

Supporting Information

Direct synthesis of IDM-1 aluminosilicate nanosheets with improved MTP performance

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Experimental

Chemicals

Tetraethyl orthosilicate (TEOS, Aladdin, > 99%), aluminum isopropoxide (AIP, Aladdin, > 98.5%), NH₄F (Aladdin, > 98%), HF (Aladdin, > 40%), *para*-xylene (Aladdin, > 99%). These chemicals were used as received without further purification.

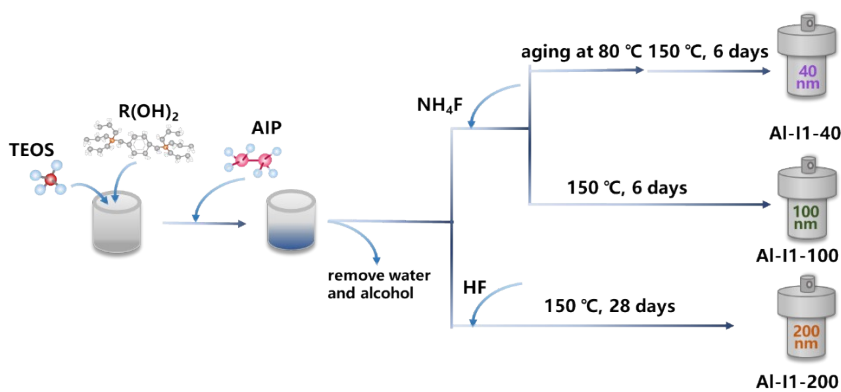
Synthesis of Materials

Synthesis of OSDA

The organic structure-directing agent (OSDA), *p*-phenylene-dimethylene-bis(tripropylammonium) (DPDBT), was prepared as previously reported.¹ 20.0 g of 1,4-bis(chloromethyl) benzene was dissolved in ethanol under stirring. Then, 100 g of tripropylamine was added and refluxed at a temperature of 353 K for 4 days. After purifying, the product was recognized by ¹H NMR and ¹²C NMR spectroscopy. Finally, the product was converted to hydroxide form using anion exchange resin (Tai-Young Chemical Co, Ltd).

Synthesis of *b*-oriented IDM-1 aluminosilicate (Al-I1)

The molar ratio of 1.0 SiO₂ synthesized the *b*-oriented Al-I1: 0.25 OSDA: 0.005 Al₂O₃: 0.5 NH₄F/HF : 15 H₂O. First, OSDA, AIP, and TEOS were added in a Teflon vessel under stirring and aged at room temperature for 3 hours. Then, ethanol was evaporated under magnetic stirring at 353 K. The *b*-oriented aluminium-containing IDM-1 was denoted as Al-I1-*x*, where *x* is the sheet thickness along *b*-axis. Al-I1-40 was synthesized in two-step: NH₄F was used as an F source, and the mixture was pretreated at 353 K for 24 h and then crystallized at 433 K for 6 days. To investigate the effect of low-temperature pre-crystallization, Al-I1-100 was prepared similarly to Al-I1-40 without preliminary aging treatment. In addition, Al-I1-200 used HF as an F source and crystallized at 433 K for 28 days. The synthesis process is described in **Scheme S1**.



Sche

me S1. The synthesis process of *b*-oriented Al-I1.

In our exploration of aging procedures, we designed three aging methods: the first, pre-crystallize at 353 K for 24 hours (denoted as two-step); the second, after pre-crystallization at 353 K for 24 hours, turn to 373 K for 24 hours (denoted as three-step); the third, the sample was pre-crystallized at 353 K, 373 K and 393 K in turn for 24 hours, respectively (denoted as four-step). These gels were finally subjected to crystallization at 423 K for 6 days (Fig. S1).

All of these zeolite materials were obtained by centrifugation, washed three times, dried at 373 K for 12 h, and calcined for 6 h at 823 K in air.

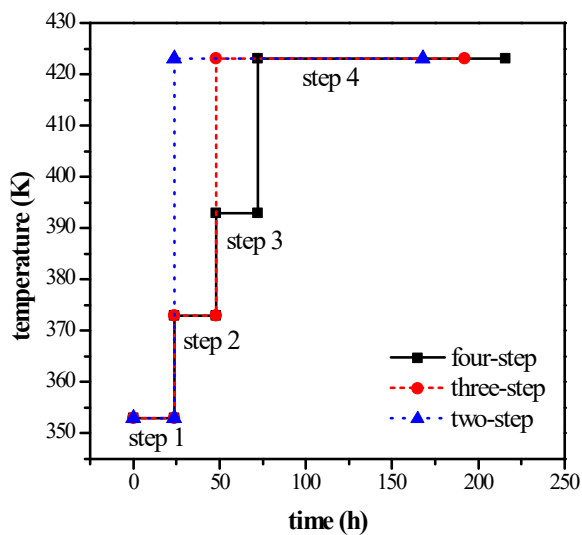


Fig. S1 Three kinds of aging steps were used for synthesizing Al-I1.

Synthesis of *b*-oriented ZSM-5

For control experiment, the *b*-oriented ZSM-5 zeolites were synthesized following a reported protocol using a growth solution with the molar ratio of 1.0 SiO₂ : 0.08 - 0.15 TPA⁺ : 0.005 Al₂O₃ : 0.8 NH₄F : 30 H₂O.² Firstly, TPAOH, TEOS, and H₂O were added to a Teflon vessel under stirring and subjected to a pre-crystallization step at 353 K for 12 h. After cooling to room temperature, NH₄F was added into the Teflon vessel and crystallized under static conditions at 353 K for 24 h and further at 373 K for 3 days. The solid products were collected by vacuum filtration, washed with deionized water until a near-neutral pH, and dried overnight at 333 K. Subsequently, after ion-exchange with 1 M NH₄Cl for three times at 333 K for 3 h, and calcined at 823 K for 6 h, the ZSM-5 nanosheets obtained were denoted as Z5-*x* (*x* stands for the crystal length along *b*-axis).

Characterization methods

The powder X-ray diffraction (XRD) patterns were collected on a Rigaku Ultima IV X-ray diffractometer using Cu-K α radiation ($\lambda = 1.5405 \text{ \AA}$) in a scanning range of $2\theta = 2^\circ - 50^\circ$ to confirm the structure and crystallinity of the zeolites. The voltage and current were 35 kV and 25 mA, respectively.

Scanning electron micrographs (SEM) were performed on a JEOS JSM-7800F microscope at low landing energy (1 keV, in gentle-beam mode) to determine the morphology and crystal size.

Transmission electron microscopy (TEM) and backscattered electron images (BEI) were obtained on JEOL JEM 2100 plus, and JEOL JEM F200 Electron Microscope operated at 200 kV.

After activating the samples at 573 K under vacuum for at least 5 h, the N₂ adsorption-desorption isotherms were measured at 77 K on BELSORP-MAX adsorption instruments. The Brunauer-Emmett-Teller (BET) analysis was carried out using the data in the relative pressure region of $P/P_0 = 0.05 - 0.25$, which calculated the specific surface area.

The thermogravimetric and differential thermal analyses (TG-DTA) were performed on a METTLER TOLEDO TGA/DSC 3⁺ apparatus in the air at 298–1073K with a heating rate of 10 K min⁻¹.

