

SYNTHESIS AND CHARACTERIZATION OF HIGH SILICA ZEOLITES FROM COAL FLY ASH (CFA): TWO CASES OF ZEOLITE SYNTHESSES FROM THE SAME WASTE MATERIAL.

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Abstract— Zeolites H/ β and H/ZSM-11 were synthesized by the crystallization hydrothermal method (CH), using coal fly ash (CFA). Tetraethylammonium hydroxide (TEAOH), tetrapropylammonium bromide (TPAB) and tetrapropylammonium hydroxide (TPAOH) were used as structure-directing agents (SDA). The optimum conditions used in the experimentation were 140 °C and NaOH/CFA ratio=1.2 (wt/wt), during the crystallization hydrothermal method (CH), and microwave-assisted heating (MH) was used in some experiments. The structure and crystallinity of the synthesized materials were analyzed by X-ray diffraction, where the formation of the β and ZSM-11 zeolites was confirmed. The morphology of the obtained zeolites was observed by the scanning electron microscope technique. It was observed spheroidal particles for the ZSM-11 zeolite and ellipsoidal particles for the β zeolite, respectively. Both zeolites were ion exchange treated, in order to obtain the protonated form. Finally, the thermal stability and the loss of weight of the modified β zeolite were determined by using the termogravimetric and differential thermal analysis techniques. The modified zeolites were stable in the range of most gas chemical reactions (300-500 °C).

Keywords — Zeolite H/ β ; zeolite H/ZSM-11; crystallization hydrothermal method; coal fly ash, structure-directing agents.

I. INTRODUCTION

The amount of coal fly ash (CFA) generated by coal-based thermal power plants has been increased at an alarming rate throughout the world. The disposal of such a big quantity of fly ash has become an important topic. Thus, several new approaches have been adopted to utilize fly ashes not only to reduce the cost of the disposal but also to minimize environmental impact. Those elements other than calcium detected in the fly ashes exhibit a broad range of toxic effects to humans, terrestrial and aquatic life and plants. A number of these elements have the potential to bioaccumulate, including

arsenic, chromium, lead, mercury, nickel and zinc (Bridgen and Santillo, 2002). Particulate pollution is implicated in the worsening of respiratory illnesses such as asthma, and in the increasing of premature mortality from respiratory and heart diseases (Bridgen and Santillo, 2002).

Recently, intensive efforts were made to promote the recycling of fly ash through zeolitization. Zeolites are microporous crystalline aluminosilicates with three-dimensional framework structures. Due to the high thermal and good dimensional stability, they have attracted a particular attention as catalysts in acid-mediated reactions (Maxwell and Stork, 1991; Corma, 1995). By virtue of their compositional and structural peculiarities, zeolites also have many other applications in various ion-exchange, adsorption, separation, and purification processes (Breck, 1974).

Several groups (Meshram *et al.*, 2000; Rayalu *et al.*, 2001; Miyake *et al.*, 2002; Querol *et al.*, 2002; Park *et al.*, 2000; Shigemoto *et al.*, 1995; Singer and Bergaut, 1995) around the world have studied the conversion of fly ash into various types of zeolites such as Y, X, A, P, F, KM, etc. However, there are no reports on the synthesis of commercially important high silica zeolite with three-dimensional 12-membered ring channels using fly ash as a source material. Using conventional source materials, high silica β (*BEA) zeolite, with a three-dimensional 12-membered ring channels, was synthesized for the first time in early 1967 (Wadlinger *et al.*, 1967), and its structure was discerned late in 1988 (Newsam *et al.*, 1988). Crystallization of zeolite β (*BEA) draws much attention because of its unique characteristics, in particular, its acidity and potential for acid catalysis (Kiricsi *et al.*, 1994; Jones *et al.*, 1999; Corma *et al.*, 2002; Prasad Rao *et al.*, 1998; Matsukata *et al.*, 2002).

