

10 h

9-MR STT

AI-STT

Rapid Synthesis of Nine-Membered-Ring STT Aluminosilicate Zeolite from Chain Rearrangement of Lamella MWW Zeolite and Its Catalytic Performance in the Methanol-to-Olefin Reaction

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studying the impact of pore structure on catalytic performance. However, synthesizing pure-phase STT zeolites with tunable acid sites has been challenging. This study presents a rational approach for the rapid synthesis of STT zeolites from lamella Si-MWW zeolite via a chain rearrangement process, leveraging their structural similarities and the flexibility in manipulating MWW's layer structure. Both zeolites share a common chain comprising ordered arrangements of 4-, 5-, and 6-membered rings, facilitating robust and rapid (10 h) STT growth, with a broad Si/Al ratio range. The resulting Al-STT zeolites exhibited an olefin product distinct from the 8-MR CHA and 10-MR MFI zeolites in the methanol-to-olefin reaction, underscoring the pivotal role of 9-MR pore structure. The findings not only advance the understanding of zeolite synthesis but also demonstrate the potential of tailoring pore structures to enhance the catalytic efficiency in industrially relevant processes.

1. INTRODUCTION

Zeolites are crucial in catalytic processes, where their unique pore structures play a key role in determining product distribution.^{1–5} Recent advancements in theoretical studies and machine learning^{6–8} have significantly enhanced the ability to predict and optimize zeolite performance in catalytic reactions, offering insights into how structural variations affect catalytic behaviors. Despite progress, challenges in validating these predictions underscore the imperative to broaden the utilization of diverse structures, particularly those with unique pore features, yet remaining underexplored.

Among zeolites, 9-MR structures hold immense potential in shape-selective catalysis and fundamental research. However, odd-membered-ring structures are very scarce compared to even-membered ring zeolites. This scarcity may stem from their framework energy.^{9,10} In the current zeolite database, only three of the silicon-based 9-MR zeolites have stable structures, namely NAT,¹¹ PWO,¹² and STT.^{13–15} While NAT zeolite's low Si/Al ratio (1.5) limits its catalytic applications,¹¹ and PWO zeolite synthesis requires intricate organic structure directing agents (OSDA),¹² STT zeolite offers significant advantages, which can be synthesized with commercially available OSDA.^{9,13–18} Aluminosilicate form STT, also known as SSZ-23, is the first aluminosilicate zeolite to possess a 9-MR aperture.^{13–16} Featured by both 9-MR and 7-MR structures, STT comprises two-dimensional cage arrays.^{15,16} The cage arrays create channels parallel to the [001] direction, limited by the 7-MR windows (3.5 × 2.4 Å²) at their narrowest point, and parallel to the [101] direction, surrounded by the 9-MR window $(5.3 \times 3.7 \text{ Å}^2)$.^{15,16} The STT cage $(11.7 \times 8.1 \text{ Å}^2)^{19}$ is located at the intersection of the 7-MR and 9-MR channels.^{15,16}

Si-MWW

Despite their potential, synthesizing STT zeolites with tunable acid sites is challenging due to long growth cycles, narrow synthesis phase areas (easy association with CHA), and the necessity for fluoride involvement.^{16–18,20,21} Thereby, alternative routes need to be developed to overcome these issues encountered in direct synthesis.

It was reported that MWW and STT zeolites have close phase diagrams.²² More importantly, we noticed that a common chain structure exists in both frameworks. As shown in Scheme 1, a chain comprising ordered connections of 4, 5, and 6 MRs exists within the MWW structure. Interestingly, this chain's repetitive arrangement gives rise to the slightly puckered layers observed in STT zeolite, aligned parallel to the (101) crystal plane. The shared chain structure between MWW and STT zeolites, as well as the flexibility in layered structural manipulation of MWW,^{23–26} suggests the

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potential for synthesizing STT from MWW through an ADOR-like (assembly–disassembly–organization–reassembly)^{27–30} interzeolite conversion (IZC) process.^{31–35} Moreover, MWW's lower framework density compared to STT makes the transition from MWW to STT more feasible from an energy perspective.³⁶

This study optimized synthetic conditions to achieve the rapid synthesis of STT zeolites from the Si-MWW parent zeolite through an interzeolite conversion process, which involved a chain rearrangement (CR) process. The method proved efficient, requiring a short crystallization time (10 h), and robust, meanwhile offering broad adjustability in the Si/Al ratio. Evaluation of the resulting Al-STT in the methanol-to-olefin (MTO) reaction revealed olefin product selectivity between CHA and MFI, demonstrating the size transition effect of the 9-MR zeolite.

