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Realization of rapid synthesis of H-ZSM-5 zeolite by seed-assisted method for aromatization reactions of methanol or methane

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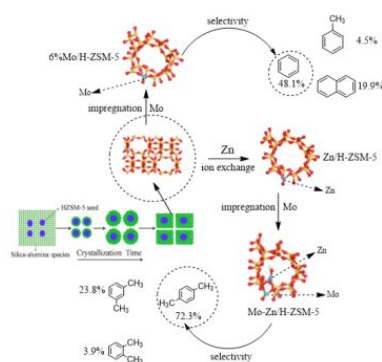
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Draft

Abstract: H-ZSM-5 zeolites are successfully synthesized within 1 h with organic-template-free system by the seed-assisted method. The synthetic method not only reduces the production cost of H-ZSM-5 zeolite, but also prevents the pollution of environment compared with the conventional synthesis process. Characterization by SEM, XRD, N₂ adsorption-desorption, NH₃-TPD and Py-IR confirms that the product of H-ZSM-5 with a high crystallinity and reveals that the rapid synthesis process in accordance with seed surface crystallization mechanism. In order to improve the aromatic selectivity on H-ZSM-5 zeolite, different concentrations of Mo and Zn catalysts were prepared by incipient wetness impregnation and ion-exchange method. Mo-Zn/H-ZSM-5-SAS-1 h have similar catalytic lifetime and higher selectivity of paraxylene in aromatics products compared with Mo-Zn/H-ZSM-5-seed in the reaction of methanol to aromatic. However, the catalytic lifetime of 6%Mo/H-ZSM-5-SAS-1 h is shorter than that of 6%Mo/H-ZSM-5-seed catalyst in methane to benzene reaction under same reaction conditions.

Keywords: Rapid synthesis, H-ZSM-5, Organic template-free, Seed-assisted, Aromatization



Scheme. 1 Schematic diagram of synthesis process.

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1. Introduction

Aromatic hydrocarbons are important chemical intermediates in fine chemical industry, which have huge industrial demand.¹ In recent decades, the methanol to aromatics (MTA) and methane to benzene (MTB) reaction over solid acid catalysts have attracted the attention of scientists and industrial organizations, because methanol is provided by different resources, such as natural gas, coal, biomass and any other carbon-based gasifiable raw materials as well as methane is provided by shale gas.²⁻⁴ H-ZSM-5 zeolite is widely applied to some solid acid catalytic processes, such as MTB reaction and MTA reaction, due to its adjustable acidity, thermal stability and a special porous structure of $5.3 \times 5.6 \text{ \AA}$ and $5.1 \times 5.5 \text{ \AA}$.⁵⁻⁸ Recently, Wei et al.⁹ reported that the coupling conversion of n-hexane with CO was carried out on H-ZSM-5 catalyst. The selectivity of aromatics was significantly improved by adjusting the H/C balance of the reactants. In addition, the laboratory was also developing MTA technology with H-ZSM-5 zeolite as catalyst. Yang et al.¹⁰ reported that the yield of aromatics was increased from 4.4% to 55.3% in MTA reaction when 0.8 Zn/H-ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 59$) zeolite was modified by alkali. Sazama et al.¹¹ used IR and solid-state NMR characterization techniques to confirm a correlation between skeletal defects and catalyst lifetime of H-ZSM-5.

A large number of organic structure directing agents (SDAs) were used in the synthesis of H-ZSM-5 zeolite by traditional method and it is expensive to use SDAs to produce zeolite. Additionally, their removal requires high temperature calcination, which leads to the H-ZSM-5 individual particles aggregation and create volatile gases that are inconsistent with environmental views.¹² Therefore, the synthesis of H-ZSM-5 with free organic-template system has attracted widely attention of some scholars.¹³ However, the long crystallization time (several days or even a week) due to slow kinetics of zeolite formation¹⁴ and low yield with SDAs-free system under hydrothermal conditions are big obstacles for large-scale production.¹⁵ In other words, it is still a challenge to synthesize zeolite with high yields and high crystallinity for rapid crystallization in free SDAs system.¹⁶ Ren et al.¹⁷ reported that the synthesis time

