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Adsorption of CO_2 on Zeolite 13X Prepared from Modified Natural Iranian Kaolin

V. Garshasbi[1], M. Jahangiri[1] and M. Anbia[2]*

[1]*Faculty of Oil, Gas and Chemical Engineering, Semnan University, Semnan, Iran*
[2]*Research Laboratory of Nanoporous Materials, Faculty of Chemistry, Iran University of Science and Technology,FarjamStreet,Narmak, Tehran 16846-13114, Iran*

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A B S T R A C T

Synthesis of zeolite 13X from modified natural Iranian kaolin at 65˚C for 72 h at various concentration of NaOH solution was investigated. Metakaolinization process was done at 900˚C for 2 h. NaOH solution with different concentrations, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4 M were separately mixed with metakaolins. A mixture of zeolite 13X, A, quartz and hydroxysodalite (HS) was obtained. The products were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The prepared zeolite 13X has been used to study the adsorption of carbon dioxide, and the results are compared with commercial zeolite 13X.

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INTRODUCTION

CO_2 is contained in natural gas, atmosphere and exhaust gas in industrial processes [1]. There is a great challenge to decrease the concentration of carbon dioxide, because the amount of CO_2 in atmosphere globally increasing which leads to 55% rise in worldwide temperature [2, 3]. Adsorption of carbon dioxide by solid adsorbents, such as metal-organic frameworks (MOFs) [4, 5], alumina [6], carbons [7, 8] and zeolites based on physical or chemical adsorption processes, has been actively investigated [9].

Zeolites are nanoporous inorganic materials with different important applications, such as in catalysis, ion exchange and separations [2, 10-14]. Its frameworks are composed of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra. Commonly, zeolites are synthesized from different sources of silica and alumina by hydrothermal treatment. To reduce the cost of synthetic zeolites, silica and alumina from chemical sources such as materials like bentonite [15], lithium slag [16], high silicon fly ash [17], paper sludge [18], bagasse fly ash [19], oil shale ash [20], coal fly ash [21], waste porcelainand kaolinite have been employed [22]. $Al_2Si_2O_5(OH)_4$ or kaolinite is a mineral clay that is consist of silica and alumina. For synthesis of zeolite 13X from kaolinite the amount of Al must be decreased or Si increased [23] in order to obtain zeolite 13X, the ratio of Si/Al values must be above 1.5.

In this work, we have synthesized the 13X zeolite from modified natural Iranian kaolin by hydrothermal treatment. The effect of NaOH concentration (1.0, 1.5, 2.0, 2.5,3.0, 3.5 and 4 M NaOH) was investigated and synthesized products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) spectroscopy. Finally, the adsorption of CO_2 on the synthesized zeolite 13X was investigated.

Material and Methods

Raw Materials

The natural kaolin (a source of silica and alumina) from Iranian sources was used for the present study. This kaolin had high amount of SiO_2 and low amount of Al_2O_3, so we modified it by acidizing to obtain convenient kaolin for synthesis of 13X zeolite. Table 1 shows the properties of raw kaolin and modified kaolin. Metakaolin was obtained by calcining kaolin in muffle furnace at 900˚C for 2 h.

* Corresponding author: Mansoor Anbia
E-mail: anbia@iust.ac.ir; Tel: 0098 21 77240516; Fax: 0098 21 77491204

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Synthesis Process

NaOH solutions with different concentrations, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4 M were separately mixed with metakaolins. The samples were homogenized at room temperature for 20 min and then the reaction mixtures were distributed in autoclave. The autoclave was kept in a conventional air oven at 65˚C for 72 h at autogenous pressure. The product was washed with deionized water to reach pH=9 and then dried at 90˚C for 12 h.

