Stepwise Synthesis of Mesoporous Carbon Nitride Functionalized by Melamine Based Dendrimer Amines for Adsorption of CO_2 and CH_4

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ABSTRACT

In this study, a novel solid dendrimer amine (hyperbranched polymers) was prepared using mesoporous carbon nitride functionalized by melamine based dendrimer amines. This adsorbent was denoted MDA-MCN-1. The process was stepwise synthesis and hard-templating method using mesoporous silica SBA-15 as a template. Cyanuric chloride and N,N-diisopropylethylamine (DIPEA, Merck) were used for functionalization of the MCN-1. Fourier transform infrared spectroscopy (FT-IR), Nitrogen adsorption-desorption analysis, Small Angle X-ray Scattering (SAXS), X-ray diffraction (XRD) and thermogravimetric analysis (TGA) were used for characterization of the adsorbent. This material was used for carbon dioxide gas (CO_2) and methane gas (CH_4) adsorption at high pressure (up to 20 bar) and room temperature. The volumetric method was used for the tests of the gas adsorption. The CO_2 adsorption capacity of modified mesoporous carbon nitrides was about 4 mmol CO_2 per g adsorbent. The methane adsorption capacity of this material was less than that CO_2. Modified Mesoporous Carbon Nitride adsorbed about 3.52 mmol CH_4 /g adsorbent. The increment of melamine based dendrimer generation on mesoporous surface increased adsorption capacity of both carbon dioxide and methane gases. According to the results obtained, the solid dendrimer amines, (MDA-MCN-1), performs excellently for CO_2 and CH_4 capture from flow gases and CO_2 and CH_4 storage.

Keywords: Carbon dioxide; Methane; Adsorption; Mesoporous carbon nitride; Melamine.

1. Introduction

Carbon dioxide (CO_2) is famous greenhouse gas in the earth's atmosphere. Its atmospheric concentration has increased in 20th century and 1st decade of present century [1-3]. CO_2 as greenhouse gas plays major roles in global warming [4]. Several methods and strategies have been proposed for removal of this gas at experimental and industrial scales [5, 6]. Most important source of CO_2 emission is fossil burning. Using alternative sources of energy such as wind energy, solar energy and tidal energy are an effective alternative using fossil energy [5,7]. Other strategies are required to remove CO_2 emission due to use of fossil energy. One of these strategies is using sequestration and capturing methods. Adsorption on porous solid is

most applicable method in CO_2 capturing. Many of these materials to remove CO_2 in recent decades [8-10] have been reported.

In addition to CO_2 adsorption, these compounds also adsorb methane (CH_4) gas. Methane, the principle component of natural gas is available in large quantities and its combustion is cleaner than other high hydrocarbon combustion. Due to low critical temperature of CH_4 (191 K); it is always in gas form at in room temperature[11]. Storing of methane in safe, cheap and convenient manner is its main problem.

One method for storing of this gas in a safe manner is to physisorb the methane onto a porous solid. Recent studies indicate that porous solid such as nanoporous materials have good potential to adsorb CO_2 and CH_4 [11,12].

Nanoporous materials such as mesoporous silica [13,14], mesoporous carbons [15,16] and metal organic framework [11,17-19] have been used for removing CO_2 and storing CH_4. Mesoporous based carbon has varied properties such as low cost, wide availability, large surface area, easy to design pore structure, surface functionalization and low energy requirements and these properties make them as promising adsorbents for capturing CO_2 and storing CH_4 [12,20]. Among mesoporous based carbon; mesoporous carbon nitrides (MCNs), mesoporous carbons with nitrogen atoms in their structure, have the potential to adsorb CO_2 due to $CO_2 - N$ interaction [20]. Functionalization of MCN with other amine groups improves CO_2 adsorption.

Many researchers, however, only focus on CO_2 and CH_4 adsorption capacity of adsorbents at low pressure but industrial processes involve high pressure.

We report here the preparation of MCN-1 using ethylenediamine and carbon tetrachloride as precursors with the SBA-15 as a hard template. This template has hexagonal morphology and was prepared by sol-gel methods. For increasing of N content, melamine based dendrimer was added on MCN-1 by stepwise reactions. The CO_2 and CH_4 capture properties of this compound has been investigated at high pressure and room temperature.