of zeolite was greatly shortened by microwave synthesis method, but it is difficult to meet the demand of industrial production due to the design and operation of the microwave reactor. Recently, a seed-assisted method was introduced to the rapid zeolite synthesis. The nano-sized zeolite SAPO-34 have been successfully synthesized using seed-assisted method in the minute-level time which has outstanding catalytic performance in MTO reaction.¹⁸ Han et al.¹⁹ reported that a fast and low-cost approach for the synthesis of sub-micron ZSM-5 from leached illite clay using the seed-assisted method. The seed plays a crucial role, and it not only promotes the growth crystal rate but also ensures the formation of pure zeolite crystal in the process of synthesis. Adding appropriate seed crystals can overcome the disadvantages of long crystallization time, low yield and low crystallinity in the organic-free template system.²⁰ The seed-assisted synthesis method may bring new possibilities to the fast and facile preparation of zeolite with excellent catalytic properties.²¹

In this paper, the authors developed a seed-assisted synthesis method without organic template system to achieve rapid synthesis of submicron H-ZSM-5 zeolite in hour-level time. The shape selectivity of H-ZSM-5-SAS-1 h catalyst was evaluated by MTA reaction or MTB reaction, and the relationship between H-ZSM-5-SAS-1 h structure and catalytic properties was discussed compared with H-ZSM-5-seed catalysts. Meanwhile, the H-ZSM-5-SAS-1 h catalysts modified with molybdenum and zinc also showed excellent catalytic performance and high selectivity of xylenes in the methanol to aromatics reaction.

2. Experimental Section

2.1 Materials

The experiment reagents including aluminum nitrate, ammonium nitrate, zinc nitrate, ammonium molybdate, sodium hydroxide, tetraethyl orthosilicate (TEOS) and methanol were analytical grade (purchased from ChengDu KeLong Chemical Industry Company of China) and were used without further purification. The 25% tetrapropylammonium hydroxide (TPAOH) was purchased from ZheJiang Maya Reagent Chemical Industry Company of China. Distilled water was used in all

experiments.

2.2 Catalyst preparation

The H-ZSM-5-seed was synthesized according to reference.²² The H-ZSM-5 was synthesized by using TEOS as a silicon source and aluminum nitrate as an aluminum source, respectively. First, the precursor solution including 6.25 g of TEOS, 0.23 g of aluminum nitrate, 0.12 g of sodium hydroxide, and 22 g of distilled water was prepared. Then, the 0.05 g/g (5 wt%) of H-ZSM-5-seed was added in the precursor solution to preparing mother gel, which was crystallized at 180°C for 0.5 to 2 h. The obtained samples were washed, dried, calcined and ion exchange with NH_4NO_3 solutions. The H-type ZSM-5 samples were obtained and labeled as H-ZSM-5-SAS-x h, where x is the crystallization time. The yield of H-ZSM-5-SAS-0.5 h, H-ZSM-5-SAS-1 h and H-ZSM-5-SAS-2 h were 54%, 93% and 92%, respectively.

The Zn-containing catalysts (Zn wt% = 5%) were prepared by ion-exchange and denoted as Zn/H-ZSM-5-SAS-1 h and Zn/H-ZSM-5-seed, respectively. In order to obtain final catalysts with a Mo loading of 0.01 g/g, the desired amount of ammonium molybdate precursor was mixed with Zn/H-ZSM-5-SAS-1 h or Zn/H-ZSM-5-seed by incipient wetness impregnation and denoted as Mo-Zn/H-ZSM-5-SAS-1 h and Mo-Zn/H-ZSM-5-seed catalysts, respectively. The Mo-containing catalysts were prepared by incipient wetness impregnation and denoted as x% Mo/H-ZSM-5-SAS-1 h and x% Mo/H-ZSM-5-seed, where x is the weight percentages of Mo content.

2.3 Catalyst characterization

The equipment type and test conditions of SEM, XRD, NH_3 -TPD, N_2 adsorption-desorption are consistent with reference.²² The solid state ^{27}Al MAS NMR was detected on AVANCE III HD600. The Py-IR analysis was carried out by FT-IR frontier system (US PE Co., Ltd.) and the contents of B and L acid were evaluated by reference to the literature.²³ The component of catalysts was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Autoscan16, TJA).

