Synthesis of aluminosilicate and borosilicate MFI type zeolite using dual–templating method

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ABSTRACT

The aluminosilicate and borosilicate MFI type zeolites were successfully synthesized by a dual-templating system using pyrrolidine tetramethylammonium hydroxide (TMAOH) as co-structure-directing agents (SDAs), in absence of inorganic cations and fluoride media. Various parameters that effect the crystallization of aluminosilicate (Al-ZSM-5) and borosilicate (B-ZSM-5) zeolites, such as the Pyrr/Si, TMA/Si and Si/Al or Si/B ratios were investigated. The obtained products were characterized by XRD, N_2 Absorption,^{13}C CP MAS NMR spectroscopy, SEM and FTIR techniques. The XRD patterns confirmed the formation a pure ZSM-5 with high crystallinity, SEM results revealed that Al-ZSM-5 and B-ZSM-5 synthesized at the same condition having different morphologies. On the other hand ^{13}C CP MAS NMR spectroscopy confirmed the incorporation of pyrrolidine and TMA into the aluminosilicate and borosilicate zeolites products. These two kinds of SDAs played a cooperative role in the crystallisation of Al-ZSM-5 and B-ZSM-5. The role of pyrrolidine was to provide the initial nucleation and selectivity, and of TMA to provide both space-filling and basicity capacities in the synthesis.

Keywords: Zeolite, Synthesis, ZSM-5, Dual-templating, Characterisation**.**
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INTRODUCTION

Zeolites are microporous crystalline materials with well-defined pore structures and geometry. Because of their properties such as thermal stability, adsorption, acidity, catalytic activity, cation exchange and molecular sieves, zeolites have been extensively used as adsorbents [1], ion exchangers and catalysts [2-5]. ZSM-5 is one of the most widely studied zeolites. It has been used in many petrochemical catalytic processes such as cracking, isomerization, aromatization and alkylation [6]. Since the synthesis of Al-ZSM-5 zeolite was first reported by Mobil in 1972 [7], considerable effort has been devoted to prepare this zeolite. ZSM-5 (MFI topology) is a high silica zeolite with interconnected two-dimensional channels surrounded by ten-membered rings with a diameter of $5,3 \times 5,6$ Å and $5,1 \times 5,5$ Å[8]. The synthesis was usually performed in the presence of an organic structure directing cation (SDA), typically tetrapropylammonium (TPA^+) and an inorganic cation, typically sodium (Na^+) under hydroxide form (NaOH)[9]. Early work by Flaningen [10] showed that fluoride-containing gels could be used to prepare MFI zeolites. The fluoride ion was used as a mineralizer (by using NH_4F or HF sources) instead of the more conventionally used hydroxide ion. This choice presents several advantages, for fewer metastable phases formation, implying a certain ease of preparation of any desired zeolite [11, 12] and for neutral medium (or acidic) enabling the incorporation of elements sparingly soluble in alkaline media such as Co^{2+}, Fe^{3+}, Ti^{4+} [13, 14]. However, a study has shown that even after calcination, fluorine remains occluded inside the MFI structure [15]. Isomorphous substitutions of metal for silicon (Si) in the lattice structure of zeolites have been studied to modify the physic-chemical properties [16-18]. For the first time, Taramasso et al, focused on the framework modification of ZSM-5 by substituting aluminium with baron [19-21]. The strength of Brönsted acid sites in B-ZSM-5 is considerably lower than that of Al-ZSM-5 and the catalytic properties of B-ZSM-5 are less than those of its aluminosilicate analogue [22], However for some special reactions, the advantage of B-ZSM-5 in comparison to Al-ZSM-5 have been claimed [18, 21], for instance in the Beckmann rearrangement [23]. In the present study, we present a dual-

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templating strategy of the synthesis of Al-ZSM-5 and B-ZSM-5 zeolites, using pyrrolidine in combination with tetramethylammonium as structure directing agents (SDAs), in the absence of inorganic cation and fluoride media. In this study, we explore the use of two organics structure directing agents. The concept used in this attempt was that SDA to provide the initial nucleation and then hope that a second could provide both the pore filling aspect as the crystal continued to grow and serve as the source of hydroxide.

