

Effect of modification of zeolite A using sodium carboxymethylcellulose (CMC)

P. Padhi^{1,*}, S. K. Rout², D. Panda¹

¹Research and Development Center, Hi-Tech Medical College and Hospital, India

²Department of Chemistry Konark Institute of Science and Technology, India

Received November 3, 2013; Revised May 19, 2014

Structural modification of zeolite A was carried out using sodium carboxymethylcellulose (CMC). The product was characterized by XRD, FTIR, FESEM, EDAS and HRTEM. As a result of the modification reaction carried out at a temperature of 80°C, the particle size of zeolite A was reduced to 668.1 nm. The particle shape changed as a result of calcination after sonication.

Keywords: Zeolite A, adsorbent, sodium carboxymethylcellulose (CMC), ultrasonication, crystal and centrifugation.

INTRODUCTION

Structurally, zeolite is a framework of aluminosilicate which is based on infinitely extending three-dimensional AlO_4 and SiO_4 tetrahedra linked to each other sharing the oxygen [1-2]. Zeolite is a crystalline hydrated aluminosilicate of group I and II elements, in particular, sodium, potassium, calcium, magnesium, strontium and barium. More than 150 synthetic and 40 naturally occurring zeolites are known [3]. They can be represented by the empirical formula $\text{M}_{2/n}\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2 \cdot y\text{H}_2\text{O}$. In this oxide formula, x is generally equal to or greater than 2, since tetrahedral AlO_4 join only tetrahedral SiO_4 and n is the valency of the cation. Initially, only natural zeolites were used, but more recently, modified and synthetic forms have been made on an industrial scale giving rise to tailor-made zeolites. The properties that make zeolites unique and under a separate category are [4]:

- Cations within the cavities are easily replaced with a large number of cations of different valency which exert electrostatic or polarizing forces across the smallest dimension of the cavity [4].
- The cations introduced into the cavities by ion exchange have separate activities; this facilitates the opportunity of dual function catalysis involving acidity along with other activities [4].
- Zeolite has a well-defined highly crystalline structure with cavities in the aluminum silicate framework which are occupied by large ions and water molecules. The openings of the

cavities range from 0.8 to 1.0 nm in diameter which is of the order of molecular dimensions. The size and shape of these pores determine which molecules would enter the cavities and which not. So they are called molecular sieves [4].

The general chemical formula of zeolite A is $\text{Na}_{12} [\text{AlO}_2 \cdot \text{SiO}_2]_{12} \cdot 27\text{H}_2\text{O}$. According to the database of zeolite structure [5], zeolites of type A are classified into three dimensional grades, 3A, 4A and 5A, all of the same general formula but with a different cation type. When 75% of sodium is replaced by potassium, it is referred to as zeolite (3A). Alternatively, replacing of sodium by calcium gives rise to zeolite (5A). Zeolite is commercially produced from hydro gels of sodium aluminate and silicate [6]. Faujasite zeolite is obtained from KanKara Kaolin clay [7] and zeolite NaX - from Kerala Kaolin [8]. Because of the presence of a large volume of micro pores and the high thermal stability of the zeolite, this material is used for purification of waste water, and soil remediation [9,10]. Synthetic zeolites are widely used as industrial adsorbents for various gases and vapors [8] and as catalysts in petroleum industry [11]. They are also used for drying of gases and liquids of low humidity content where they show a higher adsorption capacity than other adsorbents. Further, they have a high tendency to adsorb water and other polar compounds like NH_3 , CO_2 , H_2S and SO_2 and a good capacity at very low temperatures compared with other adsorbents. Pressure swing adsorption (PSA) is one of the techniques which can be applied for the removal of CO_2 from gas streams. Zeolite has shown promising results in the separation of CO_2 from gas mixtures and can potentially be used in a PSA process [12-14].

* To whom all correspondence should be sent:
E-mail: payodharpadhi@gmail.com

Perfect defect-free zeolite crystalline structures are not readily available or easy to prepare. Therefore, most of the zeolite material has defects and spaces between crystals which are larger than the pore sizes in the crystalline structures. To control the pore size different methods have been adopted for modification of zeolite [9-10, 15-21]. A lot of work has already been done in chemical modification to prepare composite membranes for gas separation. No extensive works have been done for physical modification of zeolite.