2. Materials and Methods
2.1. Synthesis of mesoporous silica SBA-15

The Figure 1 shows stepwise synthesis schematically from mesoporous silica SBA-15 to Mesoporous Carbon nitride functionalized by Melamine based Dendrimer Amines. Mesoporous silica SBA-15 (as a hard template of MCN-1 synthesis process) was prepared by sol-gel method using Tetraethylorthosilicate (TEOS 98%, Merck), triblock copolymer non-ionic surfactant $EO_{20}PO_{70}EO_{20}$ (Pluronic P123, Aldrich) and Phosphoric acid (H_3PO_4, Merck) as silica precursor template respectively. In typical synthesis, P123 surfactant (4 g) was dissolved in H_3PO_4 (9 g) by stirring for 5 h at room temperature. Then, TEOS (9.6mL) was slowly added to that solution and stirred for 24 h at 313K. The mixture was then aged at 373K for 24 h under static conditions.
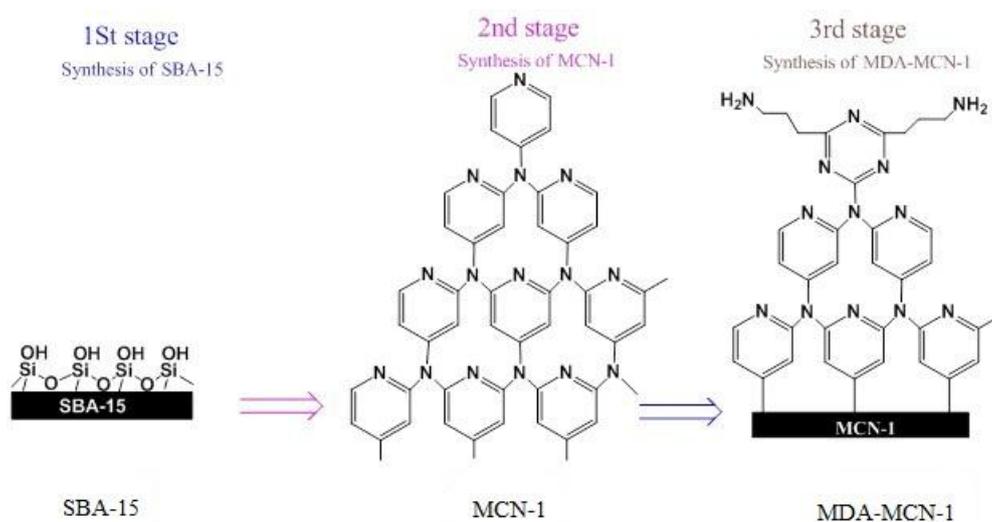
Fig. 1- Synthesis stages of MDA-MCN-1 from SBA-15 (hard template) to MDA-MCN-1.

The mixture was then allowed to cool at room temperature, and the white solid product was filtered, washed with distilled water for removing extra surfactant and then dried. The solid was calcined in a two steps procedure based on heating first at 523K for 3 hour, and then at 823K for 4 h. Complete surfactant removal was confirmed in all cases through thermogravimetric analysis and finally a white powder (SBA-15) was obtained [21].

2.2. Synthesis of MCN-1

The mesoporous carbon nitride support was synthesized by hard templating method and mesoporous SBA-15 as a template following the literature [21]. Briefly, the mixture of ethylenediamine (EDA, Merck, 2.2 g) and carbon tetrachloride (CCl$_4$, Merck, 5.4 g) was prepared by stirring at room temperature and 0.5g of calcined SBA-15 was added to this mixture. Then the EDA/CCl$_4$/SBA-15 mixture was refluxed and stirred at 363Kfor 6 hours. After that, the mixture was filtered and dried in oven for 12h. Carbonization of fine powder was performed by heat-treating in a nitrogen flow at 873 K with a heating rate of 3.0 K.min^{-1} for nearly 5 h .Then silica framework was dissolved by addition of treatment by hydrofluoric acid(5 wt% ,HF, Merck). The mesoporous carbon nitride was obtained by filtration, washing several times with ethanol, and drying at 373 K.