MATERIALS AND METHODS

II.I Materials
All the chemical reagents used in this work are given in Table 1.

Table 1: Chemical reagents

Reactant	Molecular formula	Function	Company, Purity %
Colloidal silica solution	SiO_2	Silica source	Aldrich, 40wt-%
Nitrate nonahydrate aluminium	$Al(NO_3)_3$, 9 H_2O	Aluminum source	Loba Chemie, 99%
Boric acid	H_3BO_3	Boron source	Merck, 99%
Pyrrolidine	C_4H_9N	Template	Aldrich, 99%
Tetramethylammonium pentahydrate hydroxide	$(CH_3)_4NOH, 5H_2O$	Template	Alfa-Aesar, 98%

III.II Synthesis of Al-ZSM-5 zeolite
Al-ZSM-5 zeolite was synthesized hydrothermally, both TMAOH and pyrrolidine were used as templates.

A typical starting mixture was formed using the following molar composition:

0.125 Al_2O_3 – 11 Si_2O - 1 TMA_2O - 5.5 Pyrrolidine - 200 H_2O. The procedure was as follows:

An aqueous solution of aluminium nitrate and tetrapropylammonium dissolved in deionized water was stirred for 30 mn. In the same time, we prepared the second solution, which was obtained by dissolving pyrrolidine and colloidal silica in deionised water. Both solutions were added and stirred for 1 h. The resulting gel was placed in an Teflon-lined autoclave which was heated without stirring at 150 °C for 8 days. The details of the zeolite synthesis are collected in table 2.

III.III Synthesis of B-ZSM-5 zeolite
The typical molar composition of the synthesis of B-ZSM-5 zeolite was:
0.5 B_2O_3 – 11 Si_2O - 1 TMA_2O - 5.5 Pyrrolidine - 200 H_2O. The synthesis gel was prepared by mixing the reagents in the following order: at first tetramethylammonium and boric acid were dissolved in deionized water, named solution (I). Solution (II) contained colloidal silica and pyrrolidine template dissolved in deionized water. Each solution was stirred for 30 mn to achieve a homogeneous solution. Then, solution (I) was added drop wise to solution (II) under speed agitation. The resulted mixture was stirred for 1 h at room temperature to insure homogeneity, introduced into the Teflon-lined autoclave and finally heated at 150 °C, under static conditions, for 8 days. All the crystalline solids obtained were filtered ,washed and dried at 80°c, calcined at 550°C for 6 h to remove the templates and obtained directly the acidic form H-ZSM-5 zeolite, without the need to ion–exchanging. The gel compositions and results of synthesis are tabulated in Table 3.

III.VI Characterisation
Diffractograms of the different materials were collected using a Bucker, D8 Advance diffractometer with a Cu Kα (λ = 1.54 Å). XRD patterns were determined between 2Ө angles of 2 and 40°. The crystallinity was determined from the peak area using a highly crystalline ZSM-5 sample as a reference. FT-IR spectra were recorded at room temperature using a FT-IR spectrometer (Alpha-Bruker ATR diamond), over the range 400-4000 cm^{-1}, the ^{13}C solid-state cross polarization (CP) NMR spectra of the as–synthesized borosilicate and aluminosilicate MFI type zeolite were recorded using spectrometer 400 Plus Advance III Bruker frequency of 75.5 MHz, the chemical shifts reported are relative to TMS. The specific surface area was calculated using the nitrogen adsorption data obtained with a micrometrics ASAP 2020. Micrographs of the samples were taken on a JEOL JSM-6490LV scanning electron microscope (SEM).

RESULTS AND DISCUSSION

VI.I Synthesis of Al-ZSM-5 zeolites
The hydrothermal synthesis of Al-ZSM-5 was first attempted by using TMAOH or pyrrolidine as an independent SDA. Summary of the synthesis compositions, conditions as well as characterisation results of Al-ZSM-5 samples employing mixed templating agents are presented in Table 2.