Several factors have influence on the zeolitic formation when fly ash is used as a source of Al₂O₃ and SiO₂; Höller and Wirsching (1985), investigated zeolite formation after carrying out an alkaline activation of fly ash as a function of temperature, solution composition,

and concentration in open and closed systems for long activation periods (8-40 days). A fusion with sodium hydroxide prior to hydrothermal reaction has been applied by Shigemoto *et al.* (1992) to improve the conversion of fly ash into Na-X zeolites. Recent studies (Shin *et al.*, 1995; Lin and Hsi, 1995; Singer and Berggaut, 1995; Amrhein *et al.*, 1996) have obtained high Na and K-zeolite synthesis efficiencies after carrying out an alkaline activation of fly ash in closed systems during relatively short activation periods (8-100 h).

The present research is concerned with the synthesis of zeolite H/ β (H/BEA) and H/ZSM-11 (H/MEL) from coal fly ash (CFA) and its characterization using various techniques, and also deals with the reuse of waste material as coal fly ash (CFA), converting it in active H/ β and H/ZSM-11 zeolites, employing smaller crystallization times than those reported in the literature (Kasture *et al.*, 2005), with potential use as catalysts for petrochemical processes.

II. METHODS

A. Materials

The coal fly ash (CFA) was obtained from the "Lic. José López Portillo" Thermal Power Station (JLPTPS) located in Piedras Negras, Coahuila, México, and it was collected from the electrostatic precipitators.

The reagents used in the experiments were: LUDOX[®] TM-40 colloidal silica, SiO₂ (40 wt. %, suspension in water), sodium hydroxide, 98 % purity, pellets (anhydrous), tetraethylammonium hydroxide (TEAOH) (20 wt. %, solution in water), tetrapropylammonium bromide (TPAB), tetrapropylammonium hydroxide (TPAOH) (1.0 M) and ammonium chloride (NH₄Cl). All of these reagents were supplied by Sigma-Aldrich and used as received.

B. Synthesis

Coal fly ash samples without prior treatment were used to obtain zeolites. The activation of the coal fly ash (CFA) was performed through the fusion method using NaOH as activator (Shigemoto *et al.*, 1995). The zeolite syntheses were studied as a function of a reaction time (0-95 h), maintaining the NaOH/CFA ratio=1.2 (wt/wt) and using tetraethyl ammonium hydroxide (TEAOH) as structure-directing agent (SDA) to obtain the zeolite β (*BEA). The crystallization temperature was maintained at 140°C during the hydrothermal crystallization period, in a high pressure stainless steel reactor trademark

PARR[®] Model 4521 of 1 lt in volume. Also, it was possible to obtain the zeolite ZSM-11 (MEL), using the structure-directing agent, TPAB. Most of the optimum experimental conditions used, were selected based on previous works carried out at our laboratory (Medina, 2009; De León, 2009). Table 1 shows the optimum experimental conditions used for the zeolite synthesis.

The amount of coal fly ash used in the experiments was 9.0 g and the amount of NaOH in the mixture was 10.8 g. The mixture was heated at 600°C for 1 h. For the case of synthesizing the β zeolite, homogeneous mixtures with molar composition of 6.5Na₂O:6.0(TEA)₂O:30SiO₂: Al₂O₃:840H₂O, were prepared by using appropriate quantities of the fused product, and tetraethylammonium hydroxide (TEAOH, 20 wt. %, solution in water).

For the case of the ZSM-11 synthesis, it was used the molar composition of 6.5Na₂O:6.0(TPAB): 30SiO₂: Al₂O₃: 840H₂O, and tetrapropylammonium bromide (TPAB) as SDA, in this case, it was not necessary to adjust the initial pH to 12. When the tetrapropylammonium hydroxide (TPAOH) was used as structure-directing agent, the product was an amorphous phase. For all cases, colloidal silica (40 wt. %, suspension in water) and deionized (DI) water were used. The quantity of fly ash contributes to the 100 % Al₂O₃ (1 mol) and 14 % SiO₂ (4.2 moles) of the total moles required for the synthesis of high silica zeolite (β and ZSM-11) materials (with a SiO₂/Al₂O₃=30 ratio), therefore, it was added 25.8 moles of colloidal silica to complete 100 % of total SiO₂ (30 moles). After adjusting the pH to 12 \pm 0.2 with concentrated HCl, the reaction mixture was subjected to crystallization at 140 °C. The time of crystallization was varied from 4-95 h. The solid products were recovered by filtration, washed thoroughly with deionized (DI) water, and then dried at 100 °C. Both as-synthesized β and ZSM-11 samples were calcined at 550 °C for 4 h and then subjected to ion exchange using 1.0 M ammonium chloride solution (20 ml/g of solid) at 90°C during 2 h, this process was repeated twice. Salt excess was washed by deionized water and then dried at 100 °C overnight. The dried samples were calcined at 550 °C for 3 h to obtain a protonated form (designated as H/ β and H/ZSM-11).

