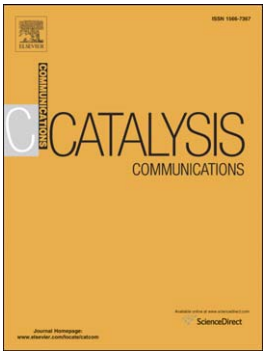

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Controllable synthesis of chainlike hierarchical ZSM-5 templated by sucrose and its catalytic performance

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Abstract

Hierarchical ZSM-5 with controllable chainlike structure was hydrothermally synthesized with sucrose as template, characterized by XRD, FT-IR, N_2 adsorption, SEM and TEM, and used for methylation of 2-methylnaphthalene. Hierarchical ZSM-5 can be rapidly synthesized, and chainlike morphology is stacked with several submicron crystals. With increasing sucrose amount in the precursor, the chain structure became more obvious, and the surface area and pore volume of mesopores increased. Narrow mesoporous distribution was centered at about 7 nm. It is thought that the formation of mesopores is related to the template role of sucrose. Chainlike hierarchical ZSM-5 exhibited high 2-methylnaphthalene conversion and 2,6-dimethylnaphthalene yield.

Keywords: hierarchical ZSM-5; sucrose; chainlike; 2-methylnaphthalene; 2,6-dimethylnaphthalene

1.Introduction

Zeolite has been widely used in industry as catalysts for its unique properties, such as high surface area, acidity, and shape selectivity, especially in the fields of oil refining and petrochemistry [1]. However, the

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micropores in zeolites often impose diffusion limitations that restrict accessibility to the internal surface of zeolites, especially when bulky molecules are involved [2]. To overcome these problems, one of the most promising ways is to prepare composites containing mesopores as well as micropores. These hierarchical materials, which combine the advantages of both zeolites and mesoporous materials, exhibit fast diffusion rates and many exposed active acidic sites [3-7]. For example, in synthesis of 2,6-dimethylnaphthalene (2,6-DMN) by methylation of 2-methylnaphthalene (2-MN), it was found that catalytic activity and stability could be significantly improved when some mesopores were introduced into ZSM-5 [6]. Templating methods are widely used to synthesize mesoporous materials [8-10]. Therefore, the cost of template and synthesis process should be considered in industrial application.

Sucrose is often chosen as a template for the synthesis of hierarchical zeolite owing to its low cost. Kustova et al. [11] reported that mesopore ZSM-5 and ZSM-11 could be synthesized by mixing silica gel with different concentration solutions of sucrose, carbonization, and crystallization through impregnating a structure-directing agent. Tong et al. [12] reported that monolithic zeolite BEA could be synthesized using the same method as that of Kustova et al. Zhu et al. [13] prepared the mesopore Silicate-1 by using porous carbon from sucrose as the template. Wang et al. [14,15] synthesized hierarchical TS-1 directly using sucrose as the meso/macroporous template by dry gel conversion. However, these processes generally need a long reaction time and several steps to prepare mesoporous zeolite. Here we report a rapid, convenient method to fabricate hierarchical ZSM-5 with a chainlike morphology by using sucrose as the template, and the effect of the sucrose amount on the structure of hierarchical ZSM-5 and catalytic performance in synthesis of 2,6-DMN by methylation of 2-MN with methanol was examined.

