

Adsorption Behaviour of Si-MCM-41 for CO₂: Effect of Pressure and Temperature on Adsorption

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Adsorption process is an alternative process for CO₂ removal which could offer solutions to the existing problems associated with absorption process. A suitable adsorbent which has high adsorption capacity and selectivity for CO₂ is required in adsorption process. Highly ordered siliceous mesoporous molecular sieve, Si-MCM-41 which has high surface area and large pore volume is an attractive candidate for use as adsorbent in the adsorption separation. Si-MCM-41 material was synthesized by hydrothermal process at 100 °C for 8 days then dried at 120 °C for 24 hours and finally calcined at 550 °C for 6 hours. Calcined Si-MCM-41 was characterized by XRD, FTIR, HRTEM and N₂ physisorption. All the characterization results confirm that the synthesized material is Si-MCM-41. Adsorption behaviour of Si-MCM-41 for CO₂ was investigated at temperatures between 25 - 100 °C and pressures from 0 - 20 bar using Rubotherm gravimetric-densimetric apparatus. Si-MCM-41 showed low adsorption capacity of 27.43 mg-CO₂/g-adsorbent at 1 bar and 25 °C. This low adsorption of CO₂ on Si-MCM-41 could be attributed to the weak interaction between the siliceous material and CO₂. Results show that adsorption of CO₂ increases with increasing pressure and at it reaches to 296.48 mg CO₂/g-adsorbent at 20 bar which can be explained as the CO₂ molecules are forced into the deep inside the pores of Si-MCM-41 at high pressure. The Si-MCM-41 material also shows an increased in CO₂ adsorption with increased temperature with 335.77 mg-CO₂/g-adsorbent adsorbed at 50 °C. However, further increase in temperature to 75 °C and 100 °C decreases the adsorption of CO₂ to 295.07 mg-CO₂/g-adsorbent and 269.86 mg-CO₂/g-adsorbent, respectively. This decrease in adsorption is suggested due to weakening of the Van der Waals forces between Si-MCM-41 and CO₂. Overall results show that Si-MCM-41 has high potential to be used as adsorbent for CO₂ removal at pressures up to 20 bar and temperatures up to 75 °C.

1. Introduction

There is a general consensus among the environmentalist, scientists and researchers that carbon dioxide (CO₂) emission is rising gradually in the atmosphere mainly due to increase in combustion of fossil fuels. Naturally, CO₂ exists in the atmosphere as a component of carbon cycle. Human activities are changing the natural carbon cycle, mainly by adding more carbon dioxide to the earth's atmosphere and by deforestation that naturally keeps the carbon cycle in equilibrium.

CO₂ gas is a prominent greenhouse gas, the accumulation of CO₂ in the atmosphere causes a "greenhouse effect", allowing incoming sunlight to penetrate but trapping heat radiated back from earth (Edmonds and Reilly, 1983). Since the industrial revolution, CO₂ emission is increasing in the atmosphere (Hofmann et al., 2009). The CO₂ is the main driver for global warming. The main source of the emission of CO₂ is the combustion of fossil fuels (i.e. oil, coal and natural gas) used for necessity of energy and transportation. Other sources of CO₂ emissions are renewable fuels like combustion of biomass and from certain industrial processes (Metz et al., 2005). About 90 % of total global CO₂ emission comes from combustion of fossil fuels excluding biomass combustion (Oliver et al., 2013). Continuous rise of CO₂ in the atmosphere due combustion of fossil fuels and deforestation has endangered this planet and

humankind due to the threat of global warming. For this purpose immediate measures are needed to reduce the CO₂ emission. This is need of the time to ponder on it seriously in order to avoid any kind of disaster in future.

Various options have been introduced for CO₂ reduction, mainly, reducing the use of fossil fuels, substituting less carbon – intensive fossil fuels for more carbon – intensive fossil fuels, replacing fossil fuel technologies with near zero – carbon alternatives, enhancing the absorption of atmospheric CO₂ by natural system and carbon dioxide capture and storage (CCS) (Oliver et al., 2013). Last option is fascinating more than above all, only for capturing of CO₂ various technologies have been introduced. CO₂ also exists as an impurity in natural gas, hydrogen gas and fuel gas productions, its presence reduces significantly the energy content of these gases (Ma et al., 2009). Currently, all commercial CO₂ capture plants use processes based on chemical absorption using solvents alkanolamine such as monoethanolamine (MEA) throughout the world. However, chemical absorption processes suffer from some major problems like high regeneration energy, large equipment size, solvent degradation, equipment corrosion and high viscosity (Xu et al., 2005). Avoiding from these problems, new cost – effective advanced approaches are needed to find for CO₂ separation.

