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The Role of Ethanol, Methyltriphenylphosphonium Bromide and Cetyltrimethylammonium Bromide as Directing Agents in Hydrothermal Synthesis of Aluminosilicate Molecular Sieve (ZSM-5) and Its Morphologies

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Abstract

Zeolite ZSM-5 presents a great source of interest in catalysis because of its shape selective properties. The absence of a relationship between the template size and shape of the structure generated during the synthesis of zeolites is illustrated by the case of ZSM-5. In this study, we have investigated the role of ethanol, methyltriphenylphosphonium bromide (MTPBr) and cetyltrimethylammonium bromide (CTABr) as neutral and cationic templates on aluminosilicate zeolite formation. Ethanol was also successfully used as a low cost template in the synthesis of ZSM-5. Although the XRD pattern of the synthesized zeolites is similar to the ZSM-5 pattern, the SEM results showed that their morphologies are completely different.

Keywords: ZSM-5; Hydrothermal synthesis; Surfactant; Morphology; Template

1. Introduction

The use of organic species as templates in the synthesis of aluminosilicate, aluminophosphate, silicoaluminophosphate, metaloaluminophosphate and many different molecular sieve materials has grown in the last twenty years [1-9]. The absence of relationship between the size and shape of template with the structure of zeolite was illustrated in the case of ZSM-5 [10]. In fact, many organic agents with different structure features promote the synthesis of ZSM-5 [11]. Zeolite ZSM-5 with MFI structure has an important role in the petrochemical and chemical industries [12]. Because of its unique structure, acidity and thermal stability, zeolite ZSM-5 can be used as catalyst in various reactions such as hydrocarbon transformation and isomerization [13]. This type of zeolite exhibits catalytic shape selectivity in the conversion of methanol to gasoline (MTG), cyclooligomerization and conversion of low molecular weight olefins and alkanes to aromatics [14]. In this study, we investigated the effect of two different templates on ZSM-5 formation. We also tried to use ethanol as a low cost template in the synthesis of ZSM-5.

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2. Experimental

2.1. Materials and Characterization

The ZSM-5 synthesis was conducted in 500 cm^3 stainless steel autoclave with stirrer. Sodium silicate (27% SiO_2, 8% Na_2O), aluminum sulfate, ethanol (96% Vol.), methyltriphenylphosphonium bromide (MTPBr) and cetyltrimethylammonium bromide (CTABr) purchased from Merck Chemical Company were used as reactant materials.

X-ray powder diffraction patterns of samples were recorded using a PW1730 diffractometer (Philips) with monochromatic Cu-K_α radiation.

The micrograph of zeolite was taken with a scanning electron microscope (NIOC, SEM 36D). FT-IR (KBr Pellets) spectra were recorded using a Shimadzu FT-IR spectrophotometer. Elemental analyses were carried out by Atomic Absorption Spectroscopy. The samples (0.012 g) were dissolved in concentrated hydrofluoric acid (2 ml) and diluted to 100 ml with deionized water in volumetric flasks.

2.2. Synthesis

ZSM-5 with ethanol as template was prepared using the reported procedure by Ugoina *et al.* [15]. The molar ratio of materials was chosen as: SiO_2/Al_2O_3=90, H_2O/SiO_2=40, OH^-/SiO_2=0.11

Aluminum sulfate solution was slowly added to the solution of sodium silicate in water containing the appropriate amount of desired template: ethanol, MTPBr and CTABr (see Tables 1-3). The reaction mixture was then stirred for 3 or 4 days at ambient temperature. It was then kept hydrothermally in autoclave at 170°C for 1 to 3 days. The crystals were filtered and washed with enough distilled water until the pH of filtrate decreased to 7.