The present study focuses on the physical modification of zeolite A to reduce particle size, as well as to achieve uniform distribution. There are different types of polymer hydrogels having temperature dependent gelation behavior, i.e., they convert to gel at elevated temperature and turn back to solution at room temperature. Further, the hydrogel has a three-dimensional network structure. Sodium carboxymethylcellulose (CMC) is a polymer that is cheap, economical, water-soluble, eco-friendly and adheres onto zeolite A. This helps to reduce the crystal size of the zeolite. Hence, CMC was used as a modifying agent for the zeolite.

EXPERIMENTAL METHOD

Materials

Raw zeolite A purchased from NALCO, India was used as the starting material for the modification experiments. The chemical composition was determined by atomic absorption spectroscopy (AAS) using Perkin Elmer AAnalyst 200/400, as shown in Table 1. Ignition loss and pH (1% in water) were found to be 21.84% and 10.3, respectively.

Table 1. Composition of Zeolite A

Molar composition: (Based on chemical analysis)	Average Chemical Composition (%)
1.0 ± 0.2 Na ₂ O	Na ₂ O 16.5-17.5
1.0 Al ₂ O ₃	Al ₂ O ₃ 27.5-28.5
1.85 ± 0.5 SiO ₂	SiO ₂ 32.5-33.5
6.0 (Max.) H ₂ O	

CMC was purchased from Central Drug House (CDH), India with the specification of technical purity (99.5 %).

Modification of zeolite

About 7.5 g of CMC was taken in a beaker, 150 mL of de-ionized water was added and ultrasonic dispersion was carried out for 5 min to make a homogeneous solution. Then 5 g of zeolite A was added to the solution. Ultrasonic dispersion was carried out for 3 h at 80°C. Finally, the zeolite was recovered from the mother liquor by repeated

cycles of centrifugation, decanting and ultrasonic redispersion in pure water until CMC was completely washed away (no bubbles observed). Modified zeolite was dried at 100°C for 3 h and calcined at 4 h at 600°C.

Characterization

The crystalline structure of the modified zeolite A was determined by X-ray diffraction using a PANalytical XPERT-PRO diffractometer with Cu-K α radiation ($\lambda=1.5406\text{\AA}$). Diffraction measurements were performed over the 2θ range from 5-80°.

The functional groups present after modification of zeolite A were determined by Fourier transform infrared spectroscopy (FTIR) using a Perkin Elmer SPECTRUM-GX FTIR spectrometer in the 4000-400 cm⁻¹ region using pellets of 0.5 mg powdered samples mixed with 250 mg of KBr.

The microstructure and the morphology of size reduction of the modified zeolite A were examined using field emission scanning electron microscopy (FESEM model ZEISS EM910).

The composition of the modified zeolite A was examined by energy dispersive X-ray spectroscopy (EDAS model ZEISS EM910).

The particle size of modified zeolite A was determined using high resolution transmission electron microscopy (HRTEM model ZEISS EM910) operated at 100 Kv, with a 0.4 nm point-to-point resolution side entry goniometer attached to a CCD Mega Vision III image processor.

RESULTS AND DISCUSSION

The powder X-ray diffraction patterns of a raw, water treated and modified zeolite A are shown in Fig. 1 (a), (b) and (c), respectively.

The patterns are plots of the X-ray intensity scattered from the sample *versus* the scattering angle (Bragg angle, 2θ). The positions and intensities of the peaks in the diffraction pattern are a fingerprint of the crystalline components present in the sample. In the samples Na₂O, Al₂O₃ and SiO₂ planes are present in the orthorhombic, rhombohedral and hexagonal unit cells, respectively. The faces [6 0 0], [6 2 2], [6 4 2], [6 4 4] are with higher intensities than [2 0 0], [2 2 0], [2 2 2], [4 2 0]. When treated with CMC, it anchored to faces [6 0 0], [6 2 2], [6 4 2], [6 4 4]. This is evident from the lowering of peak intensities. The peaks in the XRD pattern of zeolite A treated with CMC are slightly broadened, as compared to those of raw zeolite A and zeolite A treated with water. This points to a decrease in the crystallite size of the modified zeolite A.