Adsorption is the most favorable method that could be appropriate for separating CO₂ from gas mixtures. Adsorption separation fascinate due to its low energy requirement, cost advantage, and ease of applicability over relatively wide range of temperatures and pressures (Xu et al., 2005). For practical use of adsorption method, the first and most important issue is to develop a suitable adsorbent, with high CO₂ selectivity and high adsorption capacity, and which can also be operated relatively at wide range of temperatures and pressures. For this purpose, an adsorbent is needed with high surface area, large pore size and large pore volume that can adsorb large quantity of CO₂. These features are present in the mesoporous molecular sieve MCM-41.

MCM-41 is a member of M41S family synthesized by Mobil Corporation in 1992. Due to its remarkable features it has been studied widely for various applications. MCM-41 possesses numerous special features *i.e.* variable pore size (15 -100 Å and above), well-defined pore shapes (hexagonal/cylindrical), high surface area (>700 m²/g), pore volume 0.7 – 1.2 cm³/g, good thermal and hydrothermal stability, uniform pore size and shape over micrometer length scale, negligible pore networking or pore blocking effects, very high degree of pore ordering over micrometer length scale, large number of internal hydroxyl (silanol) groups (~40-60 %), high surface reactivity, ease of modification of surface properties (Selvam et al., 2001). Due to these special features it has high prospect being used as an adsorbent for CO₂ separation.

Herein, Siliceous Mesoporous Molecular Sieve (Si-MCM-41) has been synthesized and characterized by various techniques. Si-MCM-41 was investigated for its behavior towards carbon dioxide (CO₂) adsorption at low and high pressure (*i.e.* 0 – 20 bar). The effect of temperature was also investigated at four different temperatures (*i.e.* 25, 50, 75 and 100 °C) on CO₂ adsorption capacity.

2. Materials and Methods

2.1 Synthesis of Si-MCM-41

Siliceous Mesoporous Molecular Sieve (Si-MCM-41) was synthesized by hydrothermal process at 100 °C for eight days duration (Ramli et al., 2012). In a typical synthesis procedure was followed as; 18.7 g of sodium silicate (Na₂SiO₃) was dissolved in 40 g of deionized water in a beaker. In another beaker, 16.77 g of hexadecyltrimethylammonium bromide was dissolved in 50.23 g of deionized water. Then sodium silicate solution was poured into the surfactant solution and pH of the solution was maintained to 10 by adding sulphuric acid drop wise. The mixture was stirred for 30 minutes, before 20 g of deionized water was added into the solution. The mixture was then sealed in Teflon-lined stainless autoclaves and kept for eight days at 100 °C for crystallization under static condition in an oven. The obtained product was filtered, washed with copious amount of deionized water and then dried at 120 °C for 24 h. The as-synthesized Si-MCM-41 was calcined at 550 °C for 6 hours at heating rate of 5 °C/min.

2.2 Characterization

The X-ray diffraction (XRD) analysis of Si-MCM-41 was carried out using Bruker D8 Advance diffractometer (Germany). The scanning was performed in the $2\theta = 1^{\circ}$ - 10° scale with 0.010° step size and 4 s step time. Fourier transform infrared (FTIR) spectrum was recorded at room temperature on a SHIMADZU 8400S spectrometer. The FTIR spectra were obtained in the 400-4,000 cm⁻¹ region in the transmittance mode. Surface morphology was examined by Variable Pressure Field Emission Scanning Electron Microscopy (VPFESEM). VPFESEM micrograph was acquired on a ZEISS 55 Supra VP microscope at accelerated voltage of 7.00 kV and at 30,000 magnifications. The pore shape and

arrangement was examined using Zeiss Libra 200FE High Resolution Transmission Electron Microscope (HRTEM). Nitrogen adsorption-desorption analysis was carried out by using Micromeritics ASAP 2020 volumetric adsorption analyzer, using Nitrogen (N₂) gas as an adsorbate at -196 °C over 0.01 to 1 relative pressure (P/P₀). Prior to the analysis, pristine Si-MCM-41 samples were degassed for 2 h at 250 °C.

