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Effect of template type and template/silica mole ratio on the crystallinity of synthesized nanosized ZSM-5

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Abstract

The crystallinity of nanosized ZSM-5 zeolite from precursors mixtures containing different template types, tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide and tetrabutylammonium hydroxide, and different template/silica mole ratios, 0.215, 0.322, 0.43 and 0.537, has been studied. The produced samples were investigated using XRD, SEM, FT-IR and BET surface area measurements. Physicochemical investigations showed that the obtained products by different type of templates and different template/silica mole ratios were ZSM-5 phase. The as-synthesized ZSM-5 sample prepared by using tetrapropylammonium hydroxide template and 0.215 template/silica mole ratio at 230 °C for 45 h had the highest crystallinity. It was found that the average crystallite size increased in the following order; tetramethyl < tetrabutyl < tetraethyl < tetrapropyl and surface area increased in the following order: TMAOH < TEAOH < TBAOH < TPAOH. By increasing template/silica mole ratios from 0.215 to 0.537 the surface area decreased and average crystallite size increased.

Keywords: Nanosized; ZSM-5; Templates; Template/silica mole ratios; Crystallinity

1. Introduction

Silica-rich porotectosilicate known as Zeolite Socony Mobil and abbreviated as ZSM-5 is a truly synthetic substance with no naturally occurring counterpart. In fact the natural analogue of ZMS-5 was discovered in Northern Victoria Land, Antarctica [1]. The synthesis of zeolites from hydrogels occurs through a polycondensation process of polyanions aluminosilicate precursor directed by the so-called structure-directing agents or templates. Templates can either be neutral or charged, organic or inorganic molecules. They can play several roles in a zeolitization process. They alter the chemistry of the gel and favor the formation of typical oligomers in solution. They direct the condensation of these units into a specific framework, which they stabilize through electrostatic and dispersive interactions in the micropores in which they are trapped [2–9]. The framework structure [10] consists of bi-directional intersecting channels, one straight and the other sinusoidal with a 10-membered ring opening. A generic name 'Pentasil' was proposed for these types of zeolites. In the last decade, ZSM-5 zeolite has received much attention and importance in petroleum refining and chemical industries due to its unique shape-selective properties [11,12]. This zeolite has also found applications in synfuels production, NO abatement, production of fine chemicals and intermediates [13].

The major features of ZSM-5 zeolite, from the point of view of catalysis, are the high thermal stability, resistance to deactivation, high acidic activity and molecular shape selectivity arising from a unique framework structure. These characteristics are responsible for their unique selectivity in reactions of aromatic molecules. These properties distinguish ZSM-5 zeolites from Y and mordenite type zeolites. In general zeolite ZSM-5 is synthesized in a hydrothermal system containing an alumina source, a silica source and an organic template molecule. The tetrapropylammonium ion (TPA) was the first organic molecule, which was reported [14] to be capable of inducing ZSM-5 formation. Later investigations showed that the use of TPA allows the synthesis of ZSM-5 zeolites with a Si/Al ratio ranging from 25 to infinity. Other organic molecules reported to induce ZSM-5 formation are, for

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example, 1,6-hexanediol [15] and 1-propanol [16]. A review on the use of different templates in zeolite synthesis has recently been given by Lok et al. [17]. Derouane and Gabelica and coworkers [18–20] investigated the process of forming the ZSM-5 phase and the role of the alkali metal cations, using the templates TPA-Brand tetrabutylammonium bromide.

The aim of the present study was to investigate the effect of type of templates and template/silica mole ratios on the crystallinity of the nano-sized ZSM-5. The structural properties of the prepared ZSM-5 were also explored.

2. Experimental

2.1. Materials and procedure

The alumina source employed was sodium aluminate (Aldrich). The silica source employed was fumed silica (Aldrich). The alkaline source was sodium hydroxide pellets (A.R) and template sources employed were tetramethylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium hydroxide and tetrabutylammonium hydroxide (Fluka, 20%) as (TMAOH, TEAOH, TPAOH and TBAOH), respectively.