Table 1. Starting gel composition, synthesis conditions and product obtained with ethanol (T) as template

Run	T/SiO_2	Aging Time (day)	Crystallization Time (day)	Products
1	1.5	3	2	Amorphous*
2	1.5	2	4	Amorphous*
3	1.5	4	5	Amorphous*
4	1.5	6	3	Amorphous*
5	1.5	6	2	ZSM-5 + Amorphous
6	1.5	7	3	ZSM-5 + Amorphous
7	1.5	3	1	ZSM-5 + Amorphous
8	2.5	3	1	ZSM-5

SiO_2/Al_2O_3 = 90, H_2O/SiO_2 = 40

* Partially contains ZSM-5

Table 2. Starting gel composition, synthesis conditions and products obtained with MTPBr (T) as template

Run	T/SiO_2	Aging Time (day)	Crystallization Time (day)	Products
9	0.015	3	1	ZSM-5 + Amorphous
10	0.03	3	1	ZSM-5
11	0.042	3	1	ZSM-5

SiO_2/Al_2O_3 = 90, H_2O/SiO_2 = 40

Table 3. Starting gel composition, synthesis conditions and products obtained with CTABr (T) as template

Run	T/SiO_2	Aging Time (day)	Crystallization Time (day)	Products
12	0.015	3	1	Amorphous
13	0.015	4	1	Amorphous
14	0.015	4	2	ZSM-5 + Amorphous
15	0.015	3	3	ZSM-5 + Amorphous
16	0.042	3	3	ZSM-5

