Synthesis and Characterization of Amine-modified Mesoporous Santa Barbara Amorphous-15 for Carbon Dioxide Sequestration at High Pressure and Room Temperature

M. Anbia*, M.J. Habibi, M. Babaei, S. Salehi

Research Laboratory of Nanoporous Materials, Faculty of Chemistry, Iran University of Science and Technology, Farjam Street, Narmak, Tehran, Iran

**Abstract**

Amine-modified mesoporous Santa Barbara Amorphous (SBA)-15 adsorbent has been prepared by impregnation method using tetraethylenepentamine. The samples of this modified SBA-15 have been characterized by small angle X-ray scattering (SAXS), Scanning electron microscopy (SEM), Nitrogen adsorption-desorption isotherm and FT-IR. The adsorption capacity of CO$_2$ on unmodified and modified samples were measured at high pressure (up to 20 bar) and room temperature and were 2.69, 4.02 and 3.62 mmol CO$_2$/g for SBA-15, TEPA (55%)-SBA-15 and TEPA (65%)-SBA-15, respectively. The increment in the CO$_2$ adsorption capacity of amine modified mesoporous material (TEPA (55%)-SBA-15) is attributed to the increased amine mass interaction with CO$_2$. Further increase of amine content clogs the pores of the sorbent which results in slight reduction of CO$_2$ adsorption in TEPA (65%)-SBA-15.

**Keywords:** CO$_2$ Adsorbent Materials, Tetraethylenepentamine, Santa Barbara Amorphous (SBA)-15, Gas Separation

**1. INTRODUCTION**

The emission of greenhouse gases is a serious environmental problem of present era which contributes to the global warming and air pollution [1-4]. Among the greenhouse gases, Carbon dioxide is significantly increased in the recent decades. Since the time of the industrial revolution, global increment of the atmospheric concentration of CO$_2$ has been about 100 ppm (36%) [5]. Human activities such as burning of fuels at homes and industrial units have increased CO$_2$ emission to atmosphere [6-9]. The control of CO$_2$ emission has become an important research topic which is of interest to many researchers [10].

The emission of CO$_2$ may be reduced through several ways [11-15]. The best way is the replacement of fossil fuels with environmentally friendly biofuels and improvement in energy efficiency with capturing CO$_2$ from fuel sources [9, 16]. In the last few decades, several methods have been proposed for CO$_2$ removal [1, 2, 16, 17]. Absorption with chemical reaction using aqueous solutions of alkanolamines is one of the methods for carbon dioxide removal. But this method has disadvantages such as high energy consumption for solvent regeneration, equipment corrosion and amine’s flow problems. To overcome these problems [18, 19], functionalization of amine groups with grafting or impregnation methods onto porous supports have been used [20-23].

There are many porous supports such as active carbons, zeolites, silica mesoporous and metal-organic framework which are used for carbon dioxide removal. A recent review by D’Alessandro et al. [2] describes these porous materials used for CO$_2$ adsorption, discussing important aspects such as their advantage and disadvantage, in addition to adsorption capacity.

During the past few years, silica mesoporous materials such as MCM-41 [5, 10], MCM-48 [14, 21], SBA-15 [24, 25], SBA-12 [18] and KIT-6 [26] were used as porous materials to remove carbon dioxide.
These materials have several remarkable features such as high surface area, ordered pore size and easily functionalized surface [24, 27], but the CO₂ adsorption capacity of the unmodified mesoporous support is low because there are no induced strong reactions between pure silica surface’s residual hydroxyl groups and CO₂ molecules. Therefore, the increment of CO₂ adsorption capacity by grafting or impregnation of amine groups such as mono, di- and tri-amines has been studied by different research groups [16, 24]. However, the available data shows that CO₂ adsorption capacity values vary from 0.5 to 3.43 mmol CO₂ per g adsorbent at low pressure [16], while industrial situations involve with process at high pressure and room temperature.