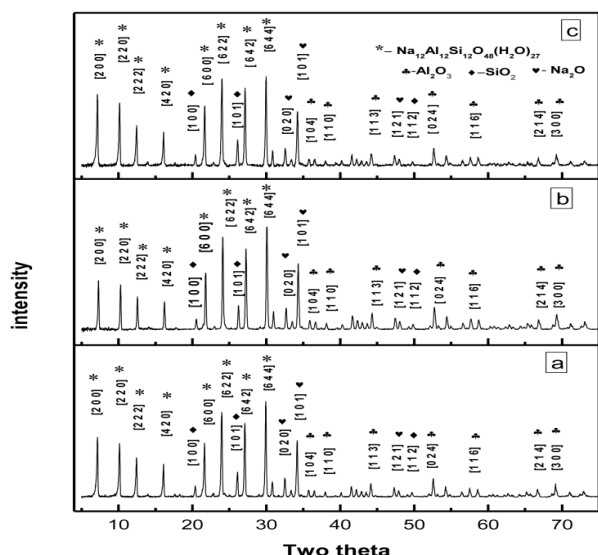


Fig.1. X-ray diffraction patterns of (a) raw zeolite A, (b) zeolite A treated with water and (c) zeolite A modified with CMC.

During modification, the temperature does not exceed 80°C. It is found that during sonication, the local heat caused by inter-particle collisions (for ~10 μm particles) could reach 2600-3400°C [22]. Thus, it is possible that the modification of the supplied zeolite A could take place at a lower macroscopic temperature because of the extremely high local temperatures generated during sonication. It is observed that sub-micro particles cannot be separated by stirring. Sonication is one of the most effective methods for dispersing the particles; however a stabilization technique like centrifugation must be used to prevent high agglomeration once sonication stopped. Higher temperature might de-mature the CMC structure and interaction is prompted at elevated temperature. That is why we picked up 80°C as a reaction temperature well below the boiling point of the solution. Calcination does not change crystallinity, and 600°C calcination cannot remove the anchored CMC from the zeolite faces, which is evident from the low-intensity peaks [1 0 1], [6 4 4], [6 2 2], [6 4 2], [1 0 1].

The FTIR spectra of raw zeolite A treated with water and modified with CMC are shown in Fig. 2(a), 2(b) and 2(c), respectively.

The absorption peaks are discussed individually. A characteristic strong and broad band at 3400 cm⁻¹ is seen due to O-H stretching vibrations [23]. The band at 2100 cm⁻¹ is due to Si-H stretching, vibration [24,25]. The deformation band at 1640 cm⁻¹ confirming the presence of bound water [23], pre-dominant in Fig. 2 (b), is related to the (H-O-H) bending vibration of water molecules adsorbed on zeolite. The band at 1150 cm⁻¹ appears because of

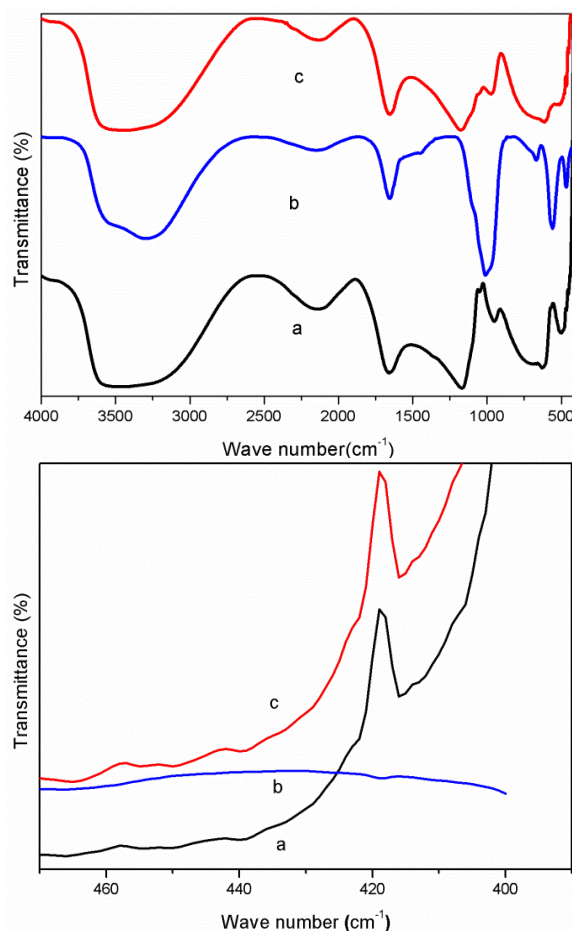


Fig. 2. FTIR spectra of (a) raw zeolite A, (b) zeolite A treated with water and (c) zeolite A modified with CMC.