SiO_2/Al_2O_3 = 90, H_2O/SiO_2 = 40

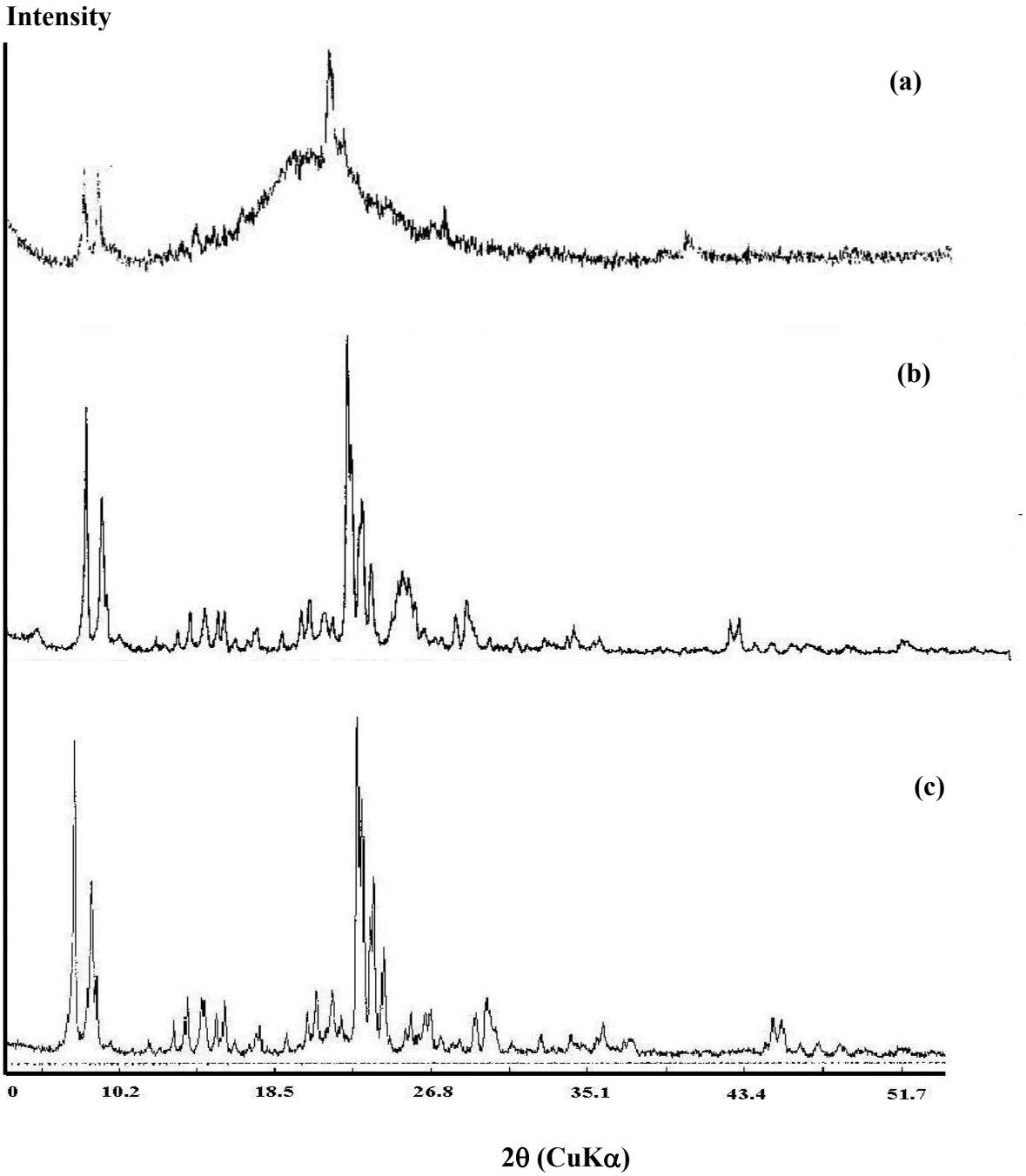

Figure 1. XRD pattern of (a) amorphous phase (runs 1, 2, 3, 4), (b) ZSM-5 and amorphous (runs 5, 6, 7), (c) ZSM-5 (run 8).

3. Results and Discussion

According to the results shown in Table 1, the hydrothermal transformation of gels with molar ratios of runs (1, 2, 3, 4) with ethanol as template, were amorphous (Fig. 1-a). Alternatively, by changing aging and crystallization times, ZSM-5 with small amount of amorphous compound was obtained (Fig. 1-b). By increasing ethanol/SiO_2 ratio to 2.5 (run 8), pure phase of ZSM-5 was formed (Fig. 1-c). The XRD pattern was similar to that of ZSM-5 [18]. In these reactions, the pH was adjusted to 11 by adding appropriate amount of concentrated H_2SO_4 (0.6-0.8 ml).

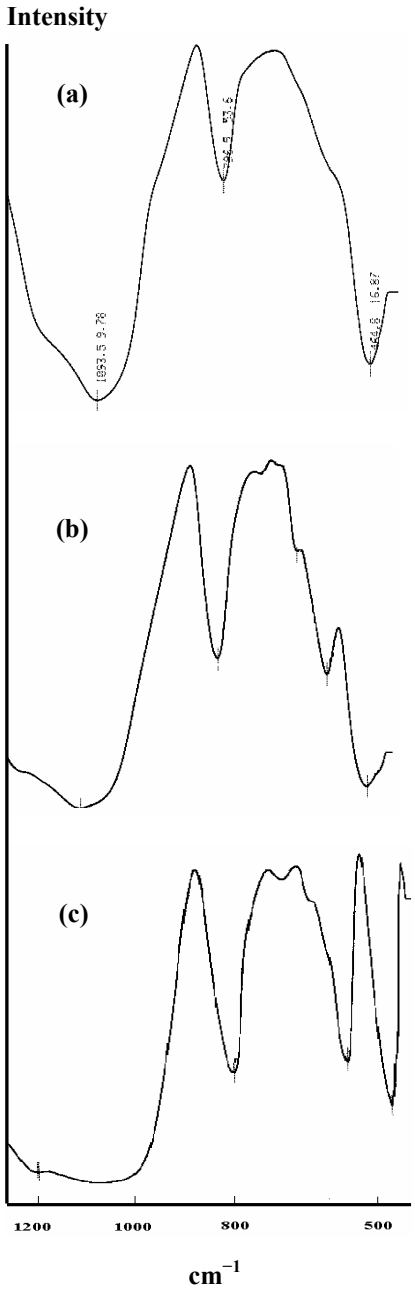

Figure 2. FTIR spectra of (a) amorphous phase, (b) ZSM-5 + amorphous (runs 5, 6, 7), (c) ZSM-5 (run 8).