2. EXPERIMENTAL SECTION

2.1. Materials. For the Si-MWW and Al-STT samples' synthesis, *N*,*N*,*N*-trimethyl-1-adamantylammonium hydroxide (TMAdaOH, 25% aqueous solution, Adamas-beta), hexamethylenimine (HMI, 98%, Energy Chemical), fumed silica (SiO₂, CAB-O-SIL M5), and sodium aluminate (NaAlO₂, Aladdin) were used. All the reagents were used as received without further purification.

2.2. Preparation Method. 2.2.1. Synthesis of Si-MWW. The Si-MWW parent was synthesized according to the literature³⁷ with a molar composition of 1 SiO₂:0.25 TMAdaOH:0.31 HMI:44 H₂O. First, the TMAdaOH aqueous solution was thoroughly mixed with HMI, and then fumed silica was added. After stirring overnight, the final mixture was transferred to a PTFE lined stainless steel autoclave and heated at 150 °C for 5 days while rotating at 30 rpm. The assynthesized product was filtered, washed with deionized water, and dried at 70 °C overnight. The dry powder was calcined in air at 600 °C for 10 h in order to remove the organic structure directing agent.

2.2.2. Synthesis of Al-STT. The gel molar composition for the synthesis of Al-STT was $1 \text{ SiO}_2:1/x \text{ NaAlO}_2:20 \text{ H}_2\text{O}:0.2-0.5 \text{ TMAdaOH}$. Si-MWW (calcined form) was used as the silicon source. First, Si-MWW was mixed with TMAdaOH aqueous solution and stirred for 1 h, and then, NaAlO₂ was added to the above mixture. After stirring overnight, the final mixture was transferred to a PTFE lined stainless steel autoclave and heated at 200 °C for 10 h under static conditions. The as-synthesized products were centrifuged, washed with deionized water, and dried at 70 °C overnight. The dry powder was calcined in air at 600 °C for 10 h. The final products were denoted as Al-STT-*x*, where *x* represents the Si/Al ratio of the initial gel.