2. Experimental

2.1 Synthesis of chainlike hierarchical ZSM-5 zeolites

Chainlike hierarchical ZSM-5 was synthesized by hydrothermal crystallization. The detailed synthesis procedure is as follows: tetrapropylammonium hydroxide (TPAOH, 25 wt%, aq; YueyangYutai Chemical Technology Development Co., Ltd., China), sodium aluminate ($NaAlO_2$, Sinopharm Chemical Reagent Co., Ltd.) and distilled water were first mixed and stirred for 30 min until a clear solution is obtained. Then tetraethyl orthosilicate (TEOS, Sinopharm Chemical Reagent Co., Ltd.) was dropwise added to the solution under stirring and agitated for 2 h until a clear gel was obtained. The composition of the resultant precursor is $1SiO_2/0.011Al_2O_3/0.25TPAOH/30H_2O$. Finally, different amounts of sucrose were added to the mixture, and agitated for another 2 h. The precursor was charged into a stainless-steel autoclave and crystallized at 170 ^oC for 72 h. The products were filtered, washed with deionized water, dried at 120 ^oC and calcined at 550 ^oC for 10 h. Zeolites synthesized with different amounts of sucrose were denoted as MZSM-5(x) (x=0-2.0), where x represents the mass ratio of sucrose to SiO_2.

To investigate the effect of crystallization time on the structure, the precursor with a ratio of sucrose to SiO_2 of 2.0 was crystallized at 170 ^oC for 4 h or 8 h. The products were expressed as MZSM-5(2.0)-4h and MZSM-5(2.0)-8h, respectively.

2.2 Characterizations

X-ray diffraction (XRD) patterns of the samples were obtained on a D/Max2400 diffractor (Rigaku) with CuKα radiation at 40 kV and 40 mA. FT-IR spectra of the structure band region (1400-400 cm^{-1}) were investigated on an EQUINOX55 spectrometer. The framework SiO_2/Al_2O_3 molar ratio was determined by XRF spectroscopy on a SRS3400X instrument after the sample was washed with 1 M HCl at 80 ^oC for 4 h to remove extra-framework aluminum. BET specific surface area of the samples was determined by nitrogen adsorption using ASAP 2020 apparatus at -196 ^oC. The samples were outgassed at 300 ^oC for 2 h prior to adsorption. Scanning electron microscopy (SEM) studies were performed on a FEI NOVA NanoSEM 450

instrument. Transmission electron microscope (TEM) images were recorded with a Philips Tecnai G^2 20 operated at 200 kV.

2.3 Catalytic reaction

Methylation of 2-MN with methanol on ZSM-5 was used as the probe reaction and carried out in a fixed-bed micro-reactor of 10 mm-i-d under atmospheric pressure. About 0.67 g catalyst was first activated at 500 ^{o}C for 2 h under N_2 flow, and then cooled down to 400 ^{o}C. The liquid reactants including 2-MN, methanol and mesitylene (as the solvent) in molar ratio of 1:5:3 were introduced into the reactor by a metering pump and preheated before passing to the reactor in 10 ml/min N_2 flow. The weight hourly space velocity of 2-MN was 0.5 h^{-1}. The products were analysed by a FID-type gas chromatogram with a 30 m TCIcaps DMN capillary column. 2-MN conversion, 2,6-DMN selectivity and 2,6-DMN yield were calculated by the method of ref. [16].

3. Results and discussion

3.1 *Structure of hierarchical ZSM-5 zeolites*

Fig.1 shows the XRD patterns of the samples synthesized with different amounts of sucrose. All the samples showed the typical peaks of MFI structure, and no amorphous aluminosilicate was detected. Almost the same relative intensities were obtained on the MZSM-5(x) shown in Fig.1a, indicative of high crystallinity, which can be further confirmed by FT-IR spectra in Fig.1c. The FT-IR spectra of MZSM-5(x) samples clearly showed the presence of a band at 550 cm^{-1} assigned to the asymmetric stretching mode of double five-membered rings of MFI-type zeolites, and the optical density ratio (ODR) of the 550 and 450 cm^{-1} bands was above 0.7 in all samples, suggesting high crystallinity of the MFI structure of MZM-5(x) [17]. Additionally, Fig.1b also shows that ZSM-5 with high crystallinity could be obtained for a crystallization time of only 4 h, suggesting the time-saving of this method.

