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Synthesis of SAPO-34 zeolite from laponite and its application in MTO reaction

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Abstract: In this work, SAPO-34 zeolite with high catalytic activity was successfully synthesized by hydrothermal method from laponite as the single Si source. Compared with the traditional method of synthesizing zeolites from clay, the laponite after swelling can be directly used in the synthesis process of zeolite. The crystallization behavior of SAPO-34 synthesized from laponite was investigated by XRD, FTIR, N2 adsorption - desorption, SEM-EDX, ICP-MS and DR-UV-Vis. The process can be summarized as follows: the Si and Mg elements were produced by the depolymerization of laponite, then the primary building units of SAPO-34 zeolite were formed under hydrothermal conditions, and finally the crystal nucleus began to form and crystallization was triggered. Compared with the conventional SAPO-34 synthesized from TEOS, the SAPO-34 synthesized from laponite exhibited higher selectivity to light olefins and longer lifetime, which can be attributed to the suitable strength of acidity. This work points to a straightforward route to the synthesis of SAPO-34 from laponite.

space and high surface areas. ^[15, 16] Owing to its high surface areas and layered structure, laponite can be used as promising material with high reactivity to synthesize zeolite. Yet to the best of our knowledge, the application of laponite as raw material to synthesize zeolite as Si source has not been reported yet.

In this study, laponite after swelling was used in the synthesis process of zeolite as silicon source without calcination or acidbase treatment. Laponite itself contains Li and Mg atoms, which were subsequently introduced into the framework of SAPO-34 zeolite. Modification of SAPO-34 catalyst with metal cations can change its surface properties and improve the catalytic performance of SAPO-34 catalyst.^[17] This work points to a facile and green route to the synthesis of SAPO-34 containing metal cations via the depolymerization and reorganization of laponite. The research broadens the range of raw materials for the synthesis of zeolite and improves the added value of laponite.

Results and Discussion

Introduction

Zeolites have been widely applied in the chemical industry benefiting from their uniform molecular sized pores, excellent catalytic activity and great stability.^[1, 2] Silicoaluminophosphate zeolite SAPO-34 with CHA topological structure has been proven to be the best catalyst for the production of ethylene and propylene in the methanol to olefins (MTO) reaction because of its shape selectivity and moderate strength of acidity.^[3] The conversion of methanol to olefins (MTO) provides an efficient route for converting carbon containing resource into light olefins through methanol as intermediate.^[4, 5] At present, traditional SAPO-34 zeolites are synthesized mainly from chemicals by adding organic templates and crystallizing under hydrothermal conditions. The properties of zeolite vary greatly due to the different of raw materials.

In recent years, researchers have noticed the great potential of minerals in zeolite synthesis, such as kaolinite^[6-8], halloysite^[9], diatomite^[10, 11], coal fly ash^[12], and palygorskite^[13]. In the above methods, the raw materials activation processes are usually calcinated or treated by acid or alkali, which lead to a large number of energy consumption and waste liquor. Herein we report a green strategy to synthesize SAPO-34 zeolite directly from laponite as a new silicon source for the synthesis of zeolite. Different from the above-mentioned mineral materials for synthetic zeolite, the laponite does not need calcination or acid - base treatment before the synthesis of zeolite.

Laponite is a layered hydrous magnesium silicate, consisting of a layer of octahedrally coordinated magnesium oxide and two parallel layers of tetrahedrally coordinated silica in 1:2 stoichiometric ratio. ^[14] Some of the Mg atoms in the framework of laponite are replaced by Li atoms. Laponite has received extensive attention benefiting from its flexibly adjusted interlayer Characterization of zeolite

XRD patterns of laponite and the samples synthesized at 180 °C for different time are shown in Fig. 1. It shows that the intensity of peaks of laponite were almost disappeared after heating under hydrothermal conditions for 4.5 h (Fig. 1 S-4.5), implying that the laponite was depolymerized in hydrothermal condition, and the structure of SAPO-34 was not formed in this period. When the crystallization time was prolonged to 9 h as shown in Fig. 1 (S-9), the characteristic peaks of SAPO-34 appeared. S-9 sample exhibited a chabazite (CHA) framework peaks structure with characteristic diffraction at $9.5^\circ, 12.8^\circ, 16.2^\circ, 20.5^\circ$ and $30.8^\circ,$ typically for SAPO-34 as reported in literatures, [18, 19] suggesting the synthesis of SAPO-34 zeolite from laponite clay is reliable. When the crystallization time was prolonged to 54 h, no additional peaks appeared or disappeared during an extra 45 h after the characteristic peaks of SAPO-34 had been appeared, which suggests that the SAPO-34 zeolite obtained from the laponite is very stable.

