

# Insights of CO<sub>2</sub> adsorption performance of amine impregnated mesoporous silica (SBA-15) at wide range pressure and temperature conditions



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## ABSTRACT

Beside IGCC, efficient storage and transportation of CO<sub>2</sub> and other gases require pressurize conditions. CO<sub>2</sub> and other gases adsorption on solid sorbents at high pressure and various temperatures are extremely important as long as the environmental purification via gas capture and separation and gas transpiration are concern. The main objective of the present research was to investigate the effect of amine impregnation on the CO<sub>2</sub>, methane and nitrogen adsorption capacity of mesoporous silica (SBA-15). Ordered mesoporous silica (SBA-15) was prepared and modified with ammonium hydroxide solution to introduce NH<sub>2</sub> functional groups within the pores of materials to produce modified SBA-15 (MSBA-15). The newly prepared materials were characterized with X-ray diffraction analysis, thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and Brunauer–Emmett–Teller (BET) analysis were performed to measure pore volume as well as the surface area of both the unmodified and modified samples. Results revealed that the crystal structures of SBA-15 were matched with that of MSBA15; yet, pore volume of the modified material was almost reduced to 50% of the pristine material indicating amine loading into the pore channels. Importantly, gas sorption capacity was investigated at 200 bars and three different temperatures of 318 K, 328 K, and 338 K by using state-of-the-art gravimetric Rubotherm<sup>®</sup> magnetic suspension sorption apparatus. Gas sorption experiments showed that modified mesoporous silica adsorbed 1.6164 mmol/g of CO<sub>2</sub> at 1 bar which is almost double than that of 0.6462 mmol/g adsorbed by unmodified material. Quantitative selectivity of both the materials varied as CO<sub>2</sub> > CH<sub>4</sub> > N<sub>2</sub>.

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## 1. Introduction

Nowadays more than 75% of world energy requirements are being covered by fossil fuels such as petroleum, natural gas and coal, where, this consumption moves up to 85% in the developed world (Chen, 2011). Ma et al. has studied the emission of CO<sub>2</sub> with energy consumption in a case study of a small town (Tianjin city) in China and has found that the growth of CO<sub>2</sub> emission increases every year by about 4.48% when only coal was used as the energy source (Chun et al., 2011). Despite significant efforts and developments on energy harvesting by using other alternative sources, fossil fuel seems to be the primary energy sources until the

development of renewable and/or alternative energy resources for the next century (Chiari and Zecca, 2011; Höök and Tang, 2013). It has been estimated that per capita consumption of fossil fuel drastically increases globally with raise in energy demands due to the changing life standards and alarming escalation in world population (Anastasi et al., 1990; Haggin, 1991). Therefore, energy demand grows proportionally to these socio-economic growth and such growth results in uncontrollable exploitation of fossil fuel, which is the major source of CO<sub>2</sub> emissions. Toxic emissions have threatened the global habitat due to significant increase in sea salinity and it is also argued that CO<sub>2</sub> emissions and other greenhouse gas emissions also cause increase in global average temperatures. A mathematical approach proposed by Zhang et al. suggested that significant quantity of fine particulate matter released during mineral handling impose severe impact on the wind speed and height particularly under weak wind condition (Zhang et al., 2013), whereas coal particulate friction velocity influenced by the humidity also severely

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affect the environment (Zhang et al., 2012b). Recent studies have shown that CO<sub>2</sub> emission alarmingly increases as a result of strong dependency on energy consumption (Bauer et al., 2015). Additionally, it has been estimated that during less than half a year, owing to the longer life time, CO<sub>2</sub> emitted by a new coal based power plant radiate more heat than that produced by combustion of coal due to the greenhouse gas effect (Caldeira, 2015). Assessment of replacing natural coal with natural gas for energy production with the objective of low CO<sub>2</sub> emission to benefit the environment revealed that electricity generation through gas still requires CO<sub>2</sub> control strategies.

Nevertheless, pre-combustion (Lee et al., 2011, Martín et al., 2011), post-combustion (Fauth et al., 2012) and oxyfuel combustion (Stadler et al., 2011) CO<sub>2</sub> capture technologies (Pera-Titus, 2014) and storage have been under utilization since long to effectively reduce the emission of various gases. Investigations for marginal improvements for a while in order to mitigate the severe environmental effects of anthropogenic gaseous emissions and also store them safely in various forms are underway. Monoethanolamine (MEA) has been utilized as a CO<sub>2</sub> capture agent for several decades since mid-1950s; however, energy required to regenerate the MEA or similar amine based solvents for cyclic CO<sub>2</sub> capture process on large scale have both economic and environmental drawbacks that needs serious attention. On the other hand, the newly developed IGCC (Integrated Gasification Combined Cycle) power plant technology requires pre-combustion CO<sub>2</sub>/H<sub>2</sub> separation at above ambient temperature and high pressure of about 40 bars (Field and Brasington, 2011; Couling et al., 2012; Raksajati et al., 2013). Pressure swing adsorption for CO<sub>2</sub> removal has been considered as a promising technique based on the low energy requirement in IGCC power plant systems (Schell et al., 2013). System like IGCC where CO<sub>2</sub> needs to be captured at high pressure and elevated temperature, require the most porous solid sorbents with adequate surface area, excellent CO<sub>2</sub> capturing efficiency and repeated applicability (Couling et al., 2011).

Solid sorbents such as activated carbon, MCM-41 (Mobil Composition of Matter No. 41) and composite of mesoporous silica and zeolite-A which can be regenerated economically and used repeatedly with almost unchangeable capturing efficiency are considered to be the most suitable materials for large scale industrial applications (Siriwardane et al., 2001; Guo et al., 2006; Gray et al., 2008; Khalili et al., 2013; Roth et al., 2013; Zhou et al., 2013; Su et al., 2014). Although, physical absorbents such as activated carbon, zeolites and molecular sieves can adsorb more CO<sub>2</sub> at ambient condition, but, these materials lost CO<sub>2</sub> capturing efficiency at high temperature and also affected by the humid environment (Choi et al., 2011; Kizzie et al., 2011). Metal organic frame work (MOFs) and covalent organic polymers (COPs) are found to be interesting materials with very good texture properties which make these solid sorbent capable to capture great amount of CO<sub>2</sub> (Patel et al., 2013; Xu and Hedin, 2014; Hu et al., 2015). However, oxidation, large scale synthesis of MOFs and manufacturing cost of COPs are still major concerns which hinder the large scale application of these materials until they become economically viable (Choi et al., 2009; Liu et al., 2012a,b; Xu and Hedin, 2014). Amine modified commercial activated carbon has shown excellent performance at a pressure of 41 bar (Chidi Ogbuka, 2013) however, additional energy was required to desorb CO<sub>2</sub> completely and performance of the used material was comparatively lower than the fresh sample (Houshmand et al., 2012).

Among the various solid sorbents SBA-15 possess special advantages of intrawall pores (Ravikovitch and Neimark, 2001), open ended mesoporous channels interconnected through narrow micropores (Galarneau et al., 2001) and oxygen vacancies on the outer surface (Zeleňák et al., 2010), which may play a key role in the adsorption process. Enhancing the affinity of solid sorbent toward

CO<sub>2</sub> by amine functionalization has been emerged as an effective technique to increase the capturing capacity of solid materials (Yan et al., 2011a,b; Cai et al., 2014; Jing et al., 2014). CO<sub>2</sub> capturing efficiency has been strongly dependent on amine loading and pore volume of the solid aminated sorbent, where studies (Zhang et al., 2012a) have shown that, manganese modified SBA-15 has excellent re-generation capability when used for desulfurization of hot coal gases (Veneman et al., 2012).