3.2 N_2 adsorption/desorption

Fig.2a illustrates nitrogen adsorption/desorption isotherms of the MZSM-5(x) samples. All the samples showed a combined types I and IV isotherms. At low relative pressure, the adsorbed amount has an obvious increase, indicative of the existence of the micropores. The hysteresis loop at P/P_0=0.6-1.0 is mainly attributed to the capillary condensation in the open mesopores, indicating the hierarchical structure. Moreover, the hysteresis loop becomes more obviously with the amount of sucrose in the precursor. The BJH pore diameter distribution shown in Fig. 2c indicates that the samples prepared without or with lower ratio of sucrose to SiO_2 have broader and larger pore size distribution. With increasing the amount of sucrose, the pore size becomes narrow and is centered at about 7 nm. As listed in Table 1, the surface area and pore volume of the micropores decreased, whereas the mesoporous surface area and pore volume increased with increasing sucrose-SiO_2 ratio, implying that the formation of mesopores is mainly related to the sucrose.

Fig. 2b and 2d showed that the ZSM-5 sample crystallized only for 4 h was also hierarchical, with the pore diameter distribution still centered at about 7 nm. Short crystallization time had no obvious effect on mesoporous dimensions.

3.3 SEM and TEM images

The SEM images of hierarchical ZSM-5 are shown in Fig. 3. In the absence of sucrose, randomly dispersed crystals of ZSM-5 were observed (Fig. 3a). When sucrose was added to the precursor, the chainlike morphology of individual particles appeared (Fig. 3b), and the length of chain became more obvious and longer as more sucrose was added (Fig. 3c to 3e). The SEM images of MZSM-5(2.0) (Fig. 3d and 3e) show that the chainlike morphology is stacked with several submicron zeolite crystals. This stacking into chains was sufficiently robust that it was not destroyed by sonication for 4 h (Fig.3f), indicating that this morphology is not formed by simple aggregation but strong force between the crystals.

TEM image (Fig. 3g) of MZSM-5(2.0) further revealed the chainlike structure and the stacking of the building units of ZSM-5 submicron zeolite crystals. Fig. 3h shows that the chainlike morphology was formed by stacking the crystals along the [010] direction. The zeolitic phase alternated with the mesoporous phase (Fig. 3i and 3j), indicating the presence of hierarchical zeolite.

Based on the above results, it can be obviously obtained that the presence of sucrose in the precursor of the zeolite is critical for the formation of the chainlike and mesoporous structure. As known, the sucrose contains polar C-OH groups, which will interact with polar species. Therefore, it is thought that the sucrose template can be present in forms of aggregations or assemblies of aggregations, which can interact with the aluminosilicate species through hydrogen bonding. Such interactions may play a significant role in directing the formation of chainlike and hierarchical structure. Moreover, the hydrothermal condition is not only preferable to the crystallization of aluminosilicate species, but also to the carbonization of the sucrose in some extent[15-16]. That is, the sucrose may play the roles of both soft and solid templates in the formation of hierarchical ZSM-5.

3.4 Methylation of 2-MN

2,6-DMN, a precursor of 2,6-naphthalenedicarboxylic acid in the synthesis of polyethylenenaphthalate, can be synthesized by methylation of 2-MN with methanol over ZSM-5 for its moderate acid, suitable pore sizes and high selectivity [18,19]. Therefore, catalytic performances of MZSM-5(x) samples in synthesis of 2,6-DMN were investigated. MZSM-5(0) exhibited the lowest catalytic activity than other MZSM-5(x) samples (Fig.4a) despite the most acidic amount (Fig.4b). The results in NH_3-TPD profiles show that the total acidic amount of MZSM-5(x) decreased with increasing sucrose amount, suggesting that the addition of sucrose to the precursor is unprofitable to the incorporation of Al into the framework of ZSM-5, which can be further confirmed by the increasing framework SiO_2/Al_2O_3 ratio of MZSM-5(x) samples shown in Table 1.

