

## A new method for synthesis of BEA type boro-titanosilicate catalysts: dry cogel impregnation method

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**Abstract :** A combination of two methods of zeolites synthesis has been employed for the preparation of boro-titanosilicate zeotype catalysts with BEA structure. Hence, the large-pore beta zeolite-like materials containing Ti and B atoms have been synthesized following a method based on the wetness impregnation technique, accordingly, amorphous  $\text{SiO}_2\text{-Ti}_2\text{O-B}_2\text{O}_3\text{-TEA}_2\text{O}$  solids have been impregnated with a template solution using tetraethylammonium hydroxide (TEAOH) as a structure-directing agent. However, the amorphous powders have been prepared according to the general procedure of dry gel conversion method. It was observed that the properties of the [Ti]-BEA catalysts samples are found to be strongly dependent on the method used to prepare the amorphous cogel. Furthermore, the crystallization process was carried out under hydrothermal conditions. It was observed that the properties of the [B,Ti]-BEA samples are found to be strongly dependent on the method used to prepare the amorphous cogel. X-ray diffraction patterns show the BEA structure type of the obtained materials and FT-IR spectroscopy analysis of the samples indicates that titanium atoms are located mainly in the tetrahedral framework position and that boron atoms has two kinds of coordination namely tetragonal and trigonal one. It should be noted that the [B,Ti]-Beta samples prepared by the new method (DCI : Dry Cogel Impregnation ) exhibit better crystallinity and more important microporous volume as well as different morphology and crystal size compared to the conventional wetness impregnation method.

*Keywords: isomorphous substitution, Ti-Beta, boro-titanosilicate, sol-gel process, dry gel method, wetness impregnation method.*

### Introduction

The synthesis and characterization of [Ti]-Beta zeotype, having the BEA structure with a three-dimensionally accessible large pore system (6.4 x 7.6 Å), have been studied by many research groups [1]. In this way, Cambor et al. [2,3] have reported the incorporation of titanium into the structure of Beta zeolite. It was found to be more active in the oxidation of bulky molecules such as branched and cyclic alkanes and alkenes using  $\text{H}_2\text{O}_2$  or tert-butyl hydroperoxide (TBHP) as an oxidant than the [Ti]-MFI (TS-1) whose pore diameters are (~5.5 Å), and consequently, it imposes more diffusion restriction [4-6]. Furthermore, the technological parameters for obtaining 213-Epoxy-1-propanol (glycidol) as a result of allyl alcohol epoxidation by 30 wt %  $\text{H}_2\text{O}_2$  over Ti-Beta catalyst have been optimized [7]. This product can be used for the manufacture of surface active agents, which are the components of the cosmetic formulations, shampoo, bath fluids, toothpastes, detergents and disinfectants. Moreover, it finds application in the production of pharmaceuticals [7].

It should be noted that synthesis of zeolites and zeotypes by novel and convenient method is an interesting aspect of research that is of most importance for catalysts preparation. The titanosilicate zeotypes have been prepared not

only by the conventional hydrothermal synthesis, but also by other methods, such as dry gel conversion [8-11], wetness-impregnation (co-gel) [12], seeding [13] and fluorides [14,15] methods. They have been employed, particularly, in an effort to reduce the framework aluminium atoms since a small amount of Al is necessary in the conventional hydrothermal synthesis of [Ti]-BEA using tetraethyl-ammonium hydroxide (TEAOH) as a structure-directing agent (SDA), on the other hand, to reduce silanol defects, which decreases the oxidation activity [16]. Furthermore, for mild oxidation catalytic reactions, the decomposition of hydrogen peroxide was caused by the strong acid sites, so that the yield on [Al, Ti]-BEA decreased compared to [Ti]-BEA. This was observed for [Al, Ti]-MFI and [Ti]-MFI [17, 18]. Hence the presence of Al and large concentration of internal and external silanol groups confer a rather hydrophilic character on Ti-Beta in contrast to the organophilic characteristics of TS-1. Moreover, the incorporation of boron into the [Ti]-Beta framework, generating a weak acid sites, is expected to hardly modify the oxidation properties of the catalyst [19]. This fact has already been observed in case of [B,Ti]-MFI synthesized first by Trong On et al.[20]. We have prepared samples of [B,Ti]-BEA and tried to investigate the synthesis parameters using two