A series of experiments has been carried out under the following conditions: fumed silica as silica source; sodium aluminate as source of alumina; 40 silica/alumina mole ratio; 0.215 template/silica mole ratio; 9.5 H_2O/SiO_2 mole ratio; 0.133 Na_2O/SiO_2 mole ratio; and 22 CH_3OH/SiO_2 mole ratio has been carried out.

The desired hydrogel was prepared by mixing the reagents in the following order; 0.212 gm of NaOH was dissolved in 19.6 gm of distilled water, the required amount of 20% template was added dropwise to the sodium hydroxide solution with stirring for 30 min. Then 13.75 gm of fumed silica was added drop wise. The resulting mixture (I) was stirred for 30 min. Another 0.212 gm of NaOH was dissolved in 19.6 gm of distilled water, 1.1 gm of sodium aluminate and 196 ml of methanol, as structure directing agent, were added to the sodium hydroxide solution with stirring for 1 h. The resulting mixture (II) was added dropwise to mixture (I) with stirring and the resulting gel was stirred for 1 h. Finally, the creamy gel was put into 500 ml parr unlined autoclave at 230 °C for 45 h. At the end of experiment the autoclave was quenched immediately with cold water. The solid product was filtered and washed with distilled water until the pH is dropped from 11 to 9. The product was then dried at 110 °C overnight. The unlined autoclaves were cleaned with 10% NaOH at 160 °C prior to each experiment to avoid adventitious seeding.

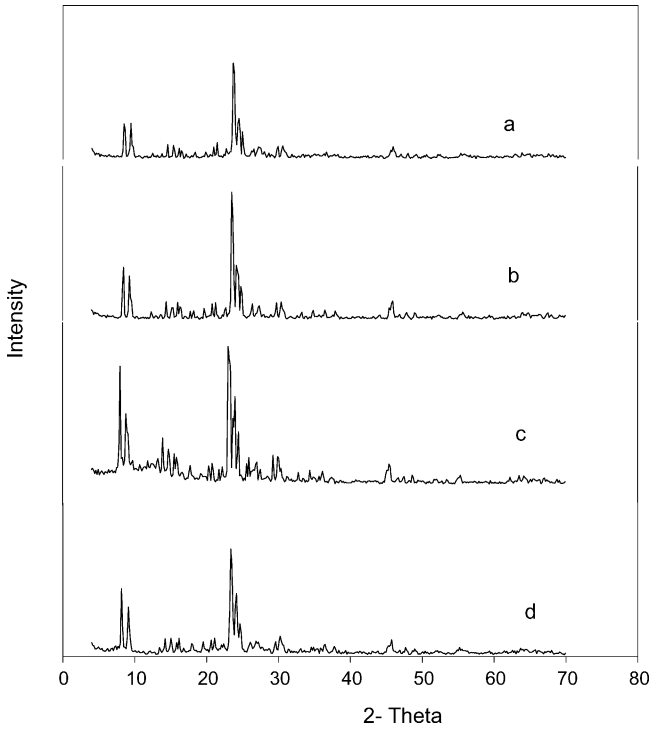

Fig. 1. Effect of type of templates on crystallinity % of as-synthesized samples where: (a) TMAOH, (b) TEAOH, (c) TPAOH and (d) TBAOH.

Table 1
Effect of type of templates on structural parameters of as-synthesized samples

Type of templates	Structural parameters (Å)			Unit cell V (Å)^3
	a	*b*	*c*	
Standard ZSM-5-tetrapropyl	20.022	19.899	13.383	5332.0
TBAOH	19.8	19.74	13.3	5198.3
TPAOH	19.92	19.92	13.36	5301.3
TEAOH	20.08	19.61	13.4	5276.5
TMAOH	20.04	19.78	13.38	5303.7

2.2. Characterization

X-ray diffraction (XRD) patterns and average crystallite size were collected with Bruker axs, D8 Advance. The crystallinity was determined from the peak area between $2\theta = 22$ and 25° using a highly crystalline ZSM-5 sample (ZSM-5 820NAA supplied by Mobil company Japan) as a reference. Surface areas were recorded using Nova 2000 series, Chromatech. The FT-IR spectra were recorded using Jasco FT-IR-460 plus. Morphology of the zeolite samples were investigated using scanning electron microscope, Jeol scanning microscope model JSM5410.