2.4 Catalysis reaction and products analysis

The MTB reaction was carried out in a continuous-flow fixed bed reactor. The quartz reactor with 650 mm long and 8 mm inner diameter. Prior to the experiment, the catalyst was pretreated in a nitrogen stream (20 mL/min) at 700°C for 30 min, and then 20 mL/min CH₄ as the reagent and 5 mL/min N₂ is input into the 0.4 g catalyst bed. In order to prevent product condensation, the gas sampling valves and reactor outlet pipeline were kept at 180°C. The reaction products were analysed on an online gas chromatograph (Ruimin GC-2060) with a FID using a OV-101 capillary column (50 m × 0.25 mm × 33 μm) to detect CH₄ and aromatics and TCD using a HayeSep D packed column (6 m × 3 mm) to detect H₂, N₂, CO, CH₄, CO₂, C₂H₄ and C₂H₆.²⁴ The CH₄ conversion and products yield are calculated on a carbon number basis using N₂ 0.20 L/L (20 vol%) as the internal standard.²⁵ The MTA reaction process and the product analysis methods were similar to the reference.^{22,26}

3. Results and Discussion

3.1 XRD and ²⁷Al MAS NMR Analysis

Fig. 1 presents the XRD patterns of H-ZSM-5-seed and H-ZSM-5 at different crystallization times, which shows that the crystals are MFI topology and no other peaks could be observed, indicating a high purity of the products. The diffraction peaks of the MFI topology were observed after 30 min hydrothermal synthesis and the crystallinity of the sample gradually increased with the crystallization time prolonged. The diffraction peak of the sample was very sharp after 1 h hydrothermal synthesis, and the intensity of the diffraction peak did not change significantly with the further increase of the hydrothermal synthesis time (2 h), indicating that the crystallinity of the sample was completed. Compared to traditional hydrothermal synthesis using crystallization time of more than 24 h, H-ZSM-5 seeds promoted the crystallization of H-ZSM-5 in a shorter period of time (1-2 h).²⁷ XRD patterns indicated that H-ZSM-5-seed played important role for faster crystallization rate in the system and the formation of pure H-ZSM-5 material in the system.

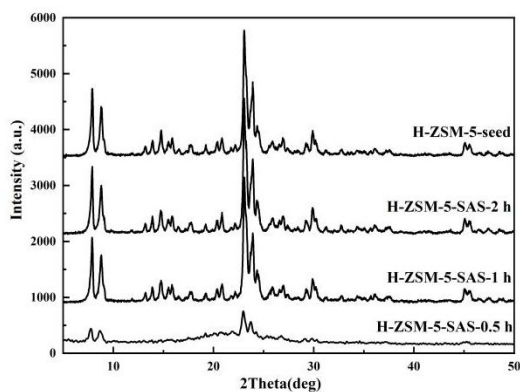


Fig. 1 XRD patterns of all samples

The active sites were determined by the spatial distribution of Al atoms with the available tetrahedral sites (T-sites) in the zeolite lattice.²⁸ Therefore, the chemical environment of the framework Al in H-ZSM-5-seed and H-ZSM-5-SAS-1 h samples was detected by ²⁷Al MAS NMR and the result is shown in the Fig. 2. There are a main resonance peak at ~55.5 ppm and a minor resonance at ~0 ppm in zeolite with low SiO₂/Al₂O₃ ratio (SiO₂/Al₂O₃ ≤ 107).²⁹ In the experiment, a sharp high peak at 52.600 ppm and a very small peak at -2.472 ppm were measured on H-ZSM-5-seed and H-ZSM-5-SAS-1 h, which were in line with the peaking characteristics of H-ZSM-5. The majority of the tetrahedrally coordinated Al within the framework structure, while only a small portion of the latter is associated with the octahedrally coordinated Al.

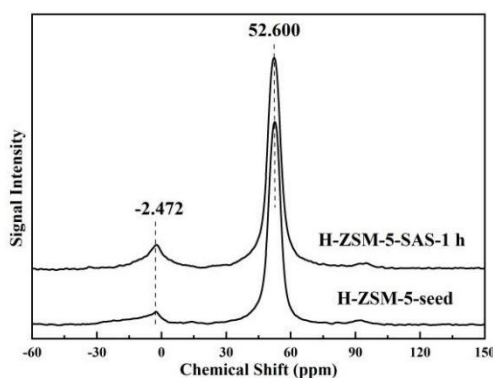


Fig. 2 1D ²⁷Al MAS NMR spectrum of H-ZSM-5-SAS-1 h and H-ZSM-5-seed samples

3.2 SEM Analysis

The surface morphology of H-ZSM-5-seed and H-ZSM-5-SAS-1 h was studied by SEM analysis (Fig. 3). It shows that after crystallized for only 1 h, the H-ZSM-5-SAS-1