different procedures : First, the wetness-impregnation method, which was simpler and required a lower reaction volume and proceeded with shorter synthesis time compared to the hydrothermal crystallization of a liquid gel [22-24]. It has been developed first by Padovan et al. [21] and used for synthesis of titanosilicates [Ti]-MFI (TS-1). In this work, however, the synthesis of materials has been carried out by a new method. It is a combination of the wetness impregnation method according to the procedure reported by Uguina et al. [23,24] and the general procedure of preparing the solid powders in the dry gel conversion method according to Bandyopadhyay et al. [27]. We have tried to explore the physical properties of the samples namely, crystallinity, porosity and crystals' size and morphology under the synthesis conditions of both methods: the wetness impregnation method (WI) and the dry cogel impregnation method (DCI), since they are strongly dependent on the preparation method.

Thus, the aim of the present work is to apply the novel technique to BEA type borotitanosilicates synthesis and to examine the mutual effect of both elements on the crystallization of [B, Ti]-BEA zeotypes and their final properties.

## 1. Experimental

### 1.1. Materials

The raw materials used in our syntheses were as follows: boric acid  $H_3BO_3$  (Labosi 99.5%), aluminium nitrate ( $N_3O_9Al$ ,  $9H_2O$ , Prolabo), tetraethylorthosilicate (TEOS)  $C_8H_{20}O_4Si$  (Aldrich 99%), tetra-n-ethylammonium hydroxide  $C_8H_{21}NO$  (Aldrich 20%), tetra-n-butylorthotitanate TBOT ( $C_{16}H_{36}O_4Ti$ ) (Merck), isopropanol ( $C_3H_8O$ ) (Acros Organic 99.5%).

### 1.2. Synthesis of materials

The synthesis of [B,Ti]-BEA was performed following the general wetness impregnation technique described elsewhere [22,23] and it involves two steps:

- (i) Preparation of the cogel, which is an amorphous  $SiO_2$ - $TiO_2$ - $B_2O_3$ -(TEA) $_2$ O solid, is carried out by the sol-gel method which leads to the formation of Si-O-Ti bonds prior to crystallization process, so that the Ti atoms are stabilized in a polymeric  $SiO_2$  network preventing the  $TiO_2$  precipitation.
- (ii) The crystallization of the amorphous impregnated xerogel was carried out via the conventional hydrothermal process after having impregnated the xerogel with the template solution of TEA<sup>+</sup> cations. Thereafter, the solid re-orders its polymeric network into

BEA structure in a solid-solid transformation as it was reported by Serrano et al. [25].

Thereby, the crystallization of the BEA type boro-titanosilicate takes place in a supersaturated system obtained by incipient wetness impregnation of the dry cogel with the template solution according to the procedure Uguina et al. [22]

#### 1.2.1. Synthesis I : Crystallization of [B,Ti]-Beta by the wetness impregnation method

In this method described elsewhere [21,23, 24], the co-gels were prepared by two-step sol-gel process as mentioned above. In the first step, TEOS is hydrolyzed at room temperature with a 0.05 M HCL aqueous solution for 2 h. Then, a solution of boric acid  $H_3BO_3$  is added. The obtained mixture is then cooled to 0 °C by means of an ice bath, and solution of TBOT dissolved in isopropyl alcohol is added dropwise. The clear solution obtained is stirred for 30min at 0 °C. In the second step, the dropwise addition of 20% TEAOH solution allowed to reach the gel point and eventually obtaining the co-gel. After gelation, the solids are dried at 110 °C overnight and ground to give a powdered material.