C. Characterization

The products were identified by the X-ray powder dif

Table. 1. Experiments carried out in order to synthesize ZSM-11 and β zeolites.

Exp.	SDA Type	Time (h)	Temperature (°C)	Source of silica and alumina	Zeolite
1	TPAB	45	140	Fly ash + silica	P
2	TPAOH	41	140	Fly ash + colloidal silica	Amorphous
3	TPAOH	4 (†)	140	Fly ash + colloidal silica	Amorphous
4	TPAB	4 (†)	140	Fly ash + colloidal silica	Amorphous
5	TEAOH	5 (†)	140	Fly ash + colloidal silica	Amorphous
6	TPAB	40	140	Fly ash + colloidal silica	ZSM-11
7 (‡)	TEAOH	20	135	Pure reagents	Beta-V
8	TEAOH	95	140	Fly ash + colloidal silica	Beta-1
9	TEAOH	48	140	Fly ash + colloidal silica	Beta-2

(†) Microwave-assisted heating.

(‡) Formulation from literature (Robson and Lillerud, 2001).

Table 2. Chemical composition of the coal fly ash utilized.

Components	Composition (wt. %)
SiO ₂	56.70
Al ₂ O ₃	23.74
Fe ₂ O ₃	5.98
CaO	3.90
Na ₂ O	0.41
TiO ₂	1.09
K ₂ O	1.49
MnO	0.02
MgO	0.74
SO ₃	0.66
ZrO ₂	0.05
P ₂ O ₅	0.05
SrO	0.05
ZnO	0.02
LOI (loss on ignition)	5.06

fraction (XRD) recorded on an Xpert Phillips PW340 diffractometer using Cu-K α ($\lambda=1.5405$ Å) radiation. The crystallinity of the β samples was studied with reference to a highly crystalline β sample, which was considered to have 100 % crystallinity. The relative crystallinity of the β samples was determined from the sum of the areas of the peaks from $2\theta = 20^\circ$ and 24° , according to the method reported by Selvam *et al.* (2007). The morphology of the crystalline products was studied using a Phillips XL 30 scanning electron microscope (SEM) with conventional sample preparation and image techniques. Thermogravimetric and differential thermal analyses were performed on a simultaneous TG-DTA (Pyris Diamond, Perkin Elmer). The sample was heated up at a rate of $10^\circ\text{C}/\text{min}$ from room temperature to 900°C under nitrogen atmosphere. Element chemical analysis was done by means of the X Ray Fluorescence (XRF) technique, using a Thermo Electron Corporation Spectrophotometer Model S4.

III. RESULTS AND DISCUSSION

Preliminary experiments were carried out in order to optimize the conditions of the experimentation. In experiment 1, it was synthesized a zeolite type P, this product contains low silica and is not adequate for our objective. From experiments 2 through 5, the reaction product was an amorphous phase. Microwave-assisted heating did not enhance the formation of a crystalline phase. Experiment 6 led to the formation of ZSM-11 zeolite. In experiment 7, it was carried out a verified β formulation (Robson and Lillerud, 2001) in order to obtain a reference sample (Beta-V). In experiments 8 and 9, there were synthesized the β zeolites (Beta-1 and Beta-2), using fly ash as raw material.

A. Element Chemical Analysis

The chemical composition of the coal fly ash was determined by means of element chemical analysis by using the X Ray Fluorescence (XRF) technique, and it is shown in Table 2. As can be seen from Tab. 2, the fly ash sample can be classified as “Class F” type with SiO₂, Al₂O₃ and Fe₂O₃, as the major constituents and content of CaO less than 10 %.