2.3. Characterization. The X-ray diffraction (XRD) patterns were obtained on a Rigaku Smart Lab 9 kW X-ray diffractometer (45 kV, 200 mA) with Cu K α radiation (λ = 1.5406 Å). The N₂ sorption isotherms were measured by using a Micromeritics 3FLEX physical adsorption analyzer at -196 °C. The samples were degassed at 200 °C for 5 h before the measurement. The surface area and pore volume were determined by Brunauer-Emmett-Teller (BET) and t-plot methods, respectively. The NH₃ temperature-programmed desorption (NH₃-TPD) experiments were performed on a PCA-1200 chemical absorber. 75 mg of the sample was placed in a quartz reactor under flowing Ar at 500 °C for 1 h. NH₃ adsorption was carried out in the mixture of 10% NH₃ in Ar at 150 °C for 40 min, and the physically adsorbed NH₃ was removed by flowing Ar at 150 °C for 40 min. The NH₃-TPD was carried out from 100 to 600 °C at a heating rate of 10 °C min⁻¹, and the NH₃ desorption signal was detected by a thermal conductivity detector (TCD). ²⁷Al magic-anglespinning nuclear magnetic resonance (²⁷Al MAS NMR) experiments were performed on an Agilent DD2-500 MHz spectrometer at 130.2 MHz using a 4 mm MAS NMR probe with a spinning rate of 14 kHz. Chemical shifts were referenced to tetramethylsilane (TMS). The elemental contents of the samples were analyzed using an Avio 220 inductively coupled plasma optical emission spectrometer (ICP-OES). 10 mg of the sample was dissolved in hydrofluoric acid and diluted to 25 mL with deionized water. The thermogravimetry and derivative thermogravimetry (TG-DTG) experiments were performed on a thermogravimetric analyzer (TGA/DSC-1) from room temperature to 800 °C at a heating rate of 10 °C min⁻¹ in air. Scanning electron microscopy (SEM) images were obtained using a JSM-7610F Plus field emission scanning electron microscope at 10 kV. Transmission electron microscopy (TEM) images were observed on a JEM-2000EX field emission transmission electron microscope at 200 kV, and high-resolution transmission electron microscopy (HRTEM) images were observed on a JEM-F200 field emission transmission electron microscope at 200 kV. The UV Raman spectra were recorded by a homemade UV Raman spectrograph with a spectral resolution of 2 cm^{-1} . The exciting source was the laser line from an intracavity double-frequency Lexel laser (Lexel Inc.) with a wavelength of 244 nm at a laser power of 3 mW. The pyridine-adsorbed IR spectra were carried out on a Bruker Tensor 27 instrument. The calcined samples were dehydrated at 500 °C for 1 h under a vacuum of 1.0×10^{-2} Pa, and then, pure pyridine vapor was adsorbed at room temperature for 10 min. After reaching equilibrium, the pyridine-adsorbed system was evacuated at 150, 300, and 450 °C. The IR spectra were recorded at the corresponding temperatures.

2.4. Catalytic Reaction. The methanol-to-olefin (MTO) reaction was performed in a quartz tubular fixed-bed reactor at atmospheric pressure. 0.3 g of catalyst (40–60 mesh) was loaded in the quartz reactor and activated at 550 °C in a N₂ flow of 30 mL min⁻¹ for 30 min before starting each reaction run, and then the temperature was adjusted to 450 °C as required. The methanol was fed by passing N₂ carrier gas with a velocity of 39 mL min⁻¹ through a saturator containing methanol at 12 °C, which gave a weight hourly space velocity (WHSV) of 1 h⁻¹. The reaction products were analyzed using an online gas chromatograph (Agilent GC 7890N) equipped with a flame ionization detector (FID) and a Plot-Q column. The conversion and selectivity were calculated on the basis of



Figure 1. XRD patterns (a) and NH₃-TPD profiles (b) of Si-MWW and Al-STT-x; ²⁷Al MAS NMR spectra (c) of Al-STT-x and SEM images of Al-STT-25 (d), Al-STT-50 (e), and Al-STT-100 (f); x represents the initial Si/Al ratio for the STT synthesis.

Table	1.	Svnthesis	Parameters an	ıd Ph	vsicochemical	Properties	of Al-STT	with	Different	Si/Al	Ratios
		- /			/						

run	initial Si/Al ^a	OSDA/Si	Si/Al ^b	$\operatorname{acid}_{\operatorname{total}}(\mu\operatorname{mol}/g)^c$	$S_{\rm BET} (m^2/g)^d$	$S_{\rm micro} ({\rm m}^2/{\rm g})^d$	$V_{\rm micro} ({\rm cm}^3/{\rm g})^d$
1	25	0.2	17.9	248	539	487	0.19
2	50	0.2-0.4	48.8	160	527	482	0.19
3	100	0.3-0.5	93.2	99	568	518	0.20
4	∞^e	0.5			459	422	0.16
ac: / 11 :	$b_{\rm D} = b_{\rm D} = b_{\rm D}$	ICD OEC CD.	$d_{\mathbf{D}}$	N	- TATA		

Si/Al in the initial gel. ^bBy ICP-OES. ^bBy NH₃-TPD. ^aBy N₂ physisorption. ^bSi-STT.