The solid-state ²⁷Al and ²⁹Si MAS NMR spectra were obtained on a VARIAN VNMRS 400WB NMR spectrometer using the single-pulse method at a frequency of 79.43. The ²⁷Al MAS NMR spectra were

recorded at 104.18 MHz, a spinning rate of 9 kHz, and a recycling delay of 4 s. ²⁹Si MAS NMR spectra were acquired with a 7.5 mm T3HX probe at the spinning rate of 3 kHz and a recycling delay of 60 s.

The acid amount was determined by temperature-programmed desorption of ammonia (NH₃-TPD) technique on a Micrometrics Auto Chem II Chemisorption Analyzer. 0.1 g of sample was pretreated in a helium stream (25 mL min⁻¹) at 873 K for 1 h. The adsorption of NH₃ gas was carried out at 323 K for 1 h. The sample was flushed with helium at 373 K for 2 h to remove physics-adsorbed NH₃ of catalyst surface. The TPD profiles were then recorded at a heating rate of 10 K min⁻¹ from 353 K to 1073 K. The Brønsted and Lewis acid sites of the sample were characterized by IR spectra of pyridine adsorption on a Nicolet Nexus 670 FT-IR spectrometer. After the evacuation of a self-supported sample wafer at 723 K for 1 h, pyridine adsorption of the sample was carried out at 298 K for 0.5 h. IR spectra were collected after the evacuation at the required temperature.

Adsorption and diffusivity measurement

The adsorption and diffusivity of organic molecules were measured by thermogravimetric analysis. By recording the mass change with time and temperature, the diffusion coefficient could be calculated by Fick's second law calculation formula. The experimental operation was as follows: about 8 mg calcined samples were pretreated at 623 K for 2 h in an N₂ gas flow to remove adsorbed water firstly. After pretreatment, the sample was cooled to 298 K, and the organic vapor was blown into the chamber by N₂ flow (30 mL min⁻¹) until the weight of the samples didn't change. We used *para*-xylene as adsorption substrate to quantify the effect of crystal morphology on diffusion resistance. Fick's second law was adopted to estimate the effective diffusion coefficient.^{3, 4} At the beginning of the adsorption process, the solution of this equation can be well approximated as:

$$\frac{q(t)}{q(\infty)} = \frac{6}{\sqrt{\pi}} \sqrt{\frac{D_{\text{eff}}}{R^2}} \sqrt{t}$$

$q(t) / q(\infty)$: the normalized hydrocarbon uptake;

D_{eff} : the diffusivity;

R : the characteristic diffusion length;

t : time.

Methanol to propylene (MTP) reaction.

The zeolite powder was pressed and sieved to 40 - 60 mesh. The catalyst (0.1 g) was loaded in a fixed-bed quartz tubular reactor with an inner diameter of 8 mm. For each test, the catalyst was activated at 773 K in an N₂ gas flow for 60 min. After the temperature declined to 723 K, methanol was pumped into the reactor by passing the carrier gas (N₂, 30.0 mL min⁻¹), which gave a WHSV of 2.0 h⁻¹. Methanol conversion was performed under atmospheric pressure. The products of the MTP reaction were analyzed using a gas chromatograph (Kechuang GC- 9800) equipped with an HP- PLOT/Q capillary column (30 m × 0.32 mm × 20 μm) and an FID detector. The total analyzing time for each run was 50 minutes. The methanol conversion X , product selectivity S_i and yield Y_i have been defined as:

$$X = \frac{F_{inlet} - F_{outlet}}{F_{inlet}} \times 100\%$$

$$S_i = \frac{n_i F_i}{\sum n_j F_j} \times 100\%$$

$$Y_i = \frac{n_i F_i}{F_{inlet}} \times 100\%$$

where F_{inlet} and F_{outlet} are the inlet and outlet carbon molar flow rate of the reactant (methanol and dimethyl ether), respectively, and F_i is the molar flow rate of effluent product i with n_i carbon atoms.

Theoretical method

The surface formation energy of three low-index IDM-1 crystal surfaces with different thicknesses was studied using the molecular dynamics (MD) method based on the Forcite module in Materials Studio. The isothermal-isobaric (NPT) ensemble with constant particles (N), a constant temperature of 298.15 K, and a constant pressure of 101325 Pa was used in our simulation. The Universal force field was chosen to describe the interactions among the atoms in our work. The Nose thermostat and Berendsen barostat were used to adjust the temperature and pressure during the MD simulations. Two stages of MD simulation with an NPT ensemble were performed successively. For the first stage, a total simulation time of 50 ps with a time step of 1 fs was performed to get the balance state. While another 50 ps with the same parameters in the first stage was used to calculate the statistically average energy of the system.

The surface formation energy (γ) was calculated according to the equation :

$$\gamma = (E_{slab} - X * E_{bulk})/2A$$

where E_{slab} is the total energy of the surface slab obtained with MD simulation, X means the number of the crystal cells in the system, E_{bulk} is the energy of the mono-crystal cell, and A is the surface area. The more positive the surface formation energy (γ) is, the harder the surface forms.

Analysis of organic species occluded in used zeolite catalysts

The used catalysts in MTP reaction was removed from the reactor and rapidly cooled to room temperature, and a part of the sample (50 mg) was transferred to a centrifuge tube and dissolved in 1.0 mL of 15% HF. To ensure the solid was completely dissolved, the acid treatment lasted about 3 hours. Then 1.0 mL CH_2Cl_2 (Aladdin) were added to the solution, which used to extract the liberated organic molecules from the aqueous phase. Hexachloroethane (Aladdin) was used as an internal standard. After 15 minutes, the organic phase and the water phase were separated. The organic phase was collected and analyzed using a gas chromatograph with an Agilent 6890 GC system equipped with an HP-5MS column and an Agilent 5977A Network Mass Selective Detector.

The coke content (in percentage) of discharged catalysts was calculated by thermogravimetric analysis (TGA). The used catalysts were collected from the reactor for different reaction times, and the average coke deposition rate is defined as follows:

$$R_{\text{coke}} = \frac{C \times M}{T \times M}$$

where R_{coke} ($\text{mg g}_{\text{cat}}^{-1} \text{h}^{-1}$) is the average coke deposition rate, C (%) is the lost weight between 523 K and 923 K in discharged catalysts determined by TGA, T (h) is the reaction time, and M (g) is the amount of catalyst.

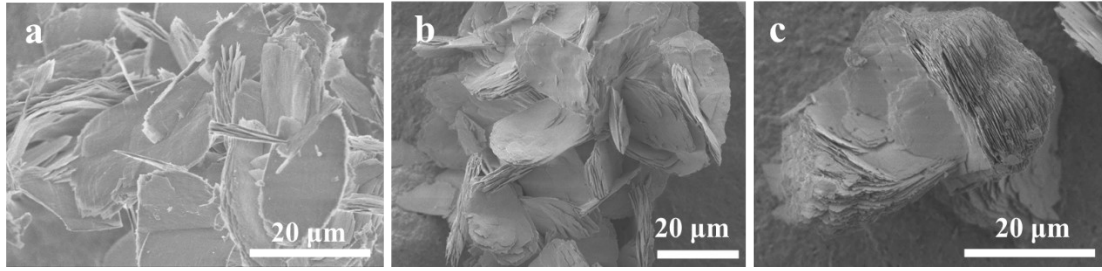


Fig. S2 SEM images of *b*-oriented (a) Al-I1-40, (b) Al-I1-100 and (c) Al-I1-200 zeolites.