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Figure 1. XRD patterns of laponite and the samples synthesized at 180 $^\circ C$ for 4.5 h (S-4.5), 9 h (S-9), 18 h (S-18), 36h (S-36) and 54 h (S-54).

To get a better understanding of the crystallization process, the laponite and the samples synthesized at 180°C for different time were carefully investigated by SEM, as shown in Fig. 2. The laponite shows a lamps shape consisting of lamellas (Fig. 2a). After heating the reactant for 4.5 h, the laponite particles were depolymerized and formed a large number of spherical particles spontaneously (Fig. 2b). After 9 h of heating, the ellipsoidal particles gradually grew into cubes with rough surface (Fig. 2c). With the prolongation of crystallization time, SAPO-34 crystals with rough surface tended to be regular cubes and the particles size of SAPO-34 remained unchanged (Fig. 2d, e, and f), which are in accordance with the XRD results.



Figure 2 SEM images of laponite and the samples synthesized at 180 $^{\circ}$ C for 4.5 h (S-4.5), 9 h (S-9), 18 h (S-18), 36h (S-36) and 54 h (S-54).

The FTIR was applied to analyze the change of chemical states of laponite and the samples synthesized at 180 °C for different time. As shown in Fig. 3, the peak at 635 cm⁻¹ is assigned to the exisiting 6 rings, ^[20, 21] which confirms the formation of the CHA structure. The spectrum of laponite shows the peak at 1008 cm⁻¹, relating to Si-O vibrations and the peak at 649 cm⁻¹, corresponding to the Mg-OH bending vibration. ^[22] It is worth noting that after crystallization for 4.5 h, the peak at 649 cm⁻¹ almost disappeared, resulting the Mg-O octahedrons in laponite are destroyed. In addition, the peaks have been weaken

obviously at 1008 cm⁻¹ and 480 cm⁻¹, which indicates that the Si-O vibrations of the tetrahedral sheet are broken. The results show that in the early stage of the crystallization, the thermally activated laponite has been already depolymerized in the alkaline environment, which is also consistent with the results of Fig. 2b. Meanwhile, when crystallization time exceeded 4.5 h, the peak strength at 649 cm⁻¹ also gradually increased, indicating that the double 6 rings of SAPO-34 zeolite began to form and gradually strengthened. The vibration band at 720 cm⁻¹ is assigned to the symmetric stretching vibration of P-O (or Al-O), while that at 1100 cm⁻¹ is credited for the asymmetric stretching vibration of O-P-O.^[23] The peak at 480 cm⁻¹ can be credited for [SiO4] tetrahedron stretching vibration, revealing that the Si species depolymerized from laponite have incorporated into the tetrahedral framework of SAPO-34 during the crystallization process.[21]



Figure 3. FTIR spectra of the laponite and the samples synthesized at 180 °C for 4.5 h (S-4.5), 9 h (S-9), 18 h (S-18), 36h (S-36) and 54 h (S-54).

The nitrogen adsorption-desorption isotherms of the laponite and the samples synthesized at 180 °C for different time are shown in Fig. 4. Different from S-18, S-36, and S-54, the hysteresis loops are observed at P/P₀=0.6-0.9 for laponite, S-4.5 and S-9 samples. The obvious hysteresis loop at $P/P_0 = 0.6$ -0.9 denotes the mesopore in the material.^[24] The hysteresis for S-9 represents the inter-crystalline mesopore, while the hysteresis for laponite and S-4.5 represents the intracrystalline mesopore (fig. 2 b and c), which shows the SAPO-34 zeolite with defects in the crystals has been formed when the crystallization time reaches 9 h. The adsorption isotherms exhibit steep uptakes in the region $P/P_0 < 0.1$, which is due to the existence of microporous structure. As can be seen, the sample S-4.5 initially shows lower nitrogen uptake than laponite in the region P/P₀<0.1, implying that the laponite has been degraded in the reaction system. It can be noticed that the adsorption-desorption isotherm of samples tends to be type I curves with the increase of heating time, which indicates that the SAPO-34 crystals became more and more regular. These results are consistent with the analysis above. Physicochemical properties of laponite and the samples synthesized at 180 °C for different time are further summarized in the Table 1. It is noteworthy that when the crystallization time was prolonged to 18 h, the relative crystallinity reached 94.9%, indicating that the SAPO-34 zeolite with high crystallinity can be obtained in a short time by using laponite as silicon source. Additionally, during the crystallization process, the S_{mcico} and V_{mcico} of the samples increase, and the increasing trend is basically consistent with its