#### 1.2.2. Synthesis II: Crystallization of [B,Ti]-Beta by the dry cogel impregnation method

In this new method, we call the dry cogel impregnation method, we followed the former steps, except that in order to obtain the xerogels we have adopted the technique used in the general dry gel method (DGC) which has been classified by Matsukata et al. [26] as two separate methods: the vapour-phase transport method in which the dry gel is crystallized in the vapor of steam and volatile template and the steam-assisted method (SAC) used when the template is non-volatile, so that the dry gel crystallized in presence of vapor of steam. In both methods, the drying process was carried out according to the general procedure reported by Banyopadhyay et al. [27]. The gel was dried at 80-90 °C over an oil bath with continuous stirring allowing evaporation of water. When the gel becomes thick and viscous, it was homogenized by hand using a Teflon rod until it dried. An amorphous solid was formed and was ground into a fine powder.

For both methods, the synthesis was carried out by wetness impregnation of the dried  $SiO_2$ - $TiO_2$ - $B_2O_3$ -(TEA) $_2$ O co-gels with a 20% TEAOH aqueous solution. The mixture

is transferred into PTFE-lined autoclaves and heated hydrothermally at 150 °C for 7 days under autogenous pressure. The post-synthesis treatment of these two reference samples is as follows: the crystalline products were washed several times with distilled water, dried overnight at 110 °C and calcined at 550 °C for 6 hours. The molar compositions of gel are as follows: 0.04 B<sub>2</sub>O<sub>3</sub> : x TiO<sub>2</sub> : 1 SiO<sub>2</sub> : 0.14 (TEA)<sub>2</sub>O : (x = 0.0067, 0.0123, 0.0303 and 0.1)

First, we optimized the SiO<sub>2</sub>/B<sub>2</sub>O<sub>3</sub> ratio while the temperature and the period of crystallization are constant. We tried to study the influence of the titanium quantity upon the properties of the obtained materials. We notice that crystallization of BEA structure has failed in the absence of boron in the reaction mixture.

### 2.3 Characterization of samples

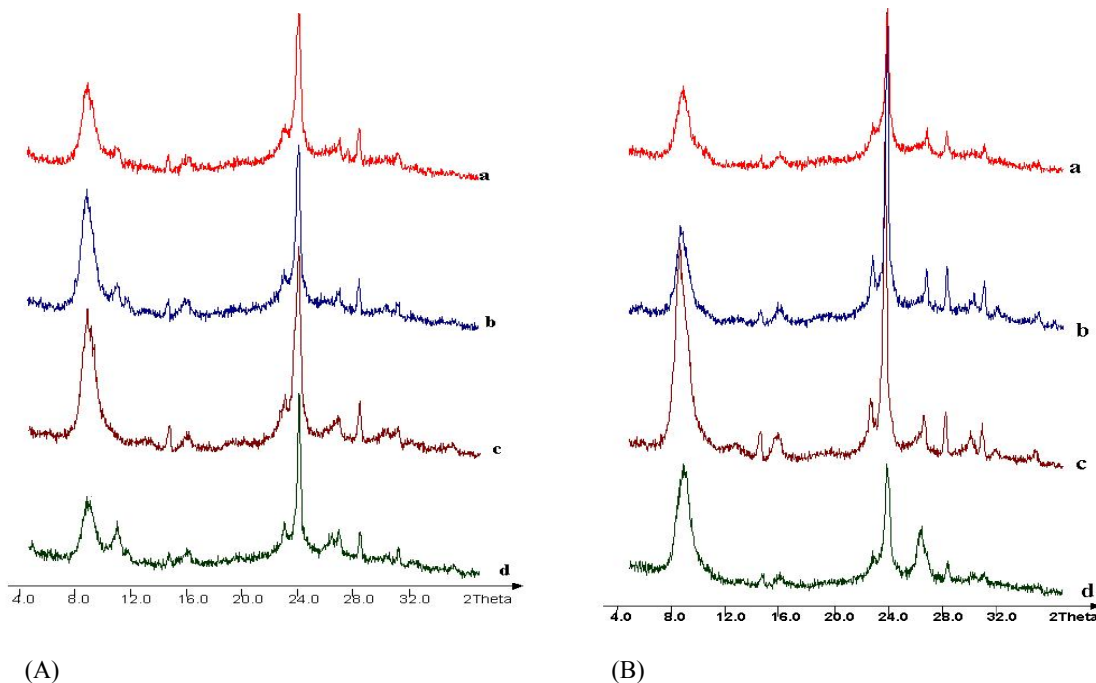
The phase purity and crystallinity of the as-synthesized and calcined samples were determined by powder X-ray diffraction (XRD). X-ray powder diffraction (XRD) patterns were collected on a Philips PW 1830 diffractometer (CuK $\alpha$ :  $\lambda$  = 1.5406 Å, 40 kV, 20