Si-O-Si asymmetric stretching [26] which is insignificant in Fig. 2(b) due to the presence of excess water molecule in the pores of zeolite A treated with water. The band appearing at 1034 cm⁻¹ [27] related to T-O-T (T=Si and/or Al) stretching is more intense in zeolite A treated with water as shown in Fig. 2 (b) because of the excess of water molecules. The asymmetric Al-O stretch of Al₂O₃ is located at 950 cm⁻¹ [28]. The bands at 557 cm⁻¹ and 620 cm⁻¹ (in the region of 500 - 650 cm⁻¹) are related to the presence of double rings (D4R and D6R) in the framework structure of these zeolites [28]. The band at 557 cm⁻¹ also could represent the beginning of the crystallization of a zeolite with double rings [29]. The bands at 420 cm⁻¹ and 490 cm⁻¹ (in the region of 420-500 cm⁻¹) are related to internal tetrahedral vibrations of Si-O and Al-O in SiO₂ and Al₂O₃ [28]. The two most intense bands of the zeolite usually occur at 860-1230 cm⁻¹ and 420-500 cm⁻¹, as shown in Fig.2. The first is assigned to an asymmetric stretching mode and the second one to a bending mode of a T-O bond. All these bands are more or less dependent on the crystal structure. The mid regions of the spectra contain the

fundamental framework vibration of Si (Al) O₄ groupings [30]. The bands in the region 400-420 cm⁻¹ are related to the pore opening or motion of the tetrahedral rings, which form the pore opening of the zeolite [1]. This is shown in the case of raw zeolite A and zeolite treated with CMC but in the case of water-treated zeolite the bands are missing, which is clearly evident from the spectra. The noise level of the bands in the region 400-420 cm⁻¹ decreased in the case of zeolite A treated with CMC which indicates that the rough zeolite surface is smoothed by the application of CMC.

The FESEM studies of raw zeolite A, zeolite A treated with water and that modified with CMC are shown in Fig. 3 (a), 3 (b) and 3 (c), respectively. The particle size of the raw zeolite A is in the range