h exhibits irregular hexagonal morphologies with smooth external surface, which is similar to that of H-ZSM-5-seed. The particle size distribution of H-ZSM-5 zeolite was obtained by Nano measurer analysis software (Fig. 3). The H-ZSM-5-SAS-1 h has a very large particle size ranging from 200 nm to 650 nm, while H-ZSM-5-seed only from 80 nm to 240 nm. The zeolite crystal growth rate of H-ZSM-5-SAS-1 h was calculated as 225 nm/h, which is very high compared with the literature about 100 nm/h.^{6,30} According to the characterization results of SEM, we speculate that the fast synthesis of H-ZSM-5 with submicron-sized is based on the seed surface crystallization (SSC) mechanism.

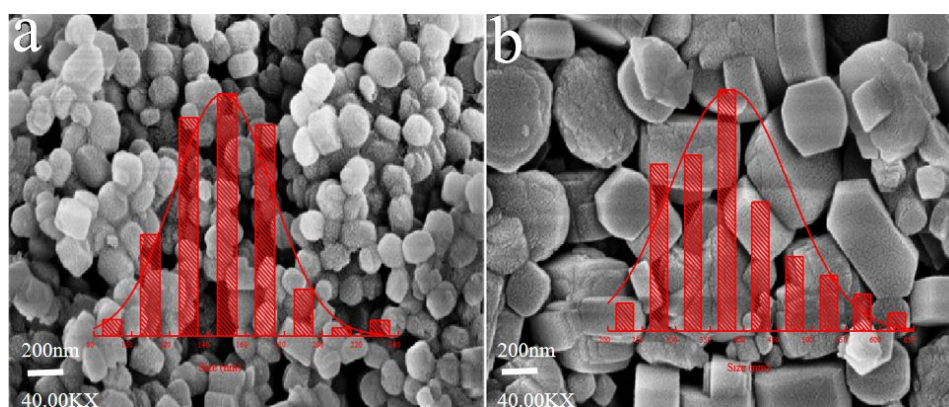


Fig. 3 The SEM images and particle size distribution of (a) H-ZSM-5-seed and (b) H-ZSM-5-SAS-1 h

3.2 N₂ adsorption-desorption Analysis

Table 1 The textural properties of H-ZSM-5-seed and H-ZSM-5-SAS-1 h zeolite

Samples	Surface area			Pore volume			Si/Al ^g	Si/Al ^h
	(m ² .g ⁻¹)			(cm ³ .g ⁻¹)				
	S _{BET} ^a	S _{Meso} ^b	S _{Micro} ^c	V _{Total} ^d	V _{Meso} ^e	V _{Micro} ^f		
H-ZSM-5-seed	407	27	380	0.44	0.26	0.18	38	34
H-ZSM-5-SAS-1 h	404	52	355	0.46	0.30	0.16	40	52

^a BET surface area, ^b S_{Meso} = S_{BET} - S_{Micro}, ^c t-plot micropore surface area, ^d Pore volume at $p/p_0 = 0.99$, ^e V_{Meso} = V_{Total} - V_{Micro}, ^f t-plot micropore volume, ^g ICP analysis and ^h EDS analysis

The N₂ adsorption-desorption isotherms and textural properties of all samples are shown in Fig. 4 and Table 1, respectively. BET surface area and micro-pore volume of H-ZSM-5-SAS-1 h are 404 m²/g and 0.16 cm³/g, which were closed to those of H-ZSM-5-seed.³¹ However, the mesopores surface area of H-ZSM-5-SAS-1 h was larger than that of H-ZSM-5-seed. Compared with the H-ZSM-5-seed sample, H-ZSM-5-SAS-1 h was a typical type IV isotherms with an upward turn hysteresis loop at relative pressure higher than $P/P_0 = 0.4$, it shows that there were more mesopores in H-ZSM-5-SAS-1 h samples.⁵ This is more conducive to the combination of the molybdenum or zinc species with acidic sites of zeolite to form more efficient composite catalysts. In addition, the mesoporous structure of catalyst provides a more convenient route for reactants molecules enter into active sites of catalyst and macromolecular intermediates can be diffused more easily.³² Therefore, the yield of target product and the stability of catalyst are improved. In the process of seed-induced rapid synthesis, the precursor solution of Si can quickly penetrate around each zeolite seed, and effectively adsorb on the zeolite seed particles. Then more secondary nuclei on the surface of zeolite seed were formed by hydrolyze the precursor of Si. Therefore, the nucleation process of a single SiO₂ molecule was replaced, resulting in more mesopore were formed in H-ZSM-5-SAS-1 h sample.³⁰