Less incorporation of Al and the formation of non-framework Al resulted in a decrease in total acidity. Therefore, higher 2-MN conversion on chainlike ZSM-5 is mainly related to the existence of mesopores. The mespores can decrease the diffusion resistances of reactants and products into and out the pore channels, and provide many exposed active sites. Especially, 2-MN conversion remains above 20% after 10 h when sucrose/SiO_2 ratio is 0.5. MZSM-5(1.0) exhibited better catalytic stability. However, less acidic amount on MZSM-5(2.0) contributes to low 2-MN conversion despite its more mesopores.

Fig.4c shows that MZSM-5(0) has the highest selectivity to 2,6-DMN, and chainlike ZSM-5 synthesized with sucrose have lower 2,6-DMN selectivity. Since 2,6-DMN synthesis by the methylation of 2-MN with methanol is a shape-selective reaction, the existence of mesopores is not beneficial to improve the selectivity [6]. Moreover, 2,6-DMN selectivity on chainlike ZSM-5 samples gradually decreased with increasing the sucrose/SiO_2 ratio. However, the highest 2,6-DMN yield was obtained on chainlike MZSM-5(1.0) for its high conversion of 2-MN (Fig.4d). Higher catalytic activities and better stability provide an opportunity for further modification by Zr or Fe to improve the selectivity and yield of 2,6-DMN [20-22].

4. Conclusion

Chainlike hierarchical ZSM-5 was synthesized in a short time by using sucrose as template, and the chain length and mesoporous structure of ZSM-5 can be controlled by the amount of sucrose in the precursor. This method of adding the sucrose to the precursor of ZSM-5 is facile and effective. It is thought that the sucrose plays an important function in driving the submicron zeolite crystals to form a chainlike structure. Chainlike hierarchical ZSM-5 samples exhibited high catalytic activities and 2,6-DMN yield, which is related to more mesopores.

Acknowledgements

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Table 1 SiO_2/Al_2O_3 molar ratio and textural properties of MZSM-5(x) samples

Sample	SiO_2/Al_2O_3 molar ratio*	S_{BET} (m^2/g)	S_{mic} (m^2/g)	S_{ext} (m^2/g)	V_{total} (cm^3/g)	V_{mic} (cm^3/g)	V_{meso} (cm^3/g)
MZSM-5(0)	102	405	226	179	0.32	0.10	0.22
MZSM-5(0.5)	108	406	217	189	0.33	0.10	0.23
MZSM-5(1.0)	136	397	202	195	0.36	0.10	0.26
MZSM-5(1.5)	138	397	179	218	0.36	0.08	0.28
MZSM-5(2.0)	141	399	159	240	0.39	0.08	0.31

*: by XRF

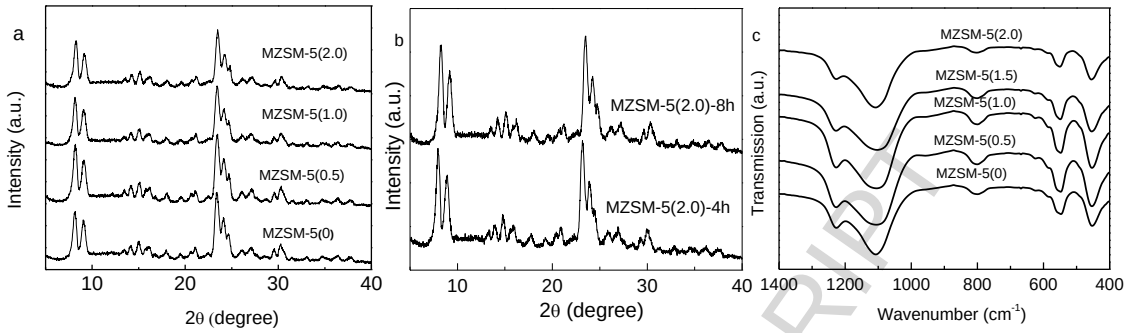
Figure captions

Fig.1 XRD patterns (a,b) and FT-IR spectra of MZSM-5 (x) samples

Fig.2 Nitrogen adsorption-desorption isotherms (a,b) and pore distribution (c,d) of the samples.