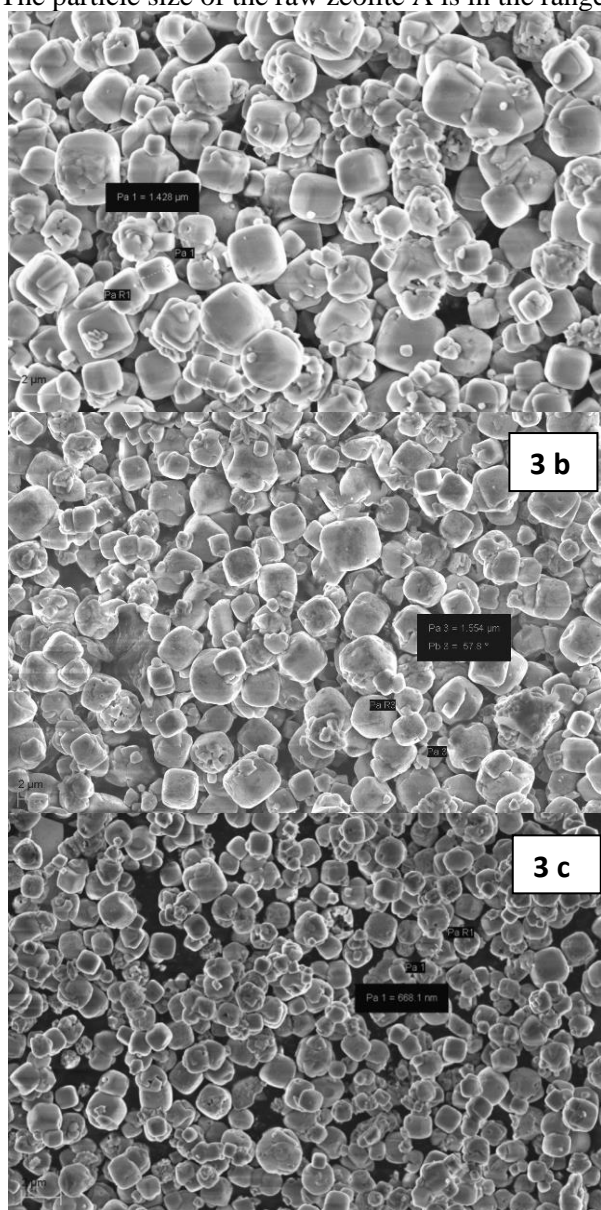


Fig.3. FESEM micrographs of (a) raw zeolite A, (b) zeolite A treated with water and (c) zeolite A modified with CMC.

of 2.5-3.5 μm with high agglomeration, which remains unchanged in case of zeolite A treated with water. After modification with CMC the particle size was found to be lower than 2 μm, in some cases being from 668.1 nm to 1 μm with better dispersion. Also the shape of the modified particles changed to slightly spherical one, as observed in Fig. 3 (b). This may be a result of calcination.

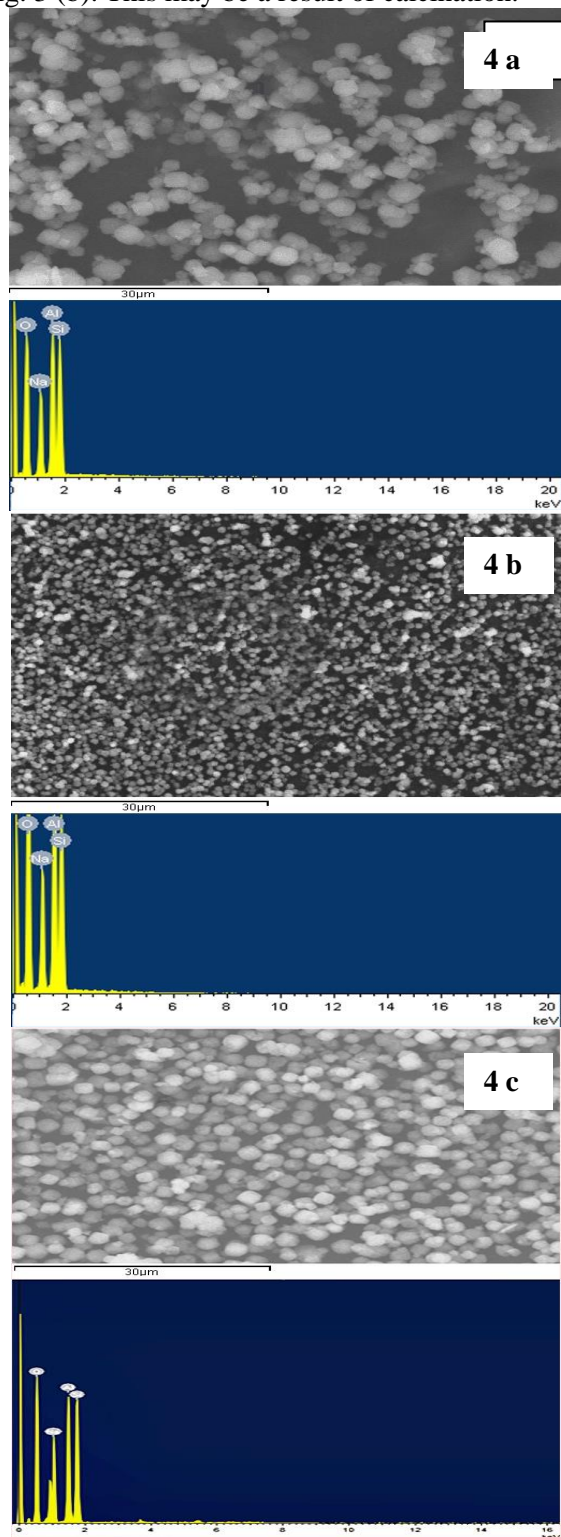


Fig.4. EDAS of (a) raw zeolite A, (b) zeolite A treated with water and (c) zeolite A modified with CMC.