mA). The crystal size and morphology of the samples were monitored by scanning electron microscopy (SEM) using Philips XL 30 ESEM. KBr pellet technique was used to perform FT-IR spectroscopy of the samples using a Genesis ATI Mattson FT-IR spectrometer; the samples were ground with KBr and pressed into thin wafers. Nitrogen adsorption isotherms were collected at 77 K on Micrometrics Gemini II 2370 area analyser.

## 2. Results and discussion

### 3.1 X-Ray diffraction

Identification of the phases present in the solids was done using X-ray powder diffraction. In case of zeolite Beta, the  $d_{(304)}$  interplanar distance of the BEA structure was calculated using the diffraction peak at  $2\theta = 22.85^\circ$ . For both methods I and II, the samples synthesized employing lower titanium content presented higher crystallinity the reduction in crystallinity might be attributed to a possible higher radiation absorption by titanium present in the solid, causing a decrease in intensity of the diffraction peaks[28].



**Figure 1.** Powder X-ray diffraction patterns of calcined borotitanosilicate synthesized by (A) method I and (B) Method II with different values of  $x = \text{TiO}_2/\text{SiO}_2$  : (a) 0.0067, (b) 0.0123, (c) 0.0303, (d) 0.1

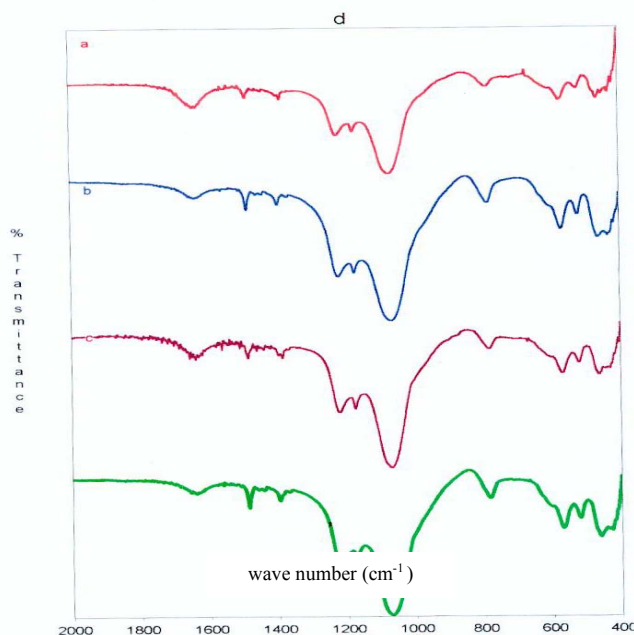
Although, the fact that crystallinity did not increase after 36 h, the solid yield carried on increasing for

higher crystallization times, also the titanium content in the solid continued increasing since there

was a decrease in the  $d_{(304)}$  interplanar distance in agreement with other works [28]. The X-ray diffraction patterns of the calcined WI-[B,Ti]-BEA and DCI-[B,Ti]-BEA samples with different titanium contents are shown in figures . The data presented in figure 1 show that the materials prepared by both methods were highly crystalline. The XRD patterns in this work were typical of the BEA topology. The crystallinity of the samples is evaluated by measuring the surface area in the range  $2\theta \approx 7.70^\circ$  and  $2\theta \approx 22.85^\circ$ . All the samples showed the characteristic peaks of BEA structure see figure 1 . When  $x = \text{TiO}_2/\text{SiO}_2 \geq 0.03$ , the crystallinity is the best for WI-samples and DCI-samples. Also, when the molar ration of  $x \geq 0.10$ , then the cristallinity is found to be reduced by ca. 50%.