To investigate the removal of CO₂ in industrial process, we have functionalized the 2-D SBA-15 type silica mesoporous, using different amount of tetraethylenepentamine (TEPA) by impregnation treatment. We have characterized the resulting materials by various techniques and have studied their CO₂ adsorption behavior by volumetric measurements at high pressure and room temperature.

2. MATERIALS AND METHODS

2.1 Reagents and Materials All materials such as poly (ethylene oxide)-poly (propylene oxide)-poly (ethylene oxide) block copolymer non-ionic surfactant EO₂₀PO₇EO₂₀ (Pluronic P123, Merck), Tetraethyl orthosilicate (TEOS 98%, Merck), tetraethylenepentamine (TEPA 99%, Merck), hydrochloric acid (HCl 37%, Merck), ethanol (EtOH, Merck) used in the synthesis SBA-15 as structure-directing agent, precursor of Si, amine source, catalyst and solvent respectively, were of analytical grade.

2.2 Synthesis of SBA-15 SBA-15 was prepared by hydrothermal synthesis using dilute solutions of the nonionic block copolymer surfactant Pluronic P123 following the literature [28]. Briefly, P123 (4.0 g) was dissolved in 2 M HCl (150 mL) at room temperature. TEOS (9.6 mL) was added to that solution slowly and stirred for 24 hours at 40 °C. The mixture was aged at 100 °C for 24 h under static conditions. The solid product was filtered, washed with deionized water and dried for 2 h at 100 °C. The prepared samples were termed: TEPA(x)-SBA-15 (x was 55 wt% and 65 wt%).

2.4 Characterization Two adsorbents, TEPA (55%)-SBA-15 and SBA-15 support were examined by Small Angle X-ray Scattering using Swaxs Hecus (model S3-MICRO) equipment. The diffraction data were recorded in the 20 range of 0.6–10° with a scanning rate of 5°/step (step 20 =0.02°). Nitrogen adsorption-desorption isotherms of the samples were measured at 77K using Micromeritics model ASAP 2010 analyzer. The specific surface area was obtained employing BET method and the pore size distribution was evaluated by Barrett-Joyner-Halenda (BJH) method. Transmission infrared (IR) spectra were obtained by DIGILAB FTS 7000 spectrometer, as KBr discs. Particle morphology and compositional analysis of these adsorbents were carried out using scanning electron microscopy (Philips model XL-30 microscope). The samples were coated with gold in order to increase their conductivity before scanning.

2.5 CO₂ Adsorption Measurements The CO₂ adsorption capacities of TEPA (x)-SBA-15 samples were evaluated employing volumetric method and the set-up used is shown in Figure 1. At first, 0.5-1 g of a sample was loaded in the adsorption reactor (HP vessel) and attached to the system, then to degas the system, temperature was increased to 433 K and the valves 4, 3 (see Figure 1) were opened. After that, the vacuum pump was turned on and the system was vacummed for 1.5 h (without any loss of crystallinity) under the given thermal conditions. After de-gassing, the system was cooled to room temperature. The CO₂ was adsorbed by opening the valves 2 & 3. The pressure of HP vessel decreased due to some dead volume in reactor (including hollow space and the connected tubes) and some adsorption. The dead volumes were calculated via helium test and subtracted from total pressure change. By measuring the dead volumes, one could calculate the exact pressure decrease due to the carbon dioxide adsorption.
CO₂ adsorption amount (mol) was calculated by using real gas equation, PV=ZnRT. Where n, P, V are amount (mol), pressure and volume of CO₂ gas adsorbed in HP reactor respectively. T was 298 K, the gas temperature and R denotes the universal gas constant 8.314 J mol⁻¹K⁻¹. Z is compressibility factor at related pressure.

3. RESULT AND DISCUSSION

3.1. XRD Analysis
The small angle X-ray scattering pattern of SBA-15 and TEPA (55 %)-SBA-15 are shown in Figure 2. XRD pattern of two synthesized adsorbents exhibits three peaks (1 0 0, 1 1 0, 2 0 0) at 2θ < 2° which can be indexed as 2D hexagonal lattice [29]. Consequently, modification of hexagonal SBA-15 type mesoporous do not seriously damage the overall ordered structure of the mesoporous silica.

