



## Solid amine sorbents for CO<sub>2</sub> capture by chemical adsorption: A review

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### ABSTRACT

Amines are well-known for their reversible reactions with CO<sub>2</sub>, which make them ideal for CO<sub>2</sub> capture from several gas streams, including flue gas. In this respect, selective CO<sub>2</sub> absorption by aqueous alkanolamines is the most mature technology but the process is energy intensive and has also corrosion problems. Both disadvantages can be diminished to a certain extent by chemical adsorption of CO<sub>2</sub> selectively. The most important element of the chemical adsorption of CO<sub>2</sub> involves the design and development of a suitable adsorbent which consist of a porous support onto which an amine is attached or immobilized. Such an adsorbent is often called as solid amine sorbent. This review covers solid amine-based studies which are developed and published in recent years. First, the review examines several different types of porous support materials, namely, three mesoporous silica (MCM-41, SBA-15 and KIT-6) and two polymeric supports (PMMA and PS) for CO<sub>2</sub> adsorption. Emphasis is given to the synthesis, modifications and characterizations -such as BET and PXRD data-of them. Amination of these supports to obtain a solid amine sorbent through impregnation or grafting is reviewed comparatively. Focus is given to the adsorption mechanisms, material characteristics, and synthesis methods which are discussed in detail. Significant amount of original data are also presented which makes this review unique. Finally, relevant CO<sub>2</sub> adsorption (or equilibrium) capacity data, and cyclic adsorption/desorption performance and stability of important classes of solid amine sorbents are critically reviewed. These include several PEI or TEPA impregnated adsorbents and APTES-grafted systems.

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### 1. Introduction

The emission of greenhouse gases into atmosphere, especially carbon dioxide (CO<sub>2</sub>), is a worldwide acknowledged problem. In this respect, CO<sub>2</sub> emitted from point sources, such as fossil fuel based power plants, has to be captured, utilised and stored (CCUS). The four general ways of handling CO<sub>2</sub> in large scale are oxy-fuel-, pre-, and post-combustion captures and the capture

associated with industrial process streams [1]. Common CO<sub>2</sub> capture techniques -amongst others-are (i) gas-liquid absorption, (ii) gas-solid adsorption and (iii) separation by a membrane. The choice of an appropriate technique involves several factors, such as source and composition of the gas stream and CO<sub>2</sub> capture procedure that is whether it is pre- or post-combustion [2]. However, the most mature capture process is CO<sub>2</sub> absorption by aqueous alkanolamine solutions [3]. Here, CO<sub>2</sub> is selectively absorbed by the reactive solvent followed by the regeneration in a desorber. However, this process is energy intensive due to high reboiler duty requirement of current solvents and the widespread application of this technology is still limited since it increases the cost by 25–40% [4]. Other major drawbacks include -amongst others-corrosion and solvent degradation. As a viable alternative to gas-liquid absorption, processes based on either physical or chemical adsorption of CO<sub>2</sub> by solid adsorbents are currently

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being developed [5–11]. Here, regeneration of solid adsorbents requires much less energy than the solvent systems [12].

An adsorption process can be carried out continuously by two different modes; namely, pressure swing adsorption (PSA) and temperature swing adsorption (TSA). Both processes have two identical columns filled with adsorbent particles and while one of them is adsorbing, the other desorbs or the column is regenerated concurrently. PSA operates at nearly constant temperature and on the principle of adsorption at high pressure followed by desorption at low pressure [12]. Desorption often takes place at near atmospheric pressure while the pressure of adsorber is significantly high. On the other hand, a TSA process is based on adsorption at low temperatures in one column (i.e. adsorber) together with concurrent desorption in another column (i.e. regenerator) at high temperature while the process pressure is nearly constant. In both TSA and PSA, CO<sub>2</sub> -containing feed gas is switched from one column, which is nearly loaded with adsorbed CO<sub>2</sub>, to the other which is already regenerated. Therefore, each one of two columns becomes an adsorber first followed by being a regenerator in turn. Hence the process is called temperature swing adsorption (TSA). The most important property of the adsorbents is the CO<sub>2</sub> adsorption (or equilibrium) capacity.

