) or SOD-NSs (10 wt%). Product distribution a) with and b) without large molecules.**Table S9.** Product distribution in LDPE cracking reaction without any catalysts and with conventional SOD crystals (10 wt%) or SOD-NSs (10 wt%). Product distribution with (left side) and without (right side) large molecules.

| | No catalyst | Conventional SOD crystals (10 wt%) | SOD-NSs (10 wt%) | No catalyst | Conventional SOD crystals (10 wt%) | SOD-NSs (10 wt%) |
|----------------|-------------|------------------------------------|------------------|-------------|------------------------------------|------------------|
| C_1 | 21.2 | 25.6 | 22.7 | 21.4 | 26.1 | 24.1 |
| C_2 | 23.4 | 23.6 | 25.2 | 23.6 | 24.1 | 26.8 |
| $C_2^=$ | 37.4 | 36.7 | 31.9 | 37.8 | 37.5 | 33.9 |
| C_3 | 6.42 | 5.07 | 6.06 | 6.48 | 5.17 | 6.44 |
| $C_3^=$ | 10.0 | 6.65 | 7.61 | 10.1 | 6.79 | 8.09 |
| $i\text{-}C_4$ | 0 | 0 | 0 | 0 | 0 | 0 |
| $n\text{-}C_4$ | 0.174 | 0.154 | 0.107 | 0.176 | 0.157 | 0.114 |
| $C_4^=$ | 0.453 | 0.151 | 0.514 | 0.457 | 0.154 | 0.546 |
| C_5 | 0.316 | 0.335 | 0.693 | | | |
| Others | 0.601 | 1.69 | 5.27 | | | |
| Sum | 100 | 100 | 100 | 100 | 100 | 100 |

SUPPORTING INFORMATION

Table S10. XRD peak positions and full widths at half maximum for MFI-NSs and conventional MFI crystals.

| Peak (2 θ) | Full width at half maximum (°) | |
|--------------------|--------------------------------|---------------------------|
| | MFI-NSs | Conventional MFI crystals |
| 8.0 | 0.130 | 0.123 |
| 8.9 | 0.171 | 0.147 |
| 13.9 | 0.169 | 0.112 |
| 14.8 | 0.169 | 0.135 |
| 17.8 | 0.160 | 0.120 |
| 20.8 | 0.162 | 0.171 |
| 23.1 | 0.204 | 0.109 |
| 23.4 | 0.130 | 0.189 |

**Figure S27.** Williamson-Hall plots of MFI-NSs (red) and conventional MFI crystals (blue). In the equations, β is full width at half maximum, η is internal strain, K is Scherrer constant, λ is the X-ray wavelength, and D is crystallite size. The Scherrer constant used was 0.94. The estimated D s for MFI-NSs and conventional MFI crystals are 56 nm and 72 nm, respectively.

SUPPORTING INFORMATION

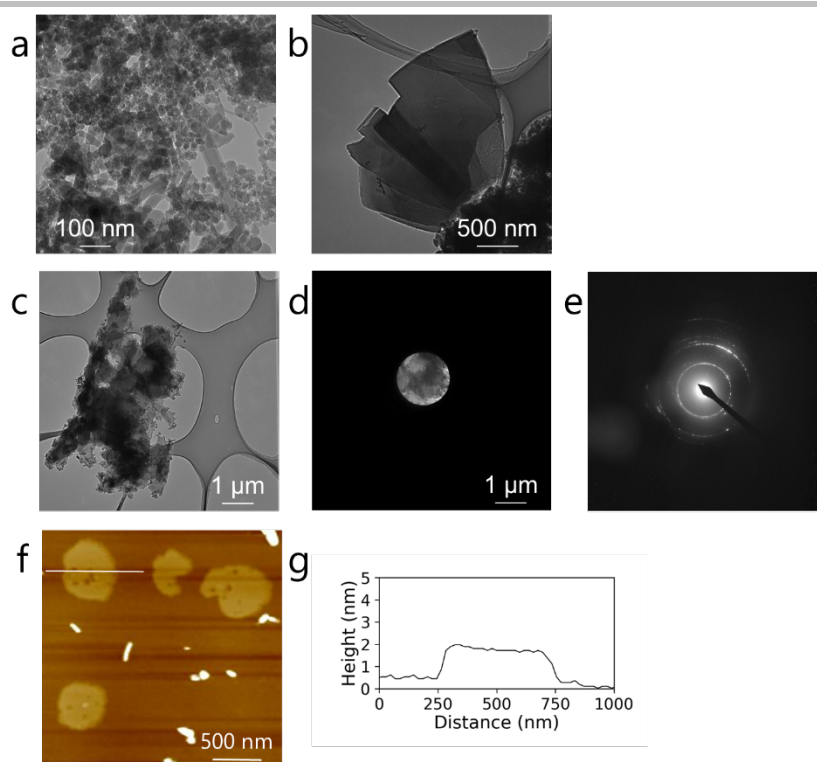


Figure S28. TEM and AFM photographs of MFI-NSs. TEM photographs of a) small MFI-NSs and b) large MFI-NSs. TEM photographs c) without and d) with selected area diffraction aperture. e) SAED pattern. f) AFM photograph and g) cross section of one of the synthesized MFI-NSs.