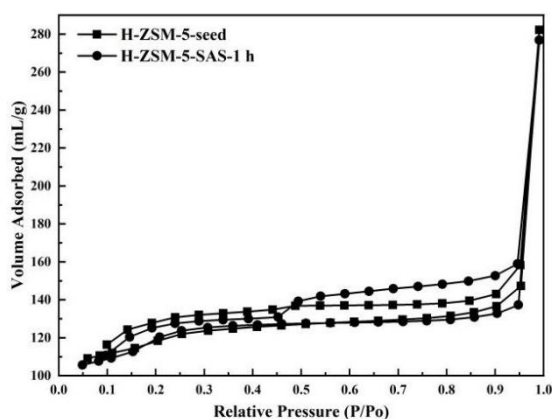


Fig. 4 N₂ adsorption-desorption isotherms of H-ZSM-5-seed and H-ZSM-5-SAS-1 h

3.3 The acidity Analysis

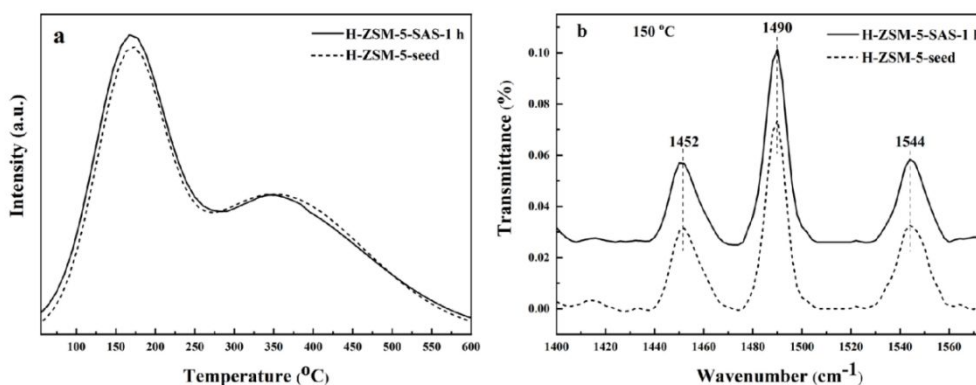


Fig. 5 (a) NH_3 -TPD profiles and (b) Py-IR spectra of H-ZSM-5-seed and H-ZSM-5-SAS-1 h

The acid properties of H-ZSM-5 was determined by NH_3 -TPD (Fig. 5a) and Py-IR (Fig. 5b). As illustrated in Fig. 5a, the spectra of the H-ZSM-5-SAS-1 h displays two distinct desorption peaks. A low temperature (about 160°C) peak is assigned to weak acid sites, and high temperature (about 350°C) peak is assigned to strong acid sites.³³ In addition, the H-ZSM-5-SAS-1 h shows similarly temperature and peak areas relative to that of H-ZSM-5-seed, which indicates the similar strength and number of total acid sites in these two samples.¹¹ Fig. 5b represents the comparison of H-ZSM-5-SAS-1 h and H-ZSM-5-seed to the Lewis and Brönsted acidity. Bands at around 1452 and 1544 cm^{-1} are assigned to L and B acid, respectively.³⁴ According to Py-IR spectra, we calculated that the concentration of L and B acid sites at 150°C for H-ZSM-5-SAS-1 h were 0.037 and 0.024 mmol/g, which were similar to those of H-ZSM-5-seed (0.038 and 0.021 mmol/g). The total Si-Al ratio of samples and partial Si-Al ratio on the surface of samples was tested by the ICP and EDS as well as the results is shown in the Table 1. There is almost the same total Si-Al ratio of H-ZSM-5-SAS-1 h and H-ZSM-5-seed sample.

