



Synthesis and property modification of MCM-41 composited with Cu (BDC) MOF for improvement of CO₂ adsorption Selectivity



Nesa Esmailian Tari^a, Azadeh Tadjarodi^a, Javad Tamnanloo^b, Shohreh Fatemi^{b,*}

^a Research Laboratory of Inorganic Materials Synthesis, Department of Chemistry, Iran University of Science and Technology, 16846-13114 Tehran, Iran

^b School of Chemical Engineering, College of Engineering, University of Tehran, Enghelab Avenue 11365-4563 Tehran, Iran

ARTICLE INFO

Article history:

Received 11 October 2015

Received in revised form 2 April 2016

Accepted 26 April 2016

Available online 6 May 2016

Keywords:

Cu(BDC) MOF

MCM-41-Cu(BDC) composite

MCM-41

CO₂ adsorption

CH₄ adsorption

CO₂/CH₄ selectivity

ABSTRACT

MCM-41/Cu(BDC) composite was synthesized as a selective adsorbent, by facile microwave method with high capacity and selectivity towards CO₂ adsorption. MCM-41 pores surface was functionalized with 3-cyanotripropyltriethoxysilane as the linker between MCM-41 and Cu(BDC) metal organic framework (MOF). The specific surface area of the functionalized MCM-41 with —COOH terminated groups of Cu (BDC) MOF was improved 73% from 624 to the specific surface area of the MCM-41 composited with 1084 m²/g, from lonely MOF to composited MCM-41/Cu(BDC) MOF, respectively. Adsorption isotherms measurements of CO₂ and CH₄ by the synthesized composite were carried out at ambient temperature and pressure range of 1–40 bar, by volumetric method. The isotherms of the composite revealed enhancement of CO₂/CH₄ selectivity about 15% at 4 bar and 13% at 40 bar compared to the initial MCM-41 and MOF materials, respectively. Formation of MOF inside the MCM-41 pores, has led to the formation of new micropores with effective active sites and more tendency towards CO₂ adsorption against CH₄. The recyclability of the composite material for the adsorption of CO₂ and CH₄ was investigated three times and the results revealed only 1% decrease of CO₂ and CH₄ adsorption capacity after the cycle sequences.

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1. Introduction

Increasing world population has led to growth usage of energy sources such as fusel fuels and natural gases. CO₂ and CH₄ are the major compositions of the outlet gas from the natural energy sources usage, and they are the most responsible materials for accumulation of greenhouse effect gases and consequently global warming [1]. Removal of CO₂ from natural gas is an important task in upgrading natural gas in which presence of CO₂ as an impurity reduces the energy content of natural gas and leads to pipeline corrosion [2]. Therefore, searching for an adsorbent with high selectivity of CO₂ is necessary. Since now several technologies have been used for CO₂ removal includes, absorption, cryogenic distillation, membrane separation and adsorption [2]. Among these technologies, adsorption in porous materials has attracted more attention due to its economic and energetic efficiency. Over the years, many porous materials such as zeolites, activated carbon, ZSM-5, mesoporous materials and metal organic

frameworks (MOFs) have been studied for CO₂ and CH₄ adsorption and separation [3,4].

Among aforementioned adsorbents, MOFs have attracted scientists' attention due to their unique properties. MOFs are a class of porous materials which are formed from metal ions or clusters as nodes and organic ligands as linkers. MOFs generally have high surface area and due to the possibility of using various organic ligands it is possible to tune their pore size and volume [5,6]. These materials are mainly being studied for hydrogen storage [7], gas separation [8], CO₂ sequestration and catalysis [9,10]. Most of the MOFs have been synthesized by hydrothermal/solvothermal heating methods which need high temperatures and long times about 1–7 days based on the type of MOF [11,12]. In order to decrease the synthesis time and obtaining high yield, many studies have reported synthesizing MOFs by other methods such as ultrasonic, microwave assisted and mechano-chemical [13–15]. Beyond mentioned methods, microwave synthesis represents a major breakthrough in synthetic chemistry methodology, a dramatic change in the way chemical synthesis is performed and in the way it is perceived in the scientific community. In coordination with a rapidly expanding applications base, microwave method can be effectively applied to synthesis any reaction scheme, creating faster reactions and improving yield.

* Corresponding author.

E-mail address: Shfatemi@ut.ac.ir (S. Fatemi).

Microwave irradiation suggests great advantages as the simplest and fastest technique while selective dielectric heating, due to difference in the solvent and reactant dielectric constants, can provide significant improvement in reaction rates [16].