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relative crystallinity.

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Figure 4. The nitrogen adsorption-desorption isotherms of the laponite and the samples synthesized at 180 °C for 4.5 h (S-4.5), 9 h (S-9), 18 h (S-18), 36h (S-36) and 54 h (S-54).

Table 1. Physicochemical properties of laponite and the samples synthesized at 180 °C for 4.5 h (S-4.5), 9 h (S-9), 18 h (S-18), 36h (S-36) and 54 h (S-54).

Sample	SBET	S _{mcico}	S _{exter}	V _{total} ^a	V _{mcico} ^b	Relative	
s	(m² g⁻	(m² g⁻	(m²	(cm³ g⁻	(cm³ g⁻	Cystallization	
	¹)	¹)	g⁻¹)	1)	1)	° (%)	
laponite	368	240	128	0.188	0.059	0	
S-4.5	335	0	335	0.806	0	0	
S-9	623	557	66	0.354	0.211	42.1	
S-18	642	614	28	0.257	0.230	94.9	
S-36	712	697	15	0.277	0.260	98.4	
S-54	718	705	13	0.286	0.269	100	

^aVolume adsorbed at $p/p_0 = 0.99$.

^bDetermined by the t-Plot method.

^cBased on the crystallinity of S-54.

In order to investigate the acidity properties of the SAPO-34 zeolite, NH₃-TPD was carried out and the results are shown as Fig. 5. The temperature of desorption indicates the strength of acidity and the peak area of desorption refers to the amount of acidity.^[25] As shown in the Fig. 5, neither laponite nor S-4.5 has strong acid sites. Meanwhile, when heating time exceeds 4.5 h, the strong acidity peak of samples appeared. The samples are observed similar acidity patterns with peaks at >300 °C and <300 °C due to strong and weak acidic sites respectively.^[26] The weak acid sites are assigned the defect structural OH groups (including Si-OH, P-OH and Al-OH), and the strong acidic sites are assigned to Si-OH-Al hydroxyl groups.^[27] The acid areas of samples (S-9, S-18, S-36 and S-54) are different, which depends on the amount of Si contents in the skeleton of zeolite. On the other hand, the acid amounts of samples may also be related to their microporous characteristics (especially the microporous area). Table 1 shows that the micropore areas of the above samples are different and in order S-54 $(718m^2/g) >$ S-36 $(712m^2/g)$ > S-18 $(642m^2/g)$ > S-9 $(623m^2/g)$, which are basically consistent with the acid amounts order of the samples. The strong acid amounts are usually produced by the isomorphic substitution of silicon atoms for aluminum or phosphorus atoms in the framework of luminophosphate [AIPO4] microporous molecular sieves.[28] With the increase of crystallization time, the strong acid amounts of SAPO-34 zeolite are gradually enhanced and stabilized, which implies that the Si

species from the depolymerized laponite are gradually involved in the reaction. The acid amount of the samples synthesized from laponite are further summarized in the Table 2.



Figure 5 NH₃-TPD analysis of the laponite and the samples synthesized at 180 $^{\circ}$ C for 4.5 h (S-4.5), 9 h (S-9), 18 h (S-18), 36h (S-36) and 54 h (S-54).

Table 2. The acid	amount of th	e samples	synthesized	from	laponite	
(mmol NH ₃ g ⁻¹).						