2.3. Synthesis of MDA-MCN-1

The MDA–MCN-1 was synthesized from cyanuric chloride (2, 4, 6-trichloro-1, 3, 5-triazine, Merck) and EDA following the literature [21]. In typical synthesis, 5.5 g of Cyanuric chloride and 7.1 ml of N, N-diisopropylethylamine (DIPEA, Merck) were dissolved in dried tetrahydrofuran (THF, Merck, 300 ml) and stirred at 273Kfor 3 h. MCN-1 was added to the mixture and stirred for 24 h at 273K. Then the mixture was filtered and the solid was rinsed sequentially by dried methanol (CH$_3$OH, Merck), dichloromethane (CH$_2$Cl$_2$, Merck) and tetrahydrofuran. The resultant solid was refluxed in mixture of EDA (4 ml), dissolved in dried tetrahydrofuran (300 ml) for 24 h.

The replacing of chlorine atoms in cyanuric chloride by the amine groups of the EDA were occurred easily and that HCl (formed during the substitution reaction) was trapped by DIPEA. The material was filtered and rinsed by dried methanol, dichloromethane and tetrahydrofuran, in sequence. This resulting substance is referred to as MDA–MCN-1. Figure 2 shows Schematic illustration of each product in every stage of synthesis process [21].

2.4. Characterization

Nitrogen sorption isotherms were measured with a Micromeritics 2020 analyzer at 77 K. Before
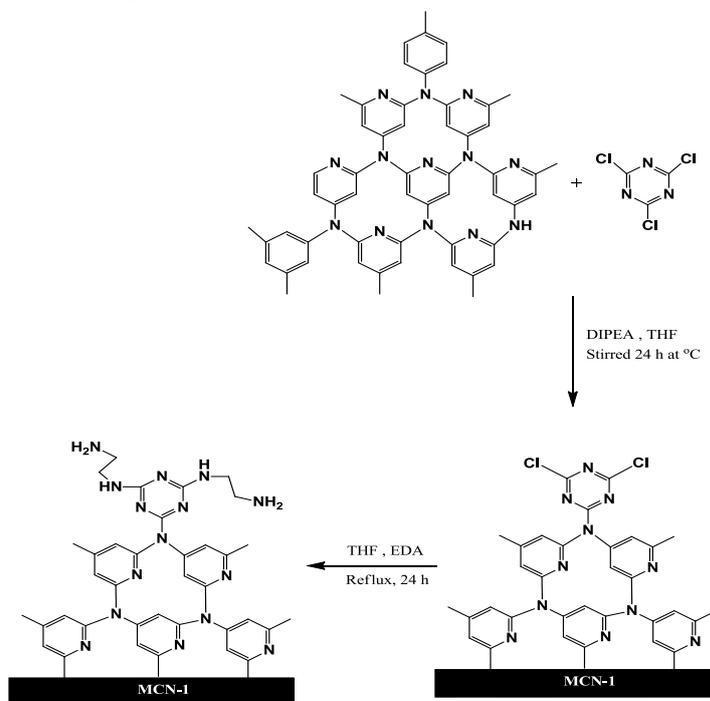
Fig. 2- Synthesis of MCN-1 functionalized by melamine-based dendrimer amine (MDA-MCN-1) [21].

measurements, the samples were degassed at 363K in a vacuum for 3 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas (S_{BET}). The pore size distributions were calculated from the adsorption branches of isotherms by using the Barrett-Joyner-Halenda (BJH) model. The total pore volumes (V_t) were estimated from the adsorbed amount at a relative pressure P/P_0 of 0.99. A thermogravimetric analyzer (NETZSCH TG 209 F1, Iris) was used to determine the thermal stability of materials in nitrogen atmospheres with a heating rate of 10.0 $K.min^{-1}$. Small-angle X-ray scattering (SAXS) measurements were carried out on a Hecus small-angle X-ray scattering system (model S3-MICRO$_{pix}$) using Cu-Kα radiation (50 kV, 1 mA). Fourier transform infrared (FT-IR) spectra of the samples were measured on a Shimadzu IR solution 8400 spectrometer using the usual KBr pellet technique. XRD patterns were recorded on Bruker d8 advance using Cu–Ka (k = 1.54 A°) radiation.