The intensities of the XRD peaks for TEPA (55 %)-SBA-15 decreases slightly and the peaks shifted to a little higher 2θ angles. Hence, the observed decrease and shift of XRD peak intensity is probably due to the pore filling effect of channels in mesoporous support and the anchoring ligands on the outer surface of support [29].

3.2. N₂ Adsorption-desorption Isotherms Analysis
Data on surface area and pore diameter were measured by standard N₂ adsorption isotherms. The BET method provides the information about surface area. The BET-based curves of SBA-15 and TEPA (55%)-SBA-15 are shown in Figure 3. The nitrogen adsorption isotherm of the calcined SBA-15 is typical reversible type IV, and adsorption isotherm (S-shape) and H1 Hysteresis the characteristic of a mesoporous molecular sieve. After amine loading, the IV type isotherm and H1 hysteresis are still preserved. The BET surface area of SBA-15 was 937 m².g⁻¹. After amine loading, surface area was reduced from 937 to 247 m².g⁻¹.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Surface Area (m².g⁻¹)</th>
<th>Pore Diameter (nm)</th>
<th>Pore Volume (cm³.g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15</td>
<td>937</td>
<td>6.55</td>
<td>1.17</td>
</tr>
<tr>
<td>TEPA (55%)-SBA-15</td>
<td>247</td>
<td>5.65</td>
<td>0.34</td>
</tr>
</tbody>
</table>

Pore diameter and pore volume were measured by BJH method. Figure 4 illustrates BJH curve of two synthesized absorbent and is based on the pore condensation phenomena. This method is applicable only in the mesoporous or microporous region. Pore diameter and pore volume of SBA-15 support was 6.55 nm and 1.17 cm³.g⁻¹, respectively. But, in the TEPA (55%)-SBA-15, these parameters were decreased to 5.65 nm and 0.34 cm³.g⁻¹, respectively. In addition, the pore volume is reduced from 1.17 to 0.34 cm³.g⁻¹ indicating that most likely the pores are blocked by the TEPA groups. Table 1 shows textural properties of SBA-15 support and TEPA (55%)-SBA-15.
3. 3. FT-IR Analysis Figure 5 shows the FT-IR spectra of calcined SBA-15 and TEPA (55%)-SBA-15 in the scan range from 400 to 4000 cm\(^{-1}\). A broad peak with high intensity around 3450 cm\(^{-1}\) on the unmodified SBA-15 indicates the O–H stretching vibrations of silanol groups and adsorbed water molecules. This peak with same intensity was seen on FT-IR spectrum of amine modified SBA-15, which indicates that there is no reaction between TEPA and OH-silanols in SBA-15 support. The band around 960 cm\(^{-1}\) can be attributed to Si–O vibration in Si–OH group in siliceous SBA-15. The characteristic band at 1031 cm\(^{-1}\) is due to the Si–O in stretching mode in Si–O–Si structure. The IR bands at 3422 and 3277 cm\(^{-1}\) are due to asymmetric and symmetric NH\(_2\) stretching. N–H and C–H vibration bands are seen at 1539 and 1463 cm\(^{-1}\) respectively. The bands at 2973 and 2854 cm\(^{-1}\) are assigned to the CH\(_2\) asymmetric and symmetric stretching modes of the TEPA in amine modified SBA-15 [29]. In addition, two bands at 1180 and 1004 cm\(^{-1}\) are related to N–C stretching modes of the TEPA molecules.

3. 4. Scanning Electron Microscopy The morphologies of the prepared unmodified SBA-15 and TEPA (55%)-SBA-15 mesoporous are shown in Figure 6. It can be seen that all the samples are composed of uniform and long fibrous aggregates. No difference in fibrous morphology is seen before and after functionalization of silica mesoporous. This obviously indicates that the shape of particles is not changed and morphology of samples have remained after modification.

3. 5. Isotherms of CO\(_2\) Adsorption Figure 7 shows the CO\(_2\) adsorption capacity of SBA-15, TEPA (55%)-SBA-15 and TEPA (65%)-SBA-15 at 20 bar and room temperature. Unmodified SBA-15 support possesses low CO\(_2\) adsorption capacity about 2.69 mmol/g.