Although, surface area and pore volume significantly reduced (Buonomenna et al., 2013) with functionalization (Chang et al., 2009; Wang et al., 2007), however, SBA-15 modified with various types of amines through different techniques (Builes and Vega, 2012) has the capability of adsorbing the highest content of CO<sub>2</sub> and can be regenerated economically for multiple use as an efficient sorbent. By comparing modified (with varying quantities of aminopropyltrimethoxysilane (APS)) SBA-15 with zeolite 13X for CO<sub>2</sub> adsorption at a pressure of 0.05 bars, the later has shown high adsorption capacities, owing to the availability of more adsorption sites (Bollini et al., 2012a), while the available adsorption sites were saturated in aminated SBA-15. Pristine SBA-15 has better performance than activated carbon at elevated temperature of 338 K for CO<sub>2</sub> capturing, whereas 3-aminopropyl-triethoxysilane (APTS) modified SBA-15 has shown more stable performance at room temperature (Chang et al., 2009). In addition, Chang et al. (Chang et al., 2003) has shown that APTS grafted material can be easily regenerated in the presence of H<sub>2</sub>/H<sub>2</sub>O, representing the hydrothermal stability of the modified material. Study has revealed that SBA-15 aminated by one amino group (Aminopropyl) with highest quantity of N (7.3%) has excellent adsorption capacity at a lower pressure, while the adsorption capacity was further increasing with increase in pressure (Sanz et al., 2012). The highest and stable adsorption capacity of amine modified SBA-15 was mainly attributed to the provision of adsorption site by NH<sub>2</sub> functional group, silane linkage and the interaction of CO<sub>2</sub> with nearest neighbor grafted amine on SBA-15 surfaces (Danon et al., 2011). Highest CO<sub>2</sub> adsorption on polyethyleneimine (PEI) impregnated SBA-15 was attributed both to the physisorption (on the surface) and chemisorptions (in the micro-pores) processes (Yan et al., 2013a,b). In order to further increase the CO<sub>2</sub> capturing efficiency at high pressure and make use of the entire space of the mesoporous structure, supercritical propane has been used to diffuse APS into the intra-channels of mesoporous SBA-15 (Huang et al., 2013). Results revealed that, although surface area and pore volume were significantly reduced with this process, however, a reasonable increase in the CO<sub>2</sub> adsorption was observed. Even though, many efforts have been made so far, however, development of material with longer stability (Khatri et al., 2006), high adsorption capacity at elevated pressure and recyclability is still remains as a challenge. Since SBA-15 has a suitable porous structure, which can accommodate both amine (as an attractive site) and CO<sub>2</sub> within the free channels as well as on the outer surface, therefore, this study was conducted to explore whether this material can be considered as an efficient sorbent for high pressure adsorption of CO<sub>2</sub>, which can be used in IGCC power plants. In this study we investigated the possibility of using modified material (MSBA-15) for CO<sub>2</sub>, methane and nitrogen adsorption at high pressure of about 200 bars and compared its performance with pristine material.

## 2. Experimental

### 2.1. Synthesis and functionalization of SBA-15

Ordered mesoporous silica (SBA-15 powder) was prepared through already established techniques (Buonomenna et al., 2013; Chen et al., 2008), with a small modification, using tri-block

copolymer, pluronic P123 (obtained from Sigma-Aldrich) as a structural template agent and tetraethyl orthosilicate (TEOS, 99%, Sigma-Aldrich) as an organo-silica source. In a typical procedure, one gram of P123 was dissolved in 30 mL of 2 M HCl (hydrochloric acid) followed by addition of 7.5 g of deionised water and 2.08 g of TEOS. After mixing through stirring the slurry was poured in a nalgene bottle and was stirred again at 38 °C for 24 h. The mixture was further treated hydrothermally at 95 °C for 72 h. The final product was filtered at least 5 times using deionised water and was then dried at 50 °C for 10 h. In order to remove the template, sample was further calcinated for 5 h at 550 °C with a temperature increase rate of 1.5 °C min<sup>-1</sup>. The final product was labeled as SBA-15 and was kept in a glass vial for further experimental tasks.

On the other hand, functionalization of SBA-15 was accomplished by dissolving 1.0 g of newly prepared SBA-15 in 5.0 mL of 50 wt.% NH<sub>2</sub>OH solution followed by addition of 2.0 mL deionized water. To certainly introduce the function molecules (NH<sub>2</sub>) into the pores of silica materials, mixture was stirred at room temperature for about 3 h. The resulting slurry was filtered on a glass frit by vacuum, washed with 5 mL of deionized water. The product was dried in 5 days at room temperature using vacuum desiccator. After weighing (1.1 g) the final product was labeled as MSBA-15 and was stored for characterization and further experiments.

## 2.2. Characterization of SBA-15 and MSBA-15

Thermal stability investigation was carried out with Perkin Elmer Pyris 6 TGA machine, where, materials were heated in N<sub>2</sub> environment from 30 °C to 800 °C at the rate of 5 °C min<sup>-1</sup>. Fourier transforms infrared spectra of materials were taken with Bruker Vertex 80 FTIR spectrometer in the range of 4000–400 cm<sup>-1</sup>. Morphology of the samples was studied with scanning electron microscope (FE-SEM-Nova Nano-450, Netherlands). D2 PHASER from Bruker was used to investigate the crystal structure of modified and non-modified SBA-15 materials. BET measurement and de-gassing of the samples were performed with Micromeritics ASAP 2420 surface and porosity analyzer. Prior to surface area and pore volume measurement samples were degassed at 150 °C for 5 h under vacuum.

## 2.3. High pressure adsorption–desorption study

BET analysis were used for low pressure CO<sub>2</sub> uptake at 273 K and 298 K, however, magnetic suspension balance (MSB) from Rubotherm Prazisions Messtechnik GmbH equipped with automated Teldyne Isco 260D pump was used to measure the high pressure CO<sub>2</sub> adsorption of the materials. Details of the experimental set up for high-pressure gas measurement has been mentioned somewhere else (Karadas et al., 2011). In a typical procedure, known amount (0.10–0.2 g) of sample was degassed for 5 h at 150 °C and was then kept in MSB sample holder for further evacuation at various temperature as required for 5 h. The maximum set pressure (200 bars) was applied step-wise by increasing the pressure gradually from 1 bar up to 200 bars. Each pressure point took about 75 min to gain the set point of pressure and temperature, record four different sets of measurements and collect the data points. The system is fully automated and the pressure goes to next higher point after completing the previous measurement point. The system was brought to atmospheric pressure subsequently by evacuation through a stepwise reduction of pressure 200 bars to evacuation stage in order to achieve the desorption characteristics of the materials.