2.5. CO_2 and CH_4 adsorption

The CO_2 and CH_4 adsorption capacities of MDA-MCN-1 samples were evaluated using volumetric method and the setup is shown in Figure 3. 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 433K and the valves 8, 9 and 10 (see Figure 3) were opened. After that, the vacuum pump was turned on and the system was vacuumed for 1.5h (without any loss of crystallinity) under the given thermal conditions. After de-gassing, the system was cooled to room temperature. The CO_2 or CH_4 was adsorbed by opening all valves except valves 3, 5 and 10. 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 tests and subtracted from total pressure change. By measuring the dead volumes, one could calculate the exact pressure decrease according to the carbon dioxide or methane adsorption.

3. Result and discussion

3.1. Structural and textural properties of adsorbent

Figure 4 shows the FT-IR spectra of unmodified MCN-1 (Figure 4a) and MDA-MCN-1 (Figure 4b) in the scan range from 400 to 4000 cm^{-1}. There are three major bands at 1276, 1606 and 3406 cm^{-1} in Figure 4a. These bands are related to aromatic C-N stretching, aromatic ring modes and the stretching mode of N-H groups in the aromatic ring, respectively. The bands of terminal CH_3 groups are at 2864 and 2902 cm^{-1}. A shoulder at 1417cm^{-1} is corresponded to a Sp^3 C-C bond or disordered Sp^2 graphitic domains, and bonds below 933cm^{-1} to graphitic Sp^2 domains. There are new bands at 1434 and 1546 cm^{-1} in FT-IR spectrum of MDA-MCN-1. These bands show an aromatic triazine ring in the MDA-MCN-1 sample and confirm that the melamine-based dendrimer are formed. MDA-MCN-1 spectra reveal new bands at ~1649and~1544cm^{-1}, which are related to the C=N stretching in the triazine ring. N-H stretching bands can be observed at 3124-3500 cm^{-1}. The bands at 2813 and 2661 cm^{-1} correspond to CH_2 groups [21].

The nitrogen adsorption isotherms of MCN-1 and MDA-MCN-1 samples are shown in Figure 5 and are of type IV according to the international union of pure and applied chemistry

Fig. 3- Setup for gas adsorption capacity test.
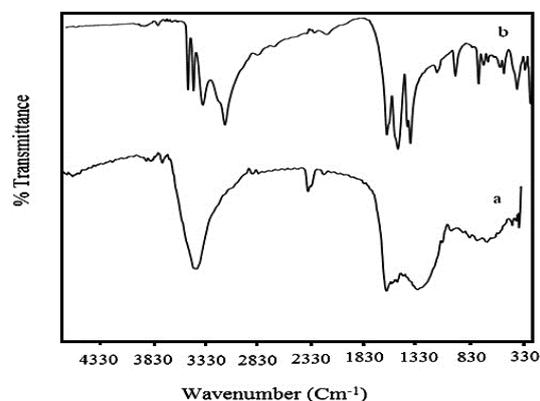
Fig. 4- FT-IR Spectra of MCN-1 (a) and MDA-MCN-1 (b) [21].

(IUPAC) indicating that the prepared samples are mesoporous compounds. The samples exhibit a total pore volume of 0.12 and 0.53cm³g⁻¹ and a specific Brunauer-Emett-Teller (BET) surface area of 102.24 and 505.65 m²g⁻¹ for MDA-MCN-1 and MCN-1 respectively. [21]

Table 1 shows the effective mesoporous diameter increasing as the dendrimer is formed inside the adsorbent. This abnormal increase in the diameter after the functionalization with amine group (from 4.23 nm to 4.74 nm for functionalization with melamine dendrimer), is due to either the stereo effect or the channel blocking by amino group [10]. It is also interesting that there is a dramatic decrease in the volume adsorbed (0.12 cm³.g⁻¹) on MDA-MCN-1 as compared to the MCN-1 (about 0.53 cm³.g⁻¹) [21].