TABLE 1. properties of natural kaolin before and after modification

composition	Content (%)	
	kaolin	Modified kaolin
SiO_2	74.98	56.40
Al_2O_3	17.42	31.68
Fe_2O_3	0.54	0.26
TiO_2	0.96	0.28
CaO	1.62	0.65
MgO	0.27	0.24
Na_2O_3	1.04	0.31
K_2O	0.03	0.03
P_2O_5	0.12	0.11
L.O.I	3.02	10.04

Characterization Techniques

Chemical composition of kaolin was determined by Bruker S4 wavelength X-ray dispersive fluorescence spectrometer (WDXRFS), with a Rh X-ray tube. The X-ray powder diffraction (XRD) patterns were recorded on a Philips PW1140/90 diffractometer using Cu-Kα target (40 kV, 25 mA) at the scan rate of 2^0/min and at 2θ angles rangingfrom 5^0 to 80^0 with step size of 0.02^0.

Infrared transmission spectra of the samples were made by the KBr wafer technique. The spectra were recorded on Fourier transform infrared spectrometer system 2000 FT-IR (Perkin-Elmer).

Scanning electron microscope (SEM) micrographs were taken with a JEOL JSM-6300F scanning electron (15 kV). The energy dispersive X-ray spectrometer (EDXS) attached to the SEM was used to conduct elemental analysis of samples.

RESULTS AND DISCUSSION

Characterization of Adsorbent

From Table 1, it is observed that the main constituents of the natural kaolin were silica (74.98%) and alumina (17.42%). After modification, these percentages were silica (56.40%) and alumina (31.68%). Fig. 1 shows the XRD pattern of metakaolin and natural kaolin. Kaolinite is identified by its characteristic X-ray diffraction peaks at 12.30˚ and 24.60˚2θ that has been reported earlier [24]. The XRD pattern of metakaolin obtained by heating natural kaolin for 2h at 900˚C resembled others, except for the peaks due to admixed impurities. XRD pattern after heating shows a significant change in compare to the untreated kaolin pattern. Highest diffraction peaks are very common in metakaolin amorphous structure that corresponds to the presence of quartz.

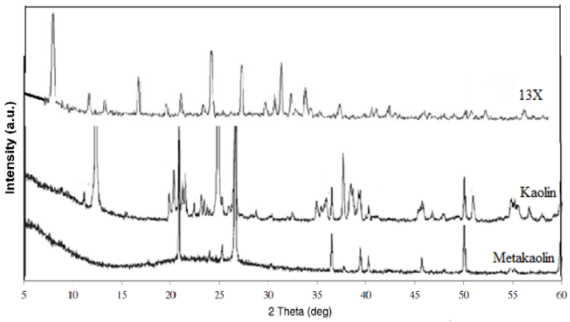

Figure 1. XRD pattern of kaolin, metakaolin and commercial zeolite 13X

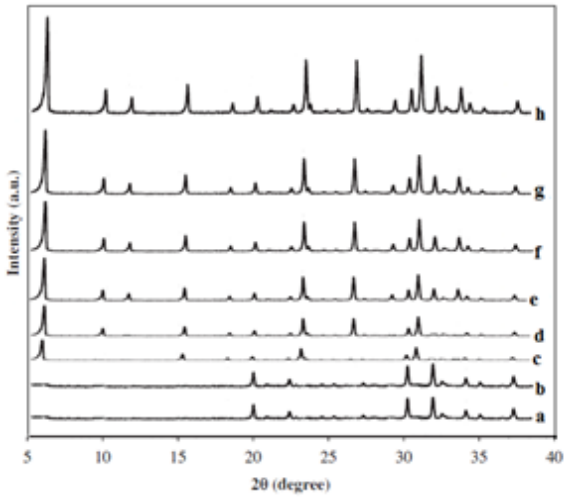

Figure 2. XRD pattern of zeolite 13X and associated phases obtained by hydrothermal synthesis: (a) 1.0 M NaOH, (b) 1.5 M NaOH, (c) 2.0 M NaOH, (d) 2.5 M NaOH, (e) 3.0 M NaOH, (f) 3.5 M NaOH, (g) 4.0 M NaOH, and (h) commercial zeolite 13X.