Table 2
Effect of type of templates on crystallinity, surface area and average crystal size of as-synthesized samples

Type of templates	Crystallinity of ZMS-5 (%)	Surface area (m^2/g)	Average crystal size (nm)	Formed phase
TMAOH	46.6	285	159.9	ZSM-5
TEAOH	74.7	292	76.3	ZSM-5
TPAOH	97.3	358.21	55.8	ZSM-5
TBAOH	77.1	321.2	87.2	ZSM-5

3. Results and discussion

3.1. Effect of template type

The variation of the type of templates as TMAOH, TEAOH, TPAOH and TBAOH could affect the crystallinity of the prepared ZSM-5 and played a noticeable role in its crystallization process.

Fig. 1 shows those XRD patterns of samples that were crystallized by using different type of templates. The results show that the patterns of samples synthesized using different type of templates show that the only formed phase is ZSM-5. Table 1 illustrate the effect of type of templates on structural parameters of the obtained samples compared to those of the standard sample. The findings reveal that the structural parameters of as-synthesized samples, which were prepared by using different type of templates, are near from those of standard sample due to the formation of only ZSM-5 phase. The effect of type of templates on surface area, crystallinity %, and average crystal size of as-synthesized samples are summarized in Table 2. The results emerge that the crystallinity % of the produced samples increased from 46.6 to 97.3% by using TMAOH, TEMOH and TPAOH, respectively, then decreased to 77.1% by using TBAOH, respectively.

The interaction energy increases with increase in the number of alkyl groups, where interaction energy increase in the following order: (−1.73 ev) tetramethyl < (1.74 ev) tetraethyl < (4.59 ev) tetrapropyl < (4.65 ev) tetrabutyl; this is due to the fact that here the number of methyl group is changing which affects the negative charge on the central nitrogen, as well as with increase in the number of methyl groups the interaction with framework also increases. It is observed that up to TPA with increase in alkyl chain length the distance between central nitrogen and framework increases. In case of TBA the same rule holds good with an additional effect of the conformation of the molecule adds up, which results in the unfavorable interaction with the framework in comparison to TPA [21]. Average crystal size increased in the following order; tetramethyl (159.9 nm) < tetrabutyl (87.2 nm) < tetraethyl (76.3 nm) < tetrapropyl (55.8 nm) and surface area increased in the following order: TMAOH < TEAOH <

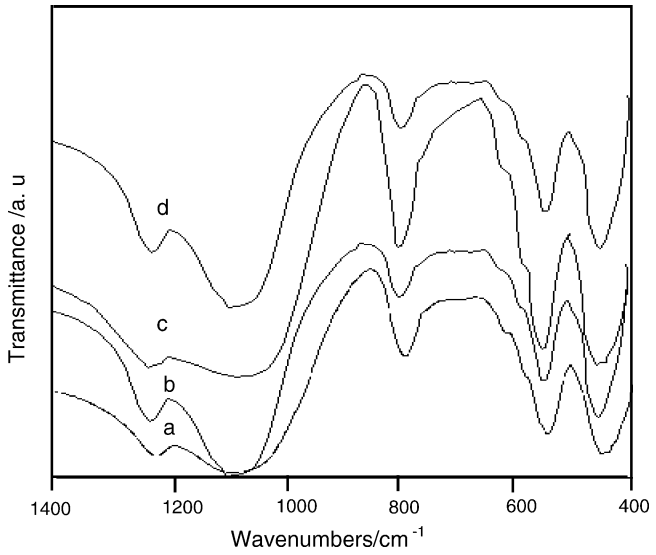

Fig. 2. IR spectra of as-synthesized samples obtained by using different type of templates where: (a) TMAOH, (b) TEMOH, (c) TPAOH, (d) TBAOH.