## 3. Results and discussions

Fig. 1 shows XRD pattern of SBA-15, where the single intense peak at  $2\theta = 0.924^\circ$  and two weak peaks at  $2\theta = 1.606^\circ$  and  $1.869^\circ$  are the characteristic peaks corresponding to (1 0 0), (1 1 0) and (2 0 0) planes respectively (Calleja et al., 2011). A small shift toward the larger diffraction angles in our case as compared to the literature (Li et al., 2013) may be attributed to the difference in the synthesis techniques and calcinations temperature. The existence of highly intense peak for (1 0 0) plane along with the two consecutive peaks for (1 1 0) and (2 0 0) planes reveal that the newly prepared material has p6mm symmetry with well-defined 2D hexagonal and mesoporous structure. XRD pattern of modified material (MSBA-15) exactly matched with the pristine SBA-15 indicating that structure of materials remained unaltered after grafting amine function group.

Additionally, content of the grafted amine was enough to modify the chemical properties like surface charges and polarity inside the pore channels and on the outer surface of the material due to NH<sub>2</sub> attachment as proposed in Fig. 2. However, the attached functional group was not in large concentration which may lead to crystal modification and channel structure alteration as evident elsewhere (Wang et al., 2012).

FTIR, analysis of modified and non-modified materials shown in Fig. 3 confirmed the formation of SBA-15 owing to the presence of the characteristic peaks of silicate materials. The strongest bands at 450 cm<sup>-1</sup>, 890 cm<sup>-1</sup> and 1078 cm<sup>-1</sup> correspond to the Si–O–Si bending, Si–O stretching and asymmetric stretching mode of SiO<sub>4</sub> skeleton (Kruk et al., 2000; Danon et al., 2011).

The relatively small peaks at 1630 cm<sup>-1</sup> can be associated to the presence of adsorbed water while the broad but weakest band at around 3453 cm<sup>-1</sup> can be associated to the presence of silanol O–H stretching mode (Cheraghali et al., 2013). Yan et al. (2011a,b) observed evidences of primary (NH<sub>2</sub>) and secondary amine at around 1569 cm<sup>-1</sup> and 1653 cm<sup>-1</sup> respectively in case the of poly(ethyleneimine) (PEI) modified SBA-15. However, due to the very small quantity of amine (i.e. NH<sub>2</sub>) inserted into the pore of material, observation of such peaks was very challenging in our case which could be evidenced through ATR signals. Nevertheless, as shown in the inset of Fig. 3 redshift of the broad band in the range of 3100–3500 cm<sup>-1</sup> can be assigned to the stretching mode N–H bond indicating the presence of minute quantity of amine group (Yan et al., 2011a,b).

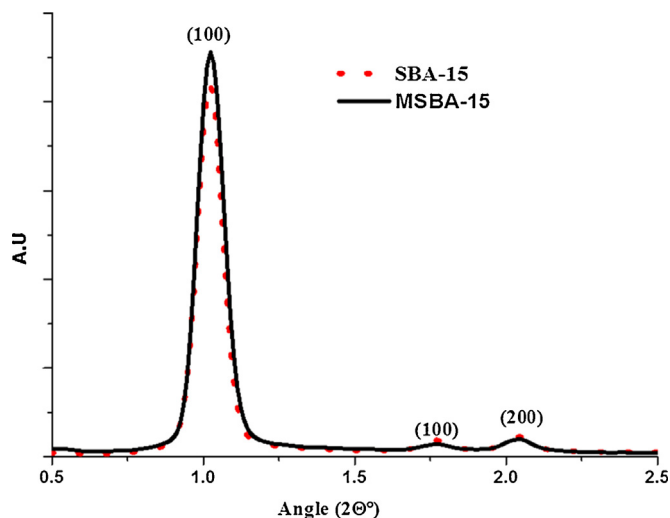


Fig. 1. XRD pattern of SBA-15 and MSBA-15, showing intense peaks for (1 0 0) plane, characteristic peak of SBA-15 and two weak peaks for (1 1 0) and (2 0 0) planes indicating 2D hexagonal SBA-15 structure.

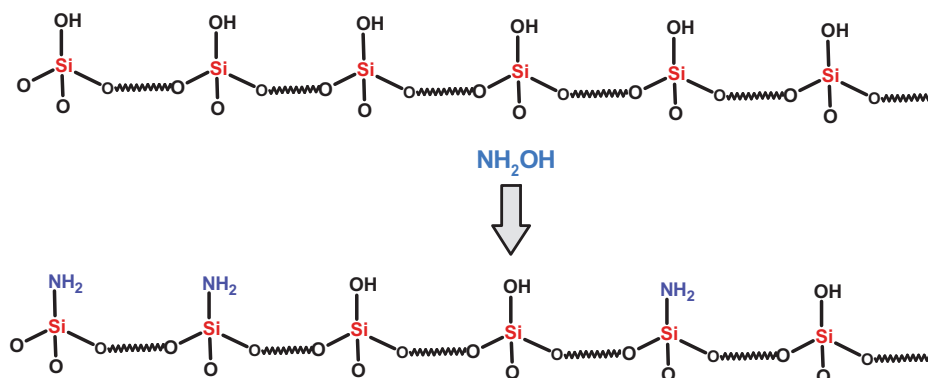


Fig. 2. Schematic of SBA-15 and MSBA-15 showing replacement OH molecule with  $\text{NH}_2$ .

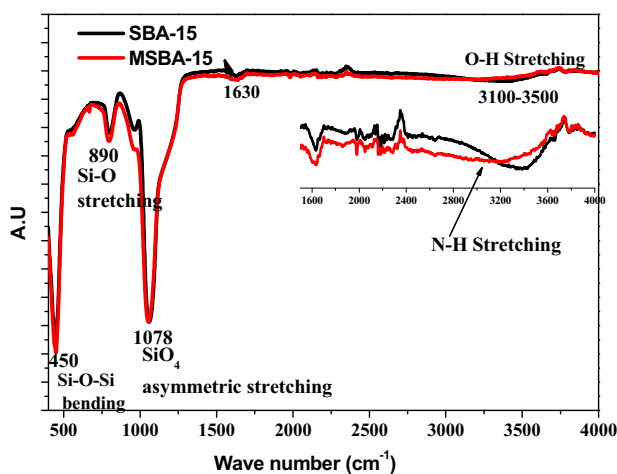


Fig. 3. FTIR analysis spectra of SBA-15 and MSBA-15, where the inset shows red shift in the peak at around  $3100\text{ cm}^{-1}$  to  $3500\text{ cm}^{-1}$  is an indication of the N-H stretching.

Scanning electron micrographs (SEM) shown in Fig. 4 reveals that material has multi-sizes agglomerates ranging from approximately 100 nm to about 1200 nm, with the average particle size of about 600 nm. Smaller and average size particulates have very smooth and uniform faces while the larger agglomerates (about  $1\text{ }\mu\text{m}$ ) have shown some voids on the outer surface indicating assembly of tiny particles to form micrometer size particles (Tadjarodi et al., 2013). Formation of larger size agglomerates and assembling of tiny particles may be attributed to the high sintering temperature during the nucleation process. Zhao et al. (1998) have also observed almost similar effect of aggregation at high calcination temperature. Since copolymer pluronic P123 has been used as a template agent, thus most of the as synthesized materials possess ordered structures with regular geometrical shapes. Likewise XRD, SEM analysis also confirmed that, attachment of amine function group only modifies the surface and pore chemical properties while the physical structure of the material remains unaltered after grafting amine function group on the material.