The XRD pattern of different products that is synthesized from different concentration of NaOH is shown in Fig. 2. The formation of synthesized zeolite 13X in the products was detected, by comparing its d-values with d-values of commercial zeolite 13X sample. The characteristic peaks of zeolite 13X are the most important change observed in the XRD patterns. The synthesized products matched the characteristic peaks of zeolite 13X at 2θ values of 6.12˚, 10.00 ˚, 11.73 ˚ , 15.43 ˚,18.42 ˚,20.07 ˚,23.31 ˚,26.65 ˚,29.21 ˚,30.30 ˚,30.94 ˚,31.98 ˚,33.59 ˚ and 37.34 ˚. Fig. 2a, 2c and 2d illustrates the XRD pattern of the product which was obtained from the sample with 1.0 M, 1.5 M and 2.0 M NaOH solution that has significant amount of metakaolin (amorphous) was observed. With increasing NaOH concentration the results indicated that the synthesized zeolite products obtained from 2.5–4.0 M

NaOH concentrations containzeolite 13X as the major constituent phase.

Fig. 3 illustrates the IR spectra of different synthesized samples of zeolite 13X by reacted kaoline and commercial zeolite 13X. Spectrum a in Fig. 2 shows the broad band of metakaolin in the range from about 920 cm^{-1} to about 670 cm^{-1} and is assigned to Al-O bonds in Al_2O_3. During the reaction between NaOH and metakaolin, SiO_2 and Al_2O_3 are transformed to aluminosilicates. Their vibration bands in the IR spectrum are replaced by a single band around 1000 cm^{-1}, characteristic of Si–O–Al bonds in TO_4 tetrahedral [24].

The appearances of the zeolite produced from metakaoline at various concentrations of NaOH is shown in SEM micrographs (Fig. 4). According to the experimental results of this work, the data obtained by SEM correlate and agree with the mineralogical composition of the zeolite products, which was determined through XRD results.

CO_2 Adsorption Isotherms

Fig. 5 shows the CO_2 adsorption isotherms of the zeolite 13X samples. 13X-M related to zeolite 13X that is produced from metakaolin and 13M-C is identified as commercial zeolite 13X. The 13X-M and 13X-C exhibited a CO_2 uptake of 255 and 265 mg/g, respectively; at 25°C and 20bar, whereas only 8mg/g was absorbed by kaolin. The high CO_2 uptake by zeolite 13X-C was attributed to its microporous structure with charge-compensating cations in the cavities [4]. The CO_2 capture capacities of 13X samples in this study were compared with different zeolites and several other CO_2 adsorbents reported in literature (Table 2).

TABLE 2. comparison of the CO_2 capture by different adsorbents

Sample	Adsorption temperature (°C)	CO_2 uptake (mg/g)	Reference
13X-C	25	265	This work
13X-M	25	255	This work
Zeolite 13X	25	223	[25]
Zeolite 13X	25	211	[9]
Activated carbon	25	99	[7]
MCM-41	75	8.6	[26]
MOF-5	30	38	[27]

CONCLUSION

Synthesis of zeolite 13X from modified natural Iranian kaolin at 65˚C for 72 h in various concentration of NaOH solutions is made. Metakaolin was obtained by calcining kaolin in muffle furnace at 900 ˚C for 2h. The zeolite 13X that was produced by this process, was characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). All results are in good agreement with literatures.