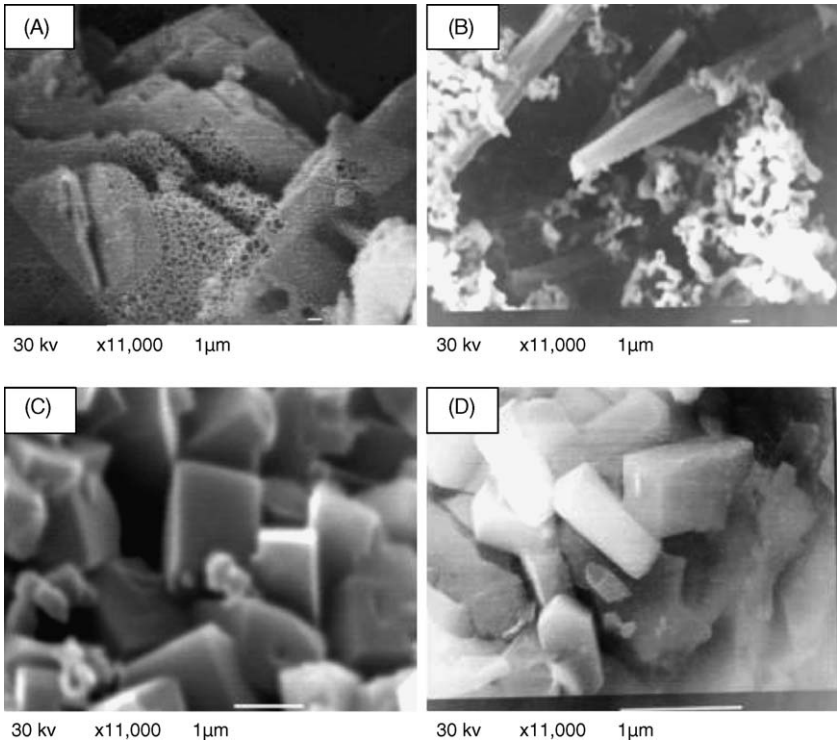

Fig. 3. SEM images of samples prepared by using different type of templates, where in (A) TMAOH, (B) TEMOH, (C) TPAOH and (D) TBAOH.

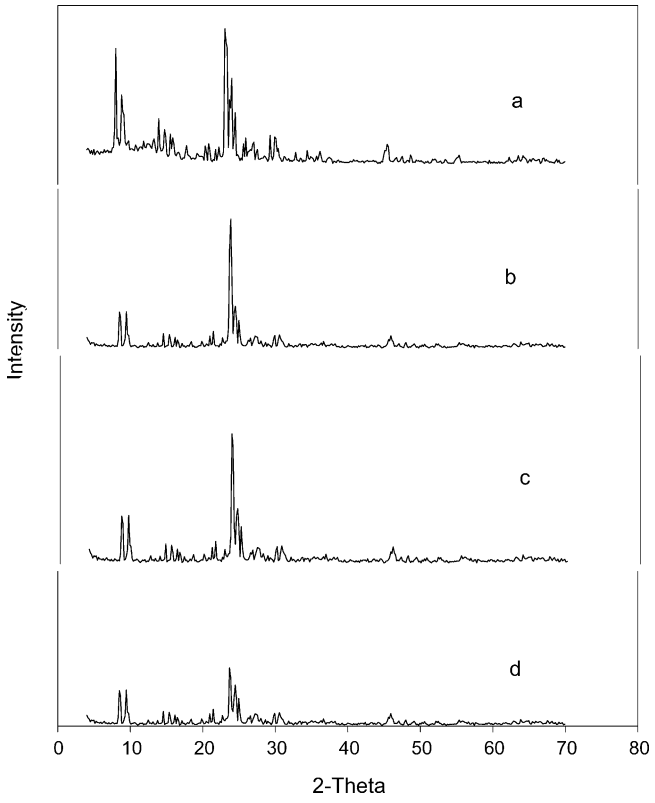

Fig. 4. Effect of template/silica mole ratios on crystallinity, of as-synthesized samples where: (a) 0.215, (b) 0.322, (c) 0.43 and (d) 0.537.

Table 3
Effect of template/silica mole ratios on structural parameters of as-synthesized samples

Template/silica mole ratios	Structural parameters (Å)			Unit cell V (Å)^3
	a	*b*	*c*	
Standard ZSM-5-tetrapropyl	20.022	19.899	13.383	5332.0
0.215	19.92	19.92	13.36	5301.3
0.322	20.02	19.74	13.32	5264.0
0.43	20.1	19.96	13.4	5376.0
0.537	20.1	19.88	13.36	5338.5

TPAOH due to increase in the crystallinity of the produced samples. The surface area decreased in case of TBAOH due to decrease in the crystallinity.