3.5 Conversion and product distributions of MTA and MTB

The yield of light aromatics over pure HZSM-5 zeolite catalyst is not meet the demand of industry. Therefore, in order to improve the yield of light aromatics, Mo and Zn were incorporated into H-ZSM-5-SAS-1 h zeolite by impregnation and ion exchange methods, respectively. Fig. 6b shows the performance of Mo-Zn/H-ZSM-5-SAS-1 h catalyst in MTA reaction under 450°C and 0.1 MPa (0.02 MPa methanol), total

flow rate 25 mL/min and 0.5 g catalyst. The yield of light aromatics (BTX) reached 68.5 % at TOS = 3 h and the yield of light aromatics (BTX) remains at 45.74% when the TOS = 98 h. The Mo-Zn/H-ZSM-5-SAS-1 h catalysts provide similar product distribution and lifetime to the Mo-Zn/H-ZSM-5-seed catalyst (Fig. 6a). The yield of BTX was decreased with the increase of reaction time. At the same time, the yield of C₁₋₂, C₃, C₄ and C₅₊ increases slowly with increasing reaction time. As we all know, paraxylene (PX) is recognized as the significant valuable aromatic hydrocarbons, since it is an important raw material for producing terephthalic acid. However, outer surface acidity of H-ZSM-5 zeolite significantly influences the selectivity of PX in the MTA catalytic reaction. With the increasing of surface Si/Al molar ratio (Table 1), surface acidity of H-ZSM-5-SAS-1 h catalyst is decreased and the isomerization of PX to o-xylene and m-xylene is effectively depressed,³⁵ resulting in the selectivity of PX in aromatics products were increased from 67.8% to 72.3% as well as barely changed of total aromatics selectivity over Mo-Zn/H-ZSM-5-SAS-1 h catalyst (Fig. 7).

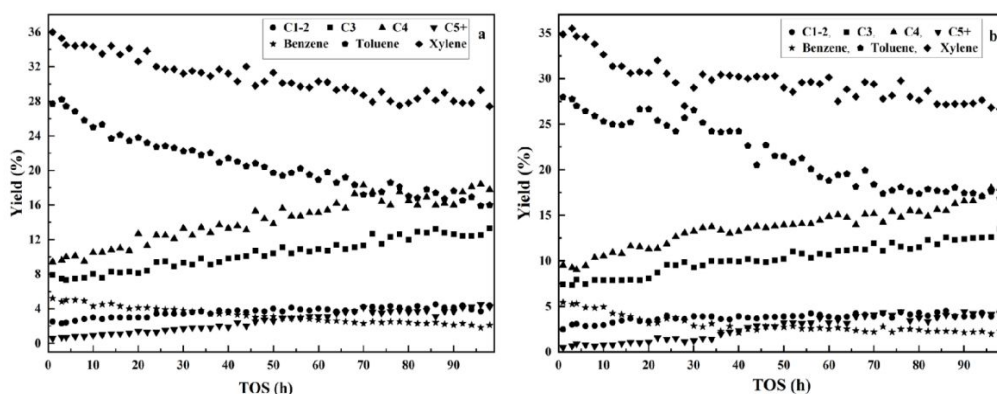


Fig. 6 Time-dependent yield of products over (a) Mo-Zn/H-ZSM-5-seed and (b) Mo-Zn/H-ZSM-5-SAS-1 h catalyst