Table 4. Chemical composition of synthesized zeolite (ZSM-5)

Run	SiO_2 (%)	Al_2O_3 (%)	Na_2O (%)
8	96.6	1.94	1.33
11	95.0	1.93	2.90
16	94.9	2.34	2.55

The FT-IR spectra of products of runs (1, 7 and 8) are shown in Figure 2. Systematic identification of the structure framework of many synthetic zeolites has been carried out at 2000-400 cm^{-1} [19,20]. The strong vibration mode at 1073 cm^{-1} is due to the internal tetrahedral vibration (T-O stretching) and the peak at 460 cm^{-1} is assigned to its bending. It should be mentioned that the pattern of spectra at 800-400 cm^{-1} agrees with the ZSM-5 type zeolite [21].

According to the results shown in Table 2, the hydrothermal transformation of gels with molar ratios of run (9) with MTPBr as template was ZSM-5 plus amorphous. In fact, in this case we had to decrease the T/SiO2 ratio because in run (8) the ethanol was as solvent and template but in this case (run 9), the template is a salt and we had to change the ratio because of its solubility limitation problem.

Pure ZSM-5 was formed (run 11) by increasing the ratio from 0.015 to 0.042 and keeping the aging and crystallization times constant. The XRD pattern (Fig. 3-a) was similar to that of ZSM-5.

According to the results of Table 3, the hydrothermal transformation of gels with CTABr as template (runs 12, 13) was amorphous. By increasing crystallization time (run 14) from 1 to 2 days, or decreasing aging time (run 15) from 4 to 3 days, the products were ZSM-5 plus amorphous. By keeping the aging and crystallization times (run 16) constant and only increasing T/SiO2 from 0.015 to 0.042, ZSM-5 was formed as pure phase.

XRD pattern and FT-IR results of runs 11 and 16 are shown in Figures 3 and 4, respectively. These results are consistent with ZSM-5.

Tables 1 and 2 also show the results regarding the effect of the templates on the formation of silicalites (runs 7-9). In these experiments the SiO_2/Al_2O_3, H_2O/SiO_2, aging and crystallization time were kept constant and only the type and molar ratio of template (T/SiO_2) were changed. It was found that with T/SiO_2=2.5 ($T=C_2H_5OH$, run 8) and MTPBr and CTABr with T/SiO_2=0.042, (runs 11, 16) pure ZSM-5 was formed. The chemical analyses of products (runs 8, 11, 16) are given in Table 4.

Scanning electron micrographs (SEM) of zeolites (runs 8, 11, 16) are given in Figure 5. The results show that the morphologies of the zeolites prepared with ethanol, MTPBr and CTABr are different. The first micrograph (Fig. 5-a) is similar to ZSM-5 micrograph, which has been prepared previously [22,23]. The second micrograph (Fig. 5-b) shows that crystals are flat hexagonal with clean and smooth surfaces. The third micrograph (Fig. 5-c) is semispherical with 4.66 μm in diameter. Dimensions of synthesized ZSM-5 are given