 CH_2 . Dimethyl ether (DME) was considered to be a reactant in the calculation.

resonance centered at ~0 ppm suggests the presence of a very small number of extraframework aluminum species.³⁸

3. RESULTS AND DISCUSSION

3.1. Rapid Synthesis of Al-STT from Si-MWW. By employing Si-MWW as the silica source, upon optimization of the synthesis conditions, STT zeolites with varied Si/Al ratios $(Si/Al = 18 - \infty)$ were successfully synthesized within 10 h. Figures 1a and S1a depict the X-ray diffraction (XRD) patterns of the parent zeolite Si-MWW and the resulting STT zeolites, showcasing characteristic STT diffraction peaks¹⁶ with high crystallinity. This observation is further supported by scanning electron microscopy images (SEM, Figures 1d-f and S1b,c), revealing prism-like morphology of STT zeolites, averaging around 1 μ m in size. Variations in thickness are evident among zeolites with different Si/Al ratios. N2 sorption isotherms of the STT samples (Figure S2) show type I isotherms representing the microporous structure, with corresponding surface area and micropore volume data presented in Table 1. Noteworthy is the close alignment of the actual Si/Al ratios in the samples with those in the initial synthetic gels (Table 1), validating the efficacy in introducing Al. Compared to the parent MWW zeolite with minimal ammonia adsorption, the Al-STT samples exhibit an ammonia adsorption performance consistent with their Si/Al ratios (Figure 1b). Higher Al content correlates with enhanced ammonia adsorption and acid quantity (Table 1), confirming the successful endowment of acidity to the STT zeolites. ²⁷Al MAS NMR spectra provide further evidence of Al incorporation. As shown in Figure 1c, Al-STT zeolites with initial Si/Al ranging from 25 to 100 exhibit a major chemical shift centered at ~55 ppm, belonging to the tetrahedrally coordinated framework Al. The weak wide

Taking the synthesis of Al-STT-50 as a case study, the influence of various synthesis factors was explored. Table S1 lists the ingredients of the initial synthetic gel for Al-STT-50, and Figure S3 displays the XRD patterns of the obtained samples under different conditions. At a fixed H₂O/Si ratio of 20, pure-phase STT was obtained at OSDA/Si ratios ranging from 0.2 to 0.4. When the OSDA concentration was too low (OSDA/Si = 0.1, Table S1, run 1), the final product exhibited an eroded MWW layer structure accompanied by an amorphous phase, underscoring the importance of adequate OSDA for STT structure formation. Conversely, an excessive OSDA concentration (OSDA/Si = 0.5, Table S1, run 6) resulted in CHA impurity, aligning with literature reports suggesting that high OSDA concentration favors CHA phase formation.²⁰ In addition, at a fixed OSDA/Si ratio of 0.2, increasing the H₂O/Si ratio to 40 (Table S1, run 2) scarcely yielded any STT phase, with only characteristic MWW peaks retained, emphasizing the necessity of optimal alkalinity for STT production. It is noteworthy that a high temperature proved essential for the rapid synthesis of STT, as incomplete conversion of MWW to STT was observed at reduced temperature (180 °C, Table S1, run 3). Exploration of different Si/Al ratios revealed a higher likelihood of CHA impurity formation with increased Al content (Si/Al = 12.5) in the synthesis system, as depicted in Figure S4.

3.2. Crystallization Process of Al-STT-50. The transition process from Si-MWW to Al-STT-50 was monitored throughout a hydrothermal treatment spanning 0 to 10 h, utilizing XRD, N_2 physisorption, and TG analysis. A unique transformation process from the 3D MWW structure to the 2D



Figure 2. XRD patterns (a) of as-synthesized samples obtained during Al-STT-50 crystallization at different synthesis times; pore volume and solid mass yield (b), N_2 sorption isotherms (c) of the calcined samples, and TG profiles (d) of as-synthesized samples.