Figures 2 and 3 depict the FTIR spectra in the 2000-400  $\text{cm}^{-1}$  range of the lattice vibrations of the as-synthesized WI-[B,Ti]-Beta ( $\text{Si}/\text{Ti}=33$ ) and as-synthesized and calcined WI- and DCI-[B,Ti]-Beta samples. It can be seen that the spectral features of as-synthesized samples are different from those of the calcined ones. All the calcined samples [B,Ti]-Beta show a neat band at  $\sim 951 \text{ cm}^{-1}$  that might be attributed to an asymmetric stretching mode of  $[\text{SiO}_4]$  unit bonded to a  $\text{Ti}^{4+}$  ion ( $\text{O}_3\text{SiOTi}$ ) in tetrahedral positions, to the same mode of vibration a band at  $960 \text{ cm}^{-1}$  is observed in [B,Ti]-MFI by Shibata et al. [29] and in [Ti]-MFI prepared in fluoride medium by Grieneisen et al. [30] and has been used as the fingerprint to

### 3.2 Framework FTIR spectra



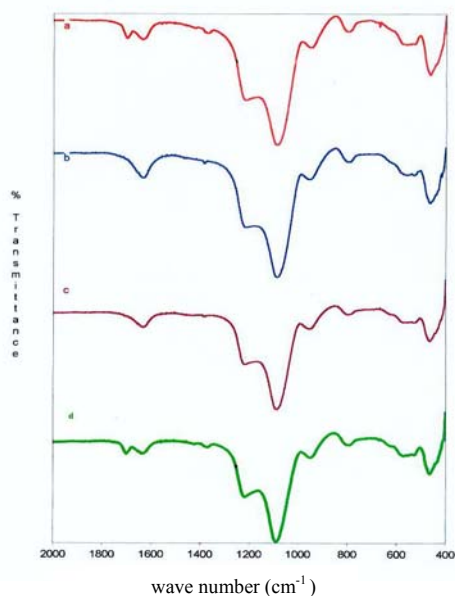
**Figure 2.** FTIR spectra of as-synthesized boro-titanosilicate (method I) with different values of  $x = \text{TiO}_2/\text{SiO}_2$  : (a) 0.0067, (b) 0.0123, (c) 0.0303, (d) 0.1

characterize the presence of framework Ti in the MFI structure and to confirm the presence of the Ti framework [31]. Also, Jahn et al. [28] has observed a band in the  $955\text{-}960 \text{ cm}^{-1}$  region in the IR spectra the calcined [Al, Ti]-BEA.

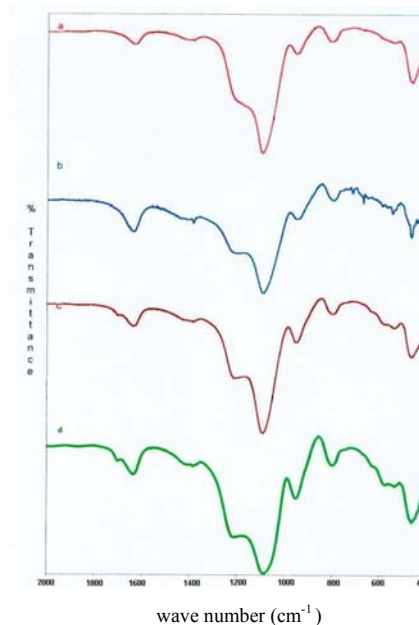
A characteristic band at  $\sim 900 \text{ cm}^{-1}$  due to the framework tetrahedral  $\text{B}(\text{OSi})_4$  entities was observed in each of the as-synthesised samples, and could be assigned to the stretching of the Si-O-B bond [32,33].

In the spectra of the calcined samples, the band might be shifted to  $\sim 940 \text{ cm}^{-1}$ , it was reported that the shift is so important in [B]-BEA [27], the shift might have resulted from the differences in the water coordination environment of the framework boron atom [33] and thus it overlapped with the band at  $950 \text{ cm}^{-1}$  but it might disappeared after calcinations, and hence the tetrahedral coordination of boron

became trigonal. It was reported that direct air calcination of boron BEA leads to partial loss of tetrahedral boron, formation of trigonal boron and loss of crystallinity to some extent [27]. But the recovery of tetrahedral boron after calcination seemed difficult in [B]-BEA even in a careful stepwise calcination of the samples in the presence of nitrogen. [27].