Figure 6 shows the Small angle X-ray scattering spectra for MCN-1 (Figure 6a) and MDA–MCN-1(Figure 6b). Both these synthesized adsorbents exhibit a single strong peak (1 0 0) in its XRD pattern followed by two additional peaks (1 1 0, 2 0 0) which can be indexed on a hexagonal lattice .The pattern is similar to the XRD pattern of the parent mesoporous silica template SBA-15, although some peak broadening is observed as compared to the parent SBA-15. Consequently, the bonding of the melamine-based dendrimer amines complexes inside the mesoporous channels of MCN-1 does not seriously perturb the overall ordered structure of the mesoporous carbon nitride. [21]

The powder diffraction pattern of MCN-1 also shows a single broad diffraction peak (Figure 7) close to 26.1 Aº, corresponding to an interlayer d-spacing of 0.341 nm, which is similar to the d-spacing obtained in the non-porous CN spheres. This indicates turbostratic ordering of the carbon and nitrogen atoms in the graphene layers of MCN-1. A pronounced additional peak is found at 17.6, corresponding to a distance d = 0.503 nm. The 17.6 small angle peaks presumably relate to an in-plane structural packing motif, such as the hole-to-hole distance of the nitride pores in the crystal. [22]

Thermogravimetric curves of two samples are recorded in Figure 8. Organic loadings in the MCN-1 and MDA-MCN-1 sample were calculated from the weight loss determined by TGA. The main decomposition of MCN-1 (Figure 8a) starts at around 873 K, which can be attributed to the

Fig. 6- SAXS patterns for (a) MCN-1 and (b) MDA-MCN-1 [21].

Fig. 5- Nitrogen adsorption-desorption isotherms for MCN-1 (a) and MDA-MCN-1 (b) [21].

Table 1- Structural properties of MCN-1 and MDA-MCN-1 [21]

Adsorbent	SBET (m²g⁻¹)	Mean pore diameter (nm)	Total pore volume (m³g⁻¹)
MCN-1	505.6	4.2	0.53
MDA-MCN-1	102.2	4.74	0.12
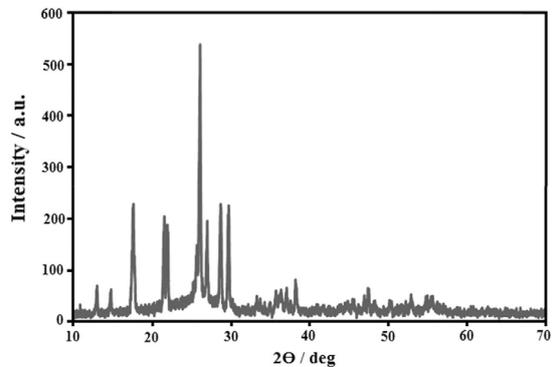
Fig. 7- XRD pattern of MDAMCN-1.

release of small molecules including N_2 and NH_3 of samples. The significant mass loss of MDA-MCN-1 material (Figure 8b) occurs at 678 K which can be attributed to the decomposition of dendrimer part of sample. This result shows that samples (MCN-1 and MDA-MCN-1) have high thermal stability compared to earlier species [21].

3.2. Adsorption behavior

CO_2 and CH_4 adsorption capacity of MCN-1 and MDA-MCN-1 at 20 bar and room temperature are listed in Table 2. Figure 9 shows CO_2 and CH_4 adsorption isotherms on MDA-MCN-1 at 20 bar and room temperature. The CO_2 adsorption isotherm of synthesized absorbent is a typical type IV isotherm according to the IUPAC classification. The adsorption capacity for an isotherm increases with increase in pressure and reaches the saturation state and then remains constant. As shown in Table 2, after the functionalization with melamine-based dendrimer amine, the adsorption amounts of both gases increased, but the relative increase quantity of CO_2 adsorption capacity was more than that of CH_4. The enhancement of adsorption capacity of the both gases after the functionalization with melamine dendrimer is because of an increase in

the pore diameter of MDA-MCN-1 compared with MCN-1. The higher adsorption capacity CO_2 to CH_4 on MDA-MCN-1 is due to the chemical interaction between CO_2 and amine groups. CO_2 has acidic nature, consequently with incorporation of amine groups in the MCN-1, the interaction of CO_2 with adsorbent is improved. The melamine includes a mixture of various amine groups (primary, secondary and tertiary amine groups). Therefore, these materials can provide a range of active sites by varied basic strength. Chemical reactions occurred between primary amine (RNH_2) and secondary amine (R_2NH) groups and CO_2 produce the carbamate species according to following Eqs:

$$CO_2 + 2RNH_2 \leftrightarrow RNH_3^+ + RNHCOO^- \qquad (eq. 1)$$
$$CO_2 + 2R_2NH \leftrightarrow R_2NH_2^+ + R_2NCOO^- \qquad (eq. 2)$$
$$RNHCOO^- + H_2O \leftrightarrow RNH_2 + HCO_3^- \qquad (eq. 3)$$
$$R_2NCOO^- + H_2O \leftrightarrow R_2NH + HCO_3^- \qquad (eq. 4)$$
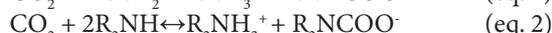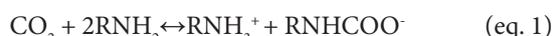
Mesoporous materials used for CO_2 and CH_4 adsorption from the literature are given in Table 3 and Table 4, respectively. Experimental conditions of previous literature is shown in Table's Columns and it shows that most of experimental work reported earlier was done at low pressure and room temperature.

It is clear that under similar conditions, MDA-MCN-1 has an excellent adsorption capacity at high CO_2 partial pressures.

4. Conclusions

CO_2 and CH_4 capturing and storing are important environmental issues which have also industrial applications. Their emission to atmosphere affects to global warming and air pollution. In this work, MDA-MCN-1 material was synthesized by stepwise reactions and the CO_2 and CH_4 adsorption capacity of this material have been studied at high pressure and room temperature. CO_2 and CH_4 adsorption capacities of prepared samples are about 4 and 3.52
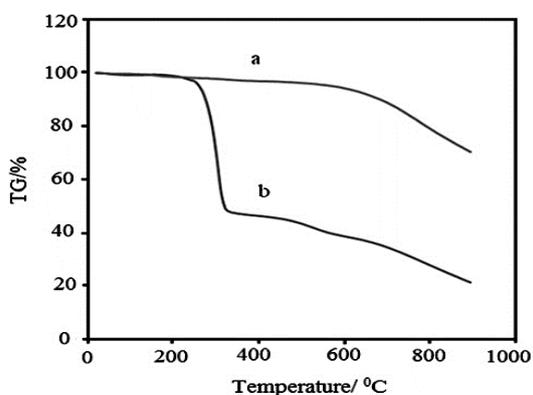
Fig. 8- The thermogravimetric curves of the MCN-1 (a) and MDA-MCN-1 (b) in nitrogen atmosphere [21].

Table 2- Gas adsorption capacity of MCN-1 and MDA-MCN-1 at 20 bar and room temperature

Adsorbent	gas adsorption capacity (mmol/g)	
	CO_2	CH_4
MCN-1	3.14	3.21
MDA-MCN-1	4	3.52
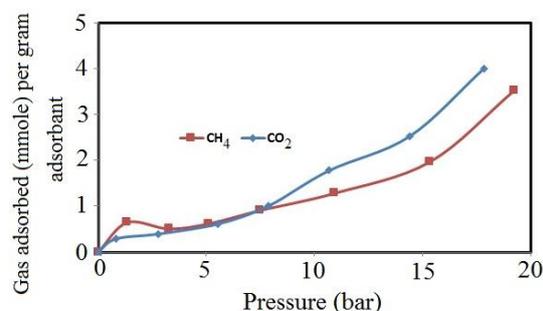
Fig. 9- CO_2 and CH_4 adsorption isotherms of MDA-MCN-1.

Table 3- Comparison adsorbents used for CO2 adsorption from the literature and this work

Sample	Conditions	Capacity (mmolg^{-1})	Ref
MIL-101	10 bar, 298 K	0.85	[17]
PEHA-MIL-101	10 bar, 298 K	1.3	[17]
Ordered mesoporous carbon	13 bar, 298 K	2.21	[12]
MCN/C	1 bar, 298 K	2.35	[15]
MCN-1	1bar, 308 K	1.08	[15]
MCN-1	17.85 bar, 298 K	3.14	This study
MDA-MCN-1	17.85 bar, 298 K	4	This study

Table 4- Adsorbents used for CH4 adsorption from the literature and our work

Sample	Conditions	Capacity (mmolg^{-1})	Ref
Mesoporous carbon	100 bar	1.05	[16]
MOF-235	1 bar and 5 bar	1.8 , 2.7	[11]
Ordered mesoporous carbon	100 bar	3.26	[12]
MCN-1	20 bar	3.21	This study
MDA-MCN-1	20 bar	3.52	This study

mmol gas per g adsorbent, respectively. This solid dendrimer amines adsorbent is very effective for CO_2 and CH_4 capturing and storing.

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