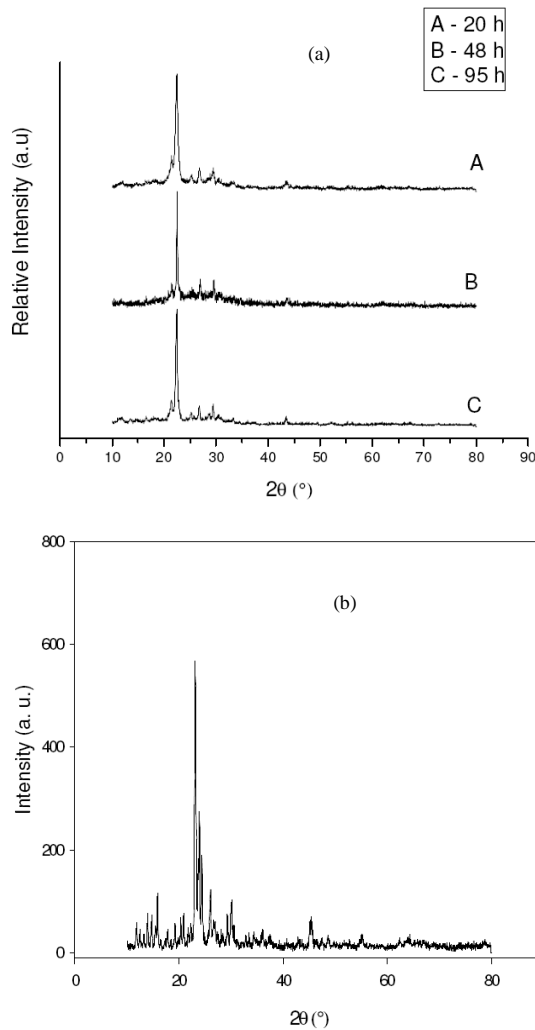


Fig. 1. XRD powder patterns of a verified β (Beta-V) (A) and two β (Beta-1 and Beta-2) (B, C) zeolites (TEAOH/SiO₂=0.2): a) 20 h (A), 48 h (B), 95 h (C); and ZSM-11 zeolite (TPAB/SiO₂=0.2): b) 40 h.

B. X Ray Diffraction (XRD) Analysis

The XRD powder patterns obtained for the verified β (Beta-V) (A) and two β (Beta-1 and Beta-2) (B, C) (ICCD 49-0673) zeolites (SiO₂/Al₂O₃=30) as-synthesized are shown in Fig. 1(a). The XRD pattern obtained for the ZSM-11 (ICCD 73-1138) zeolites (SiO₂/Al₂O₃=30) as-synthesized is shown in Fig. 1(b).

The XRD powder patterns of β zeolites were compared with that of the standard zeolite *BEA as reference sample (verified β), prepared with pure reagents. The diffraction peaks are coincident with those corresponding to the *BEA zeolitic structure. These peaks are well defined, indicating that the sample consists of β zeolite with a high crystallinity (100 %). A well-crystallized β phase was obtained after 95 h, designated as as-synthesized Na/ β (β sodium form). The relative crystallinity of the Na/ β samples at 95 and 48 h of crystallization time, was 92 % and 32 %, respectively. The

crystallinity was determined from the sum of the areas of the peaks between $2\theta = 20-24^\circ$ by using the Sietronics XRD Trace Processing Program, version 3.0. The crystallinity of the ZSM-11 zeolite was not determined because the lack of a reference sample. The characteristic peaks for beta zeolite appear at 7° , 22° , 28° and 42.5° , meanwhile for ZSM-11 zeolite appear at 15° , 23° , 24° , 30° and 45° on 2θ scale.

Also, the XRD powder patterns for protonated H/ β and H/ZSM-11 zeolites were obtained as is shown in Figs. 2(a) and 2(b). No changes were observed in the crystallinity of the structure due to the post-synthesis treatments, for both zeolites, this means that such treatments do not affect neither the former structure of the H/ β nor the H/ZSM-11 zeolite.

