Journal of Research in Ecology

An International Scientific Research Journal

ISSN No: Print: 2319 –1546; Online: 2319– 1554

Original Research

Characterization of zeolite or carbon nanotube composite prepared by hydrothermal method

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ABSTRACT:

With the usage of hydrothermal method, a hybrid composite of NaY zeolite and amine Modified Multi Walled Carbon Nanotube (MWCNT) has been combined and the resulted composite of NaT/CNT (NC composite) was defined through X-Ray Diffraction (XRD), Brunauer-Emmett-Teller (BET) surface area analysis, Scanning Electron Microscopy (SEM) and Fourier Transform Infrared (FT-IR) spectroscopy. The results showed that crystal structures of NC composite are similar to the structures of pure NaY zeolite. In contrast, the surface area and pore volume of the NC composite had been developed. The production of MWCNTs and NaY combination leads to the increased nucleation sites which finally results in the formation of smaller zeolite crystals. Moreover, due to the increased micro-pore volume, gas adsorption capacity and selectivity of NC composite have increased. It is worthy to note that NC composite is a useful material for separating and purifying the gases.

Keywords:

Carbon nanotube, composite, zeolite

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Article Citation:
Babaei M, Anbia M and Kazemipour M
Characterization of zeolite or carbon nanotube composite prepared by hydrothermal method
Journal of Research in Ecology (2017) 5(2): 895-900

Dates:
Received: 22 Nov 2016 **Accepted:** 30 Nov 2 016 **Published:** 16 Aug 2017

Web Address:
http://ecologyresearch.info/documents/EC0202.pdf

Journal of Research in Ecology

INTRODUCTION

The zeolites have been used in a wide range of applications of adsorption and separations of the gases for many years. Owing to their specific physical and chemical properties, as well as their cost-effectiveness and availability. Some applications of this material in different fields are presented briefly in the following:

- **Application in the environment**

Its application in the environment includes the adsorption of heavy toxic elements from the soil, water absorbent and preservative as a hydro reservoir and absorption of toxic metals, harmful gases (nitrogen and sulfur, etc.,) and undesirable combinations of water

- **Water and wastewater refinery**

In water refinery, zeolites are used for the removal of heavy metals and also removal of ammonia in sludge

- **Aquaculture**

To delete toxic nitrogen and sulfur gases in water, to function as a buffer substance and prevent sudden changes in the pH of the pool, to reduce water salinity and for physical and chemical purification of water naturally, zeolites are used.

- **Agriculture**

For fertilizer production, enhancing cationic and fertile exchanges, controlling the smell and as animal feed additives, zeolites are used.

- **Industrial applications**

In industry, zeolites are used as an application in the management of nuclear waste, drying of mineral and industrial oils, pozzolanic cement production and as a molecular sieve

The modification of zeolites can improve their physical properties such as surface area, pore volume and their adsorption capacity. Common modifications of zeolites for improvement of adsorption capacity are incorporation of amine groups into their structure (Bezerra *et al.,* 2011; Chen *et al.,* 2013) and employing different metal ions (Lopes *et al.,* 2010; Zhao *et al*., 2007).

Carbon Nanotubes (CNTs) are cylinders with one or more layers of graphene and with open or closed end that are called Single-Wall Nanotube (SWNT) or Multi-wall Nanotube (MWNT). In recent years, many studies are carried out on the carbon structures and their applications. Its major reason is their expected structural evolution, small size, low density, high hardness, high strength (the tensile strength of the outer wall of a multi-wall carbon nanotube is approximately 100 times greater than that of aluminum and their excellent electric features. Some applications of carbon nanotubes are as reinforcement in composites