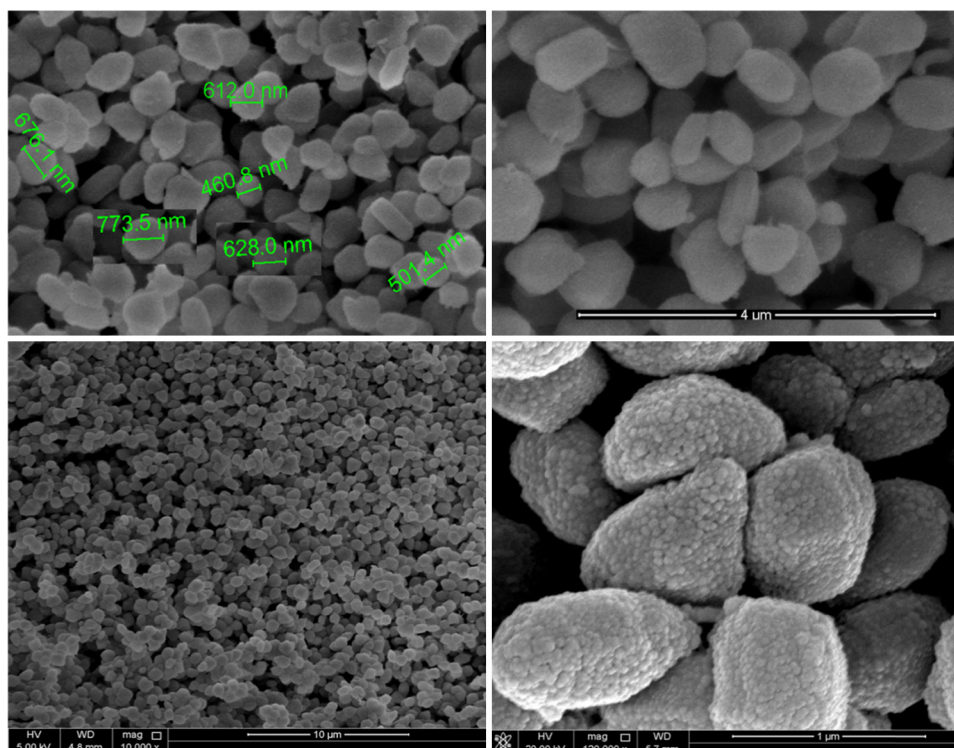


Fig. 4. Scanning electron micrographs of SBA-15 (top two) and MSBA-15 (down two).



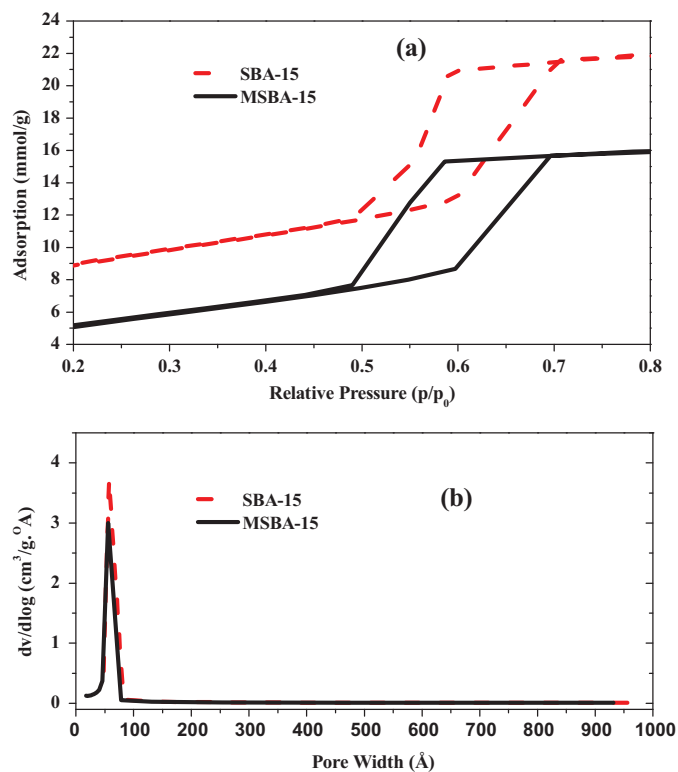
**Table 1**  
Physical parameters of unmodified and amine modified SBA-15.

Material	BET surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Pore diameter (Å)	CH <sub>4</sub> uptake (mmol/g)
SBA-15	711.8434	1.1137	77.8001	5.8239
MSBA-15	433.5696	0.5429	68.4550	4.6166

Fig. 5 shows TGA analysis obtained from Perkin Elmer for SBA-15 and MSBA-15, where both the materials have shown almost similar weight loss behavior. The initial significant weight loss up to 7% at around 100 °C is mainly associated to the vaporization of water and the following 1–2% (up to 450 °C) weight loss can be attributed to the decomposition of surfactant agent such as P123 (Song et al., 2006) and other polymeric impurities in the structure. Since, materials were sintered in nitrogen environment for thermal gravimetric analysis, therefore, it requires higher temperature to completely remove the template agent as compare to heating in air (Kruk et al., 2000). The small difference at the mid-stage (70 °C to 330 °C) decomposition of material in case of MSBA-15 is associated to the removal of amine group from aminated silica, however, above 330 °C both the materials have similar degradation characteristics. Fig. 5 further reveals that, both modified and as synthesized materials have almost similar thermal stability, but, MSBA-15 may lose the entire amine function group at temperature above than 300 °C. This bleaching of amine group from modified SBA-15 may affect the performance of material as an efficient CO<sub>2</sub> adsorbent at higher temperature such as temperature swing adsorption and will limit its application (Xue and Liu, 2011).

Table 1 shows BET surface area, pore volume, pore size and CO<sub>2</sub> uptake of as synthesized material and amine modified SBA-15. BET surface area (711 m<sup>2</sup>/g) and pore volume (1.1137 cm<sup>3</sup>/g) of SBA-15 were significantly reduced after material was modified with amine loading. This reduction in pore volume (Fig. 6b) and surface area clearly indicates that amine function group NH<sub>2</sub> has been introduced within the pore of material and occupied about one third of the free space. Nitrogen adsorption–desorption isotherms of SBA-15 and MSBA-15 (shown in Fig. 6a) have typical IV shapes and hysteresis loops between 0.5 and 0.7  $p/p_0$ .