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Table 2: Synthesis condition of Al-ZSM-5 and properties of products

Samples No.	Gel chemical conditions (molar ratio)				Crystallization		Products	BET surface area (m² g⁻¹)
	Si/Al	Pyrr/Si	TMA/Si	TMA:Pyrr	Time (days)	R.C % [a]		
Z-1	44	0.5	0	-	8	-	Amorphous	-
Z-2	44	0	0.18	-	50	-	Amorphous	-
Z-3	44	0.5	0.18	2 : 5.5	8	90	Al-ZSM-5	280
Z-4	44	0.27	0.22	2.4 : 3	10	-	Amorphous	-
Z-5	22	0.5	0.27	3 : 5.5	8	-	Amorphous	-
Z-6	7.5	0.5	0.18	2 : 5.5	8	-	Amorphous	-
Z-7	110	0.5	0.18	2 : 5.5	8	98	Al-ZSM-5	300

Crystallization temperature: 150°C
[a] Relative crystallinity calculated from XRD patterns [24].

When TMAOH or pyrrolidine were used as a single SDA, only amorphous materials were obtained, after 8 days of crystallisation (samples Z-1 and Z-2). On the other hand, when using pyrrolidine as a solely SDA, the pure Al-ZSM-5 phase was obtained, after 30 days of heating at 150 °C (sample Z-1). At the same synthesis conditions, Al-ZSM-5 zeolite was obtained when TMAOH and pyrrolidine were used as a dual-template system with TMA/Pyrr molar ratio of 2/5.5 and a Si/Al ratio of 44 and 110, after 8 days of crystallisation. Fig.2 shows representative XRD pattern of the Al-ZSM-5 zeolite synthesized by dual-templating method. The pattern verified that the product was a characteristic of MFI topology free of any impurity. However, there was difficulty in crystallizing a Al-ZSM-5 zeolite at the Si/Al molar ratio less than 22 when the amorphous phase was formed. These results reveal that the nucleation of Al-ZSM-5 zeolite requires the presence of Pyrrolidine (to specify the synthesis of Al-ZSM-5). When a mixed template system being used (Pyrr + TMA), the crystallisation time was reduced by a factor of 4-5 times. Generally TMA would then play a beneficial but structurally non-specific role in the crystallisation of Al-ZSM-5. The necessity to use TMA as a second SDA was to provide both space-filling and basicity capacities in the synthesis of Al-ZSM-5.

VI.II Synthesis of B-ZSM-5 zeolites
The gel composition and crystallization conditions for B-ZSM-5 synthesis are listed in Table 3.

Table 3: Synthesis condition of B-ZSM-5 and property of products

Samples No.	Gel chemical conditions (molar ratio)				Crystallization		Products	BET surface area (m² g⁻¹)
	Si/B	Pyrr/Si	TMA/Si	TMA:Pyrr	Time (days)	R.C % [a]		
Z-8	11	0	0.1	-	8	-	RUB-10 [b]	-
Z-9	11	0.5	0	-	8	91	B-ZSM-5	315
Z-10	11	0.5	0.1	1 : 5.5	8	96	B-ZSM-5	320
Z-11	11	0.27	0.06	0.62 : 3	11	-	Amorphous	-
Z-12	11	0.27	0.1	1 : 3	8	-	RUB-10 [b]	-
Z-13	11	0.5	0.06	0.62 : 5.5	7	100	B-ZSM-5	340
Z-14	22	0.5	0.06	0.62 : 5.5	8	88	B-ZSM-5	260
Z-15	22	0.5	0	-	8	-	Amorphous	-
Z-16	0	0.5	0.06	0.62 : 5.5	5	–	– [c]	–

Crystallization temperature: 150°C
[b] obtained with amorphous phase.
[c] No solids were obtained.