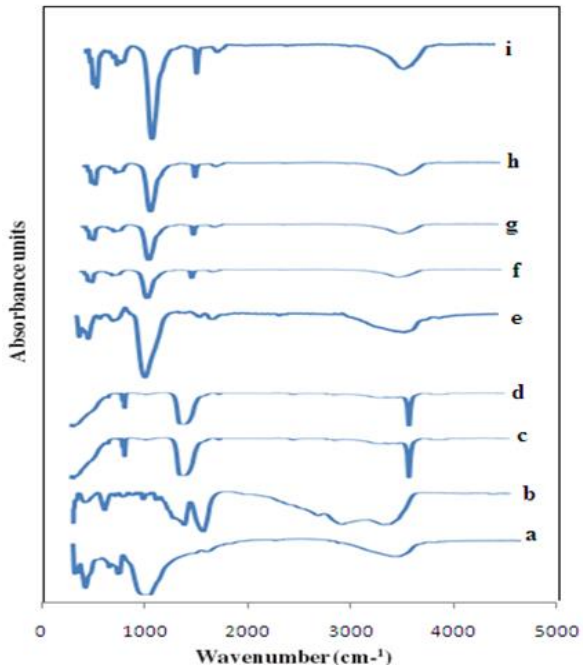

Figure 3. FTIR spectra of zeolite 13X and associated phases obtained by hydrothermal synthesis: (a) unreacted metakaolin, (b) 1.0 MNaOH, (c) 1.5 M NaOH, (d) 2.0 M NaOH, (e) 2.5 M NaOH, (f) 3.0 M NaOH, (g) 3.5 M NaOH, (h) 4.0 M NaOH, and (i) commercialzeolite 13X.

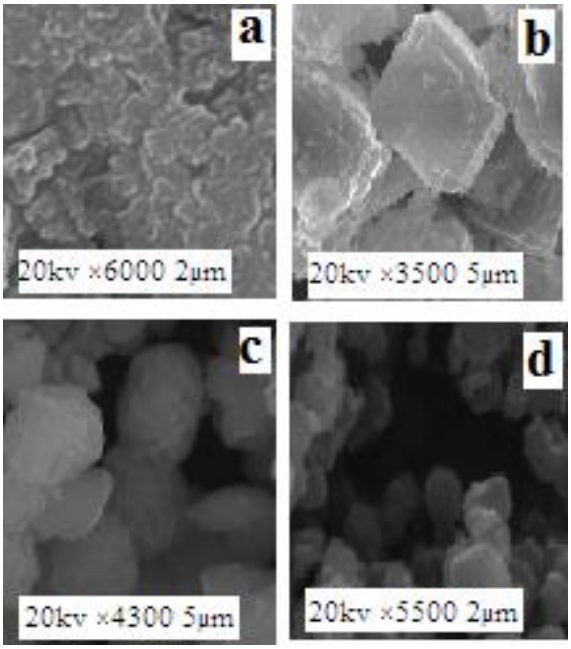

Figure 4. SEM micrographs of zeolite 13X crystals produced from metakaolin in NaOH concentrations a) 1.0M b) 2.0M c) 3.0M d) 4.0M

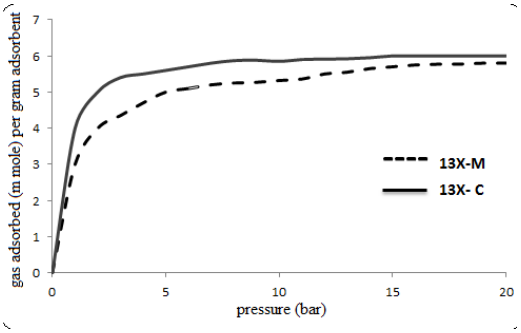

Figure 5. CO_2 adsorption by commercial zeolite 13X (13X-C) and zeolite 13X prepared by natural kaolin (13X-M)

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Persian Abstract

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چکیده

سنتز زئولیت 13X از کائولین طبیعی ایرانی در دمای ۶۵ درجه سانتی گراد به مدت ۷۲ ساعت در غلظت های مختلف محلول سود مورد بررسی قرار گرفت. فرآیند متاکائولیزاسیون در دمای ۹۰۰ درجه سانتی گراد به مدت ۲ ساعت انجام شد. محلول سود با غلظت های ۱، ۱,۵، ۲، ۲,۵، ۳، ۳,۵ و ۴ مولار با متاکائولین مخلوط شد. مخلوطی از زئولیت 13X و کواتز و هیدروکسی سودالیت بدست آمد. مشخصات محصول با آزمایش های XRD، FT-IR، و SEM مورد بررسی قرار گرفت. محصول تولید شده برای جذب دی اکسید کربن مورد استفاده قرار گرفت و نتایج با زئولیت طبیعی مقایسه شد.