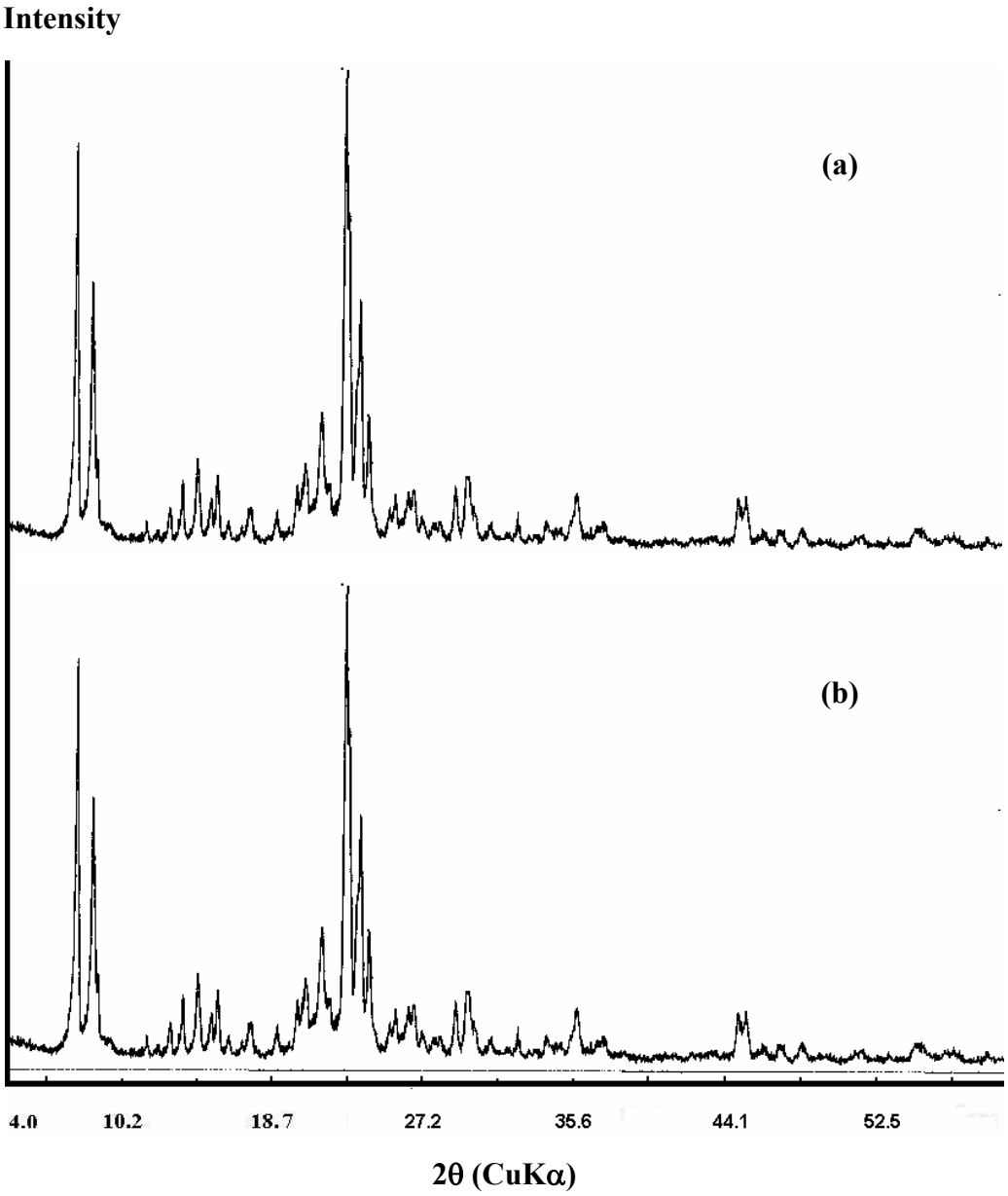

Figure 3. XRD pattern of (a) synthesized ZSM-5 with methyltriphenylphosphonium bromide (run 11), (b) with cetyltrimethylammonium bromide (run 16).

in Table 5. Although the XRD pattern of the products in the presence of ethanol, MTPBr and CTABr were similar, their morphologies are completely different.