2.3 CO₂ Adsorption Measurement

CO₂ adsorption studies were carried out by Rubotherm gravimetric – densimetric apparatus (Bochum, Germany). It is generally composed of Magnetic Suspension Balance (MSB), the automatic gas dosing and pressure control system, (containing a network of valves, mass flow meters and pressure sensors), Jumo Imago (temperature control system of electric heater), Julabo thermostat (circulating liquid to control the temperature of the sample chamber), a vacuum pump. In a typical adsorption experiment, a blank measurement of the empty sample container was carried in nitrogen gas atmosphere at 100 mL/min at 25 °C. The blank measurement was carried out to determine the mass and volume of sample container (M_{SC} and V_{SC}). After the blank measurement, the adsorbent is weighed and placed in a sample container. The cell in which the container is housed is then closed and high pressure is applied to check any leakage in the system. Leak test was performed whenever the chamber is dismantled. The adsorbent was then reactivated in the vacuum at 100 °C till there was no more weight loss, from where mass of the sample (M_S) is obtained. After reactivation, the sample was cool down to the analysis temperature. After cooling down, a buoyancy measurement was performed at the temperature desired for adsorption measurement using Helium (He) gas at flow rate of 100 mL/min. The buoyancy measurement gives the volume of suspension system (V_{SS}), from which volume of sample (V_S) is obtained. Helium gas is an inert gas that penetrates in all open pores of the materials without being adsorbed. For CO₂ adsorption measurement, first the system was evacuated to vacuum. Then the sample was exposed to flowing pure CO₂ with flow rate of 100 mL/min at desired temperature. The temperature during adsorption measurements was held constant by using thermostated circulating fluid. The data was received by *Mess Pro* software and all the operations were performed by this software.

Amount of CO₂ adsorbed was calculated using the following equation:

$$m_{CO_2} = \Delta m - (M_{SC} + M_S) + (V_{SC} + V_S) * \rho_{CO_2} \quad (1)$$

3. Results and Discussion

3.1 Characterization of Si-MCM-41

The structural properties of the Si-MCM-41 sample were characterized by XRD measurement. The XRD diffractogram of the calcined Si-MCM-41 is shown in Figure 1 and it reflects the high quality material. XRD diffractogram of MCM-41 material exhibits a typical four peaks pattern with a very strong peak a low angle (100) and three another weaker peaks at higher angle (110, 200 and 210). The absence of last three peaks suggests the disordered structure of MCM-41 (Blin et al., 2001). The XRD analysis of Si-MCM-41 displayed well-defined XRD pattern exhibits characteristic four diffraction peaks i.e. a high intensity peak and three low intensity peaks. The occurrences of these peaks on 2-theta scale are in the range of 1 – 10°. A high intensity peak (100) was found at ~2.1° and a series of three low intensity peaks 110, 200 and 210, were found at ~3.6°, ~4.2° and ~5.6° on 2-theta scale, respectively, which indicate well-ordered hexagonal structure present in MCM-41. The presence of these diffraction peaks suggests the long range order present in the frame work of Si-MCM-41 and exhibits hexagonal array of cylindrical pores (Jiang et al. 2008). All four XRD peaks can be indexed on a hexagonal lattice. The presence of one or two low angle x-ray diffraction peaks in XRD diffractogram shows the disordered structure in the material (Beck et al., 1994). XRD diffractogram suggests a highly ordered hexagonal pore structure by the existence of four well-resolved diffraction peaks at low angles (Mokhonoana and Coville, 2010).

FTIR spectrum of calcined Si-MCM-41 is shown in Figure 2. FTIR spectrum of Si-MCM-41 was obtained in the range of 400 – 4,000 cm⁻¹ in transmittance mode. A broad band around 3,500 cm⁻¹ attributed to hydrogen bonded surface silanols (Si-OH) and adsorbed water molecules due to O-H stretching while a band at around 1,635 cm⁻¹ due to bending vibration of adsorbed water molecules. A band at 964 cm⁻¹ is assigned to Si-O stretching in Si-OH and is the characteristic peak indicating formation of hexagonal phase in MCM-41 (Aniba et al., 2012). A strong band at 1,080 cm⁻¹ and with a shoulder band at 1240 cm⁻¹ attributed to asymmetric stretching vibrations of Si-O-Si bridges and a band at 794 cm⁻¹ is attributed to symmetrical Si-O-Si stretching (Grisdanurak et al., 2003).

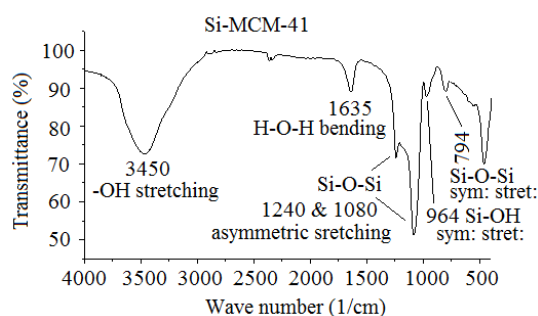
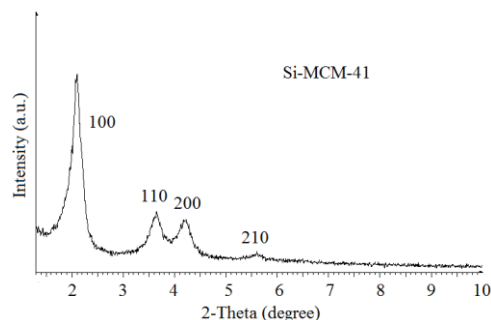