Fig.3 SEM images of MZSM-5(0) (a), MZSM-5(1.0) (b), MZSM-5(1.5) (c), MZSM-5(2.0) (d,e) and MZSM-5(2.0) by sonication for 4 h (f) and TEM images (g, h, i, j) of MZSM-5(2.0) sample

Fig.4 2-MN conversion (a), NH_3-TPD profiles (b), selectivity of 2,6-DMN (c) and 2,6-DMN yield (d) on MZSM-5(x) samples



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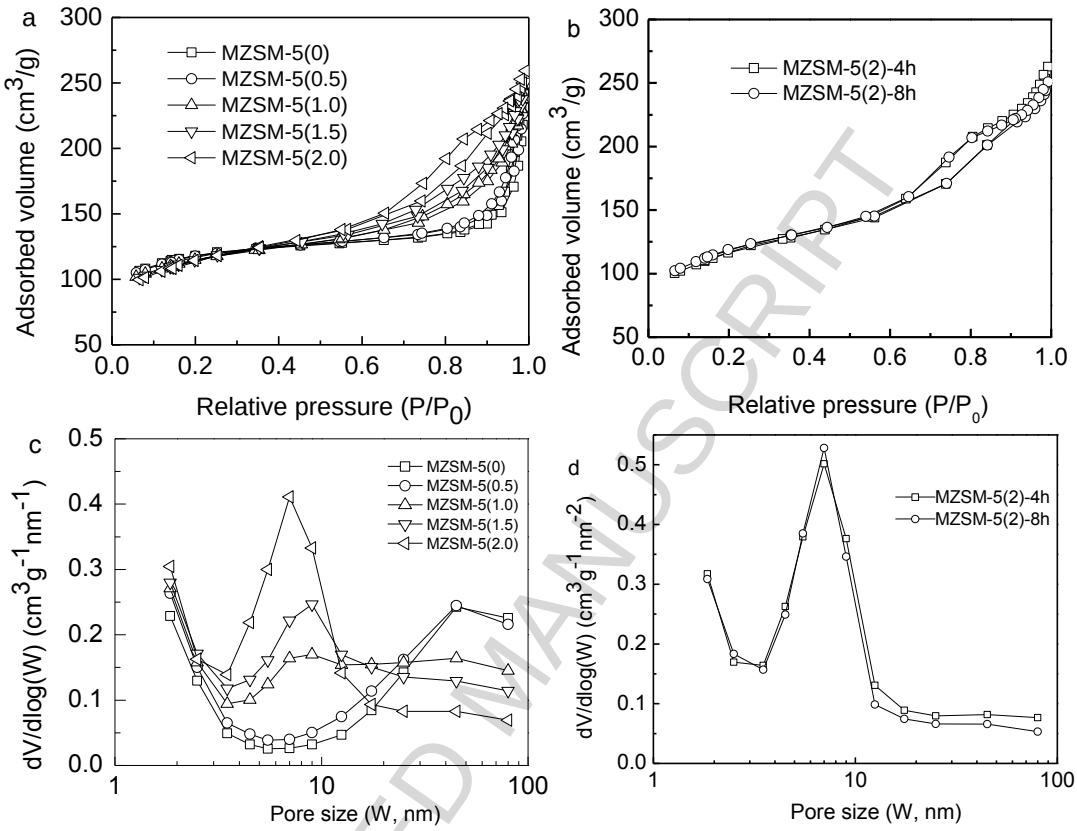