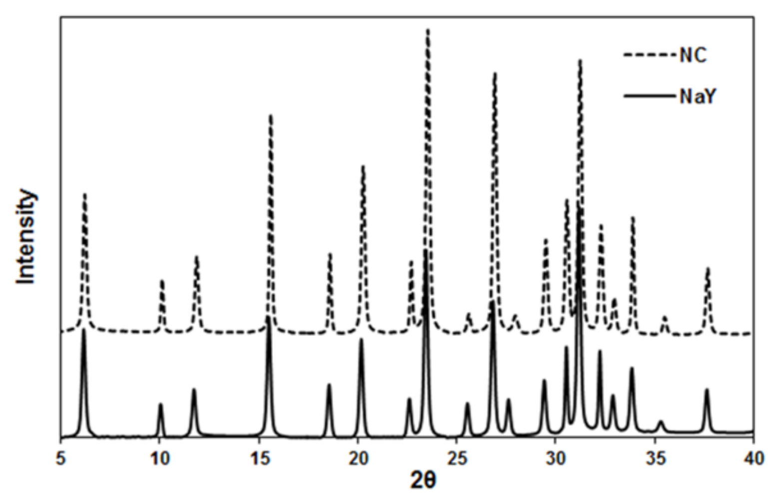

Figure 1. XRD patterns of the NaY zeolite and NC composite

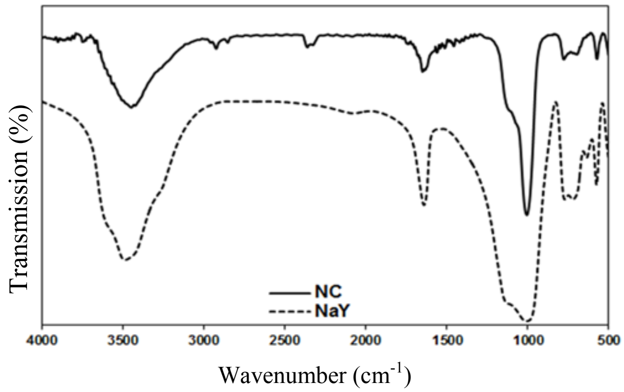

Figure 2. FT-IR spectra of NaY zeolite and NC composite

Nanotubes are one of the strongest materials. Carbon nanotube-based composites have more strength in ratio to the weight and will have a wide range of applications in industry. Their uses include

- Application in the monitors of field emission
- The use of single-wall nanotubes in the electronics industry
- Nanotube hollow structure and use as storage and fuel cell
- Making Nano-machines using carbon nanotubes

Few researches about synthesis of the carbon/ zeolite composite materials have been reported with enhanced porosity and adsorption capacity (Katsuki *et al.,* 2005; Jin *et al*., 2006). Some works have been reported on incorporation of CNTs into MOFs and their effect on adsorption performance (Xiang *et al*., 2011; Pourebrahimi *et al*., 2015). However, there are no reports about incorporation of CNTs into zeolite structures and their effect on porosity and adsorption capacity of CNT/zeolite composite. Due to low hydrothermal stability of MOF materials at high temperatures and cost-effectiveness of zeolites, in this work, the NC composite has been synthesized. Characterization of these materials was performed by X -Ray Diffraction (XRD), Fourier Transform Infrared (FT-IR) spectroscopy, Brunauer–Emmet–Teller (BET), and Scanning Electron Microscopy (SEM) analysis. The results showed that surface area and pore volume of CNT/zeolite composite has been enhanced. The results confirmed that CNT/zeolite composite can be a promising material for the adsorption and separation of gases.

MATERIALS AND METHODS

Commercially available MWCNTs, with the purity of around 95% were supplied by Neutrino Co. in Iran. The inner and external diameter of MWCNTs was in the range of 5–10 nm and 10–20 nm, respectively. The specific surface area of MWCNTs was > 200 m^2/g. For pre-treatment of MWCNTs prior to functionaliza-