(A)



(B)

**Figure 3.** FTIR spectra of boro-titanosilicate synthesized by different methods (A) Synthesis I (WI) (B) Synthesis II (DCI) with different values of  $x = \text{TiO}_2/\text{SiO}_2$ : (a) 0.0067, (b) 0.0123, (c) 0.0303, (d) 0.1

It is noticeable that a band at  $\sim 1400 \text{ cm}^{-1}$  appeared for all the samples the as-synthesized and calcined [B,Ti]-BEA samples, which indicates the of formation of trigonal boron, however, the same band appeared only after calcination in [B]-BEA sample as noticed by R. Bandyopadhyay et al.[27,34] This may suggest that the titanium incorporation affect the tetragonal coordination of boron atoms and stabilizes the trigonal boron. Also, it should be noted that in the as-synthesized samples, the IR band at  $1172.5 \text{ cm}^{-1}$  could assigned to the

presence of tetraethylammonium ( $\text{Si-O-TEA}^+$ ).

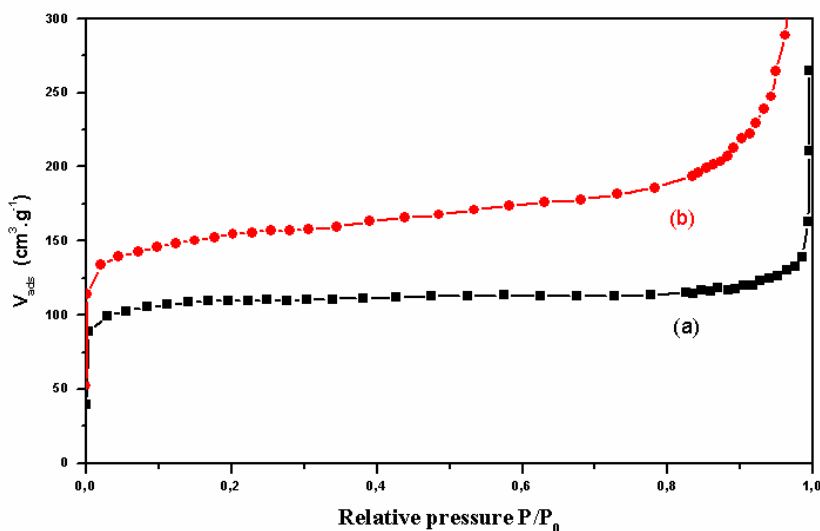
### 3.2 $\text{N}_2$ adsorption at 77 K

In order to explore the textural properties of these materials,  $\text{N}_2$  adsorption isotherms at 77K have been measured over two samples prepared by two methods namely, wetness impregnation and dry cogel impregnation methods. The results obtained are depicted in figure 4. It shows the typical isotherm of type I

characterizing the microporous structures. The isotherm corresponding to the first sample indicates clearly

the presence of micropores with pore volume of 0.232 cc/g as estimated from the t-plot analysis of the isotherm. The highly crystalline samples show a high N<sub>2</sub> adsorption at P/P<sub>0</sub> lower than 0.1 in agreement with the microporous character of these samples. The adsorption observed at P/P<sub>0</sub> above 0.9 is attributed to the presence of interparticle voids [25]. The textural data draw attention to the

fact that the DCI-[B,Ti]Beta sample shows higher microporosity (0.23 cc/g) than that of WI-[B,Ti]-Beta sample phase (0.162 cc/g) which is basically due to the method of preparation of the xerogels. Also, it is noticeable that they have very different external surfaces 159 and 104 m<sup>2</sup>/g for method II and method I respectively which might indicate that the crystal size obtained by method II is different from that obtained by method I.



**Figure 4.** Nitrogen adsorption on [B,Ti]-BEA synthesized by (a) Method I (b) Method II.

**Table 1.**

Textural data for [Ti, B]-BEA with TiO<sub>2</sub>/SiO<sub>2</sub>=0.0303 prepared by method I and method II at 150 °C.