The presence of hysteresis loops is strongly suggesting that both the materials have cylindrical mesoporous and microporous channels which were almost unaffected after amine incorporation (Calleja et al., 2011). However, a slight reduction at the two ends of the hysteresis loop and significant reduction in the differential pore volume in case of MSBA-15 may be the reason of insertion of NH<sub>2</sub> molecules in the pore channels affecting the pore volume



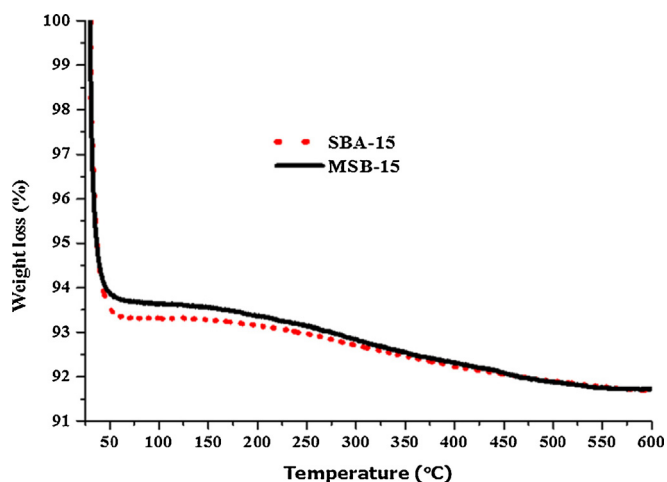
**Fig. 6.** Nitrogen adsorption–desorption isotherms (top) and pore volume distribution of SBA-15 and MSBA-15.

and pore area of the modified material (Liu et al., 2010). It must be noted that NH<sub>2</sub> molecules introduced in the channels of SBA-15 were enough in quantity to modify the chemical affinity of the free pores, but, maintain the free space available for the adsorbing gas molecules. Unlike to literature (Xue and Liu, 2011), instead of increasing the amine function group concentration and changing the type of amine molecules, a single amine function group with one specific quantity was used to enhance the capturing efficiency of the material. This incorporation of a single amine function group with a specific lower quantity was aimed to only modify the chemical behavior of the free pores for gas molecules attraction while maintaining the porosity of material almost at the same level.

Table 2 clearly indicates that by increasing temperature at constant pressure of 200 bars, CO<sub>2</sub> uptake, i.e. number of moles of CO<sub>2</sub> adsorbed is decreasing. This decline in the number of adsorbed CO<sub>2</sub> moles may be attributed to the weakening of the accessibility of CO<sub>2</sub> to active site and reduction in CO<sub>2</sub> affinity with increase in temperature. Presumably, pore volumes and surface areas of both the materials remain unaffected by increasing temperature from

**Table 2**  
CO<sub>2</sub> uptake for both SBA-15 and MSBA-15 at various temperatures and pressures.

Material	1 bar		200 bars		
	0 °C	25 °C	45 °C	55 °C	65 °C
SBA-15 (mmol/g)	0.5737	0.6462	110.34	103.078	94.38
MSBA-15 (mmol/g)	1.6164	1.6510	110.64	103.39	94.581



**Fig. 5.** Thermogravimetric analysis of synthesized material (SBA-15) and amine modified material (MSBA-15).

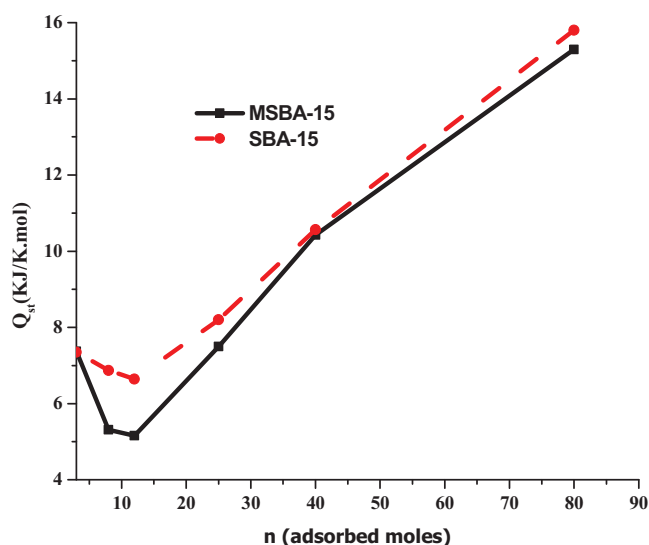


Fig. 7. Effect of adsorbed CO<sub>2</sub> quantity on the isosteric heat of adsorption in case of SBA-15 and MSBA-15.

318 K to 338 K, however, accessibility of CO<sub>2</sub> molecules to the active sites within the pore of materials became limited which in turn reduce the number of adsorbate (Bollini et al., 2012b). Additionally, adsorbed phase density of CO<sub>2</sub> is a function of temperature at supercritical elevated temperature and pressure (Sakurovs et al., 2010). This means that, at higher temperature and constant pressure, CO<sub>2</sub> molecule access to the attractive sites reduces which subsequently limiting the number of gas molecules within the pore, thus resulting in less number of moles accommodated by the micropores of materials. Furthermore, affinity of gas molecules also reduces as temperature is increasing, since gases affinity is inversely related to the absolute temperature at constant pressure.

Heat of adsorption (shown in Fig. 7) has been estimated with the standard Clausius–Clapeyron equation (Awadallah-F and Al-Muhtaseb, 2013) for different moles of CO<sub>2</sub> adsorbed by modified and non-modified SBA-15 materials at three temperatures of 318 K, 328 K and 338 K. The isosteric heat ( $Q_{st}$ ) of adsorption was calculated for selected moles of adsorbed CO<sub>2</sub> based on the slope of the linear plot obtained from  $\ln P$  vs  $1/T$ . Similar to literature (Zhou et al., 2014), a decline in the heat of adsorption was observed from around 7.3 kJ/kmol up to 5.15 kJ/kmol and 6.64 kJ/kmol for MSBA-15 and SBA-15 respectively. As shown in Fig. 7 both modified and non-modified materials behave similarly, i.e. heat of adsorption first reduces and then increases linearly with the amount adsorbed (Delgado et al., 2006).

This lowering effect in heat of adsorption in the lower range (up to 12 mol/kg) of adsorbed gas can be attributed to the strong affinity of CO<sub>2</sub> by the attractive site of materials (Himeno et al., 2005). It must be noted that initially all the attractive sites are unoccupied and have strong affinity to capture CO<sub>2</sub> molecule within the pore and on the surface of the materials. Additionally, modified MSBA-15 material possesses more attractive sites than the non-modified because of the insertion of the NH<sub>2</sub> molecule within the pore. Therefore, initially, due to the availability of the empty sites (more in modified and less in non-modified materials) strong interaction between CO<sub>2</sub> molecules and attractive site is taking place which consequently lessen the heat of adsorption. Since in case of MSBA-15 the interaction of CO<sub>2</sub> molecules with attractive sites is more due the presence of function group, therefore, the lessening effect in heat of adsorption is also larger than SBA-15 up to 12 moles/kg. After occupancy of most of the attractive sites by CO<sub>2</sub> in both the materials, adsorption increases due to the pressure increment which mostly involves condensation of the adsorbed gas,

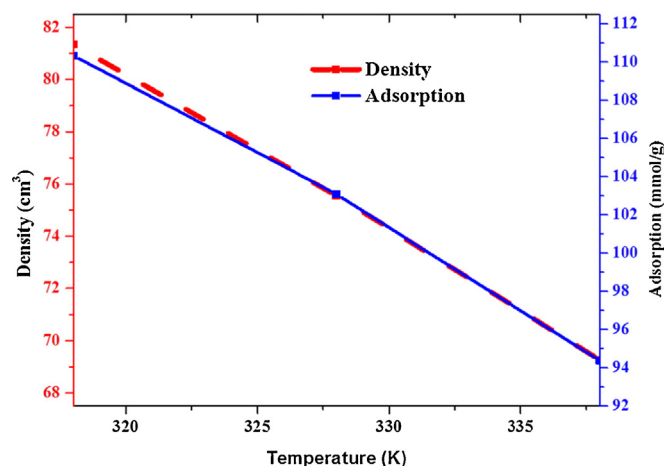


Fig. 8. Effect of temperature on CO<sub>2</sub> density and adsorption on MSBA-15.

resulting in the enhanced heat of adsorption. It is worth mentioning here that, unlike lower pressure performance, at higher pressure, both the materials adsorbed almost same value of CO<sub>2</sub> indicating ineffectiveness of amine group at high pressure and large adsorption quantities. Fig. 8 also suggest that at high pressure (or in other words at larger adsorption quantities) role of function group in the adsorption process is not very clear, but both modified and non-modified behave exactly with the same manner. It must be noted that, the maximum heat of adsorption for the adsorbed value of 80 mol/kg in our case is about 15 kJ/kmol which is the lowest as compared to other materials (Mello et al., 2011) such as amine modified SBA-15 (Zhou et al., 2014), activated carbon (Himeno et al., 2005, Awadallah-F and Al-Muhtaseb, 2013) covalent organic polymers (Dawson et al., 2011; Patel et al., 2013) and MOF (Li et al., 2011).