By loading amines onto mesoporous SBA-15, adsorption capacity is increased. Increase of carbon dioxide adsorption capacity is due to loading of amine groups. TEPA possess primary amine and secondary amine in their structures. The improvement in CO\(_2\) adsorption over functionalization of SBA-15 with amine groups is because of acid-base interaction between acidic CO\(_2\) basic and amine groups. This is explained by the fact that active alkali –NH\(_2\) group possess lone a pair of electrons on N atom which undergoes nucleophilic attack on the C atom of acidic CO\(_2\), leading to formation of carbamate through carboxyl group. The active H atom in carboxyl group can then form ion pairs through hydrogen bond with the nearby amine group, and hence stabilizes the chemisorption of CO\(_2\). However, stabilization of carbamate in the course of hydrogen bonding decreases the number of free amine groups. This indicates that, one mole CO\(_2\) stabilization requires two moles of amine groups. TEPA (55%)-SBA-15 and TEPA (65%)-SBA-15 adsorbents show CO\(_2\) adsorption capacity of 4.02 and 3.62 mmol/g, respectively. The adsorption capacity of TEPA (65%)-SBA-15 is greater than which measured for SBA-15 support but it is lower than that of TEPA (55%)-SBA-15. This exception is associated with the completely filled pores of this adsorbent and block age of the pores by the additional TEPA groups.

Figure 8 shows CO\(_2\) adsorption isotherms of SBA-15 and all amine modified mesoporous at room temperature and different pressures in the range of 0-20 bar. In the range of 0-8 bar, TEPA (65%)-SBA-15 shows the highest CO\(_2\) adsorption capacity due to amine loading on the outer surface of support and reaction with CO\(_2\). But in the range of 8-20 bar, free amines on the surface were decreases due to interaction with CO\(_2\) molecules. The CO\(_2\) adsorption isotherm on all synthesized absorbent is of a typical type IV isotherm according to the IUPAC classification. The adsorption capacity for an isotherm increases with increasing pressure and reaches the saturation state and then remains constant.
Figure 7. CO₂ Adsorption capacity chart of SBA-15 and TEPA-SBA-15 materials at 20 bar

Figure 8. CO₂ adsorption curves on SBA-15 and TEPA(x)-SBA-15 materials at 298 K up to 20 bar

4. CONCLUSION

In this work, amine modified SBA-15 is prepared using tetraethylenepentamine by impregnation method. The resulting sample was characterized by FT-IR, XRD, SEM and BET analysis. CO₂ adsorption capacity of prepared sample is measured by volumetric method. The order of CO₂ adsorption capacities for the prepared samples were SBA-15<TEPA (65%)-SBA-15<TEPA (55%)-SBA-15. Increasing the amine mass on SBA-15 increases CO₂ adsorption capacity of amine modified mesoporous material. However, with further increase of amine groups result in slight lowering of CO₂ adsorption capacity of (TEPA (65%)-SBA-15) this is due to the clogging of the pores by amine group in this sample.

5. REFERENCES


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**NOTE**

چکیده

جاذب مترودوس 15 (SBA-15) اصلاح شده با آمین از طریق روش انتقال ساری با ترا آمین تیتحتی نامنه. نمونه‌های اصلاح شده با روش‌های شناسایی مانند برآش این سیستم، ترکیب جاذب-آمیزه، نمودار ترکیبات اصلاح شده و CO2 و ترکیبات SBA-TEPA (55%)-SBA-TEPA به ترتیب ترای 15 و 15atherine که ترکیبات اصلاح شده آمیزه (TEPA) از اثر آمونیاک ترکیبات جاذب CO2 و 15 (65%)-SBA-15 و 15 (65%)-SBA-15 ذرت گری شده. از این آمیزه به عنوان اسکد حفظ حفظ و در نیمه کاهش جزئی در جاذب SBA-15 (55%)-SBA-15 مایه‌می‌شود.

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