MWW precursor and then to new 3D STT structure was observed. Initially (0 h), after overnight stirring without hydrothermal treatment, the XRD pattern (Figure 2a) exhibits a new peak at approximately 6.3° , the characteristic (002) diffraction peak of the MWW precursor,³⁹ coupled with a considerable weakening of the peak at around 7.1°. Notably, the 7.1° peak represents both the interlayer (002) and intralayer (100) diffractions of the parent 3D MWW. The (002) peak shift from 7.1° to 6.3° indicated a transition from the 3D MWW structure into an MWW precursor, with expanded *d*-spacing. Essentially, the layer space expansion was realized via OSDA insertion.^{40,41} It is hypothesized that stirring with TMAdaOH induced this transformation, allowing the OSDA to enter the MWW layer along the *c*-axis. Meanwhile, partial destruction of the interlayer and intralayer structure may occur due to the alkaline environment.⁴¹ Comparison of BET surface area and pore volume (Figures S5 and 2b) showed increased external surface area and mesopore volume due to layer disordering, alongside a reduction in micropore area and volume, in line with XRD findings.

Treatment at 200 °C for 1 h intensified the (002) diffraction peak of the expanded layer structure (Figure 2a), suggesting an increased incorporation of OSDA between the layers. Meanwhile, the mesopore volume and external surface area peaked (Figures 2b and S5), evident through a significant hysteresis loop on the N₂ sorption isotherms (Figure 2c). Additionally, after calcination, the calcined sample exhibited a broadened (002) peak (Figure S6), indicating a higher degree of disorder along the c-axis. These phenomena can be explained by the intensified etching effect of OSDA under a high temperature. There is no doubt that the loose structure and broadened interlayer space are conducive for the transition process, while the structural defects and gaps caused by local erosion create footholds for the birth of new structure. This is similar to the assembly-disassembly-organization-reassembly (ADOR) strategy, 27-30 in which the formation of layered precursors is

also crucial for the subsequent evolution of the structure, and the hydrolysis of the bonds in the original structure provides the possibility of structural rearrangement.

At 2 h, XRD patterns of calcined sample (Figure S6) show distinctive peaks of the STT structure at 8.1, 9.4, and 10.5°.¹⁶ At this time, both the solid mass and micropore content increased (Figure 2b), supporting the formation of the new STT phase. Additionally, the sample's external surface area began to decrease (Figure S5), suggesting consumption of the layer phase. Subsequent stages involved the progressive growth of the STT phase and the continuous diminution of the layer phase. At 4 h, further increase in micropore content was observed, with solid vield close to 80% (Figure 2b). By 6 h, STT became the dominant phase, and by 10 h, crystallization was completed, with the solid yield increasing over time to nearly 90%. The N₂ sorption isotherms gradually approached the type I isotherm accompanied by the disappearance of the hysteresis loop, representing a characteristic micropore structure (Figure 2c).

TG-DTG experiments were performed to verify the structural evolution with the insertion of OSDA (Figures 2d and S7; Table S2). The weight loss was roughly divided into three steps: the desorption of physisorption water (30-180 °C); the removal of the OSDA between the MWW layers (180-400 °C) and inside the zeolite channels (400-800 °C).⁴² For the first stage, with the extension of growth time, the weight loss associated with water bound to the hydrophilic groups decreased, in line with the diminishing of the more hydrophilic MWW phase.⁴³ The desorption peak of 180-400 °C was observed since 0 h and reached its highest value at 2 h, followed by a gradual decrease, indicating the insertion of the OSDA between the layers and the subsequent MWW phase depletion. In addition, the weight loss in the range of 400-800 °C kept increasing over time, suggesting the formation and gradual perfection of the STT framework.



Figure 3. TEM images of the calcined samples obtained during Al-STT-50 crystallization at different synthesis times.



Figure 4. TEM and HRTEM images of the calcined samples obtained during Al-STT-50 crystallization at 1 h (a, d), 2 h (b, e), and 10 h (c, f), respectively.