Comparing Figs. 8 and 9 it is evident that both density and adsorption are linear functions of temperature, since, adsorption is reducing with temperature exactly at the same rate as the density of CO<sub>2</sub>. It is important to mention that similar behavior of reduction in the adsorption of CO<sub>2</sub> at higher temperature have been observed in literature although with different adsorbents materials, i.e. zeolite (Sheikh et al., 1996; Cavenati et al., 2004) and mesoporous silica. It must be noted that, data of the variation of density and variation of adsorbed CO<sub>2</sub> with temperature was obtained experimentally at pressure of 200 bars, where the density variation for

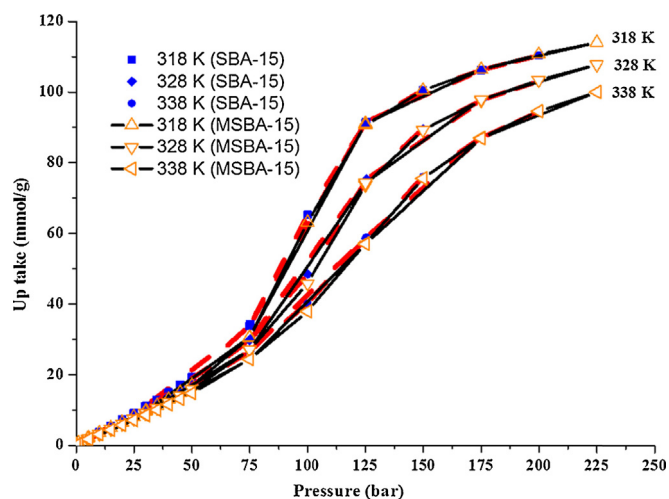
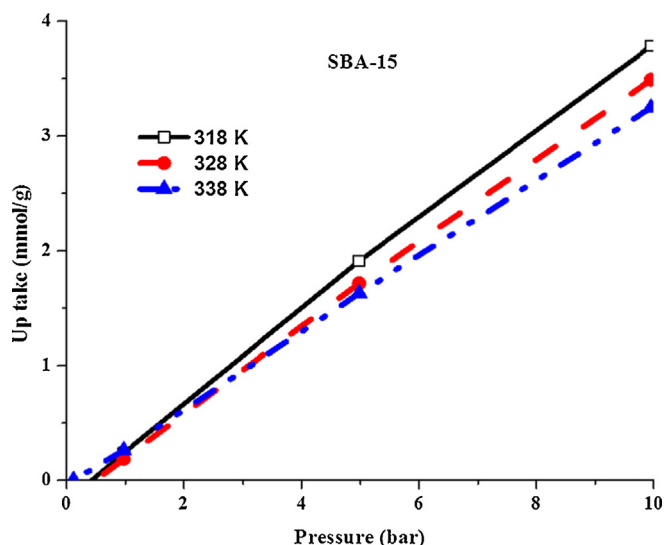


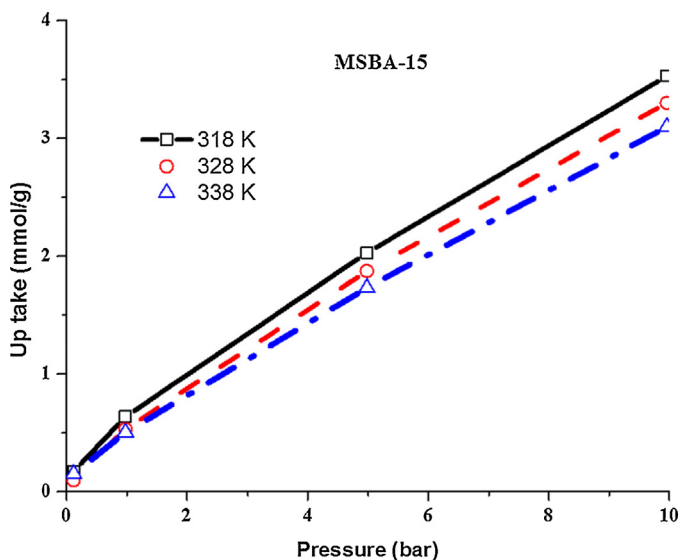
Fig. 9. CO<sub>2</sub> adsorption on SBA-15 and MSBA-15 at higher pressure of 200 bars and three different temperatures (318 K, 328 K, and 338 K).



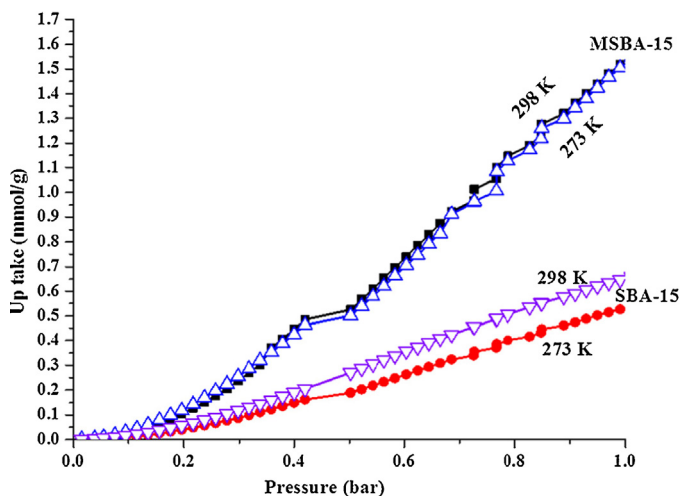
**Fig. 10.** CO<sub>2</sub> adsorption on SBA-15 at pressure of 10 bars and three different temperatures (318 K, 328 K, and 338 K).

CO<sub>2</sub> was also confirmed with NIST and REFPROP software. Mainly three factors; reduction in density, reduction in CO<sub>2</sub> affinity and high heat of adsorption are contributing to the lower adsorption at elevated temperature. Detail investigation of Figs. 9–11 reveals that difference between the adsorption isotherms at three temperatures (318 K, 328 K and 338 K) and lower pressure (<5 bar) is significantly smaller than that at pressure above than 10 bars. Additionally, this difference in the adsorption isotherms at three temperatures becomes stable beyond 10 bars indicating the only effect of pressure on the adsorption process. Zhou et al. has attributed such behaviors of the adsorption isotherms at different temperatures to the variation in the adsorption mechanisms, i.e. chemisorption at lower pressure and physisorption at higher pressure (Zhou et al., 2014). However, it can be argued that at pressure of around 1 bar decline in the affinity and density of CO<sub>2</sub> gas start, which is increasing gradually with pressure and become stable after 10 bars.