C. Scanning Electron Microscopy (SEM) Micrographs.

The morphologies of the ZSM-11 zeolite, before and after ion exchange are shown in Figs. 3(a) and 3(b), respectively. In both cases the particles have a spheroidal form. The morphologies of the β zeolite, before and after ion exchange are shown in Figs. 3(c) and 3(d), respectively. In both cases the particles aggregated with irregular form. Besides, in the protonated form, Figs. 3(b) and 3(d), both zeolites behave as catalyst in petrochemical reactions, improving the conversion of the reactants.

The ion exchange percentage (% I. E) was obtained by means of Eq. (1), using the Na^+ concentrations (% Na_0 and % Na_1 , respectively) evaluated with element chemical analysis.

$$\% \text{I.E.} = \frac{(\% \text{Na}_0 - \% \text{Na}_1)}{\% \text{Na}_0} \times 100, \quad (1)$$

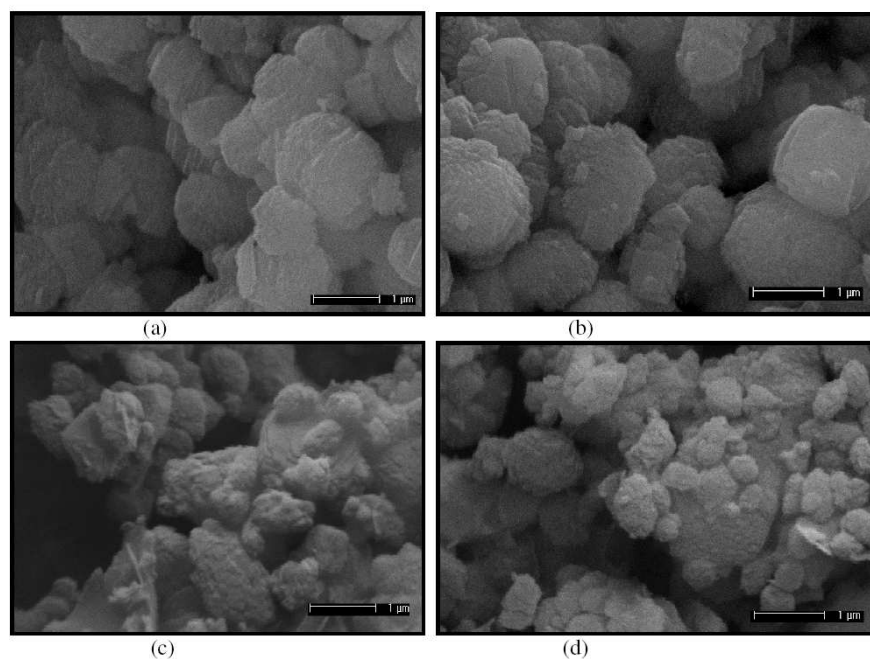


Fig. 3. SEM images (20000x) of the ZSM-11 and β zeolites: a) Na/ZSM-11, b) H/ZSM-11, (c) Na/ β and (d) H/ β , respectively.

The ion exchange percentage in H/ZSM-11 zeolite was 62 %, and in the case of H/ β zeolite, it was 94 %. As reference in Fig. 4 is shown a micrograph of the raw material utilized known as coal fly ash (CFA).

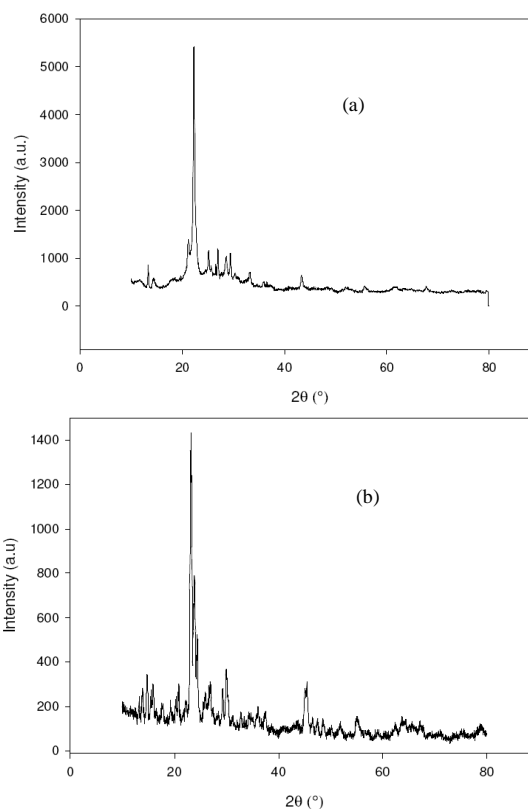


Fig. 2. XRD powder patterns for the β and ZSM-11 zeolites in protonated form: a) H/ β and b) H/ZSM-11.