Fig. S2 shows that the Al-I1 zeolites are composed of rectangular plates with similar width. To achieve the thickness of Al-I1 nanosheets, we calculated the average thickness by selecting a uniformly distributed area.

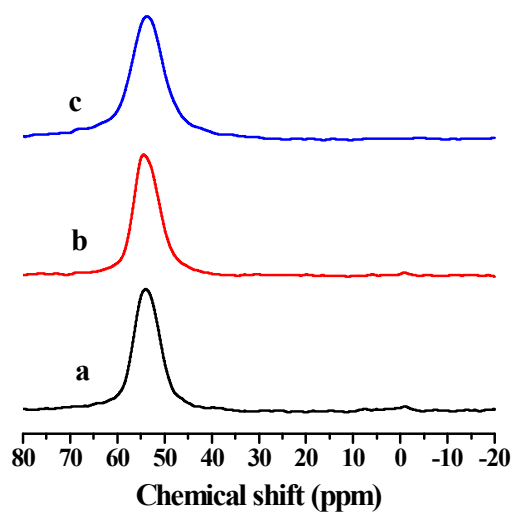


Fig. S3 ^{27}Al MAS NMR spectra of *b*-oriented Al-I1 (a) Al-I1-40, (b) Al-I1-100 and (c) Al-I1-200 zeolites.

The spectra display a main resonance in the range of 45 - 60 ppm and a very weak one centered at 0 ppm, attributed to tetrahedral and extra-framework octahedral Al species, respectively. This demonstrates that nearly all aluminum atoms are integrated into the Al-I1 framework.

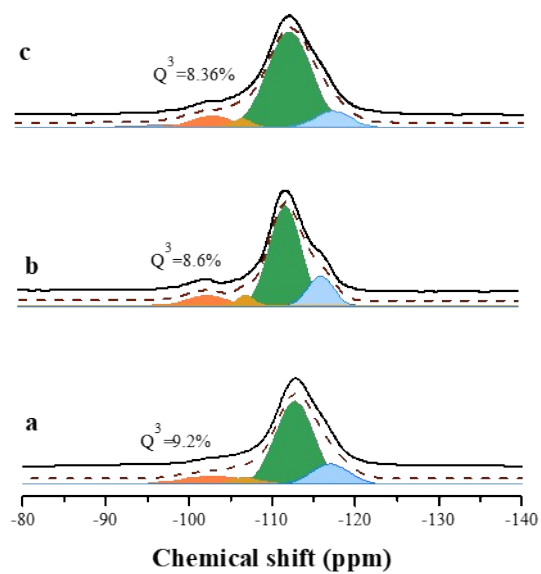


Fig. S4 ^{29}Si MAS NMR spectra of *b*-oriented Al-I1 (a) Al-I1-40, (b) Al-I1-100 and (c) Al-I1-200 zeolites.

In the previous report,¹ both $\text{Si}(\text{OSi})_3(\text{OH})$ (Q^3 sites, around -105 ppm) and $\text{Si}(\text{OSi})_2(\text{OH})_2$ (Q^2 groups, around -95 ppm) presented in pure-silica IDM-1. However, in Al-I1 aluminosilicates, only Q^3 sites were detected.

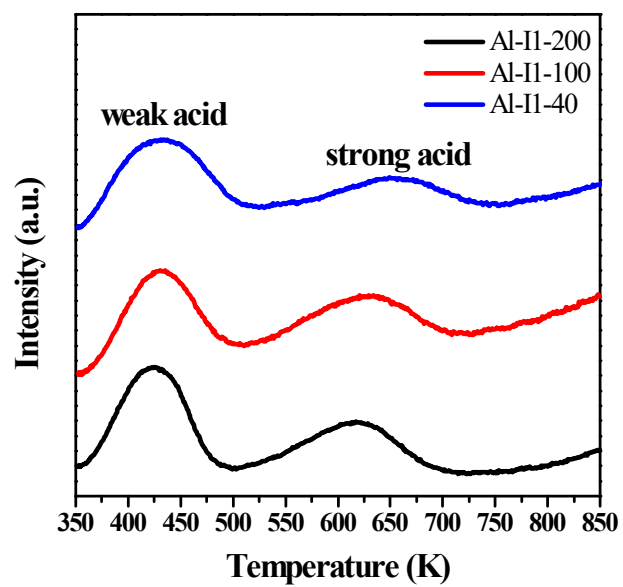


Fig. S5 NH₃-TPD profiles of calcined Al-II zeolites.

Fig. S5 shows two desorption peaks in NH₃-TPD profiles at approximately 425 and 625 K corresponding to weak and strong acid sites, respectively.

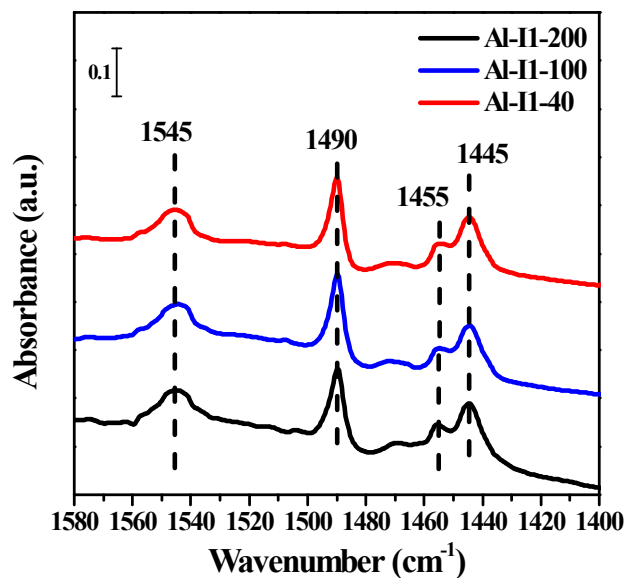


Fig. S6 Py-IR spectra (collected at after pyridine desorption at 423 K) of calcined Al-II zeolites.