Furthermore, TGA/DTA curves of synthesized ZSM-5 with ethanol (run 8), MTPBr (run 11) and CTABr (run 16) are given in Figure 6 (a-c). Figure 6 (a-c) shows three kinds of weight loss peaks. The weigh loss in lower temperature region ca.25°C to 150°C (for ethanol and CTABr) and ca.250°C (for MTPBr) may be related to desorption of water from surface and interlayer of ZSM-5. Two weight loss peaks at higher temperature ca.400°C and 550°C may correspond to the decomposition of organic templates. This may be because of the relatively strong interactions between anionic inorganic framework and cationic organic species located at different sites of the ZSM-5 framework.

In general, the organic compounds added to the starting mixtures for the zeolite synthesis remarkably modify the crystalline product types with reference to

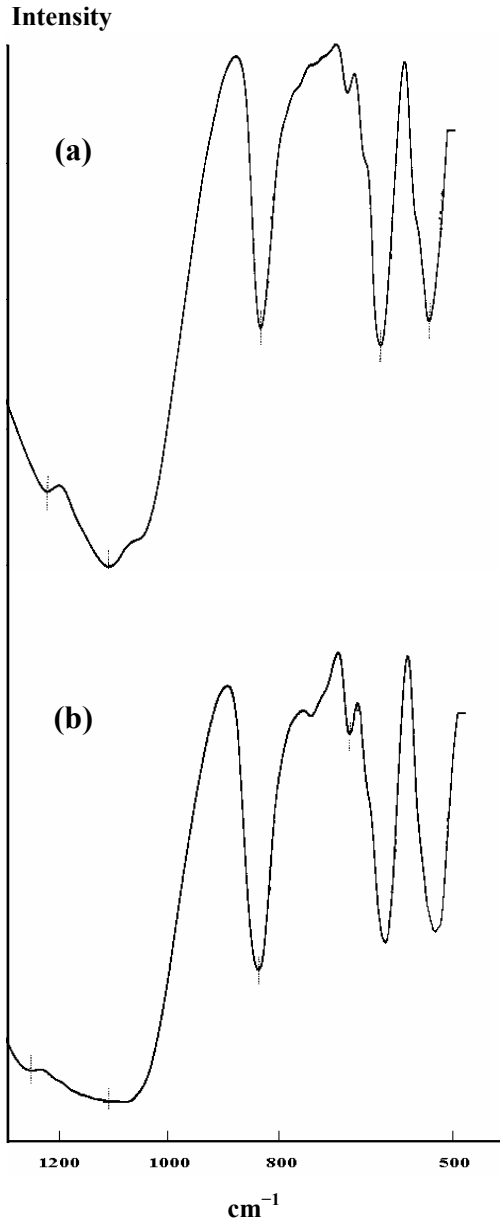

Figure 4. FT-IR spectra of (a) synthesized ZSM-5 with MTPBr run 11, (b) with CTABr run 16.