To elucidate the crystallization process more comprehensively, TEM and SEM imaging were performed to track various growth stages. As shown in Figures 3 and S8, the parent Si-MWW zeolite had a characteristic plate-like morphology, with a smooth and intact surface. After overnight stirring, the 0 h sample still maintained the overall shape and stacking morphology (Figure S8), albeit with emerging eroded holes and cracks on the plate (Figure 3), in line with increased mesopore volume. Subsequent high-temperature treatment for 1 h resulted in blurred edges of the sheets and restacking of fragmented structures (Figure S8) and a more pronounced erosion effect (Figure 3). By 2 h, scattered quadrilateral particles began to develop on the MWW surface, accompanied by a few uneven lumpy protrusions (Figures 3 and S8), which could be the first sign of the STT development, in alignment with the XRD findings (Figure 2a). Observations at 4 h (Figure 3) revealed the enrichment of the STT crystals on the periphery of the MWW layers, with a size of less than 1 μ m. As the growth time extended to 6 h, a surge of enlarged STT crystals was noticed (Figures 3 and S8), while the original MWW flakes underwent significant ablation, leaving only a small portion attached around the STT crystals, signifying STT growth utilizing MWW as nutrients. Over time, STT crystals continued to enlarge (Figures 3 and S8), demonstrating the Ostwald effect⁴⁴ by progressively consuming MWW. Ultimately, at 10 h, the STT surface appeared smooth (Figure S8), devoid of any remaining MWW flakes, indicating the culmination of the crystallization process, characterized by prism-like crystals measuring approximately $1-2 \mu m$ in size.

High-resolution transmission electron microscopy (HRTEM) imaging was employed to track the microstructure changes at key stages during the transition process (Figure 4). The initial observation at 1 h (Figures 4a and 4d) revealed widespread erosion of the MWW sheets, leading to the formation of mesoporous regions characterized by bright cracks and holes accompanied by blurring of the lattice fringes near the etching area. Despite this erosion, the integrity of the MWW structure was largely preserved with discernible lattice fringes observed in the (101) direction, corresponding to a measured d-spacing of 1.15 nm. By 2 h (Figure 4b), a significant transition occurred as STT crystals began to emerge at the margins of the MWW lamella sheet, with lower growth energy barriers at the interface.⁴⁵ Figure 4e depicts small grains exhibiting characteristic STT lattice fringes, featuring a dspacing of 0.94 nm corresponding to the (-111) plane, alongside retained MWW lattice fringes, providing clear evidence of the transition from MWW to STT. The gradual consumption of MWW ultimately led to the formation of pure STT. Remarkably, the 10 h sample exhibited a smooth,

Intensity (a.u.)

Temperature (°C)



Figure 5. UV Raman spectra (a) and NH₃-TPD profiles (b) of the calcined samples obtained during Al-STT-50 crystallization at different synthesis times.



Raman shift (cm⁻¹)



unbroken surface with uniform lattice fringes, indicative of high-crystallinity STT purity attainment (Figures 4c and 4f).

The structure evolution at the building-unit level was investigated through UV Raman spectroscopy. As shown in Figure 5a, the 0 h sample predominantly retained the characteristic vibrations of the MWW framework, with Raman bands at 266 and 342 cm⁻¹ corresponding to the 6 MRs, 399 cm⁻¹ attributed to the 5 MRs, and 489 and 518 cm⁻¹ representing the 4 MRs of the MWW structure.⁴⁶

The 2 h mark denoted a pivotal transition point in structural evolution. Signals associated with the MWW structure markedly weakened, indicating substantial degradation of both the intralayer structure and ordered layer arrangement. Concurrently, peaks indicative of the STT structure began to emerge. Notably, the T–O bending vibration around 450 cm⁻¹ originating from MWW shifted to 441 cm⁻¹. Moreover, an overall downward shift in the vibration bands of 4, 5, and 6 MRs toward lower frequencies was observed, showing characteristic peaks belonging to the STT structure, indicating uniform ring rearrangement, which could be the sign of chain rearrangement (Scheme 1). Specifically, the vibration of 4 MRs at 489 cm^{-1} shifted to 473 cm^{-1} , the 5-MR vibration band at 399 cm^{-1} shifted to 390 cm^{-1} , and a shift of the 6-MR vibration from 342 to 339 cm⁻¹ was observed. Furthermore, a new band at 217 cm⁻¹, assigned to the vibration of 7 and 9 MRs of STT, was also captured at 2 h, providing additional evidence of the emergence of the STT structure.