The XRD pattern of B-ZSM-5 zeolite is given in Figure 1. When compared with the XRD patterns in the literature, there are no other reflections than those from the ZSM-5 zeolite [24], indicating the high purity of these products.
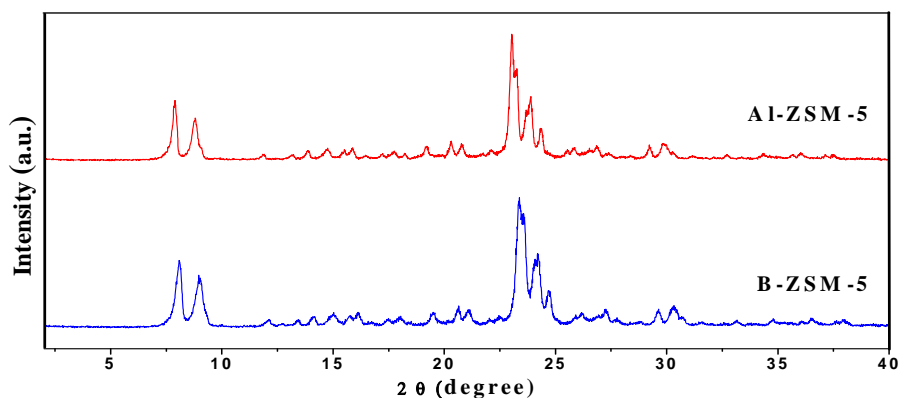
Figure 1: XRD patterns of synthesized Al-ZSM-5 and B-ZSM-5 samples

The effect of Si/B molar ratio in the initial synthesis solution was studied using ratios between 0-22. The results show, in the absence of B, the reactant remains liquid and no solid was obtained. In order to determine how the organic template concentration influences ZSM-5 formation, a series of syntheses was performed using different template contents (TMA/Si = 0, 0.06, 0.1, 0.14) and (Pyrr/Si = 0, 0.27, 0.5). Using the organic cation TMA^+ as a single SDA (presented in sample Z-8) gives RUB-10 zeolite (RUT topology), after 8 days of crystallisation, consistent with the results reported in previous studies [25, 26]. This zeolite is not completely crystallized, this maybe for lower TMA concentration. RUB-10 was also obtained using dual-templating system showed in Z-12 sample. The pattern of products synthesised with pyrrolidine as a single template shows a pure B-ZSM-5 phase, after 8 days of crystallisation, explain that the pyrrolidine favourite the nucleation and crystallization of B-ZSM-5 zeolite. The addition of TMAOH as co-template showed in Z-10 and Z-13 increase the crystallinity of B-ZSM-5 zeolites. With decreasing the amount of the two amines simultaneously (samples Z-12), only amorphous materials were obtained. These results revealed that the amount of each organic template was the key factor for the synthesis of B-ZSM-5 or RUB-10: a high proportion of TMA favoured the formation of B-ZSM-5. However, a high proportion of pyrrolidine favoured the crystallisation of B-ZSM-5. No mixture of RUB-10 and B-ZSM-5 phases was produced, suggesting that, the organic compound added as a supplementary crystallisation SDA to the synthesis mixture, no affecting the phase selectivity and its presence serves as space-filling species rather than as reserve of OH^-.