ſ.	Samples	Weak acid	Strong acid	Total acid
			-	
	S-9	0.746	0.236	0.982
	S-18	0.774	0.366	1.14
	S-36	0.784	0.388	1.172
	S-54	0.864	0.408	1.272
-				

As a silicon source for the synthesis of SAPO-34 zeolite, laponite also contains Mg and Li. To determine the elements composition of SAPO-34 synthetized from laponite, the energydispersive X-ray spectroscopy (EDX) analysis and elemental mapping was carried out. The EDX elemental mapping results and corresponding SEM image of S-54 are illustrated in Fig.6. The SEM-EDX results show that the composition of S-54 contain P-, Al-, Si- ,Mg- and O- atoms. It is well known that P -, Al -, Si -, O- are the skeleton atoms of SAPO-34, whose distribution are consistent with the SEM image (Fig. 6). So the Mg atoms of sample S-54, which are from the raw material laponite, also corresponding to the SEM image of S-54, indicating that Mg elements are introduced into the framework. Besides, no phase of MgO is found in XRD analysis, so the Mg elements are incorporated into the framework of S-54. The exact chemical composition of the sample was determined by ICP-MS. The test result is Li_{0.019}Mg₁Al_{7.1}Si_{1.83}P_{6.3}, which proves our analysis above directly.

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Figure 6. SEM images of S-54, and corresponding EDX elemental mapping (Si, O, P, AI, and Mg).

To take insight into the chemical states of Mg atoms in the SAPO-34 zeolite synthesized from laponite, diffuse reflectance UV–vis spectra was performed. The diffuse reflectance UV–vis spectra of S-T, S-9, and S-54 are given in Fig. 7. No absorption band is seen for S-T, S-9, and S-54 samples in the visible region of the spectra. In the UV region, all the samples show a broad band at about 220 - 260 nm, which attributes to Al-O charge transfer transitions of tetrahedral AlO4 species in or outside the framework. ^[29,30] Moreover, the band at 260 nm is assigned to the tetrahedral Mg species.^[31] So it can be concluded that Mg has been incorporated into the framework of SAPO-34 during the crystallization process. The results are also consistent with the results of SEM-EDX.



Figure 7. DR-UV-Vis spectra of samples: (a) S-T, (b)S-9 and (c) S-54.

Discussion on formation mechanism

From the above discussion, the crystallization mechanism of SAPO-34 synthetized from laponite can be summarized as follows: during the stirring and initial heating period of the reactants, the laponite was attacked by morpholine, Al-OH, hydroxyl ion and phosphate in the synthesis system. The ligands coordinated with Si or Mg atoms in the surface of laponite, which probably contributes to the progressive surface peeling of Mg coordinated units connected with Si atoms, implying that all or part of the Mg and Si species could turn into an amorphous state.

Then the species migrated from the laponite participated into synthesis system. The primary building units of SAPO-34 zeolite could be formed by the Mg and Si species depolymerized from laponite, phosphate anions, morpholinium cations and Al-OH at the desirable temperature.^{16, 32]} At last, the crystal nucleus began to form, and the primary building units continued to grow rapidly on the crystal nucleus. A possible reorganization procedure from the depolymerized laponite to the SAPSO-34 is schematically illustrated in Fig. 8.



Figure 8. Schematic illustration of a possible formation process of the SAPO-

34 zeolite synthesized from laponite.

Catalytic Performance on MTO Reaction

SAPO-34 catalysts are widely used as MTO catalyst to convert carbon containing resource into light olefins through methanol as intermediate.[33] To demonstrate the advantages of the SAPO-34 catalyst synthesized from laponite, the MTO test was performed. The methanol conversion as a function of time on stream over SAPO-34 catalysts at 390 °C are presented in Fig. 9 a. The catalyst lifetime obtained at 100% methanol conversion over SAPO-34 catalysts are 193 min for S-T and 318 min for S-54. More significantly, the deactivation rate of the S-54 is much lower than S-T. In order to explore the reason for the difference in catalytic lifetime of the two catalysts, NH₃-TPD test was carried out. The exact chemical composition of the S-T and S-54 were determined by ICP-MS. The test result of S-54 is $Li_{0.019}Mg_1AI_{7.1}Si_{1.83}P_{6.3}$, and the chemical composition of S-T is Si_{0.49}Al_{1.21}P₁. So the aluminum content in S-54 is higher than that of S-T. The SAPO-34 zeolite with high aluminum content was indicative of a high acid site density, and vice versa.[34] This is also in good agreement with the results of TPD. As shown in Figure 9 b, the sample S-54 has lower acidic strength and acidic concentration in the strong acid sites compared with the conventional SAPO-34 (S-T) synthesized from TEOS, which can slow down formation of the coke.[35] The Mg and Li elements can be introduced into the zeolite by using laponite as the Si source, which can deactivate the stronger acid sites of the catalyst. In addition, MeAPSO-34 catalysts exhibit better catalytic stability and light olefin selectivity during the MTO reaction as compared to parent catalyst.^[27] The catalytic performance and the product distributions are shown in Table 3. As showed in Table 3, the S-54 synthesized from laponite contributes to higher yield of light olefin than S-T. It is worth noting that compared with S-T, the light olefin selectivity of S-54 increased by nearly 10%. These results reveal that the selectivity, yield of light olefin and catalyst life of MTO reaction are significantly improved by the zeolite synthesized from laponite compared with conventional SAPO-34 synthesized from TEOS.