The EDAS studies of raw zeolite A, zeolite A treated with water and that modified with CMC are shown in Fig.4 (a), 4 (b) and 4 (c), respectively.

The EDAS was done to determine any change of composition of both raw and modified zeolite. It is seen from Table 2 that the composition, weight and atomic percentage are changing slightly. Oxygen percentage is increasing whereas Na, Al, and Si percentages are decreasing after modification. This may be due to the particle size reduction after calcination. Further, it should be noted that in both raw zeolite A and zeolite A treated with water, the distribution of the particles is not uniform, whereas in the modified one, the particle distribution is uniform and with very few agglomerations.

The HRTEM micrograph studies of raw zeolite A, zeolite A treated with water and that modified with CMC are shown in Fig. 5 (a), 5 (b) and 5 (c), respectively.

It is seen that the particle size is in the range of 2.5-3.5 μm for zeolite A (as supplied) and remains unchanged in case of zeolite A treated with water. After modification with CMC, the particle size is found to be lower than 2 μm , which confirms the reduction of the size and shape of the zeolite.

CONCLUSIONS

It is found in the present study that modification of zeolite A using CMC is possible. As a result of CMC modification, the particle size is reduced from 3 μm to 1 μm and in some cases to 668.1 nm with better dispersion. The modified zeolite A may be used for purification of waste water, soil remediation, as a catalyst, molecular sieve, ion exchanger, adsorbent and for the removal of CO_2 from gas streams.

Acknowledgments: The authors acknowledge the Ministry of Environment and Forest (MOEF), Govt. of India for its financial support with sanction letter no 19-17/2008-RE and NALCO, Govt. of India for supplying zeolite A powder.

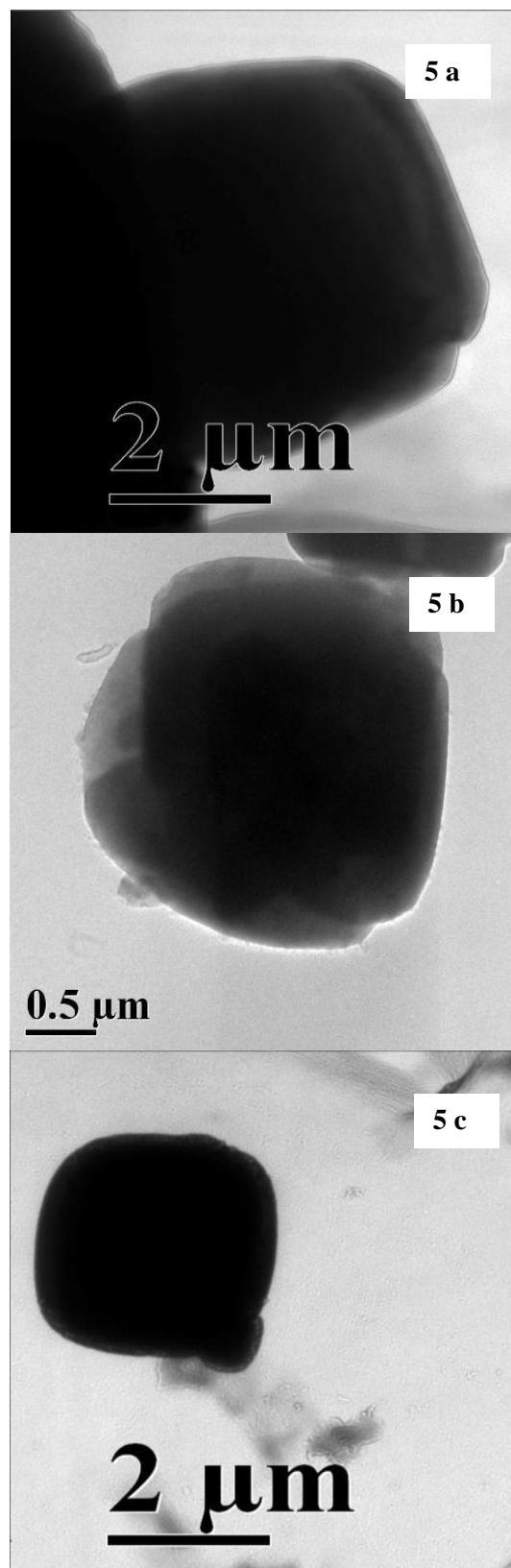


Fig. 5. HRTEM micrographs of (a) raw zeolite A, (b) zeolite A treated with water and (c) zeolite A modified with CMC.