Fig. 2 displays IR spectra of the as-synthesized samples obtained by using different type of templates. The results show that the bands near 542, 1080, 790 and 450 cm^{-1} are presented for the samples which were prepared by using different type of templates due to the formation of only ZSM-5 phase.

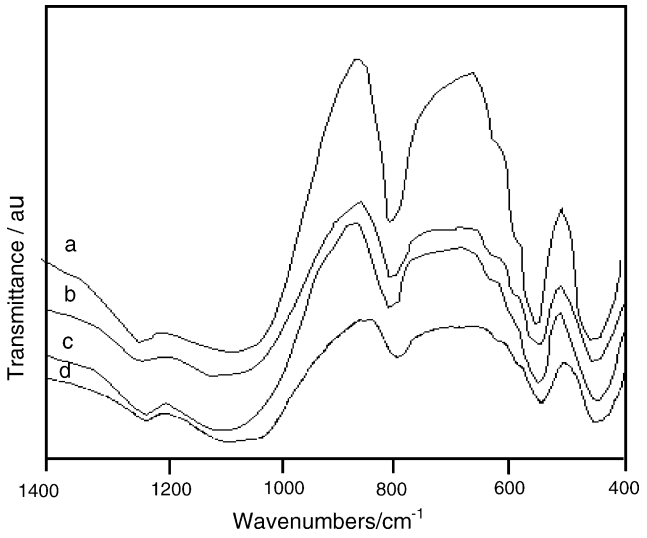

Fig. 5. IR spectra of as-synthesized samples obtained by using different mole ratios from template/silica where (a) 0.215, (b) 0.323, (c) 0.43, (d) 0.537.

Fig. 3 shows SEM images of the prepared sample using various type of templates. The results show that the sample, which was prepared by TMAOH crystallized in plate-like shaped crystals. Whereas the sample, which was prepared by TEAOH crystallized in rod-like and sphere-like shaped crystals. On the other hand, the sample, which was prepared, by TPAOH crystallized in cube-like shaped crystals and that was prepared, by TBAOH crystallized in flattened orthorhombic-like shaped crystals.

3.2. Effect of template/silica mole ratios

Template/silica mole ratios were changed from 0.215 to 0.537 under the above mentioned conditions.

Fig. 4 shows the XRD patterns of samples which were prepared by using different mole ratios from template/silica from 0.215 to 0.537. The results show that the characterized peaks of ZSM-5 zeolite phase existed and the crystallinity % of as-synthesized ZSM-5 increased by decreasing template/silica mole ratios in the following order; $0.537 < 0.43 < 0.333 < 0.215$. The effect of template/silica mole ratios on structural parameters of the obtained samples compared to the structural parameters of the standard sample were summarized in Table 3. The results reveal that there are no variations on the structural parameters of the synthesized samples at different template/silica mole ratios compared to those of the standard sample, which confirm the formation of ZSM-5 phase only. The effect of template/silica mole ratios on crystallinity %, surface area,

Table 4
Effect of template/silica mole ratios on crystallinity, surface area and average crystal size of as-synthesized samples

Template/silica mole ratio	Crystallinity of ZSM-5 (%)	Surface area (m^2/g)	Average crystal size (nm)	pH	Formed phase
0.215	97.3	358.21	55.8	10.9	ZSM-5
0.322	56	292	123.1	12.8	ZSM-5
0.43	46	285	130.2	13.9	ZSM-5
0.537	29	230	180	Above 14	ZSM-5