In pyridine(Py)-IR spectra (Fig. S6), the bands at 1455 and 1545 cm⁻¹ are assigned to Lewis acid sites (LAS) and Brønsted acid sites (BAS), whereas the bands at 1490 and 1445 cm⁻¹ are attributed to the vibrations of Py molecules adsorbed on both BAS and LAS acid sites or hydrogen bonds.⁵

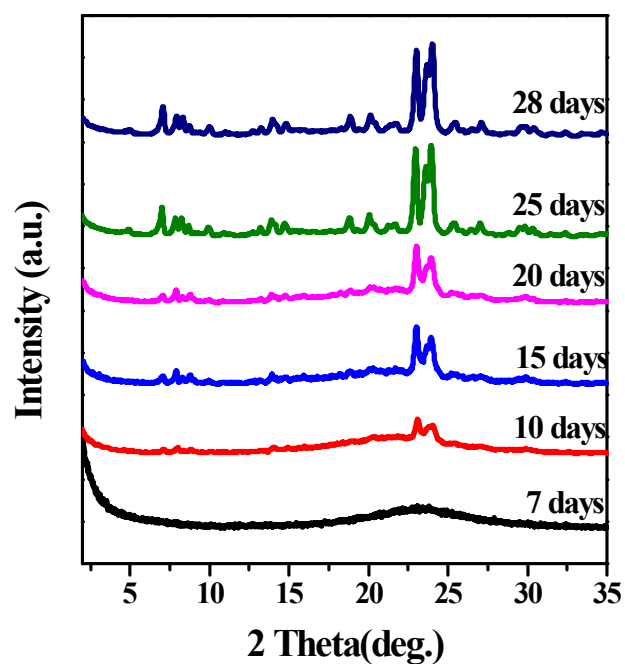


Fig. S7 PXR D patterns of as-made Al-II for different times (The mother gel molar ratio is 1.0 SiO₂ : 0.25 OSDA : 0.005 Al₂O₃ : 0.5 HF : 15 H₂O and crystallizes at 423 K) .

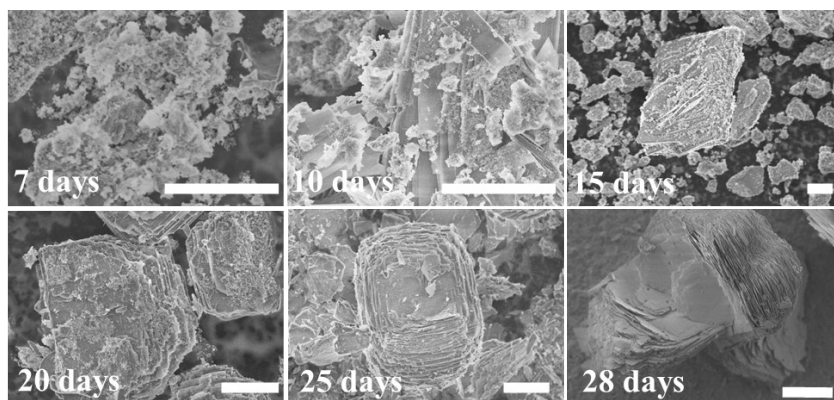


Fig. S8 SEM images of Al-II as-made for different times (scale bar, 10 μm).

As shown in Figs. S7-8, the Al-II crystals were created in 10 days, and the crystallization was completed after 28 days, when using HF as an F source.

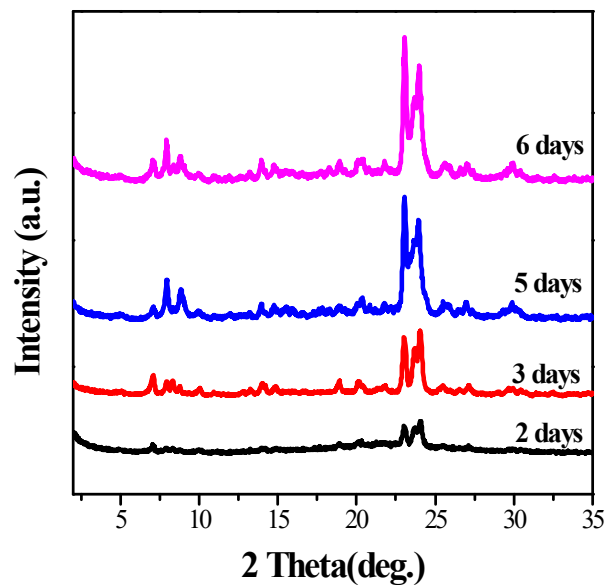


Fig. S9 PXR D patterns of Al-I1 as-made for different times. (The mother gel molar ratio is 1.0 SiO₂ : 0.25 OSDA : 0.005 Al₂O₃ : 0.5 NH₄F : 15 H₂O and crystallizes at 423 K).

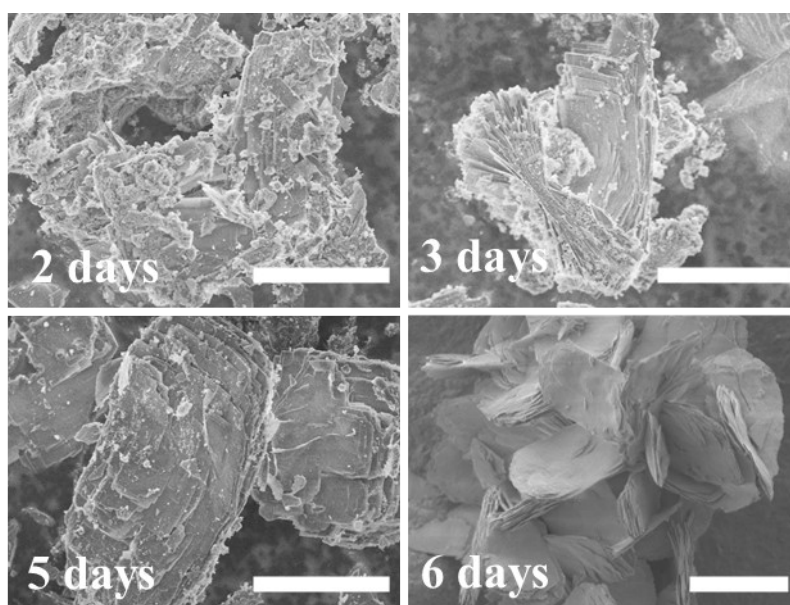


Fig. S10 SEM images of as-made Al-I1 for different times (scale bar, 20 μm).

As shown in Figs. S9 and 10, the Al-I1 crystals were obtained in only two days, and the crystallization was completed in 6 days, when using NH₄F as an F source.

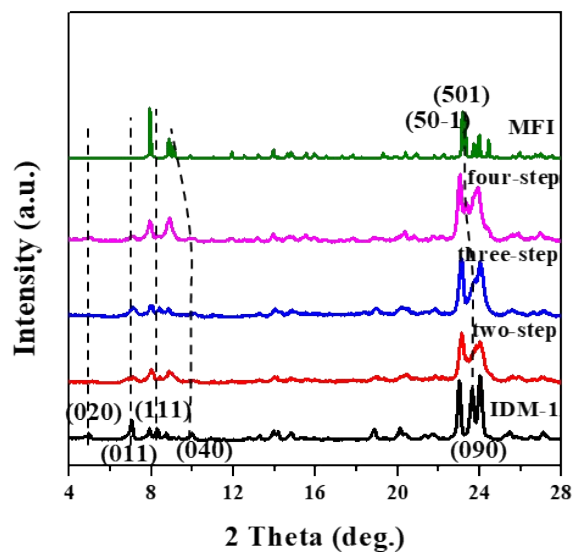


Fig. S11 PXRD patterns of the samples as-synthesized with different aging procedures.

As shown in Fig. S11, the Al-II could still retain the pure IDM-1 topology after aging, except for the four-step sample. The four-step sample showed the reflection change: the reflection (090) of IDM-1 disappeared and reflections (501) and (50-1) of MFI at lower angles appeared.