Table 2. Elemental composition of raw zeolite A, zeolite A treated with water and that modified with CMC.

Elements	Raw Zeolite A		Zeolite A treated with water		Zeolite A modified with CMC	
	Weight %	Atomic %	Weight %	Atomic %	Weight%	Atomic%
O	50.01	62.01	19.79	37.97	56.98	68.31
Na	14.03	12.10	8.22	10.98	12.47	10.40
Al	16.98	12.48	11.57	13.16	14.87	10.57
Si	18.98	13.40	11.45	12.52	15.68	10.71
Total	100					

REFERENCES:

- 1.D.W.Breck; Zeolite Molecular Sieves: Structure, Chemistry and Uses, John Wiley, New York. (1974).
- 2.J.T.Richadson, Principles of Catalysts Developments, Plenum Press, New York and London. (1989).
- 3.B.K.Marcus and W.E.Cormier: Going Green with Zeolites. *Chem. Eng. Progress.* **95**, 47 (1999).
- 4.J.R.Ugal, K.H.Hassan and I.H.Ali, Preparation of Type 4A Zeolite from Iraqi Kaolin. Characterization and properties measurements. *J. Association of Arab Universities for Basic and Applied Sciences.* **9**, 1 (2010).
- 5.Database of Zeolite Structures, (2002) /www.zeolites.ethz.ch/zeolites/stdAtlas.htm.
- 6.R.G.Copperwaite, G.T.Hutching and M.Vander Riet: Preparation and Evaluation of a Synthetic zeolite Catalyst. *J.Chem Edu* **7**, 632 (1986).
- 7.A.Y.Atta, O.A.Ajayi and S.S.Adefila Synthesis of Faujasite Zeolites from Kankara Kaolin Clay. *J. Appl. Sci. Res.* **3**, 1017 (2007).
- 8.S.Chandrasekhar and P.N.Pramada Investigation on the synthesis of Zeolites NaX from Kerala Kaolin. *Journal of Porous Materials.* **6**, 283 (1999).
- 9.C. J. Rhodes, Properties and applications of zeolites. *Sci. Prog.* **93**, 223-84 (2010).
10. G. B. Gholikandi, M. M. Baneshi, E. Dhghanifard, S. Salehi, A. R. Yari Natural Zeolites Application as Sustainable Adsorbent for Heavy Metals Removal from Drinking Water. *Indian J. Toxicology.* **3**, 3 (2010).
- 11.J.G.Speight, The chemistry and technology of petroleum, Marcel Dekker Inc, New York. 1999.
12. K.Cheu, K.Jong-Nam, Y.Yun-Jong and C.Soon-Haeng, Fundamentals of Adsorption, Proc. Int.Conf, D.Levan (ed), Klawer Academic Publishers: Boston. MA. 203 (1996).
13. R.V.Siriwardane, M.Shen, E.P.Fisher and J.P.Poston, Adsorption of CO₂ on molecular sieves and activated carbon. *Energy Fuels.* **15**, 279 (2001).
14. F.Dong, H.Lou, M.Goto and T.Hirose, A new PSA process as an extension of the Petlyuk distillation concept. *Sep. Purif. Technol.* **15**, 31 (1999).
15. S. Mishar, G. U. Rani, G. Sen, Microwave initiated synthesis and application of polyacrylic acid grafted carboxymethyl cellulose. *Carbohydrate Polym.* **87**, 2255-2262 (2012).
16. K. M. Jae, O. T. Hwan, H. S. Soo, J. S. Woo, J. H. Yong, C. D. Wook, Preparation of poly (vinyl alcohol) /silver-zeolite composite hydrogels by UV-Irradiation *Fibers and Polymers.* **15**, 101-107 (2014).
- 17.M. Ugrina, N. V. Medvidović and A. Daković: Characterization and environmental application of iron-modified zeolite from the Zlatokop deposit. *Desalination and Water Treatment* .1-13 (2013).