Unraveling the reaction mechanism is a big challenge in MTO

conversion. For the MTO process, the dual-cycle hydrocarbon pool schematic comprised of olefinic and aromatic methylation cycles has been well accepted.[36,37] In the induction period, the methanol was generated polymethylbenzene compounds, which are the most important active intermediate in the methanol conversion process.^[38] The Benzene with low methyl substitution is the active intermediate of ethylene, and the ethylene is mainly formed by (poly)methylbenzene and dealkylation cycles.[39] Another important product propylene is produced through olefin methylation and cracking cycles.^[40] During the MTO reaction, SAPO-34 zeolite synthesized from laponite possesses lower acidic concentration in the strong acid sites than SAPO-34 zeolite synthesized from TEOS. The low acidic concentration can provide a low aromatic/CH3 ratio, which is beneficial to improve the selectivity of light olefins.^[18] More comparative data on S-T and S-54 are included in the supplementary materials.



Figure 9. (a) Methanol conversion as a function of time on stream over SAPO-34 catalysts. (Reaction conditions: t = 390 °C, WHSV = 1 h⁻¹); (b) NH₃-TPD analysis of the S-T and S-54.

Table 3. Products Selectivity of SAPO-34 Catalysts during the reaction period of MTO reaction at 390 $^{\circ}$ C with a methanol feeding rate of 0.3 mL/h and corresponding WHSV of 1.0 h⁻¹.

							100
Sample	TOS	Selectivity(%)					
campic	(min)	Ethyl	Propyle	prop	C4	C5 ⁺	C2=+
5		ene	ne	ane			C₃⁼
S-T	30	22.4	34.2	20.3	10.1	4.8	56.6
0-1	193	28.2	37.5	10.6	9.5	3.8	65.7
S 54	30	27.3	37.6	11.8	9.9	4.5	64.9
0-04	318	34.6	42.3	8.5	8.3	3.6	76.9

Conclusion

In summary, SAPO-34 zeolites were synthesized and characterized by using laponite as the single Si source, and its crystallization mechanism and MTO catalytic performance were investigated as well. Laponite itself contains Li and Mg atoms which could be introduced into the SAPO-34 zeolite via depolymerization-reorganization of laponite during the crystallization process. Metal incorporation can reduce the amount of stronger acid sites and improve catalytic performance. Therefore, the preparation of SAPO-34 zeolite by using laponite as the Si source is an attractive option to enhance the catalytic performance for MTO reaction. The methodology also can be easily extended to the preparation of other zeolites.

Experimental Section

Materials

Methanol (AR 98%), aluminum isopropanol (AR 98%), tetraethyl orthosilicatewas (TEOS, 28wt% SiO2) and morpholine were all purchased from China National Pharmaceutical. Phosphoric acid (AR, 85wt%) was purchased from Aladdin Reagent Co., Ltd. Laponite RD, a synthetic hectorite, was purchased from Rockwood Additives Ltd (UK). powder and its empirical As а white composition is Na_{0.7}[(Si₈Mg_{5.5}Li_{0.3})O₂₀(OH)₄]. It is a disk-shaped clay particle with a thickness of 1 nm and a diameter of about 25 nm.[41] Deionized (DI) water was produced by water system in the lab. All reagents were invoked as purchased without any further purification. Preparation