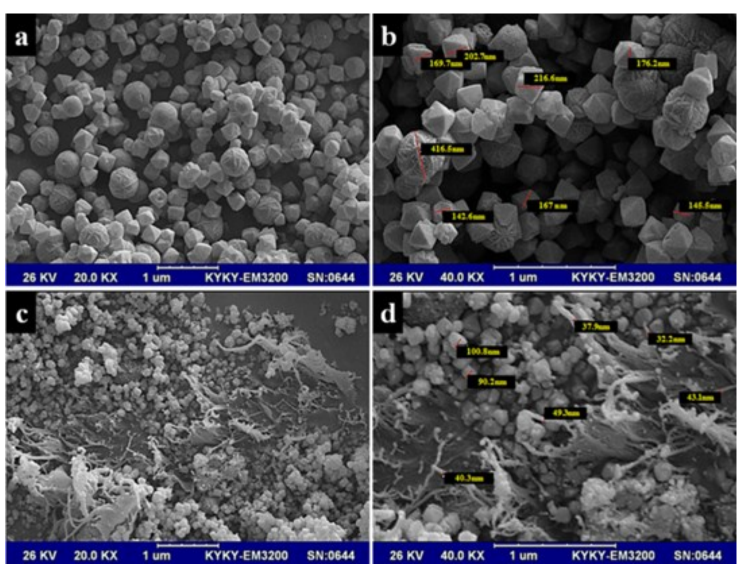

Figure 3. SEM images of NaY zeolite (a, b) and NC composite (c, d)

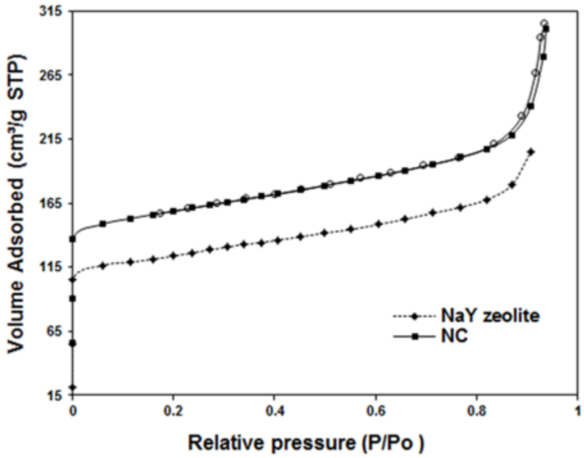

Figure 4. N_2 adsorption–desorption isotherms of NaY zeolite and NC composite at 77 K

tion, sulfuric acid (95–97%) and nitric acid (65%) were used as obtained, without further purification. 3-Amino Propyl Tri Ethoxy Silane (APTES) (purity >98%, Merck) was used for the functionalization of MWCNTs with amine groups. The materials utilized to prepare the zeolite were fumed silica (SiO_2 63% 200 mesh, China), sodium aluminate (Merck), sodium hydroxide (NaOH > 99.999%, Merck), and deionized water. The solvents used in this work were methanol and ethanol obtained from Merck. Carbon dioxide (CO_2), methane (CH_4), and nitrogen (N_2) gas cylinders with purity > 99.999 were used in adsorption experiments (*Babaei et al*., 2016).

Synthesis of NaY zeolite and NaY/CNT composite

NaY zeolite was synthesized by the following procedure. A reaction mixture with a molar composition of Al_2O_3: 3 Na_2O: 5 SiO_2: 200 H_2O was made. To prepare aluminosilicate gel, an aluminum gel (solution 1) and a silicone gel (solution 2) were prepared separately. Solution 1 was prepared by dissolving 2 g sodium aluminate in 8.79 g of deionized water. For solution 2,

Table 1. Structural properties of NaY zeolite and NC composite

Adsorbent	S_{BET} (m^2/g)	Pore volume (cm^3/g)
MWCNT	> 200	—
NaY zeolite	212	0.213
NC	407.49	0.349