V.I Infra-red analysis
The formation of ZSM-5 framework was further confirmed by the FT-IR spectra shown in Figure 2.
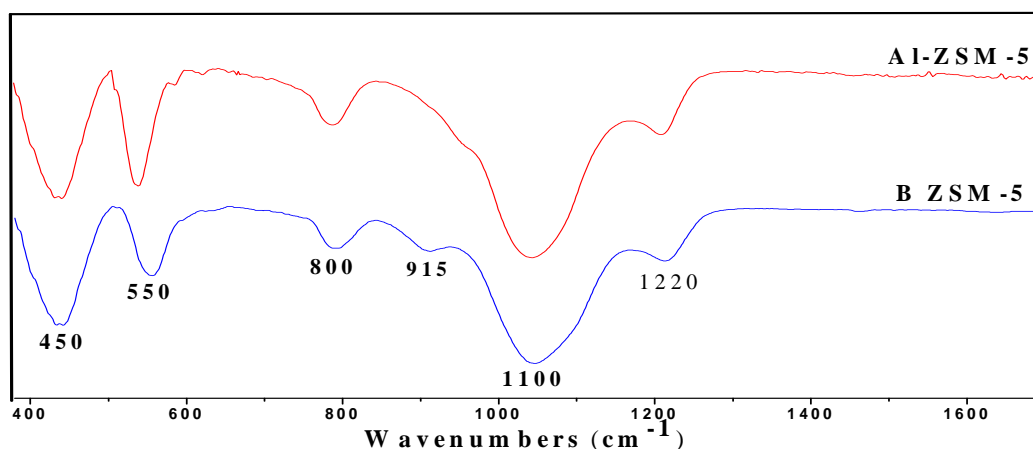

Figure 2: FT-IR spectra of synthesized Al-ZSM-5 and B-ZSM-5 samples

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The FT-IR spectra on both samples show well-defined IR absorption bands centred at 450, 550, 800, 1100, and 1220 cm⁻¹ typical from the MFI structure (pentasil zeolite) [27, 28]. The vibration band at 550 cm⁻¹ confirms the presence of a five-membered ring of the pentasil structure [28, 29]. For B-ZSM-5 zeolite, the IR peak at around 915 cm⁻¹ was documented in a previous work [30], which could be observed in all of the boron-contained zeolites, characteristic of symmetric stretching vibration of Si-O-B bond.

V.II ^{13}C solid-state CP MAS NMR analysis

Figure 3 shows the ^{13}C CP MAS NMR spectra of B-ZSM-5 and Al-ZSM-5 as made form, together with the liquid ^{13}C NMR of TMAOH and Pyrrolidine.
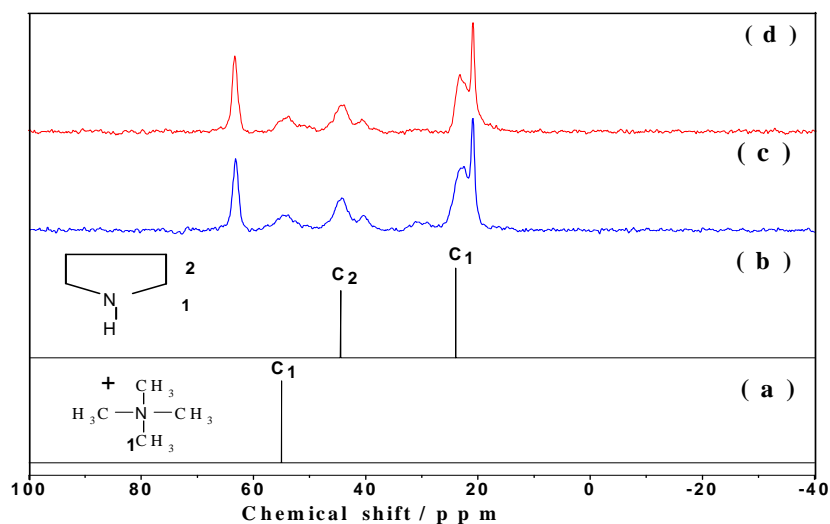

Figure 3: Liquid ^{13}C NMR spectra of: (a) TMAOH, (b) pyrrolidine, and ^{13}C CP MAS NMR as-made (c) B-ZSM-5, (d) Al-ZSM-5 synthesized by dual-templating system