Laponite suspension of 8wt/% was prepared according to the steps described by Tan et al.^[42] Laponite was gradually dispersed in deionized water to form an aqueous dispersion, and then the concentration of aqueous dispersion was adjusted to 8wt%. At last, the aqueous dispersion was sealed for one week to swell the laponite particles completely. The SAPO-34 zeolite was prepared by a hydrothermal method using morpholine (Mor) as the template. The optimized molar composition of the resulting mixtures was 1.0 Al₂O₃: 1.0 P₂O₅: 3.0 Mor: 0.6 SiO2: 80 H2O. The sources of the framework elements were aluminum isopropanol, 85wt% phosphoric acid, laponite (8wt%), water and morpholine (Mor). The synthesis gel was prepared by slowly adding 16.4g of aluminum isopropoxide powder to a solution containing 10.44g of Mor and 31.4g of deionized water with continuous stirring. After stirring for 2 h, 7.84g of phosphoric acid was added drop-wise to the above solution under stirring for 1 h. At last, 28.5g of laponite suspension (8wt%) was added into the solution under stirring for 4 hours at 30 ° C to disperse the laponite completely. The mixture was transferred into a teflon-lined stainless steel autoclave, which was heated at 180 °C for different time. The heating time was ranging from 4.5 to 54 h (4.5, 9, 18, 36, and 54), corresponding SAPO-34 samples were denoted as S-4.5, S-9, S-18, S-36 and S-54, respectively. Under the same synthesis conditions and molar composition, the sample synthesized from TEOS was named S-T, and the sample was synthesized at 180 °C for 54 h. The synthesis of S-T sample was to compare its catalytic performance with that synthesized from laponite.

All the samples were recovered by centrifugation, washing, and then oven-drying at 110 °C for 12 h. The final samples were calcined at 550 °C for 8 h in order to remove the organic templates that resided in the pores of the samples.

Characterization

X-ray powder diffraction (XRD) patterns of the SAPO-34 zeolites were recorded in the range of 5-60° on a Bruker D8 diffraction equipped with Cu K α radiation (λ = 0.154 nm, 35 kV, 40 mA). The morphology of all the samples were obtained by using a FEI QUATA Q400 field emission scanning electron microscope (SEM) with energy-dispersive X-ray (EDX) spectrometer. Nitrogen adsorption-desorption isotherms of the calcinated samples were measured at -196 °C, using a volumetric gas sorption analyzer (QuantaChrome IQ) after being degassed at 300 °C for 6 h. The surface areas were calculated using BET method, and the micropore volume were calculated by the t-Plot method. The acidity of the SAPO-34 catalysts were characterized by temperature-programmed desorption of ammonia (NH₃-TPD).^[43] The NH₃-TPD measurements were performed on a Chem BET TPR/TPD Chemisorption Analyzer, QuantaChrome instruments. The chemical composition of S-54 sample was determined by inductively coupled plasma mass spectroscopy (ICP-MS; Agilent). Diffuse reflectance UV-vis spectra of the samples of were

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performed on a Shimadzu UV-240 spectrometer. Infrared spectra of the SAPO-34 zeolites were obtained by a Nexus 670 Fourier transformation infrared spectrometer (Thermo Fisher Scientific Inc) in the range of 400-4000 cm⁻¹.

Catalytic reaction

The catalytic reaction was performed at 390 °C in a parallel fixed-bed reactor (inner diameter, 9mm) using 0.3 g of catalyst (40-60 mesh). Firstly, catalysts were activated at 500 °C in a flowing N2 (30 mL·min⁻¹) for 2 h, after cooling to the reaction temperature of 390°C, methanol was injected at a feed rate of 0.3 mL/h, corresponding to the weight hourly space velocity (WHSV) of 1.0 h⁻¹. The products were analyzed in situ by an online gas chromatograph (Bruker GC-456) equipped with a FID and a HP-plot-Q capillary column (30 m × 0.32 mm × 20 µm).

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SAPO-34 zeolite was successfully synthesized from laponite as the single Si source. laponite itself contains Li and Mg atoms, which were subsequently introduced into the structure of SAPO-34 via depolymerization-reorganization of laponite. Metal incorporation can reduce the amount of stronger acid sites and enhance the catalytic performance for MTO reaction.