As the growth time extended, the STT structure gradually improved at the expense of the original MWW structure. At 4 h, a mixture of both structures persisted. By 6 h, characteristic vibration bands of MWW were nearly undetectable, exemplified by the disappearance of the 518 cm⁻¹ band, which represents the most abundant 4-MR groups of the MWW structure. Eventually, when the intensity of the 7 and 9 MRs (217 cm^{-1}) bands belonging to the STT structure reached its zenith, the growth of STT was deemed complete.

3.3. Evaluation of Al Species. In the transition process from a pure silica MWW to an Al-incorporated STT structure, understanding Al insertion is crucial. As illustrated by the NH₃-TPD profiles (Figure 5b), Si-MWW showed minimal acidity, while all the subsequent samples exhibited distinct NH₃ desorption peaks centered at 220–230 °C (weak acidity) and 350–380 °C (medium/strong acidity),^{38,47–49} evolving as crystallization progressed. Surprisingly, the 0 h sample already exhibited a pronounced desorption peak at 220 °C and a weak peak at 350 °C, despite it predominantly retaining the MWW structure. This suggests that with the insertion of OSDA into the layers, the expanded layer space facilitated the entry of Al species, primarily in a grafted form bound with the silica hydroxyl group of Si-MWW, thus forming Lewis acid species. A small portion transitioned into the framework Al upon calcination-induced layer condensation, leading to Brønsted acidity, slightly enhanced after 1 h of hydrothermal treatment.

After 2 h of treatment, significant changes occurred in the acidity distribution. The intensity of the second desorption peak markedly increased and shifted to a higher temperature, while the lower-temperature desorption peak (230 °C) experienced slight shrinkage, indicating increased Al incorporation into the framework. As crystallization progressed, extraframework Al species attached to the surface depleted, weakening the first desorption peaks. Meanwhile, peaks at higher temperatures shifted rightward, indicating Al species migration and STT framework perfection, strengthening Brønsted acidity. By 10 h, Brønsted acidity prevailed, with minimal extraframework Al, suggesting predominant integration of Al species into the framework. Pyridine-adsorbed IR spectra (Figure S9) confirmed Brønsted acid sites created by framework Al species, with characteristic desorption peaks observed at 1542 and 1488 cm^{-1,50}

3.4. Chain Rearrangement Route. Compared with the typical interzeolite conversion (IZC), which undergoes a complete dissolution and reorganization process, $^{51-53}$ the transformation from Si-MWW to Al-STT exhibited a unique deviation, with no entire dissolution observed in the early stage. Instead, the birth of STT occurred, while the majority of the MWW structure remained largely intact (2 h). The insertion of OSDA into the MWW layers triggered subsequent structural and composition evolution, resulting in Al-inserted expanded layers. Thereby, the shared chain structure between MWW and STT, composed of ordered arrangements of 4, 5, and 6 MRs, was directly affected by the OSDA insertion, guiding a preferred reorganization of the chain toward STT structure, as shown in Scheme 2.

As previously reported, the synthesis diagrams of MWW, CHA, and STT are close.²² Especially, CHA is widely documented to be a competitive phase of the STT via the direct synthesis, and high aluminum content prefers the growth of CHA.^{20,54} Hence, the shared chain structure is crucial for ensuring the transformation toward STT. Presumably, the binding of aluminum species to the precursor in its early stages of crystallization has effectively hindered the severe dissolution of the precursor, ⁵⁵ which is essential for keeping the chains, thus facilitating the formation of the pure STT phase in aluminum-containing systems.