The signals at 24 and 46 ppm in the ^{13}C CP MAS NMR spectra, which could be found in samples (c) and (d), are assigned to -CH$_2$ in the pyrrolidine ring, these signals confirmed the integrity of pyrrolidine inside the zeolite structure. Pyrrolidine molecules may be present in the zeolite channel as unidissodiated (chemically intact) state [31], similar to that present in the liquid form. An additional signal at 57 ppm could be observed, this can be assigned to -CH$_3$ groups of the TMA$^+$ cations occluded in zeolitic framework, but the intensity of the signal due to this molecule was low. This was because the amount of TMA incorporated into the zeolite was less. These results showed that both TMAOH and pyrrolidine were occluded in the zeolite framework, suggesting that both molecules may work as SDAs towards the formation of Al-ZSM-5 and B-ZSM-5 zeolites. When TMA was used as an SDA, together with pyrrolidine, it was incorporated into the zeolite void volume even though it is more required to crystallize Al-ZSM-5 than B-ZSM-5, under this synthesis conditions. The other signals at 22, 32, 42 and 64 ppm explain that the pyrrolidine is mainly located in the channel intersection (probably protoned/charged species) represents reactions products of pyrrolidine formed during the zeolite synthesis [31].

V.III Scanning electron microscopy analysis

The SEM images of various zeolites prepared in this study are illustrated in Figure 4. It showed that Al-ZSM-5 and B-ZSM-5 samples were highly crystalline materials free of amorphous phase and other impurities.
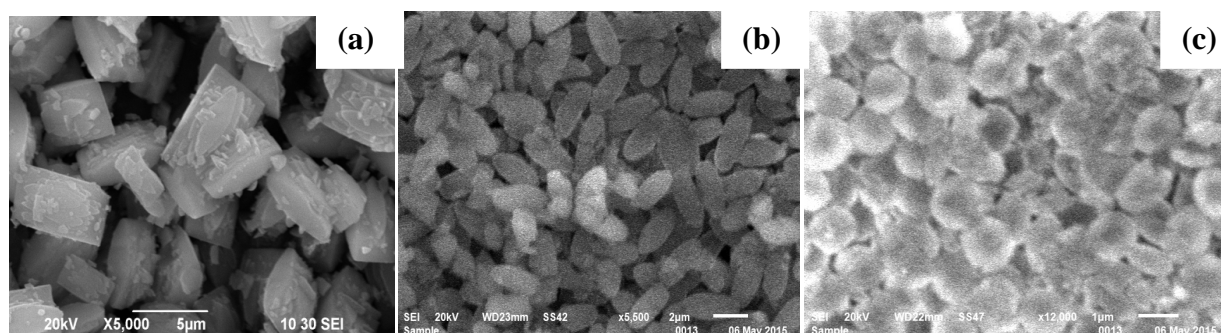
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Figure 4: SEM images of as-made: (a) Al-ZSM-5, (b) B-ZSM-5 and (c) RUB-10, corresponding to: (a) Z-3, (b) Z-9 and (c) Z-12 respectively

It can be seen that the as-synthesized samples show different crystals morphologies and sizes. The crystals of Al-ZSM-5 zeolite are hexagonal with 5 μm in length. The B-ZSM-5 zeolite showed uniform crystals with an oval shape and average diameters of (4 x 2) μm. The SEM image of RUB-10 zeolite crystals present spherical aggregates morphologies and the size of the aggregates was 1μm.

CONCLUSION

Pure and highly crystalline B-ZSM-5 and Al-ZSM-5 zeolites were successfully synthesized with a dual-templating system, consisting of pyrrolidine and TMAOH. The addition of TMAOH as co-template increases the crystallinity of B-ZSM-5 and Al-ZSM-5 zeolites with less crystallization time. The final products obtained by dual-templating system have different morphologies and crystals size. ^{13}C CP MAS NMR spectroscopic of dual-templating system reveal that TMA remain intact upon its occlusion in the zeolites Al-ZSM-5 and B-ZSM-5, however pyrrolidine was present as neutral molecules (in the channels) and protoned/charged species (probably at the channels intersection).