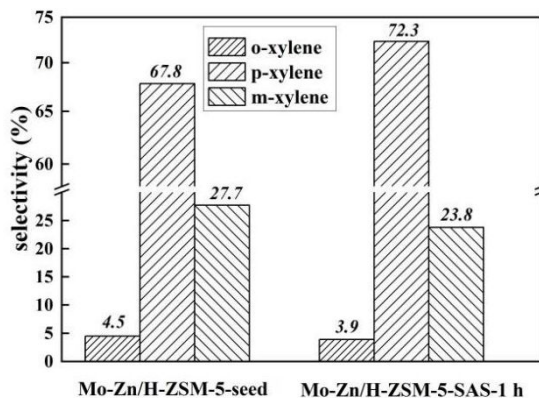


Fig. 7 The selectivity of xylene isomers with TOS = 3 h

In order to improve the benzene yield, Mo was incorporated in H-ZSM-5 zeolites by impregnation method.³⁶ With increase of Mo content, the catalytic activity of Mo/H-ZSM-5-SAS-1 h and Mo/H-ZSM-5-seed gradually increase and a maximum conversion of CH₄ and yield of benzene was achieved on the 6% Mo catalyst (Table 2). The B acid sites of H-ZSM-5-seed or H-ZSM-5-SAS-1 h are insufficient for the MTB reaction when weight content of Mo is greater than 6% in Mo/H-ZSM-5.³⁷ The maximum conversion of CH₄, around 11%, which is good agreement with the values given in the literature.^{38,39} Fig. 8 shows the performance of 6%Mo/H-ZSM-5-SAS-1 h and 6%Mo/H-ZSM-5-seed catalyst in the MTB reaction under 700°C and 0.1 MPa, total flow rate is 25 mL/min and 0.4 g catalysts. All curves of CH₄ conversion shows an induction period,^{40,41} it is due to the active sites (Mo₂C and MoO_xC_y) were formed at the beginning of the reaction, which is important for the aromatization activity of the catalyst.⁴⁰ The conversion of CH₄ reached a maximum value at 6 min, but then declines gradually with time on stream. The yield of benzene reached a maximum value at 21 min, but then declines gradually with time on stream. However, the conversion of methane and the yield of benzene over 6%Mo/H-ZSM-5-SAS-1 h catalyst with time on stream drops more rapidly than that of 6%Mo/H-ZSM-5-seed catalyst, which may be closely related to its small (nanoscale) catalyst particles. These results suggest that the 6%Mo/H-ZSM-5-seed exhibits a much slower deactivation rate than 6%Mo/H-ZSM-5-SAS-1 h.

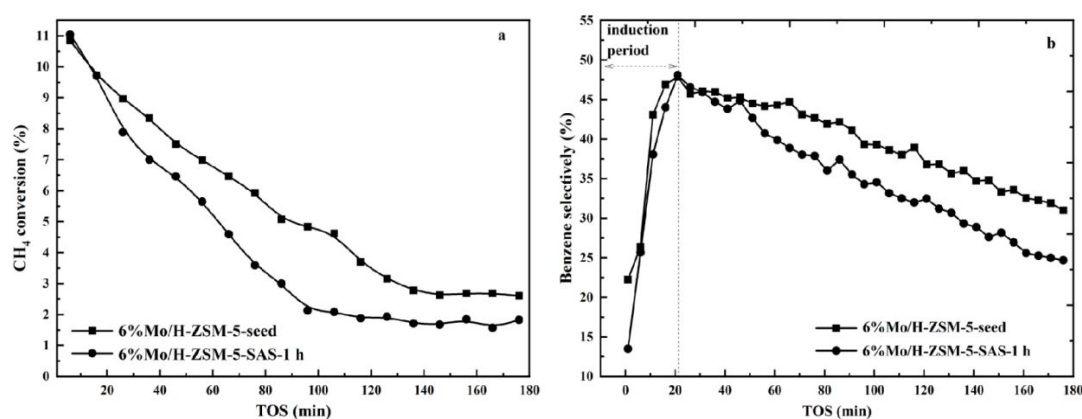
**Fig. 8** Time-dependent conversion of CH₄ (a) and selectivity of C₆H₆ (b)

Table 2 Comparison of Mo/H-ZSM-5-seed and Mo/H-ZSM-5-SAS-1 h for methane aromatization

Sample	Conversion of CH ₄ (%)	Selectivity (%)			
		C ₆ H ₆	C ₇ H ₈	C ₁₀ H ₈	coke
2%Mo/H-ZSM-5-SAS-1 h	6.9	30.9	2.1	14.2	52.8
4%Mo/H-ZSM-5-SAS-1 h	9.0	42.6	3.6	16.7	37.1
6%Mo/H-ZSM-5-SAS-1 h	11.0	48.1	4.5	19.9	27.5
8%Mo/H-ZSM-5-SAS-1 h	10.4	44.3	4.0	17.3	34.4
2%Mo/H-ZSM-5-seed	6.2	27.2	1.9	13.6	57.3
4%Mo/H-ZSM-5-seed	8.7	41.7	3.0	15.8	39.5
6%Mo/H-ZSM-5-seed	10.8	47.8	3.8	17.2	31.8
8%Mo/H-ZSM-5-seed	9.3	43.1	3.4	16.5	37.0

Reaction conditions: 0.1 MPa, 700°C, total flow rate = 25 mL·min⁻¹, 0.4 g catalyst.