Hexagonal mesoporous silica materials (HMS) are a family of siliceous materials that are recognized as one of the widely used gas adsorbents due to their large pore volume, large pore size, and good pore interconnection [17]. However, due to their low capacity and selectivity toward CO₂, several studies have been reported about modification of mesoporous silica mainly by incorporating certain basic functional groups in order to increase CO₂ adsorption capacity and selectivity. For example, Wang et al., studied the CO₂ adsorption on amine grafted SBA-14 by increasing silanol density. They found that by increasing amine loading, the CO₂ adsorption capacity was increased from 1.05 to 1.6 mmol/g at 0.15 bar and 25 °C. However, modification of SBA-15 with amine decreased the surface area significantly from 786 m²/g for SBA-15 to 147 m²/g for amine-SBA-15 [18]. In the other work, Wu et al., increased CO₂ adsorption capacity to 3.61 mmol/g in the modified disordered mesoporous silica by incorporating tetrarthylenepentamine (TEPA) in its pores at 25 °C. Also in their study, the BET surface area of the modified mesoporous silica was decreased compared to the unmodified silica [5]. Belmabkhout and Sayari, investigated CO₂ adsorption over a wide range of mesoporous silica comprised of conventional MCM-41, pore-expanded MCM-41 (PE-MCM-41) and triamine surface modified PE-MCM-41 (TRI-PE-MCM-41) in different conditions [20]. In their work, it was recognized that CO₂ adsorption capacity of TRI-MCM-41 at low pressure was the highest and it reached to 2.5 mmol/g at 0.1 bar compared to 0.49 mmol/g and 0.5 mmol/g for PE-MCM-41 and MCM-41, respectively. However by increasing CO₂ pressure up to 20 bar the mentioned order inverted and the CO₂ adsorption capacity

reached to about 8 mmol/g, 6.4 mmol/g and 5.8 mmol/g for MCM-41, PE-MCM-41 and TRI-PE-MCM-41, respectively, at 25 °C. Nearly in all of the mesoporous silica modified by amines or metal oxides the BET surface area have been decreased sharply [18–21]. Also, improving adsorption capacity which was gained by adding chemical absorption besides physical adsorption makes desorption process costly and uneconomical [18–20].

In this work, a new composite of silica mesoporous material composited by MOF structure is synthesized by using microwave as a source of energy, to reach to a high surface area and high capacity and selectivity for CO₂ adsorption. Synthesis of Cu(BDC) with a fast and simple method inside the pores and channels of a popular mesoporous silica, such as MCM-41 to achieve high specific surface area with less MOF consumption and higher yield of the adsorbent rather than pure MOF is the strategy of this research.

2. Experimental

2.1. Materials and methods

Copper(II) nitrate trihydrate (Cu(NO₃)₂·2H₂O, pure), *N,N*-dimethylformamide (DMF, 99.8%), tetraethylorthosilicate (TEOS), hydrochloric acid (HCl, 37%), ammonium hydroxide (NH₄OH, 32%), cetyltrimethylammoniumbromide (CTAB) were provided from Merck Co. Terephthalic acid (H₂BDC, 98%) and 3-cyanotripropyltriethoxysilane were purchased by sigma-Aldrich Co. All of the mentioned materials were used without further purification. XRD patterns were obtained on JEOL JDX-8030 X-Ray diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Nitrogen adsorption/desorption isotherms were obtained on a Micromeritics Asap 2020 at sorptometer at liquid nitrogen temperature. The specific

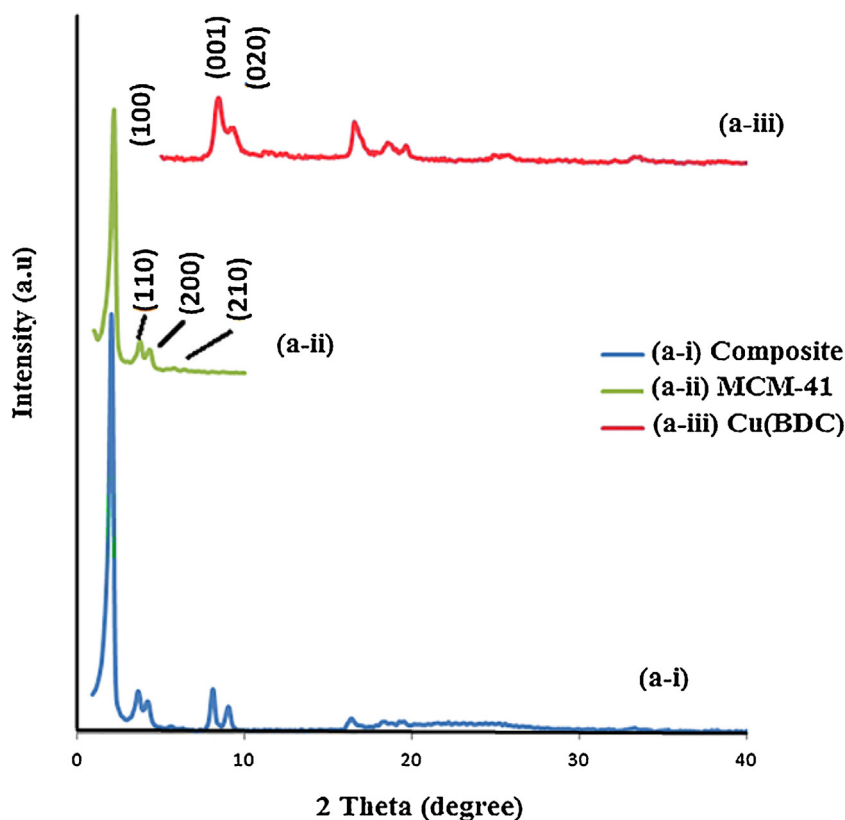


Fig. 1. XRD patterns of (a-i) composite, (a-ii) MCM-41 and (a-iii) Cu(BDC).

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