18. T. Haixiang, L. Changlin, R. Jiawen, W. Yanqin, L. Guanzhong: Synthesis of mesoporous zeolite single crystals with cheap porogens. *J. Solid State Chem* , **184**, 1820– 1827 (2011).
19. H. Long and J. L. Zuo: Effect of heat modification and bio-film on zeolite adsorption properties. *Key Eng. Materials.* **439-440** , 956-959 (2010).
20. Y. Tang, D. Zhou, and J. Zhang: Novel Polyvinyl Alcohol/Styrene Butadiene Rubber Latex/Carboxymethylcellulose Nanocomposites Reinforced with Modified Halloysite Nanotubes. Hindawi Publ. Corp. *J. Nanomaterials*, **8**, (2013).
21. H. Peng, G. Ma, W. Ying, A. Wand, H. Huang, Z. Lei, In situ synthesis of polyaniline/sodium carboxymethyl cellulose nanorods for high-performance redox supercapacitors. *J. Powder Sources*, **211**, 40-45 (2012).
22. S.J.Doktycz and K.S.Suslick, Inter particle collisions driven by ultrasound. *Science.* **247**, 1067 (1990).
- 23.H.Dogan and N.D. Hilmiglu, Zeolite-filled regenerated cellulose membranes for pervaporative dehydration of glycerol. *Vacuum.* **84**, 1123 (2010).
24. F.Ruiz, C.V-Lopez, J.G-Hernandez; D.D.Allred, G.R-Paredes, R.P-Sierra and G.T-Delgado, Meso structure of Photo Luminescent porous silicon. *J.Vacuum Sci. and Technol.* **A12**, 25 (1994).
- 25.R.R.Koropecski and R.Arce, Infrared study of the kinetics of oxidation in porous amorphous Silicon. *J. Appl. Phys.* **60**, 1802 (1986).
26. K.L.Pong, S.C.Chen and K.W.Cheah, Photo luminescence of laser ablated silicon, *Solid State Communications*, **99**, 887 (1996).
27. S.S.Rayalu, Estimation of crystallinity in fly ash-based Zeolite-A using XRD and IR Spectroscopy. *Current Science.* **89**, 25 (2005).
28. C.A.Rios, C.D.Williams and M.A.Fullen, Nucleation and growth history of zeolite LTA synthesized from ualinite by two different methods. *Appl. Clay Sci.* **42**, 446 (2009).
29. M.Alkan, C.Hopa, Z.Yilman and H.Guler, The effect of alkali concentration and solid/liquid ratio on the hydrothermal synthesis of zeolite NaA from natural Kaolinite, *Macroporous Mesoporous Materials*, **86**, 176 (2005).

P. Padhi et al.: Effect of Modification of Zeolite A using Sodium Carboxy Methyl Cellulose (CMC)

30. K. Ojha, N. C. Pradhan, A. N. Samanta, Zeolite from fly ash: synthesis and characterization, *Bull. Mater. Sci.* **27**, 555 (2004).

ЕФЕКТ НА МОДИФИКАЦИЯТА НА ЗЕОЛИТ А С НАТРИЕВА СОЛ НА КАРБОКСИМЕТИЛЦЕЛУЛОЗА (СМС)

П. Падхи^{1,*}, С.К. Рут², Д. Панда¹

¹Център за изследвания и развитие, Хай-тек медицински колеж и болница, Индия
Департамент по химия, Научно-технологичен институт „Конарк“, Индия

Постъпила на 3 ноември, 2013 г.; коригирана на 19 май, 2014 г.

(Резюме)

Извършена е структурна модификация на зеолит А с помощта на натриевата сол на карбоксиметилцелулоза (СМС). Продуктът е охарактеризиран с XRD, FTIR, FESEM, EDAS и HRTEM. В резултат на реакцията, протекла при 80⁰С размерите на частиците на зеолита са намалени до 668.1 nm. Формата на частиците се променя в резултат на калциниране след звукова обработка.