Figure 1. XRD diffractogram of calcined Si-MCM-41 Figure 2. FTIR spectrum of calcined Si-MCM-41

N_2 adsorption-desorption isotherm of Si-MCM-41 is depicted in Figure 3. N_2 adsorption – desorption analysis used to determine the surface area, pore volume and pore size distribution (Araujo et al., 2005). The surface area, pore size distribution and pore volume obtained on the basis of BET method (Brunauer et al., 1938) and BJH method (Barrett et al., 1951). Table 1 shows the BET surface area, pore size and pore volume of Si-MCM-41. From Figure 3, it can be seen that calcined Si-MCM-41 exhibits typical type IV isotherm with *H1* type hysteresis loop and capillary condensation of nitrogen at relative pressure $p/p_0 = 0.35 - 0.41$, that are the characteristic features of the isotherm related to mesoporous solids (Cheng et al., 1997). Three noticeable regions of the N_2 adsorption – desorption isotherm were observed. Monolayer – multilayer adsorption of N_2 on the walls of the mesopores was observed at low pressures ($p/p_0 < 0.35$) followed by a sharp inflection in the adsorption isotherm in a range of relative pressure $p/p_0 = 0.35 - 0.41$ due to capillary condensation of N_2 in the primary mesopores. The inflection point is associated to the pore diameter of the material. The sharpness of the inflection point (Figure 3) indicates that the synthesized Si-MCM-41 has very uniform pore diameters. The final feature of the adsorption isotherm is saturation at $p/p_0 > 0.41$ (Tai et al., 2005).

HRTEM micrograph of calcined Si-MCM-41 is illustrated in Figure 4. HRTEM analysis provides the information of the pore shape and arrangement. HRTEM analysis corroborated the findings of X-ray diffraction, FTIR, and N_2 adsorption-desorption. Micrograph shows that Si-MCM-41 exhibits long range order and regular array of uniform hexagonal pore arrangements like honeycomb structure. This well-ordered hexagonal pore structure arrangement is characteristics of typical MCM-41 consistent with the literature reported (Sayari et al. 2000).