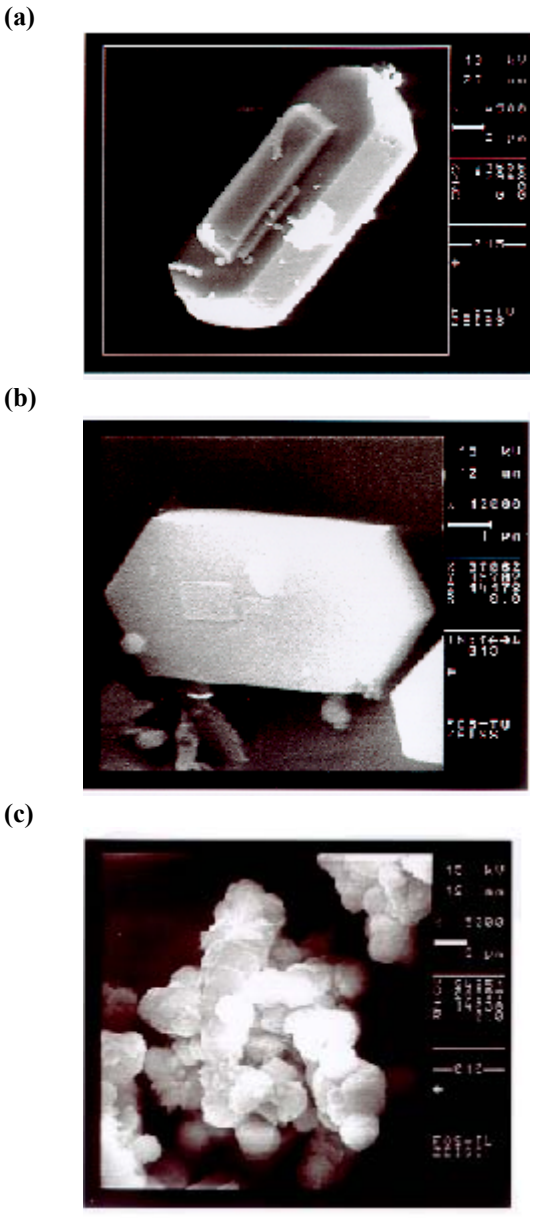

Figure 5. Scanning electron micrograph of ZSM-5 prepared with (a) Ethanol, (b) MTPBr, (c) CTABr.

Table 5. Dimensions of synthesized ZSM-5

Run	Template	Length (μm)	Width (μm)	Height (μm)	Diameter (μm)
8	Ethanol	40.40	11.33	7.27	-
11	Methyltriphenylphosphonium bromide (MTPBr)	6.11	3.05	2.69	-
16	Cetyltrimethylammonium bromide (CTABr)	-	-	-	4.66