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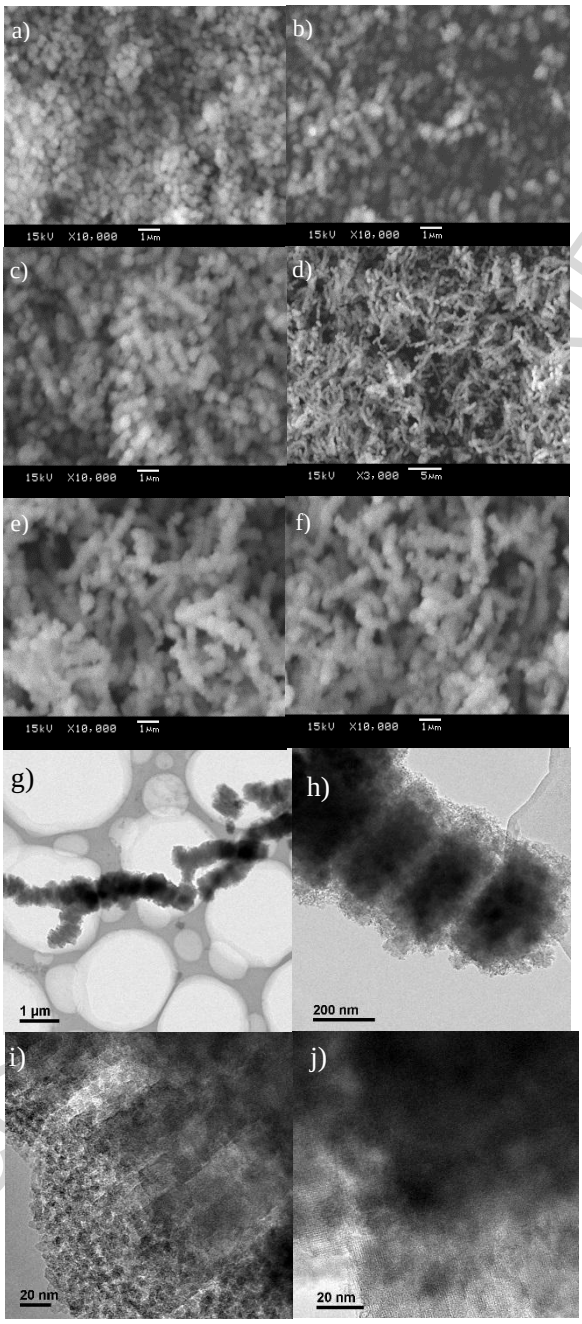


Fig. 3 SEM images of MZSM-5(0) (a), MZSM-5(1.0) (b), MZSM-5(1.5) (c), MZSM-5(2.0) (d,e) and MZSM-5(2.0) by sonication for 4 h (f) and TEM images (g, h, i, j) of MZSM-5(2.0) sample