Table 1: Textural Properties of calcined Si-MCM-41

Surface area (m^2/g)	Pore Size (nm)	Pore volume (cm^3/g)
994	3.03	1.0

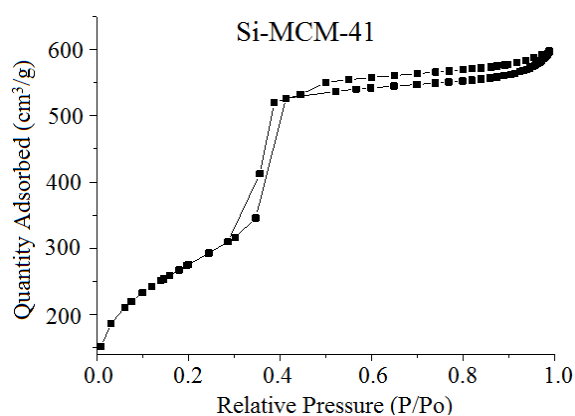


Figure 3. N_2 adsorption-desorption isotherm of calcined Si-MCM-41

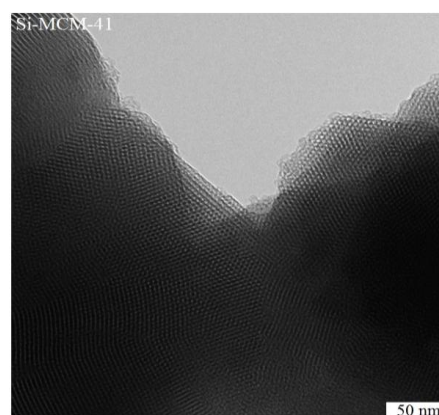


Figure 4. HRTEM micrograph of calcined Si-MCM-41

3.2 Carbon dioxide (CO₂) adsorption studies

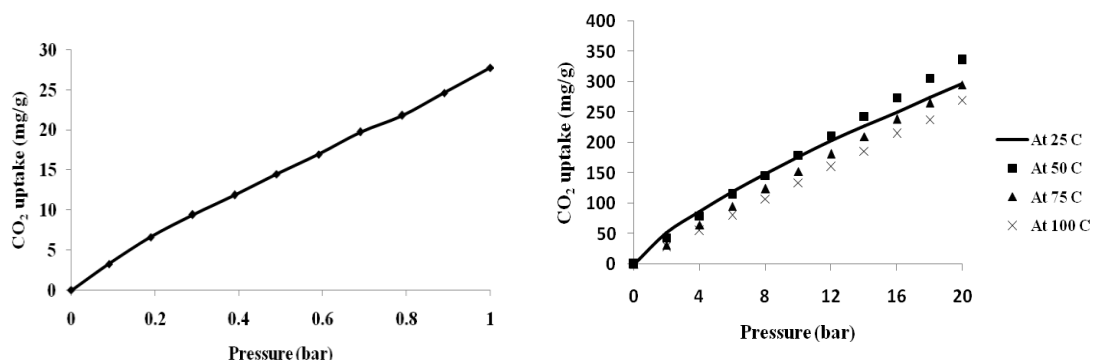


Figure 5. CO₂ adsorption isotherm using Si-MCM-41 at 25 °C and 0-1 bar

Figure 6. CO₂ adsorption isotherms using Si-MCM-41 at 25-100 °C and 20 bar

CO₂ adsorption study on Si-MCM-41 was carried out gravimetrically in pure CO₂ atmosphere at 25 °C and 1 bar pressure. Adsorption isotherm of CO₂ on pure Si-MCM-41 is shown in Figure 5. Si-MCM-41 showed adsorption uptake capacity of CO₂ is 27.78 mg/g. This low adsorption uptake of CO₂ was suggested due to weak interaction between Si-MCM-41 material and CO₂ molecules. Adsorption isotherm of Si-MCM-41 was found to be linear that shows with increase in pressure adsorption of CO₂ increased. This shows that adsorption capacity of Si-MCM-41 is dependent on pressure. The CO₂ adsorption result of Si-MCM-41 is consistent with results reported in the literature (Belmabkhout et al., 2009).

Adsorption of CO₂ on Si-MCM-41 was also studied at high pressure from 0 – 20 bar. Due to high surface area, cylindrical pore structure, large pore size and pore volume, Si-MCM-41 can accommodate large quantity CO₂ at high pressure. Figure 6 illustrates CO₂ adsorption isotherm at pressure up to 20 bar and 25 °C. Si-MCM-41 showed high adsorption capacity of CO₂ at high pressure (20 bar). The textural properties of Si-MCM-41 facilitate the CO₂ molecules to reside in pores at high pressure. This behaviour shows that with increase of pressure, CO₂ molecules are pushed inside the pores.

The effect of temperature on CO₂ adsorption isotherms was studied at 25, 50, 75 and 100 °C. Figure 7 shows that at the CO₂ adsorption capacity of Si-MCM-41 increases with increasing in temperature from 25 °C to 50 °C. However, when the temperature was further increased to 75 and 100 °C, the CO₂ adsorption decreased to 295.07 mg/g and 269.86 mg/g, respectively. This is attributed to the kinetic energy of CO₂ molecules which increases with increasing temperature thus resulted in a decrease in solubility of the gas molecules. Similar observation was previously reported by Saiwan et al. (2012).

4. Conclusions

Si-MCM-41, with uniform hexagonal pore arrangement was synthesized at 100 °C for eight days duration by hydrothermal method. Si-MCM-41 material calcined at 550 °C was characterized with XRD, FTIR, HRTEM, N₂ adsorption – desorption analyses. Characterization results verify that synthesized material is Si-MCM-41. CO₂ adsorption behavior of Si-MCM-41 was investigated from low to high pressure (i.e. 0-20 bar) and at increasing temperatures of 25, 50, 75 and 100 °C. At low pressure of 1 bar and 25 °C, Si-MCM-41 showed low adsorption capacity for CO₂ i.e. 27.78 mg/g, may be due to weak interaction. With increase of pressure up to 20 bar and 25 °C, adsorption of CO₂ increased, this behavior is suggested due to pushing of CO₂ molecules inside the pores. The rise of temperature from 25-50 °C showed increase of CO₂ adsorption i.e. 335.77 mg/g. This increase in uptake of CO₂ is suggested may be due to more available silanol groups for interaction and mobility of CO₂ molecules inside the pores. The increase of adsorption temperature at 75 °C and 100 °C showed gradual decrease in adsorption of CO₂ i.e. 295.07 mg/g and 269.86 mg/g, respectively. This behavior may be attributed to an increase in kinetic energy of CO₂ molecules at these temperatures which resulted in lesser solubility of the CO₂ molecules.

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