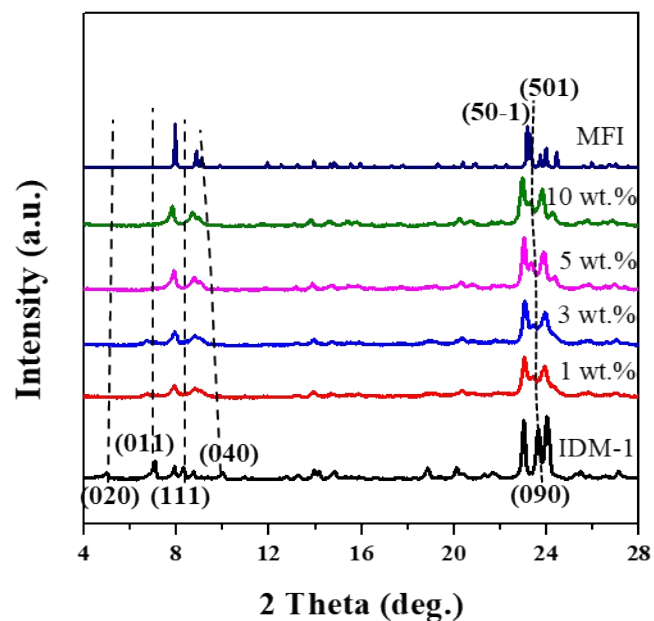


Fig. S12 PXRD patterns of the samples as-synthesized by seed-assisted method.

As shown in Fig. S12, four reflections at around 5.0°, 7.0°, 7.9° and 10.04° disappeared with the addition of Al-II seed and the peaks around 23- 25° were also changed: the reflection (091) of Al-II disappeared and the (50-1) and (501) reflections of MFI appeared.

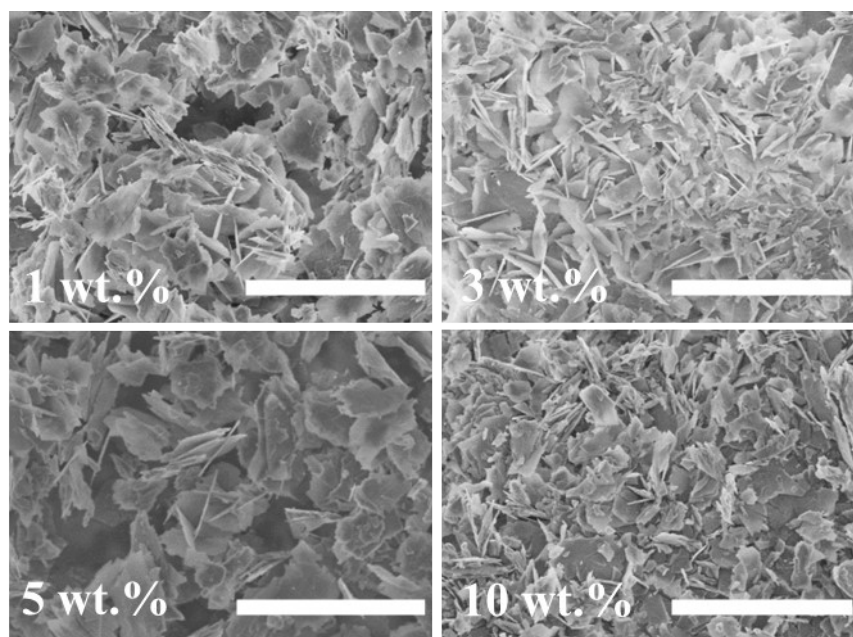


Fig. S13 SEM images of calcined samples synthesized by IDM-1 seed-assisted method (scale bar, 10 μm).

Fig. S13 shows that all of these ZSM-5 samples obtained with IDM-1 as seeds exhibited plate-like morphology.

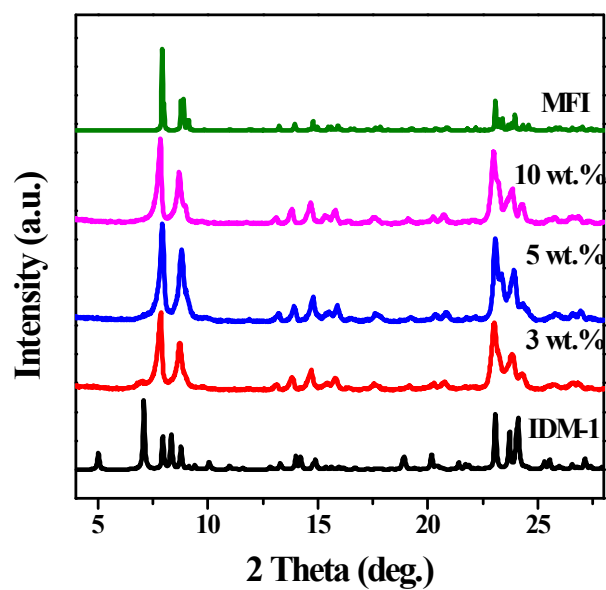


Fig. S14 PXRD patterns of calcined samples synthesized by using MFI-type Silicate-1 as seeds.

With the addition of Silicate-1 seeds, the IDM-1 structure transferred to the MFI structure. It implied that the tiny nuclei generated from two different kinds of IDM-1 and MFI seeds had similar secondary building units and finally led to the ZSM-5 zeolites.

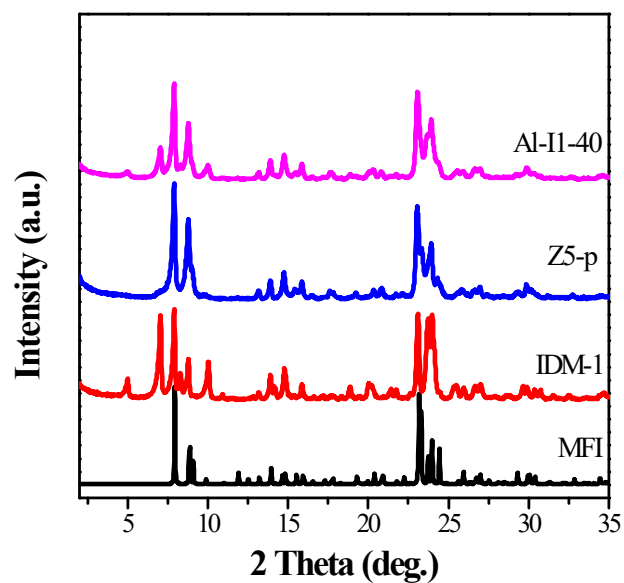


Fig. S15 PXPD patterns of calcined MFI, IDM-1, Al-II-40 and Z5-p.

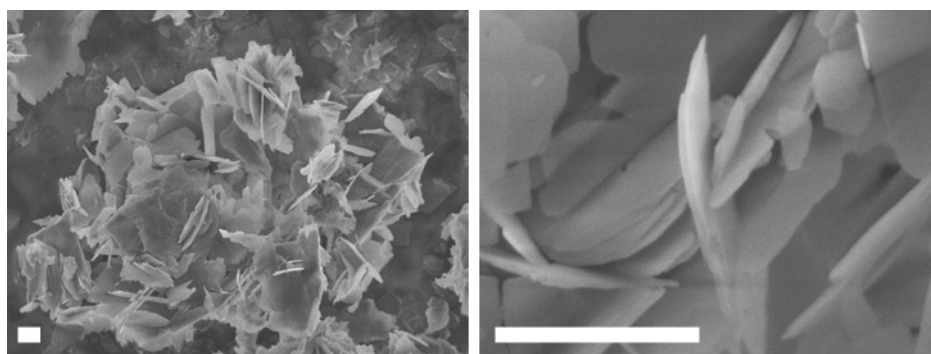


Fig. S16 SEM images of calcined Z5-p (scale bar, 1 μm).