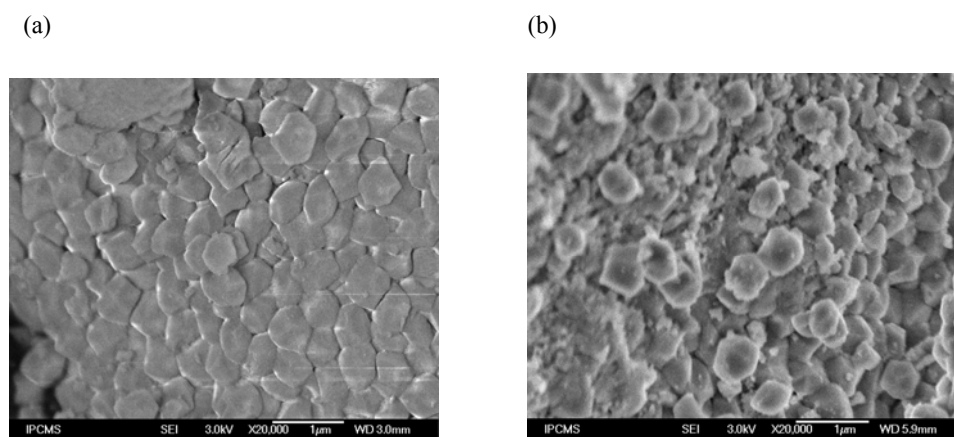
	$\bar{\phi}$ (Å)	$S_{BET}$ (m <sup>2</sup> g <sup>-1</sup> )	$V_{micro}$ (cm <sup>3</sup> g <sup>-1</sup> )	$S_{micro}$ (m <sup>2</sup> g <sup>-1</sup> )	$S_{ext}$ (m <sup>2</sup> g <sup>-1</sup> )
<b>c</b> Method I	6.2	340	0.162	189	159
<b>c</b> Method II	7.2	482	0.232	375	104

**3.4 Scanning electron microscopy**  
SEM micrographs of the as-synthesized [B,Ti]-BEA are given in figure 5

below . It is clear that the samples have high crystallinity and purity. No amorphous phase and other crystalline impurities have been

found. However, the morphology and crystal size of WI-samples are obviously different from those of DCI-samples. It should be noted that the morphology of the [B]-BEA crystals obtained by Bandyopadhyay et al. [27] using DGC method was cuboid. The WI-[B,Ti]-Beta presents crystals with shapes of truncated spheres, see figure 5 (b) whereas figure 5 (a) shows micrograph of DCI-[B,Ti]-BEA, where one can observe that the particles present an oval pattern with forms of films and the

crystalline phase consists of particles that exhibit a regular shape compared to the WI-sample. Hence, the methods used affect the particle diameter and the morphology of crystals of the crystalline phase. The [B Ti]-Beta materials synthesized using method II presents an average crystal size around 0.5  $\mu\text{m}$ , whereas those synthesized by method I presents an average crystal size around 0.3-0.5  $\mu\text{m}$  with less regularity and this may be due to the fact of the slower crystallization kinetics.



**Figure 5.** SEM micrographs of calcined [B,Ti]-BEA (sample c) synthesized by (a) method II (DCI) and (b) method I (WI)

### 3. Conclusion

A new synthesis method, namely dry cogel impregnation technique, has been successfully applied for the synthesis of crystalline borotitanosilicates. The [B,Ti]-Beta has been synthesized by wetness impregnation of amorphous  $\text{SiO}_2$ - $\text{TiO}_2$ - $\text{B}_2\text{O}_3$ -(TEA) $_2$ O xerogels with TEAOH solutions followed by crystallization under autogenous pressure. The xerogels have been prepared by drying the cogel formed by a so-gel process, according to the dry gel method. The samples obtained were of high crystallinity and purity. Compared to the original method, the dry cogel impregnation method conferred higher crystallinity and higher specific area and higher microporous volume as well. FTIR analysis of the samples revealed that titanium atoms are supposed located in the tetrahedral framework position and that boron has been incorporated in the tetrahedral sites in the as-synthesized samples but the trigonal boron does exist in all

samples. The [B,Ti]-Beta prepared by both methods clearly presents different crystal size and morphology .

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