Figs. 10 and 11 indicate that adsorption of CO<sub>2</sub> at various temperatures initially varies as 338 K > 328 K > and 318 K and increases with increase in pressure at particular temperature, however, at



**Fig. 11.** CO<sub>2</sub> adsorption on MSBA-15 at higher pressure of 10 bars and three different temperatures (318 K, 328 K, and 338 K).



**Fig. 12.** CO<sub>2</sub> adsorption by SBA-15 and MSBA-15 at 1 bar and lower temperatures of 273 K and 298 K.

around 1 bar this trend reverses to 318 K > 328 K > and 338 K. Such inversion effect in adsorption of CO<sub>2</sub> (toward lower capacities) by SBA-15 with respect to temperature was also detected in literature but at different pressure of about 0.01 bars (Gargiulo et al., 2014). Although, such reduction in adsorption capacities at elevated temperature was regarded to the weak interaction of CO<sub>2</sub> and mesoporous silica materials (Xu et al., 2002), however, we assume that, affinity of the adsorbing gas molecules is changing or in other words drastically decreasing by increasing temperature at a particular pressure which causes significant decline in the adsorption.

This inversion of adsorption from higher to lower quantity due to temperature increment is not very clear when the material was modified with amine functional group (Yan et al., 2013a,b; Xu et al., 2002). Obviously amine modified SBA-15 (Fig. 11) has larger attraction, since, amine loading enhances CO<sub>2</sub> affinity (Danon et al., 2011; Choi et al., 2011; Kuwahara et al., 2012; Buonomenna et al., 2013). Thus, affinity of CO<sub>2</sub> in case of amine modified SBA-15 may be very limitedly affected with temperature modification, however, active sites inaccessibility by CO<sub>2</sub> molecules is still taking place, which subsequently causes reduced adsorption at high temperature. Thus at around 10 bars both SBA-15 (Fig. 10) and MSBA-15 (Fig. 11) have almost similar adsorption trends at different temperatures of 318 K, 328 K, and 338 K.

It must be noted that effect of density reduction became more obvious, when both the materials were subject to standard temperature and pressure, since at lower pressure of 1 bar adsorption of CO<sub>2</sub> was almost remained stable with increase in temperature from 273 K to 298 K (Fig. 12). This stability in CO<sub>2</sub> adsorption with increase in temperature between 273 K and 298 K at lower pressure may be associated to the combined effect of the following three mechanisms. It can be assumed that by increasing temperature from 273 K to 298 K (i) significant expansion in material pores is taking place due to the negative thermal expansion (Attfield, 1998) of mesoporous silica materials (i.e. material contraction due to increase in d-spacing) (Belmabkhout and Sayari, 2009a,b), (ii) affinity of CO<sub>2</sub> toward the active sites of pores is diminishing, since affinity is inversely related to the square route of temperature (Gargiulo et al., 2014), and (iii) adsorption is simultaneously taking place both at material surface and on the inside pores. Although, Yan et al. (2011a,b) have detected an un-reasoned pore expansion behavior in SBA-15 due to the increase in temperature, at larger CO<sub>2</sub> adsorption, however, the lower CO<sub>2</sub> up take at 273 K than 298 K but SBA-15 may be mainly attributed to the lessening of

**Table 3**  
Comparison of CO<sub>2</sub> experimental and NIST densities.

Temperature (K)	Pressure (bars)	NIST density (g/cm <sup>3</sup> )	Measured density (g/cm <sup>3</sup> )		State (NIST)
			During SBA15 experiments	During MSBA15 experiments	
298	64.3	0.2427	–	–	Vapor
298	64.3	0.7105	–	–	Liquid
318	75	0.2093	0.2029	0.2018	Supercritical
328	75	0.1822	0.1796	0.1719	Supercritical
338	75	0.1649	0.1621	0.1620	Supercritical

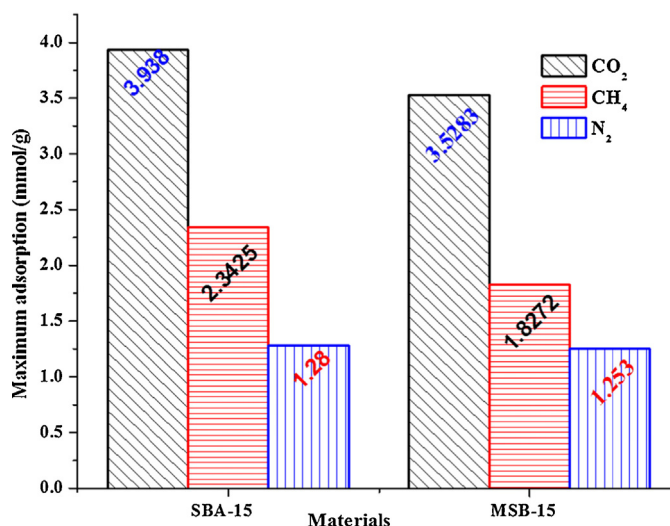
affinity with increase in temperature. Fig. 12, further reveals that at lower temperatures (273 K and 298 K) and lower pressure (up to 1 bar), effect of amine loading on SBA-15 is significant in capturing more CO<sub>2</sub>, however, function of amine group is almost negligible at higher pressure and temperature. Lower adsorption capacity at lower temperature observed in modified SBA-15 was attributed to the decrease in diffusion of CO<sub>2</sub> at lower temperature due to the presence of the PEI (poly(ethylene mine)(Yan et al., 2011a,b).

This significant CO<sub>2</sub> adsorption by MSBA-15 at lower pressure and lower temperature may be attributed to the additional affinity introduced by the amine function group (Belmabkhout and Sayari, 2009a,b). However, after achieving saturation (i.e. most of the NH<sub>2</sub> active sites in MSBA-15 are being occupied by CO<sub>2</sub>), only physical adsorption is taking place at higher pressure (above 1 bar) and higher temperatures (318 K and above), resulting in almost similar adsorption by SBA-15 and MSBA-15 (Mello et al., 2011).