*Figs. S15 and S16 show that the crystal nuclei were critical to synthesizing oriented zeolites. Considering the structural similarity between MFI and IDM-1, only when NH_4F and the Al-II crystal nuclei coexisted, the b-oriented Al-II could be achieved successfully. However, when NH_4F was added after the low-temperature preliminary aging, the ZSM-5 crystal nuclei would be created, and plate-like ZSM-5 zeolites (**denoted as Z5-P**) would be achieved.*

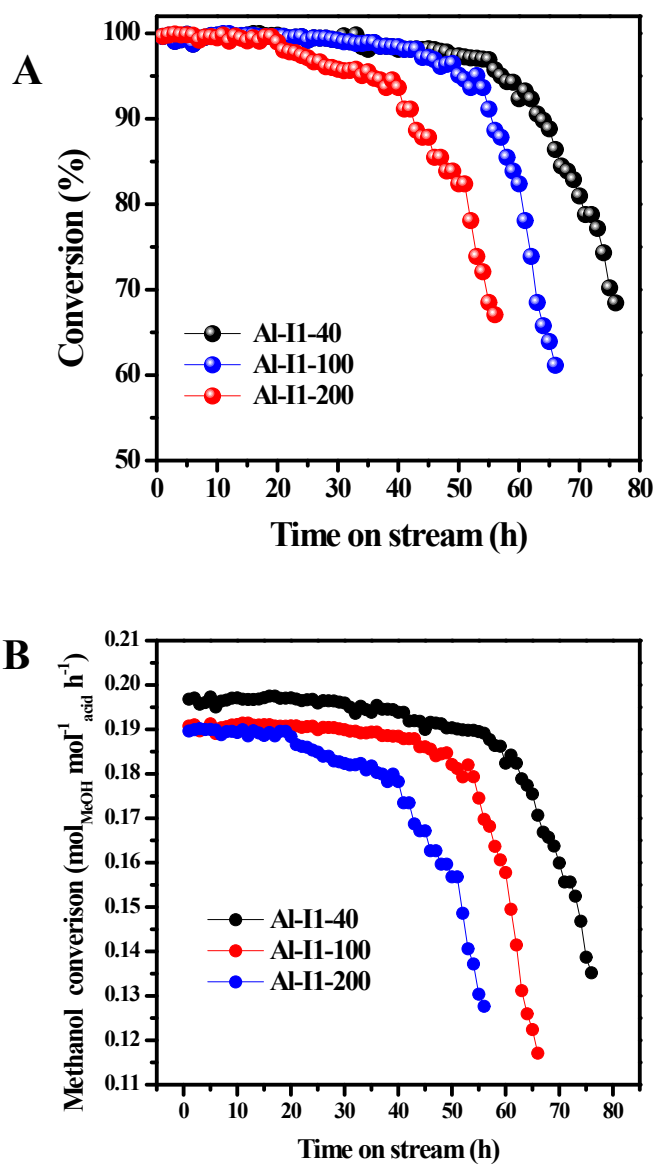


Fig. S17 (A) Methanol conversion and (B) the moles of converted methanol to per mole of acid sites per hour of *b*-oriented Al-I1 in MTP reaction.

Reaction conditions: catalyst 0.1 g, temperature, 723 K, atmospheric pressure, WSHV= 2 h⁻¹, N₂ gas flow rate 30 mL min⁻¹.

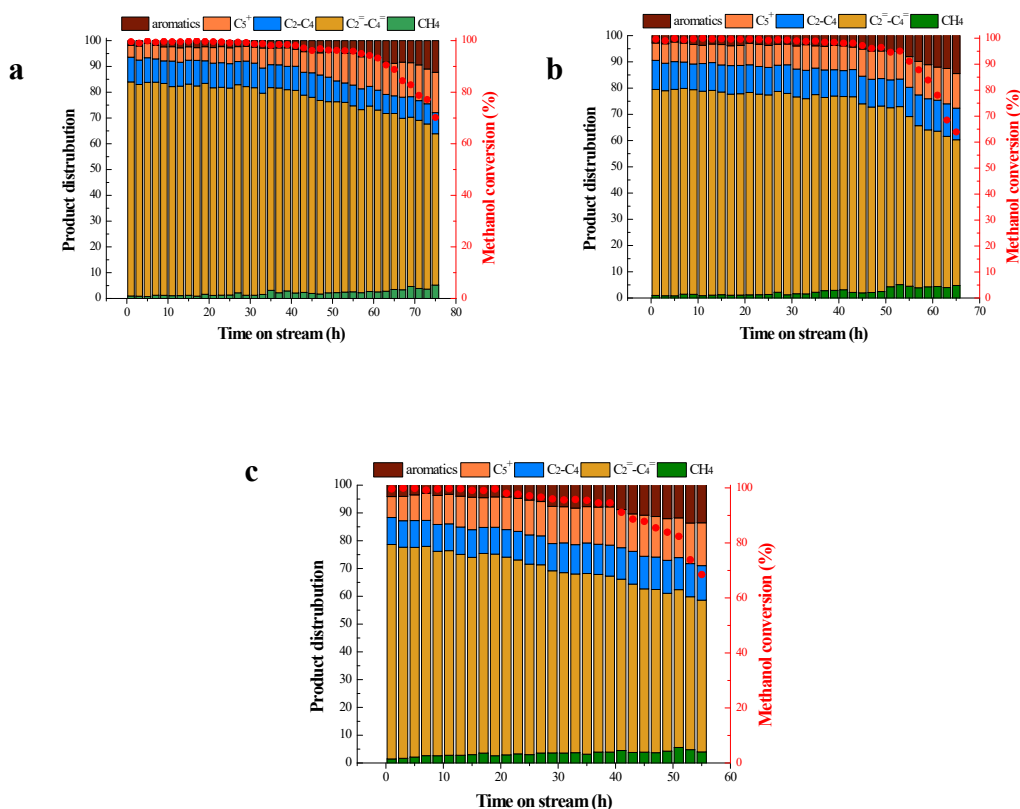


Fig. S18 MTP product distributions and methanol conversion for the *b*-oriented (a) Al-I1-40, (b) Al-I1-100, (c) Al-I1-200 zeolites.