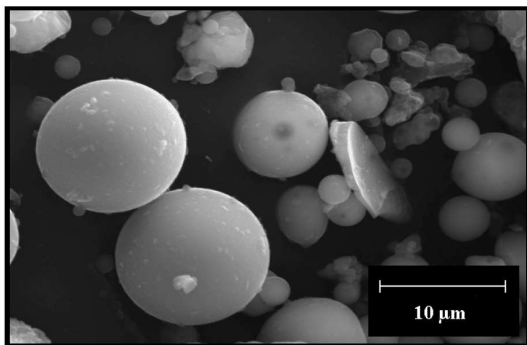


Fig. 4. SEM image of the coal fly ash (CFA) utilized as raw material.

D. Termogravimetric and Differential Thermal Analysis (TG-DTA)

The thermal stability of the H/ β zeolite was determined by using the differential thermal analysis (DTA). This zeolite was thermally stable up to 600 °C. Also, it can be observed that the largest loss of weight occurred between 30 °C and 100 °C, because of the loss of the absorbed water, beyond 100 °C until 400 °C, the structure-directing agent (TEAOH) is removed.

These observations can be visualized in Figs. 5(a) and 5(b), respectively. The H/ β zeolites can operate as catalysts because they remain thermally stable within the range of most gas chemical reactions from 300 °C up to 500 °C, since no structural changes were observed.

IV. CONCLUSIONS

It was possible to obtain a highly crystalline β (*BEA) zeolite from coal fly ash (CFA) by means of an economical process under hydrothermal conditions at 140°C and a maximum reaction time of 95 h, with a thermal stability at least up to 600°C. This was achieved with the presence of a template or structure-directing agent (SDA), using coal fly ash as raw material. The fly ash-based zeolite H/ β can operate as a potential catalyst for industrially important reactions as that of commercial zeolite *BEA. Both structure-directing agents, TEAOH and TPAB, were the key to obtain the crystallography of the β (*BEA) and ZSM-11 (MEL) zeolites, respectively.

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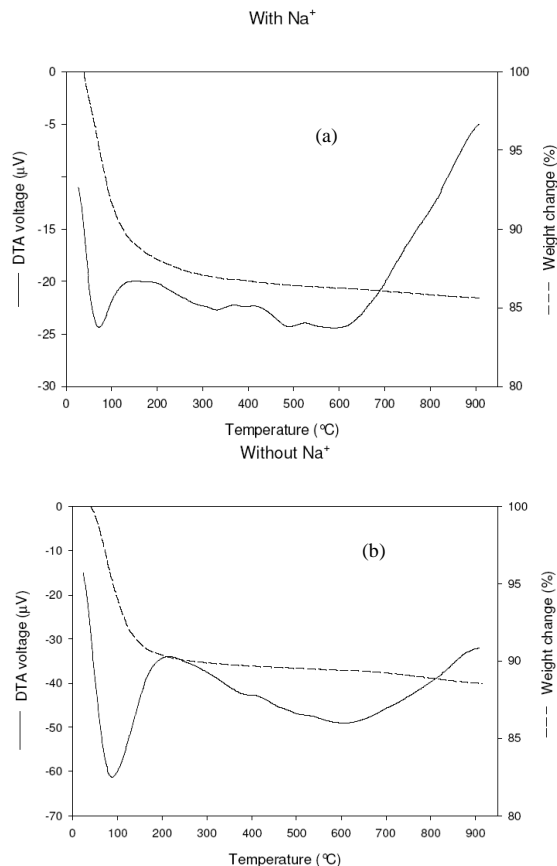


Fig. 5. TG-DTA graphs for the β zeolite: a) Na/ β and b) H/ β forms.

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