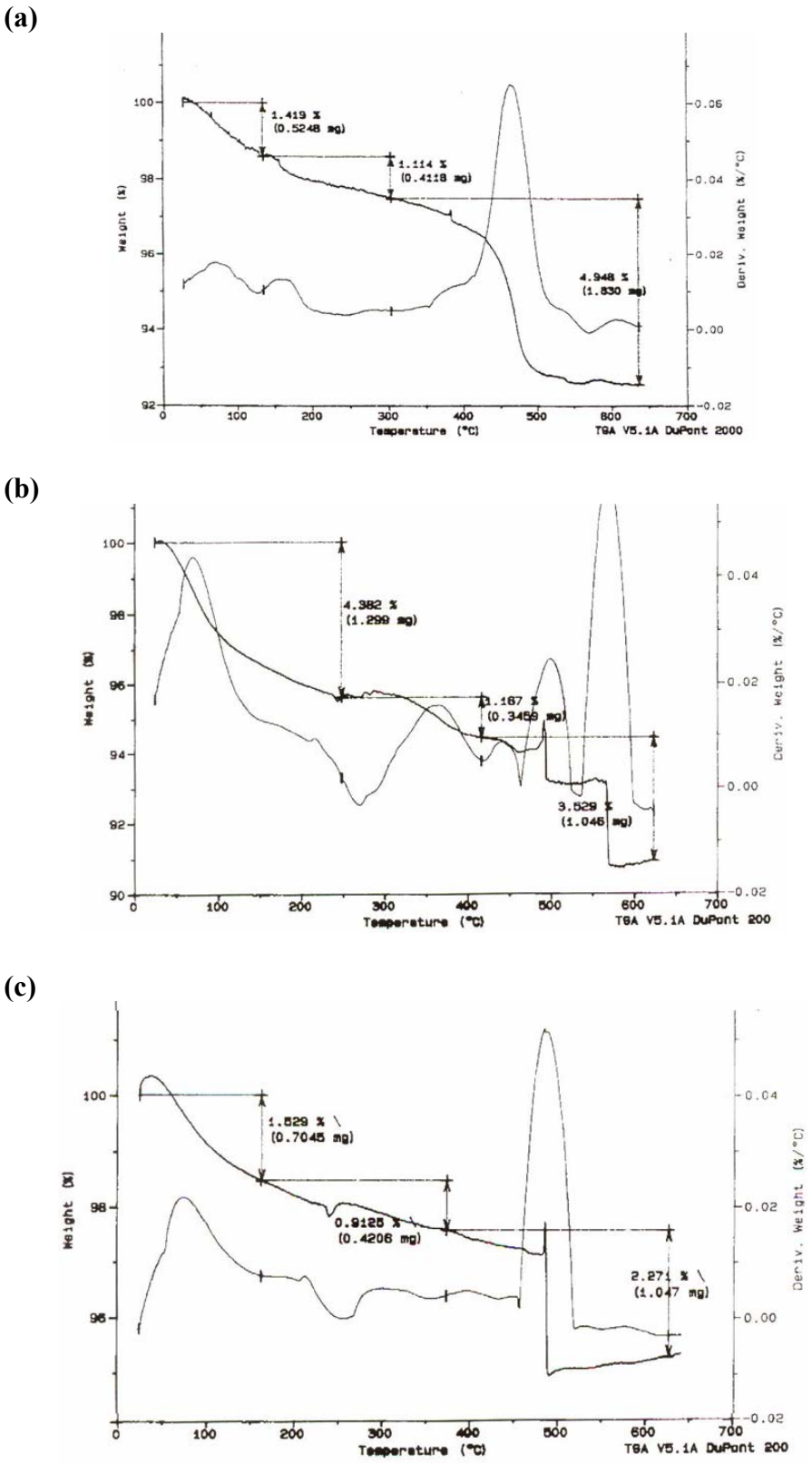

Figure 6. TGA/DTA curves of synthesized ZSM-5 obtained from (a) ethanol (run 8), (b) MT PBRr (run 11) and (c) CTABr (run 16).

both structure and composition. During the past twenty years, different methods have been reported for the synthesis of zeolites from SiO_2-Al_2O_3 gel containing organic templates. Commonly, tetrapropylamonium (TPA) salts or hydroxides and different amines and diamines have also been used as template for ZSM-5 synthesis [16].

Studies on the synthesis of ZSM-5 from a system without organic templates are indispensable from the view point of industrial utilization. In this study, we followed two main goals; firstly to improve the synthesis method of ZSM-5 with ethanol as a low cost template, and secondly to see the effect of three different templates on ZSM-5 morphologies. According to the reported article published by Uguina *et al.* [15,24], ethanol can act as a directing agent for the MFI structure. In our work, we used ethanol as solvent and directing agent. We found that formation of pure phase of ZSM-5 was possible only if ethanol/SiO_2 ratio was increased to 2.5. In the next step we tried to see the effect of three different templates on ZSM-5 morphologies. We found that without using template, no ZSM-5 was formed. Although by using ethanol and MTPBr, the morphologies were similar to that reported for ZSM-5, the morphology in the case of CTABr was completely different from the other two.

The interesting point is that, when we used CTABr as template, a microporous particle with spherical morphology was formed. Even though we didn't investigate the mechanism, the interpretation suggested by Huang et al. seems likely [17]. According to their views, thermodynamic interactions in the synthesis gel, *i.e.* the surfactant-inorganic (SI), inorganic-inorganic (II) and surfactant-surfactant (SS) interactions are the main factors in the crystallization type of products. If SI>SS>II, an orderly mesoporous phase will be formed. On the other hand, when the crystallization temperature is high enough (165-180°C), the SS interaction decreases. Therefore, the interaction order is changed to SI>SS and II>SS and the CTABr acts as directing agent toward the formation of microporous material.

4. Conclusion

It was concluded that, using ethanol, MTPBr and CTABr as templates resulted in the formation of zeolite ZSM-5 under similar conditions. It was also found that pure ZSM-5 zeolite was obtained using ethanol as low cost template. It is interesting that although the XRD patterns of the products are similar but their morphologies are completely different.

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