3.6 Discussions

A possible pathway related to the growth of the MFI-type zeolite crystal was proposed based on above characterization analysis. The fast synthesis of H-ZSM-5 with submicron-sized is based on the seed surface crystallization (SSC) mechanism (Fig. 9). From the fast synthesis of submicron-sized H-ZSM-5 which was crystallized by the SSC mechanism and no template agent was added in the crystallization process. Therefore, no new nucleus was formed, the whole crystallization process was performed exclusively on the H-ZSM-5-seed surface, where H-ZSM-5-seed functions as the nuclei.¹⁷ First, some small particles were accumulated on around of seed nanocrystals. Then, more and more small particles were generated with increasing crystallization time and they begin to aggregate into larger particles and deposit on the surface of the seed crystals. Finally, perfect H-ZSM-5 crystal was obtained when the crystallization time is 1.0 h.¹⁷ The catalytic properties depend on some key factors. Namely, the morphology characterization, acidic properties, and channel structure as discussed above, cannot be used to analyze the influence of catalyst on the reaction through just one of the factors. On one hand, the H-ZSM-5-SAS-1 h catalyst should have more higher stability than the catalyst H-ZSM-5-seed,^{22,42} mainly because it has more mesopores, which provide an additional diffusion channels for reactants or products molecules on the catalyzed substance.¹¹ On the other hand, the average crystal

size of the H-ZSM-5-seed is much smaller than that of H-ZSM-5-SAS-1 h, indicating that the diffusion path of reactants or products molecules on the H-ZSM-5-seed is shorter.^{22,43} Therefore, it is suggested that the combination effect of the mesopores structure and particle size of the Mo-Zn/H-ZSM-5-SAS-1 h is responsible for its similar catalytic performance and lifetime to the Mo-Zn/H-ZSM-5-seed exhibited in the MTA reaction. Additionally, the 6%Mo/H-ZSM-5-SAS-1 h showed a shorter lifetime than that of 6%Mo/H-ZSM-5-seed in the MTB reaction.⁴⁴ The actual location and nature of the Mo species depend on the density of the B acid sites.³⁷ H-ZSM-5-seed and H-ZSM-5-SAS-1 h have a similar density of B acid sites. As a result, the effect of Mo species location and nature become negligible for the stability of Mo/H-ZSM-5.⁴⁵ Therefore, the particle size of catalyst has larger influence on deactivation rate in the MTB reaction than that of MTA reaction.

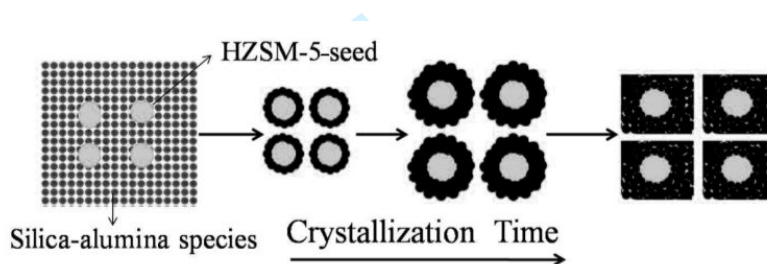


Fig. 9 Schematically illustration of the crystallization process of SSC approach.

4. Conclusions

In summary, a fast seed-induced hydrothermal synthesis process without structure-director was proposed for the low-cost and environmentally friendly production of H-ZSM-5 zeolite with high crystalline degrees. In addition, the surface area and acidity of H-ZSM-5-SAS-1 h were similar with those of typical H-ZSM-5-seed. Nevertheless, H-ZSM-5-SAS-1 h exhibits more mesopores and larger sizes, with an average diameter was 375 nm, than that of H-ZSM-5-seed. More importantly, the H-ZSM-5-SAS-1 h sample performs a similar deactivation rate and higher selectivity of PX in aromatics products that of H-ZSM-5-seed in MTA reaction, which makes it potentially available for production of aromatics from methanol. However, the deactivation rate of H-ZSM-

5-SAS-1 h sample was higher than that of H-ZSM-5-seed in the MTB reaction. Based on the characterization of samples and the deactivation behavior, the particle size has larger influence on deactivation rate of catalyst in the MTB reaction than that of MTA reaction.

Acknowledgements

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