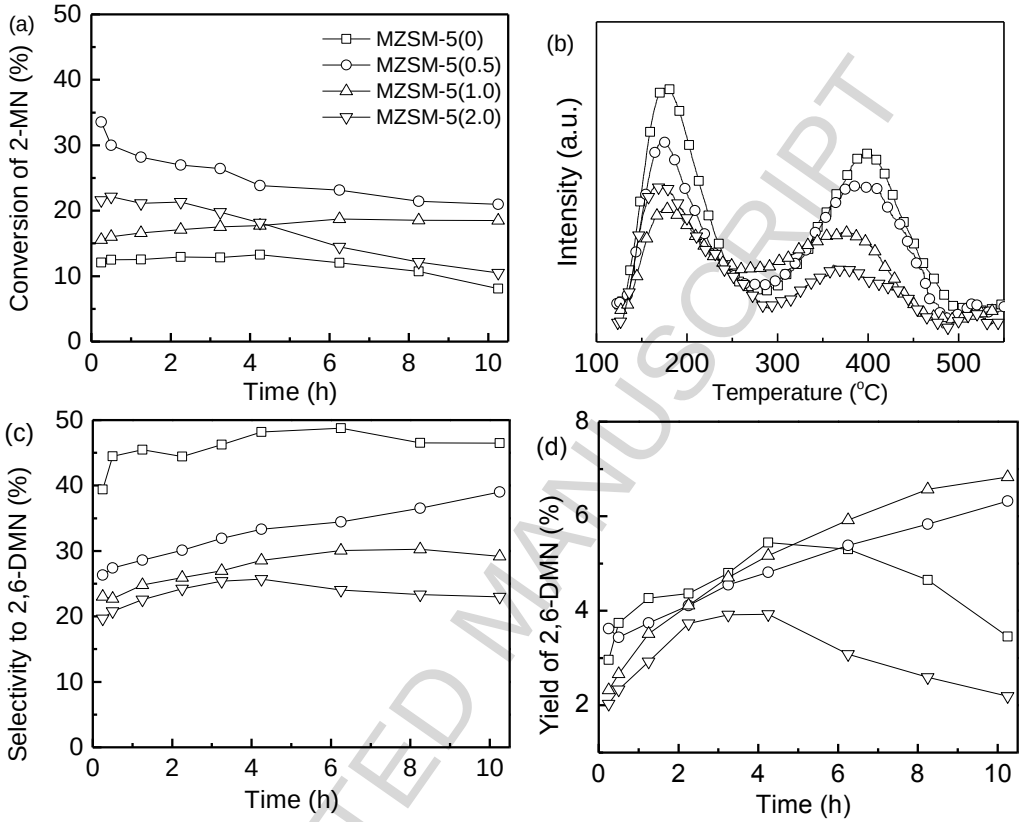
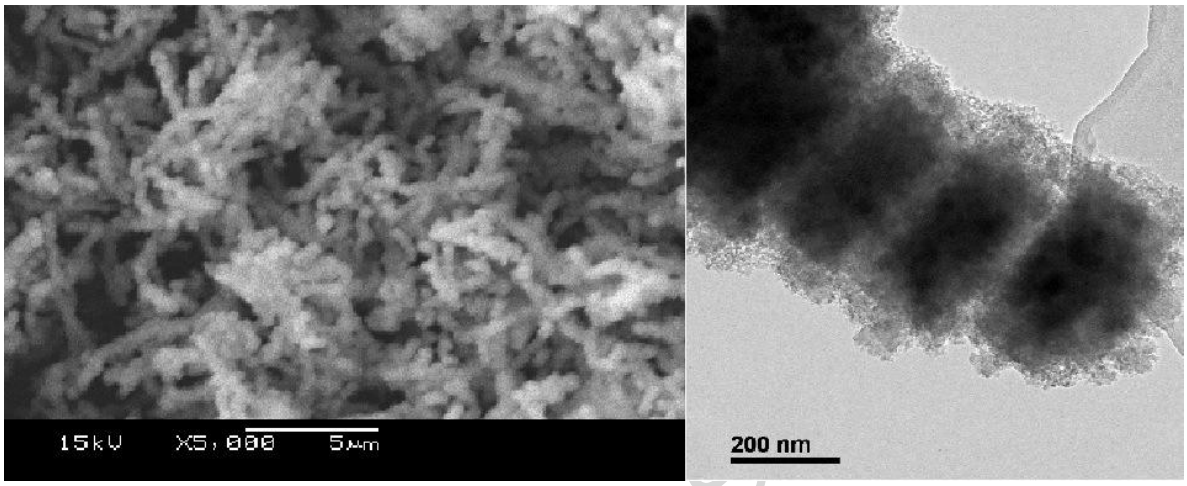


Fig.4 2-MN conversion (a), NH_3-TPD profiles (b), selectivity of 2,6-DMN (c) and 2,6-DMN yield (d) on MZSM-5(x) samples



Graphical abstract

Highlights

- Chainlike hierarchical ZSM-5 were synthesized by using sucrose as the template.
- Chainlike morphology is stacked with several submicron zeolite crystals.
- Chain length and pore structures of ZSM-5 can be tuned by added amount of sucrose.
- Chainlike ZSM-5 exhibited higher conversion and 2,6-dimethylnaphthalene yield.