3.5. MTO Catalytic Performance. The methanol-toolefins (MTO) reaction catalyzed by zeolites with shapeselective effects has attracted considerable attention in the field of C_1 chemistry.^{5,56,57} The suitable acidity and unique structural parameters of STT, positioned between the two most popular MTO catalysts, ZSM-5 and SSZ-13, prompted us to evaluate its MTO catalytic performance. As depicted in Figure 6, Al-STT-25 exhibits the longest lifetime and a



Figure 6. MTO reaction performance of Al-STT with different Si/Al ratios. Reaction conditions: 450 $^\circ$ C, WHSV 1.0 h⁻¹.

relatively stable light olefin selectivity of around 77%. The life span of Al-STT is shortened with increased Si/Al ratios, probably related to the increased crystal thickness (Figure 1) and gradually insufficient acid sites. Nevertheless, the highest olefin selectivity enhances to 84.7% for Al-STT-50 and 83.3% for Al-STT-100 (Table S3).The improvement can primarily be attributed to the decrease of acid density, which promotes the alkene-based cycle pathway while weakening the hydrogen transfer reaction.⁵⁸ Consequently, the selectivity of propene was obviously improved from 31.4% for Al-STT-25 to 38.4% for Al-STT-100, with a corresponding decrease in propane selectivity from 9.9% to 3.7% (Table S3).

The distribution of light olefins is roughly 3/4/2 for ethylene/propylene/C₄, with an average distribution around 25%, 38%, and 16%, respectively. Notably, the average propylene yield of STT catalysts is similar to that of SSZ- 13^{59-62} and ZSM-5, $^{63-66}$ while STT catalysts demonstrate obviously higher ethylene selectivity (25% of STT vs $\leq 15\%$ of ZSM-5) than ZSM-5.⁶³⁻⁶⁶ The smaller 9-MR channels (3.7 × 5.3 Å²) of STT enhance shape selectivity for ethylene compared to the 10-MR channels (5.5 × 5.1 Å² and 5.3 × 5.6 Å²) of ZSM-5.

When compared to 8-MR SSZ-13 zeolites, $^{59-62}$ a significantly lower ethylene (45% vs 25%) and higher C₄ yield were observed on STT. Compared with the point of view of Davis's article, 67 provided the MTO reaction results of ERI and LEV with similar size to STT, it seems that the selectivity of ethylene should be larger. However, during the methanol conversion process, the products ethylene and butylene are closely related, and mutual transformation occurs between these two species. It is not ruled out that the product is diffused in the form of butylene, thereby reducing the ethylene yield. Overall, the catalytic performance characteristics of STT are distinct from those of typical medium-pore ZSM-5 and small-pore SSZ-13 catalysts.

This catalyst example provides a new possibility for regulating olefin distribution, which confirms again the shape-selective catalysis principle⁵⁷ and demonstrates how to control product distribution by adjusting structural parameters. Since the structural parameters of STT zeolite are quite special, more research on the MTO mechanism of selectivity control and deactivation is still ongoing.

4. CONCLUSIONS

A novel chain rearrangement (CR) route was developed for the rapid production of 9-MR STT zeolites using Si-MWW zeolite as the parent silicon source. STT zeolites with Si/Al ratios ranging from 18 to infinity were successfully prepared with a short growth time (10 h). The mechanism of the CR process was elucidated, revealing the transformation of the 3D MWW structure into a layered precursor structure, followed by preferential recombination of the shared chain structure between MWW and STT to form the STT framework. The synthesized Al-STT zeolites were evaluated for their catalytic performance in the methanol-to-olefin (MTO) reaction, demonstrating a unique olefin selectivity profile positioned between SSZ-13 and ZSM-5 zeolites, verifying the size transition effect of the 9-MR structure in the catalytic reaction. The findings not only advance the understanding of zeolite synthesis but also highlight the potential for pore structure tailoring to enhance the catalytic efficiency in industrially relevant processes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.4c02088.

Characterization results of samples obtained via the crystallization process including XRD, SEM, DTG, N_2 physisorption, and pyridine-adsorbed IR spectra; detailed reaction results (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. W.H. performed catalyst preparation, characterization, and prepared the draft manuscript. H.W. performed SEM imaging, N_2 physisorption, and draft revision. X.Y. performed TEM imaging and draft revision. J.Z. performed TG-DTG tests. Z.F. analyzed the data and revised the draft. M.Y. performed catalytic tests, analyzed the data, and revised the draft. X.G. analyzed the data and revised the data, and revised the study, analyzed the data, and wrote the paper.

Notes

The authors declare no competing financial interest.

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