Fig. S18 shows that the light olefins selectivity remained constant at beginning state and decreased with TOS over all the samples, while light paraffin selectivity gradually declined and remained constant. Meanwhile, C₅⁺ and aromatics selectivity gradually increased due to the deactivation of catalysts, and the CH₄ selectivity gradually increased with the progress of the reaction. The light olefin selectivities, especially, the propylene and butene, significantly were increased with decrease of *b*-axis length and that indicated that olefins-based cycles was dominant over Al-I1 zeolite, and the shorter *b*-axis channel length was advantageous for the olefin-based cycle in the MTP reaction.⁶

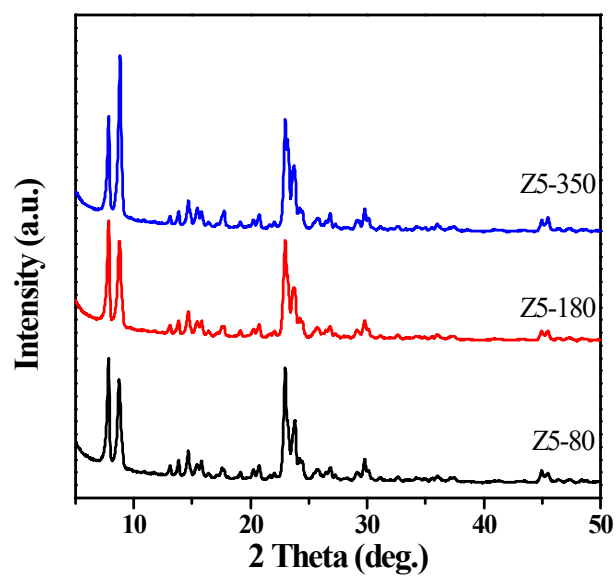


Fig. S19 PXR D patterns of calcined Z5-x.

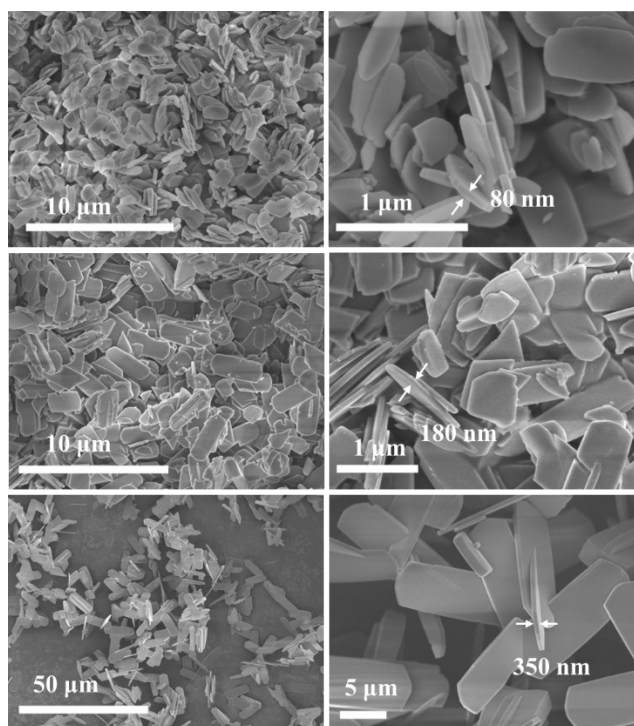


Fig. S20 SEM images of calcined Z5-x.

Figs. S19 and 20 show that the ZSM-5 zeolites for control experiment were synthesized successfully to have b-axis orientation. The length along the b-axis was about 80 nm, 180 nm, and 350 nm for Z5-50, Z5-180, and Z5-350, respectively.

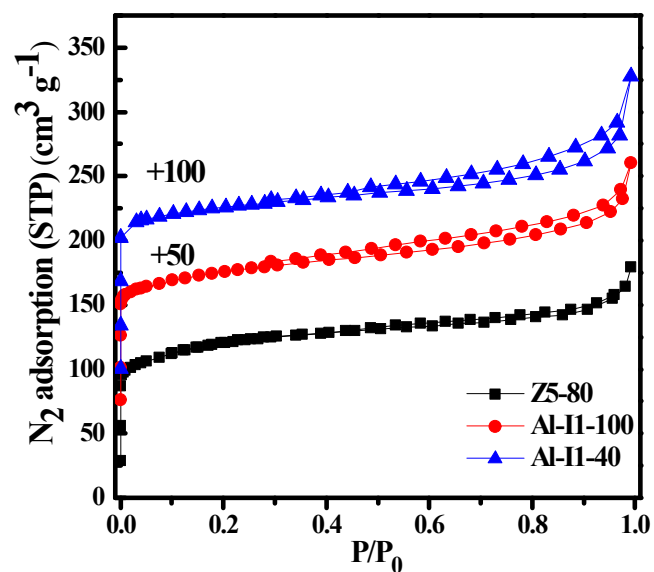


Fig. S21 N₂ sorption isotherms of calcined Al-II and ZSM-5 zeolites.

All materials possessed the type I adsorption isotherms. A steep increase was observed for both Al-II-40 and Al-II-100 at $P/P_0 > 0.2$ as a result of multilayer adsorption, which was attributed to the presence of intra-particle voids created by the expanded a -axis channels. The hysteresis loop area of Al-II was larger and more apparent, indicative of the presence of more mesopores.

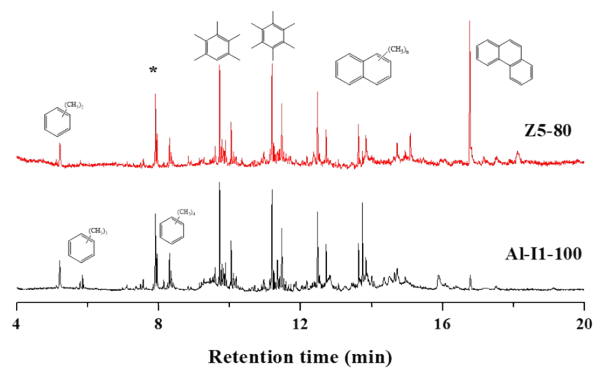


Fig. S22 GC-MS analysis of the organic species in used Al-I1-100 and Z5-80 after methanol conversion at 723 K. Hexachloroethane was used as an internal standard, indicated by the asterisk (*) in the chromatogram.

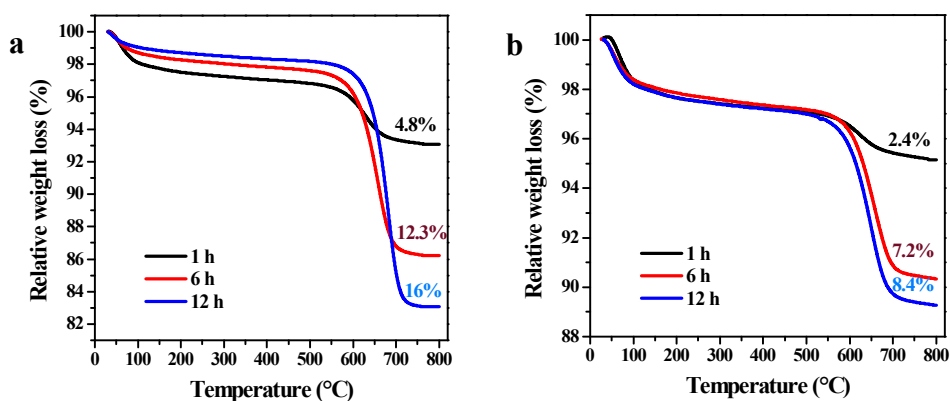
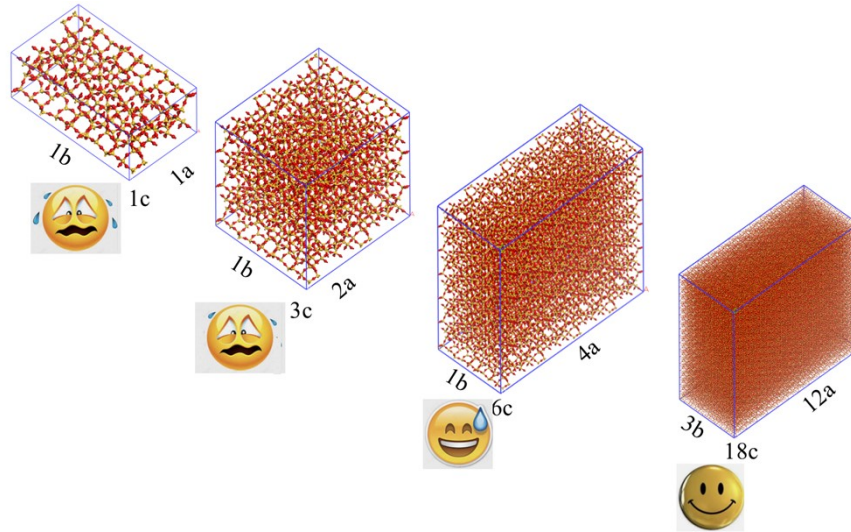