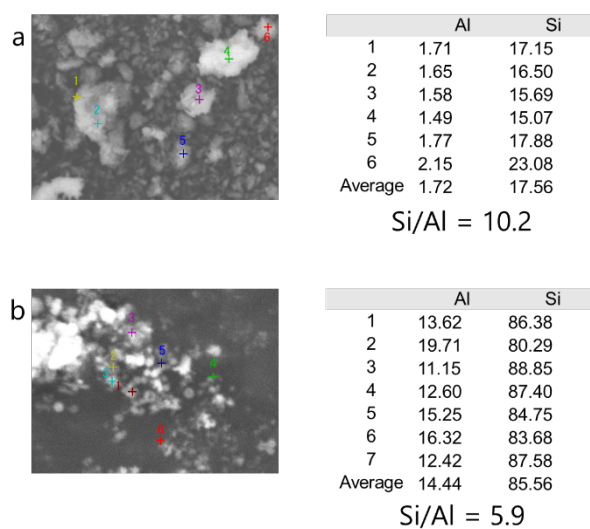


Figure S29. SEM-EDX spectra and Si/Al ratio for MFI zeolites. a) Conventional MFI particles. b) MFI-NSs..

SUPPORTING INFORMATION

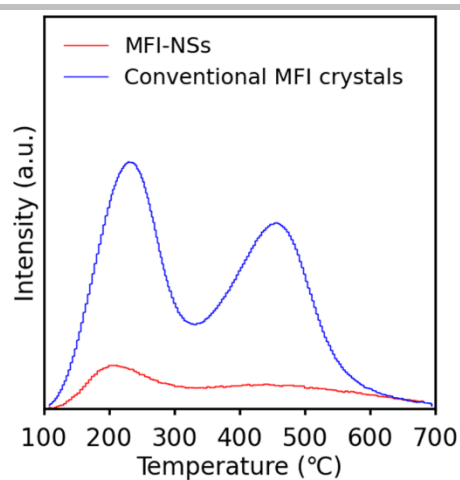


Figure S30. NH_3 -TPD profiles of MFI-NSs (red) and conventional MFI crystals (blue).

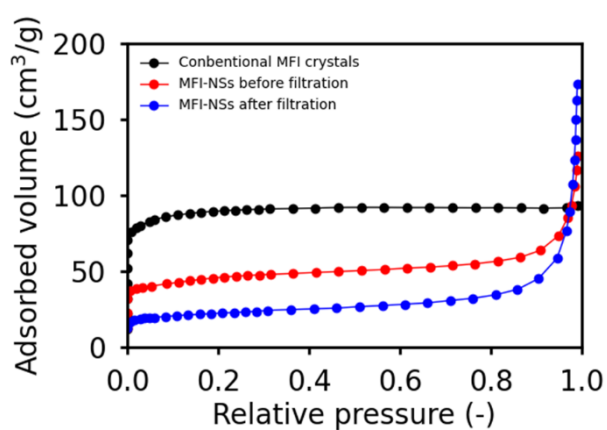


Figure S31. Nitrogen adsorption isotherms for MFI-NSs before (red) and after (blue) filtration and conventional MFI crystals.

Table S11. Specific surface area (S_{total}), external surface area (S_{ext}) and pore volume (V_{total}) of conventional MFI crystals, MFI-NSs before filtration and MFI-NSs after filtration measured by nitrogen adsorption isotherms.

| | $S_{\text{total}}^{[a]} / \text{m}^2\text{g}^{-1}$ | $S_{\text{ext}}^{[b]} / \text{m}^2\text{g}^{-1}$ | $V_{\text{total}}^{[b]} / \text{cm}^3\text{g}^{-1}$ |
|---------------------------|--|--|---|
| Conventional MFI crystals | 405 | 0.09 | 0.14 |
| MFI-NSs before filtration | 165 | 24 | 0.06 |
| MFI-NSs after filtration | 81 | 37 | 0.02 |

[a] Surface area calculated using BET method (BET surface area) applied to the nitrogen adsorption isotherm.

[b] S_{ext} and V_{total} calculated using the t -plot method applied to the nitrogen adsorption isotherm.