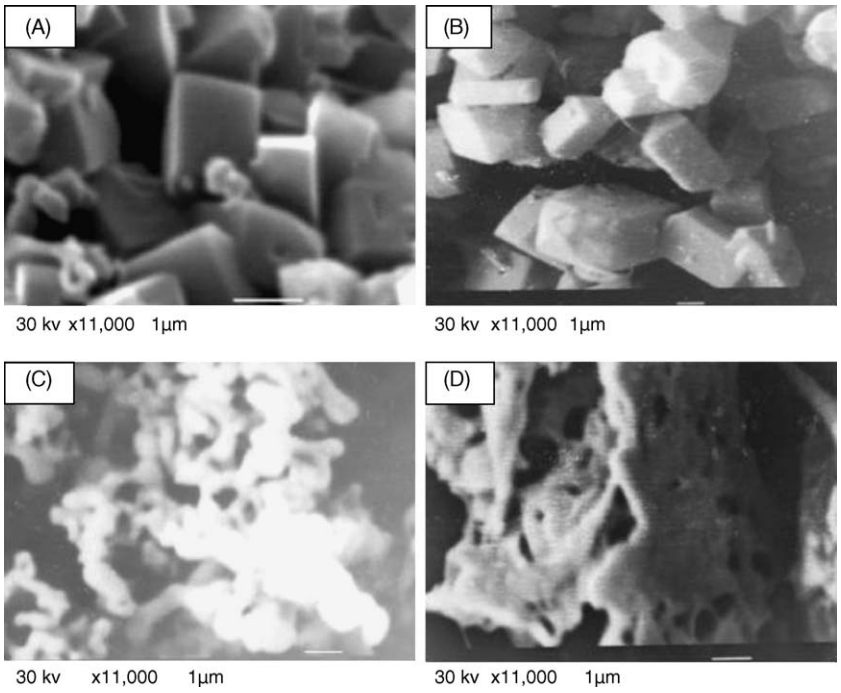

Fig. 6. SEM images of samples prepared by using different template/silica mole ratios, where in (A) 0.215, (B) 0.322, (C) 0.43 and (D) 0.537.

pH and average crystal size of as-synthesized samples were summarized in Table 4. The results in Table 4 shows that the crystallinity % of ZSM-5 and surface area decreased, whereas average crystallite size increased by increasing template/silica mole ratios from 0.215 to 0.537.

The increase in template/silica mole ratio raises the alkalinity of the mixture, leading to the decrease in the crystallization rate. Moreover, a higher pH induces an important increase in the crystallite size probably this was related to the decrease in the incorporation of Al at high pH and the role of Al species in the nucleation process [22].

Fig. 5 illustrates IR spectra of as-synthesized samples obtained by using different template/silica mole ratios. The results reveal that the bands near 542, 1080, 790 and 450 cm^{-1} were presented for all samples due to the formation of only ZSM-5 phase.

Fig. 6 shows SEM images of the prepared samples by using different template/silica mole ratios. The results show that the samples which were prepared by 0.215 and 0.322 template/silica mole ratios crystallized in cube-like shaped crystals. Whereas, sample which was prepared by 0.43 template/silica mole ratio crystallized in sphere-like shaped crystals and the sample prepared by 0.537 template/silica mole ratio crystallized in network-like shaped crystals.

The TPAOH and 0.215 mole ratio seem to be the best template type and template/silica mole ratio producing a material of 55.8 nm crystal size and has 358.21 m^2/g surface area. These result represent 97.3% of crystallinity.

4. Conclusions

The effects of type of templates and template/silica mole ratios on zeolite crystallization have been investigated. Using different type of templates and different template/silica mole ratios give ZSM-5 phase. In case of the effect type of templates and template/silica mole ratios, the crystallinity percentage of the produced ZSM-5 increased in the following order: TMAOH < TEAOH < TBAOH < TPAOH and 0.537 < 0.43 < 0.333 < 0.215, respectively. FT-IR confirmed that the samples, which were prepared by different type of templates and different template/silica mole ratios, gave ZSM-5 phase. In case of the effect of type of templates, SEM images show that the sample, which was prepared by TMAOH crystallized in plate-like shaped crystals, whereas the sample, which was prepared by TEAOH crystallized in rod-like and sphere-like shaped crystals. On the other hand the sample, which was prepared, by TPAOH crystallized in cube-like shaped crystals. The sample, which was prepared, by TBAOH crystallized in flattened orthorhombic shape crystals. But in case of the effect of template/silica mole ratios, SEM images show that the samples which were prepared by 0.215 and 0.322 template/silica mole ratios crystallized in cube-like shaped crystals and sample which was prepared by 0.43 template/silica mol ratio crystallized in sphere-like shaped crystals whereas that prepared by 0.537 template/silica mole ratio crystallized in network-like shaped crystals.

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