REFERENCES

[1] L. Maaza, F. Djafri, A. Bouchekara, A. Djafri, *Orient. J. Chem.*, **2016**,32,171-80.
[2] R. F. Howe, J. McGregor, S. F. Parker, P. Collier, D. Lennon, J. *Catal. Lett.,***2016**,146,1242-1248.
[3] Z. Ghasemi, H. Younesi, A. A. Zinatizadeh, *J. Chemosphere.*, **2016**,159,552-564.
[4] M. Rutkowska, D. Macina, Z. Piwowarska, M. Gajewska, U. Díaz, L. Chmielarz, J. *Catal. Scien. Techn.*, **2016**,6,4849-4862.
[5] W. Feng, X. Gao, C. Ding, Y. Jia, J. Wang, K. Zhang, P. Liu, J. *Appl. organometa. chem.*, **2016**,1-7.
[6] N. Hansen, T. Bruggemann, A.T. Bell, F.J. Keil, *J. Phys.Chem. C.*, **2008**,112,15402-15411.
[7] Y. G. Adewuyi, D. J. Klocke, J. S. Buchanan, *J. Appl. Catal. A.*, **1995**,131-21.
[8] International Zeolite Association, in IZA-online. org.
[9] A. Soualah, M. Berkani, M. Chater, *J. C. R. chimie.*, **2004**,7,713-720.
[10] E. M. Flanigen, R. L. Patton, *US Patent 40738651978.*, **1978**.
[11] M. A. Camblor, L. A. Villaescusa, M. J. Díaz-Cabañas, *J. Top. Catal.*, **1999**,9,59-76.
[12] S.A. Axon, J. Klinowski., *J.Chem.Soc.*, **1990**,86,3679-3682.
[13] J. Guth, H. Kessler, J. Higel, J. Lamblin, J. Patarin, A. Seive, *J. ACS. Symp. Ser.*, **1989**,398,176-195.
[14] H. Kessler, J. Patarin, C. Schott-Darie, *J. Adv. Zeolite. Sci. Appl.*, **1994**,75-113.
[15] Z. Lounis, F. Djafri, A. Bengueddach, *J. La Société. Chim. Tunisie.*, **2010**,12,97-103.
[16] C. Naccache, Y. B. Tarrit, *J. Zeolite. Scie. Techn.*, **1984**.
[17] W. Song, R. E. Justice, C. A. Jones, V. H. Grassian, S. C. Larsen. *Langmuir.*, **2004**,20,8301.
[18] S.P. Yuan, J. G. Wang, Y.W. Li, H. Jiao. *J. Phys.Chem. A.*, **2002**,106,8167.
[19] V. Sundara murthy, N.Lingappan, *J. Mol. Catal. A.*, **2000**,160,367-375.
[20] W. Zhou, S. Y. Zang, X.Y. Hao, H. Guo, C. Zhang, Y.Q. Zhang, S.I. Liu. *J. Solid. State. Chem.*, **2006**,179,855.
[21] G.P. Heitmann GD, J.P.M. Niederer,W.F. Holderich. *J. Catal.*, **2000**,194,122.
[22] M.G. Howden, *Zeolites.*, **1985**,5,334.
[23] J. Röseler, W. F. Heitmann, *J. Appl. Catal. A. Gen.*, **1996**,144,319.
[24] M. M. J. Treacy, J. B. Higgins, Collection of simulated XRD powder patterns for zeolites, Elsevier, **2001**.
[25] B. Marler, U. Werthmann, H. Gies, *J. Micropor. Mesopor. Mater.*, **2001**,43,329-340.
[26] H. Gies, J. Rius, *J. Z. kristallogr.*, **1995**,210,475-480.
[27] A. Miecznikowski, J. Hanuza, *Zeolites.*, **1987**,7,249-254.
[28] H. Asaoka, *J. Mol. Catal. A.*, **1991**,68,301-311.
[29] Y. P. Guo, H. J. Wang, Y. J. Guo, L. H. Guo, L. F. Chu, C. X. Guo, *J. Chem. Eng.*, **2011**,166-391.
[30] M.A. Camblor, A. Corma, J.P. Pariente. *J. Chem. Soc., Chem. Commun.*, **1992**,7,360.
[31] A. Thangaraj, R. Kumar, P. Ratnasamy. *Zeolites.*, **1991**,11,573-576.