3.665 g fumed silica and 1.952 g sodium hydroxide were dissolved in 33.174 g of deionized water. Solution 1 was mixed with solution 2 in a polypropylene beaker. The prepared reaction mixture was stirred by magnetic stirrer at ambient temperature for 3 days, and then the mixture was put into teflon-line autoclave and heated at 373 K in an oven for 12 h. After the performance of hydrothermal crystallization reaction, the NaY zeolite powders were filtered and dried in an oven. Before the synthesis of NaY/CNT composite, MWCNTs were pretreated and functionalized by amine groups. In the way that, first MWCNTs were stirred with a mixture of concentrated H_2SO_4 and HNO_3 (3:1, v/v) at 80º C for 6 h, and then filtrated and washed with deionized water for several times and dried at 50º C. Then, the carboxylated MWCNTs (MWCNTs-COOH) after dispersing into flasks containing APTES solution (APTES: ethanol of 1:9, v/v) was sonicated for 6 h and stirred at ambient temperature for 72 h. The mixture was filtered through 0.2 μm fiber filters and washed repeatedly with ethanol and deionized water to remove any residual APTES. Then the filtered solid was dried in an oven at 100° C for 6 h and denoted as N-MWCNT. The NC composite was also prepared under the similar hydrothermal procedures of NaY, except various amounts of N-MWCNT were well dispersed in 33.174 g of deionized water of solution 2 and sonicated for 2 h and then fumed silica and sodium hydroxide were added. The various amount of N-MWCNT was used to synthesize 15 wt% MWCNT incorporated NaY sample. The synthesized NaY/CNT composite is named as NC composite. The XRD patterns of NaY zeolite and composite were obtained with a powder X-ray diffractometer (Philips PW 1830 X-ray Diffraction) with Cu-Kα radiation source. FT-IR spectra of the samples were obtained by (FT-IR DIGILAB FTS 7000 spectrometer). The morphologies of the synthesized NaY zeolite and NC composite were identified using a KYKY-EM 3200 field emission scanning electron microscope. The porosity properties of the samples were determined by the nitrogen adsorption–desorption isotherms at 77 K using a micromeritics model ASAP 2010 sorption analyzer. The Specific Surface Area (SSA) was calculated by Brunauer–Emmett–Teller (BET) method (Dogan *et al*., 2006).

RESULTS AND DISCUSSION

The crystal structures of NaY zeolite and NC composite were identified by XRD. As shown in Figure (1), the XRD pattern of the NC composite is in perfect agreement with that of NaY zeolite, indicating that MWCNT incorporation does not destroy the formation of the crystal structure of NaY zeolite. Furthermore, in the composite, the weak peak of CNT at $2\theta = 26°$ C could not be observed because of its overlapping with high-intensity peaks of NaY zeolite. Also, after the incorporation of MWCNTs, peak intensities of the composite were higher, indicating that crystallinity of NaY zeolite crystals in NC, having been improved compared with pure NaY zeolite.

Figure 2 shows the FT-IR spectra of NaY zeolite and NC composite. In the spectrum of NC composite (b), a peak at 2370 cm–1 appears which is associated to hydroxyl groups (-OH) stretch from strongly H-bonded-COOH (Liu *et al*., 2002) and confirmed the incorporation of MWCNTs into zeolite structure. Furthermore, these spectra showed that MWCNTs incorporation did not destroy the zeolite crystal structure.

The SEM images of NaY zeolite and NC composite are shown in Figure 3. As can be seen, after MWCNT incorporation, the crystalline shape of NaY zeolite in the composite has not changed. The morphologies of NC composites displayed that the MWCNTs are well blended with NaY zeolite. It could be seen that the size of NaY zeolite crystals in the NC composite is smaller than those in the pure NaY zeolite. It is because of the increase of nucleation sites for the formation of NaY zeolite crystals by MWCNTs, leading to the smaller size of NaY zeolite crystals.

Nitrogen adsorption–desorption isotherms of NaY zeolite and NC composite at 77 K (Figure 4) are of a typical type I isotherm, which indicate the microporous feature of these composites. The pore characteristics of adsorbents are listed in Table 1. The results showed that when MWCNTs incorporate into NaY zeolite, the surface area and micropore volume of NC composite improve, due to the formation of extra micropores. Furthermore, the crystal size reduction may also contribute to the increase of the surface area of NC composite. The effect of particle size on the surface area of adsorbents had also been reported by others (Liu *et al*., 2012; Ge *et al*., 2013).

According to the findings of Liu *et al*. (2012), the decreased size of NC particles causes the increased crystal surface leading to the increase of nitrogen absorption. Furthermore, in the study of Ge *et al*. (2013) discovered that matrix membrane mixed with Cu-BTC leads to the decrease of MOF crystal size increasing the permeability of the membrane. These both studies confirm the results of current study and are in line with it.

CONCLUSION

Zeolite/carbon nanotube composite has been successfully synthesized with hydrothermal method and characterized. The surface area and pore volume of the NC composite are enhanced that it is attributed to increase of nucleation sites after incorporation of MWCNTs into zeolite. Due to the obtained results in this study, NC composite can be a suitable material for adsorption and separation of gases.

ACKNOWLEDGMENTS

The authors are grateful to Research Council of Iran University of Science and Technology (Tehran) and Islamic Azad University, Kerman branch for the financial support of this project.

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