SUPPORTING INFORMATION

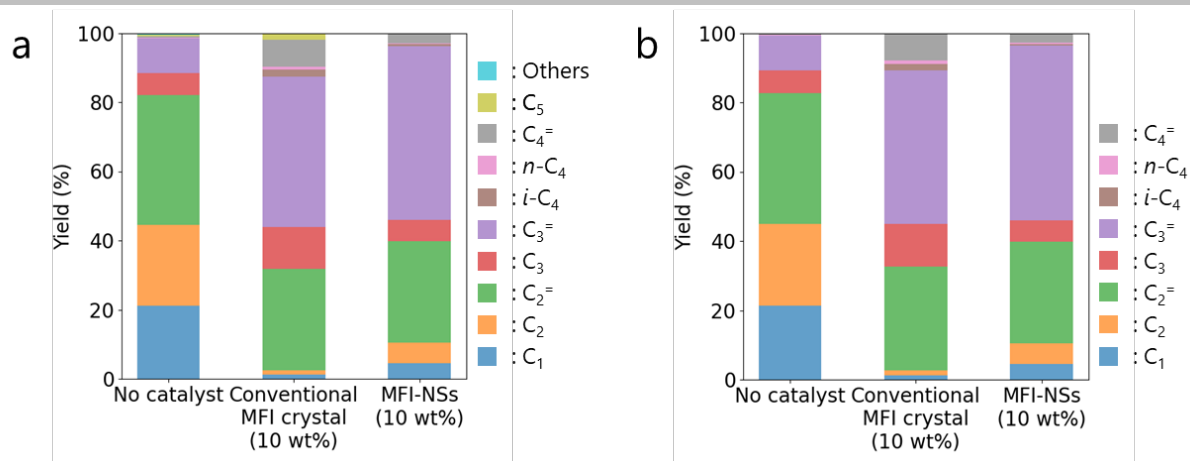


Figure S32. Product distribution in LDPE cracking reaction without and with conventional MFI crystals (10 wt%) or MFI-NSs (10 wt%). Product distribution a) with and b) without large molecules.

Table S12. Product distribution in LDPE cracking reaction without any catalysts and with conventional MFI crystals (10 wt%) or MFI-NSs (10 wt%). Product distribution with (left side) and without (right side) large molecules.

| | No catalyst | Conventional MFI crystals (10 wt%) | MFI-NSs (10 wt%) | No catalyst | Conventional MFI crystals (10 wt%) | MFI-NSs (10 wt%) |
|--------------------------|-------------|------------------------------------|------------------|-------------|------------------------------------|------------------|
| C ₁ | 21.2 | 1.16 | 4.60 | 21.4 | 4.60 | 1.19 |
| C ₂ | 23.4 | 1.38 | 5.83 | 23.6 | 5.83 | 1.40 |
| C ₂ = | 37.4 | 29.3 | 29.3 | 37.8 | 23.0 | 29.3 |
| C ₃ | 6.42 | 12.0 | 6.28 | 6.48 | 12.3 | 6.28 |
| C ₃ = | 10.0 | 43.5 | 50.3 | 10.1 | 44.2 | 50.3 |
| <i>i</i> -C ₄ | 0 | 1.97 | 0.598 | 0 | 2.02 | 0.576 |
| <i>n</i> -C ₄ | 0.174 | 0.853 | 0.265 | 0.176 | 0.873 | 0.261 |
| C ₄ = | 0.453 | 7.80 | 2.69 | 0.457 | 7.95 | 2.85 |
| C ₅ | 0.316 | 1.76 | 0.007 | | | |
| Others | 0.601 | 0.238 | 0.190 | | | |
| Sum | 100 | 100 | 100 | 100 | 100 | 100 |

SUPPORTING INFORMATION

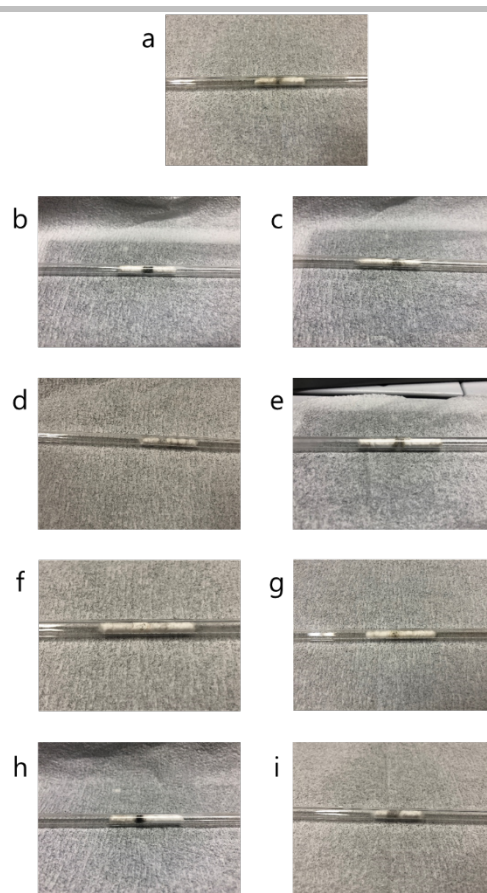


Figure S33. Quartz glass capillaries with the samples after the catalytic test: a) No catalyst. b) Conventional CHA crystals (10 wt%). c) CHA-NSs (10 wt%). d) Conventional PHI crystals (10 wt%). e) PHI-NSs (10 wt%). f) Conventional SOD crystals (10 wt%). g) SOD-NSs (10 wt%). h) Conventional MFI crystals (10 wt%). i) MFI-NSs (10 wt%).