Fig. S23 TG curves of (a) Al-II-200 and (b) Al-II-40 after MTP reaction for different times.

Fig. S23 shows the changes in deposited coke amounts on Al-II-40 and Al-II-200 after different reaction times. The Al-II-40 sample had a lower amount of deposited coke than Al-II-200 at the same reaction time. Primarily, the amount of coke deposited on Al-II-200 (coke content 16%) was almost double that of Al-II-40 (coke content 8.4%) after 15 h reaction.

Table S1 Generation energies of different surfaces of IDM-1 (kcal nm⁻²).

Different layers	100			010	001		
	1a	2a	4a	1b	1c	3c	6c
Surface energy	6.63	5.98	4.64	4.84	6.04	5.48	4.66



As shown in Table S1, when the unit cell parameters are 1:1:1, the surface formation energy of (010) surface in a unit cell is the lowest with a value of 4.84 kcal nm⁻², while they are 6.63 kcal/nm² for (100) and 6.04 kcal nm⁻² for (001), respectively. This kind of large energy difference may be caused by the different unbonded atoms exposed on the out-most surfaces. However, with the increased thickness along the a and c-axes of the crystal, the surface formation energy of (100) and (001) decreased rapidly. And when the unit cell parameter is 4:1:6, the surface formation energy required for growth in the three directions is comparable, which means that the growth of the IDM-1 crystal may according to the ration of a:b:c to 4:1:3. During the growth process of IDM-1, the decreased surface formation energy along the a-axis and c-axis will cause the increasing the relative thickness of a and c in the supercell to stabilize the system. Based on this, Al-II with different b-axis thicknesses maybe can be obtained through experimental optimization while introducing Al into the IDM-1 framework at the same time.

Table S2 Chemical compositions, texture properties and surface acid properties of calcined

Al-I1 and ZSM-5 zeolites.

Sample	Si/Al ^d	Surface area		Pore volume		Acidity by NH ₃ -TPD ^e			Acidity by Py-IR ^f		
		(m ³ g ⁻¹)		(cm ³ g ⁻¹)		(μmol g ⁻¹)			(μmol g ⁻¹)		
		S ^a _{total}	S ^b _{ext}	V ^a _{total}	V ^c _{meso}	total	week	strong	total	BAS	LAS
IDM-1 silicate	-	380	80	0.22	0.14	-	-	-	-	-	-
Al-I1-40	97	451	91	0.35	0.21	154	95	59	148	121	27
Al-I1-100	98	417	83	0.32	0.18	163	102	61	154	128	26
Al-I1-200	97	383	88	0.22	0.13	164	104	60	150	122	28
Z5-80	90	430	98	0.22	0.08	158	98	60	156	135	21
Z5-180	95	414	90	0.21	0.07	162	88	74	162	132	30
Z5-350	93	357	88	0.18	0.07	168	96	72	158	134	24

^a Calculated by the BET method.^b Calculated by the t-plot method.^c $V_{meso} = V_{total} - V_{micro}$.^d Decided by ICP analysis.^e The quantities of weak and strong acid sites determined by NH₃-TPD were measured by the amounts of ammonia desorbed at 350–500 K and 500–700 K, respectively.^f The quantities of Brønsted and Lewis acid sites were determined by Py-IR with the amounts of pyridine (Py) desorbed at 473 K.

The difference in the amount of acid determined by NH₃-TPD and Py-IR is due to the different molecular sizes of NH₃ and pyridine. NH₃ molecules can access some acid sites that cannot be approached by pyridine, and thus, more acid sites are detected by NH₃-TPD than by Py-IR.⁷

Table S3 Product distribution in the MTP reaction.^a

Sample	lifetime ^b (h)	Product selectivity (%)									
		CH ₄	C ₂ ⁼	C ₂	C ₃ ⁼	C ₃	C ₄ ⁼	C ₄	C ₅ ⁺	C _{2,4} ⁼	P/E ^c
Al-I1-40	67	1.3	12.2	0.1	57.1	0.9	14.4	7.8	6.2	83.8	4.7
Al-I1-100	58	1.6	12.1	0.1	51.8	1.0	13.1	8.8	11.5	77.0	4.3
Al-I1-200	47	2.1	12.4	0.2	50.2	0.7	9.9	8.3	16.2	72.5	4.1
Z5-80	53	3.5	13.8	0.2	47.1	0.6	10.6	8.9	15.3	71.5	3.4
Z5-180	43	3.8	14.7	0.1	44.3	0.4	10.5	8.3	17.9	69.5	3.0
Z5-350	29	4.9	16.5	0.3	40.6	0.6	8.3	7.2	21.6	66.1	2.4

^a The selectivity of the product is tested when the reaction reaches a steady state.

^b The lifetime is based on the TOS at methanol conversion $\geq 85\%$.

^c P/E is defined as $S_{\text{propylene}}/S_{\text{ethylene}}$.

Table S4 The diffusion coefficients of *para*-xylene in *b*-oriented Al-I1 and ZSM-5.

Substrate molecule	Diffusion coefficient ^a (D_{eff} / R^2 (10^{-9} s^{-1}))				
	Al-I1-40	Al-I1-100	Al-I1-200	Z5-80	Z5-350
<i>para</i> -Xylene	54.3	49.6	12.7	11.5	6.4

^a These results were calculated by Fick's second law.

Table S5. Evaluation of sample repeatability.

Sample ^a	Si/Al ^b	Yield (%)	RC% ^c
Al-I1-1	97	92	98
Al-I1-2	98	95	99
Al-I1-3	97	94	98
Al-I1-4	96	95	99
Al-I1-5	99	95	99

^a The Si/Al of synthetic gel is 100.

^b decided by ICP analysis.

^c We take the integrated intensity ratio of diffraction peaks of crystallized products and fully crystallized products within the 2θ range of $22.0-25.0^\circ$ as relative crystallinity (RC%)

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