Adsorption–desorption isotherms shown in Fig. 9 at three different temperatures (318 K, 328 K, and 338 K) and high pressure of 200 bars demonstrate type IV characteristics with a significant increase in CO<sub>2</sub> adsorption starting at pressure range of about 75 bars. This significant behavior of CO<sub>2</sub> adsorption at high pressure (above 75 bars) and high temperature can be attributed to (i) the considerable increase in the density of CO<sub>2</sub> at these particular conditions (Gensterblum et al., 2009, 2010) and (ii) to the modification of quadrupole moment of CO<sub>2</sub> (Bonenfant et al., 2008). As shown in Table 3 behavior of CO<sub>2</sub> in the supercritical condition varies from vapor to liquid (Stefanopoulos et al., 2012), which causes increase in CO<sub>2</sub> density with a major jump from 0.2427 g/cm<sup>3</sup> to 0.7105 g/cm<sup>3</sup> at 298 K and critical pressure of 65 bars. Table 3 further reveals that density of CO<sub>2</sub> adsorbed by the material is exactly matching with that of the supercritical CO<sub>2</sub> (NIST data) confirming the liquidity of CO<sub>2</sub> under these experimental conditions. However, a minute decrease in the experimental values can be the reason of difference in the density of CO<sub>2</sub> adsorbed on the surface and adsorbed within the pore of the material (Sakurovs et al., 2010). Density of CO<sub>2</sub> adsorbed on the outer surface is dissimilar to that inside the pore of the material, since, a strong interaction of CO<sub>2</sub> with Si–O–Si and Si–OH on the outer surface may modify CO<sub>2</sub> behavior on the outer surface as compare to inner pore condition. This effect is prominent in case of MSBA-15, where the surface adsorption is slightly higher than the unmodified material due to the presence of amine function group. Additionally, densities of adsorbed phase and gas phase are not identical (Poirier and Dailly, 2008; Watson et al., 2009) since, CO<sub>2</sub> volume is decreasing inside the pores of adsorbent as compared to the free condition (Schneider et al., 2004). Sharp increase in CO<sub>2</sub> adsorption at critical condition (i.e. at/and above 318 K and 75 bar) can be attributed to the combined effect of (i) abrupt decrease in volume and (ii) enhanced quadrupole moment of CO<sub>2</sub> at/and above the critical temperature and pressure. Almost similar effect of exponential increase in adsorption at the supercritical pressure and temperature range have been observed for materials such as hydrotalcite derivatives (Karadas and Atilhan, 2012), coal matrix (Krooss et al., 2002; Gensterblum et al., 2010), activated carbon (Chen et al., 1997) and covalent organic polymers (COPs), which was mainly attributed to the enhanced affinity caused by the

presence of nitrogen content in the sorbent (COPs materials) (Patel et al., 2012). Consequently, same adsorption behavior of CO<sub>2</sub> for different types of material within the same range of pressure and temperature (supercritical) would suggest combined effect of the density enhancement (of adsorbate) and strong columbic interaction (Stefanopoulos et al., 2012) between adsorbate and adsorbent active sites leading to the increased adsorption by various sorbents. Quadruple moment (Buckingham and Disch, 1963) and structural modification of CO<sub>2</sub> (Shi et al., 2005) play an important role which lead to the enhanced adsorption at supercritical condition. Quadrupole moment of CO<sub>2</sub> may increase at elevated temperature (Kemmere, 2006) and pressure (Christoe and Drickamer, 1970) introducing significantly strong columbic interaction with basic sites (Liu et al., 2013) of mesoporous SBA-15, resulting in increased adsorption. Thus, it can be concluded from above discussion that, at supercritical condition adsorption of CO<sub>2</sub> peaks up due the significant enhancement in the density and quadrupole moment. However, this substantial adsorption saturates at around 130 bars, getting stable at value of 95 mmol/g and then reaches to the maximum value of 101 mmol/g at/and above 200 bars. It is noteworthy to mention that, unlike conventional adsorbent (Krooss et al., 2002; Ustinov and Do, 2003), both SBA-15 and MSBA-15 (Fig. 9) have shown very stable performance without any decline in the adsorption characteristic even after saturation at 200 bars and beyond.

Fig. 13 shows the comparative adsorption isotherms for three main gasses (i.e. carbon dioxide, nitrogen and methane) at higher temperature of 318 K and pressure of 20 bars. Although, kinetic diameters of CO<sub>2</sub> (0.33 nm) and N<sub>2</sub> (0.36 nm) are smaller than that of CH<sub>4</sub> (0.38 nm) (Sakurovs et al., 2010), however, nitrogen adsorbed in much smaller quantity than the other two gases. Almost, similar trend in the adsorption quantities of gases (CO<sub>2</sub> > CH<sub>4</sub> > N<sub>2</sub>) has been observed in the literature for MCM-41 material (Belmabkhout and Sayari, 2009a,b; Belmabkhout et al.,



**Fig. 13.** Adsorption selectivity of CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub> on SBA15.



2009). The adsorption trend ( $\text{CO}_2 > \text{CH}_4 > \text{N}_2$ ) shown in Fig. 13 can be mainly attributed to the affinity rather than the kinetic diameters of the gases, since SBA-15 may have comparatively higher selectivity for  $\text{CO}_2$  than for the other two gases. This selective adsorption behavior of SBA-15 and MSBA-15 is advantageous for the gases separation and materials can be utilized for the flue gas separation on industrial scale. It is evident from chart bar that at 318 K and pressure up to 10 bars pressure MSBA-15 capture almost 3 times more  $\text{CO}_2$  than  $\text{N}_2$  and 2 times more than methane (Krooss et al., 2002). This represent that, selectivity of  $\text{CO}_2$  is further increasing with increase in pressure (Ho et al., 2008) and temperature (Zhao et al., 2010), which make this material more attractive for high-pressure adsorption and separation of  $\text{CO}_2$  from flue gases.

#### 4. Conclusion

Although, amine loading has reduced the surface area and pore volume almost to the half values of unmodified material, however, twofold increase in  $\text{CO}_2$  adsorption was observed in case of MSBA-15 at low pressures and temperature as compared to SBA-15 indicating effect of increased affinity due to  $\text{NH}_2$  molecule. On the other hand at higher pressure and higher temperature both modified and unmodified materials adsorbed similar quantity of  $\text{CO}_2$  suggesting saturation of the functional molecules at supercritical condition. At lower pressure of 1 bar both the materials have similar behavior of same adsorption characteristics at 273 K and 298 K, which was mainly attributed to the pore expansion of materials and reduced affinity of  $\text{CO}_2$  at temperature of 298 K. Alternatively, at higher temperatures and constant higher pressure (above 10 bars)  $\text{CO}_2$  adsorption varies as  $318\text{ K} > 328\text{ K} > 338\text{ K}$  suggesting reduction in the affinity at higher temperatures. Over all  $\text{CO}_2$  adsorption of both modified and unmodified SBA-15 at higher pressure of 200 bars was almost similar having the highest adsorption capacity of 110 mmol/g at 318 K and about 103 mmol/g at 338 K.  $\text{CO}_2$  adsorption isotherms of both the materials at three different temperatures have identical type IV characteristics with a major rise at the supercritical pressure (65 bars) and temperature which was extended up to 130 bars. This significant jump in the adsorption at supercritical condition was mainly attributed to the abrupt increase in the density as well as to the strengthening of the quadrupole moment of adsorbed  $\text{CO}_2$  at supercritical condition. SBA-15 and MSB-15 were also tested for the selective adsorption of other two flue gases (i.e. methane and nitrogen) at higher temperature of 318 K and pressure of 10 bars. Results revealed that both the materials exhibited exactly similar selectivity performance for the three gases which was recorded as  $\text{CO}_2 > \text{CH}_4 > \text{N}_2$ . Based on the present findings it can be suggested that, amine modified SBA-15 could be better option for  $\text{CO}_2$  adsorption at lower pressure and lower temperature (post combustion conditions), while pristine SBA-15 may have the better performance at higher pressure and higher temperature. Importantly, both MSBA-15 and SBA-15 have very low heat of adsorption as compared to the other solid sorbent including SBA-15 and possess strong thermal and mechanical stability when used repeatedly at elevated temperature and pressure.

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