Adsorbents for CO<sub>2</sub> capture consist of a support to which functional groups are attached by different techniques. There exists several possibilities for the support, such as mesoporous silica and the amine based functionalization (or amination) is the natural choice as CO<sub>2</sub> is a Lewis acid. Although there are several publications on CO<sub>2</sub> adsorption which are reviewed -amongst others-by Olajire [2], Samanta et al. [7] and Wang et al. [8], detailed comparative reviews for the solid amine sorbents are rare. Therefore, the aims of this paper are to present certain amount of original experimental results -often for consolidation-covering several facets of the solid amine sorbents and to compare them both among themselves and also with those reported in the literature.

## 2. Carbon dioxide adsorption

In any adsorption process, adsorbate molecules are separated selectively from a gas mixture either by making a bond together with the sorbent or by attaching themselves to the solid matrix by weak intermolecular forces (that is, chemisorption or physisorption respectively).

A certain gas, such as CO<sub>2</sub>, can then be captured by adsorption onto the surface of a specific sorbent [13,14]. CO<sub>2</sub> adsorption can be achieved by using several adsorbents such as activated carbons [15–17], zeolites [18], amine immobilized mesoporous silica types of MCM-41 [19], SBA-15 [20,21], metal-organic frameworks (MOFs) [11], microporous organic polymers (MOPs) [12] and amine-grafted sorbents [22–25]. The most important property of an adsorbent is its CO<sub>2</sub> adsorption (or equilibrium) capacity which depends strongly on the pore structure, the surface area and the degree and type of functionalization. In addition, the capacity depends on the partial pressure of CO<sub>2</sub>, temperature and humidity [25]. Dependency on CO<sub>2</sub> partial pressure is more significant for physisorption so that they are more suitable for high pressure applications. In principle, an ideal sorbent should have a high CO<sub>2</sub> adsorption capacity, high selectivity for CO<sub>2</sub> and it should also be economically regenerable without any significant cyclic performance loss [20,26].

Post-combustion CO<sub>2</sub> capture is usually carried out at ambient pressures. Therefore, chemical adsorbents with basic amine groups are most suitable. The appropriate amine-based adsorbent for a certain capture case can be developed by using one of the following two different techniques [27]:

- Surface modification of low cost carbons and mesoporous silica by a polymeric amine, such as tetraethylenepentamine (TEPA) or polyethylenimine (PEI) [28].
- Synthesizing a high nitrogen content carbon -including adsorbents-by carbonisation. Then thermal or chemical activation of a range of nitrogen compounds [29–31].

Certain functional groups, such as alkyl-amines, can be attached to various porous solid materials. Then, these functional groups enhance the CO<sub>2</sub> sorption properties so that they become suitable even for low pressure captures [32]. These amine-based adsorbents are presently very popular for CO<sub>2</sub> capture applications [8,25,33–38] since they provide high adsorption capacities, fast CO<sub>2</sub> adsorption rates and desirable desorption properties, such as easy regeneration [40]. In addition, amine-based adsorbents are tolerant to moisture, in fact the CO<sub>2</sub> uptake increases under proper humidity conditions [40–43]. Attachment of organic amines can be achieved by immobilization onto the porous surfaces by one of the following techniques: (i) impregnation, (ii) post-synthesis grafting or (iii) direct co-condensation [34]. These modifications increase CO<sub>2</sub> adsorption capacity significantly due to formation of carbamates [8]. For example, the adsorption capacity of PEI/MCM-41 adsorbent is much higher than that of pristine MCM-41 at atmospheric conditions [39]. This is due to chemical adsorption of CO<sub>2</sub> resulting in carbamate formation.

Polymeric adsorbents can also find applications for CO<sub>2</sub> capture. In fact, amine attached or immobilized polymeric adsorbents have superior performances due to their high adsorption capacities and high adsorption rates for CO<sub>2</sub> for typical flue gas temperature range of 60–80 °C. The performances vary significantly depending on the type of nitrogen functional groups of the attached amines [27]. Polymethyl methacrylate (PMMA) is a popular polymeric support whose CO<sub>2</sub> adsorption capacity can be increased by mixing it with amines [40]. In this case, it is claimed that there are both physically and chemically bonded amines on the support.

Several support materials for solid amine sorbents are currently available. In this work, three mesoporous silica (namely, MCM-41, SBA-15 and KIT-6) and two polymeric supports (PMMA and polystyrene (PS)) will be examined and compared. Adsorption/desorption and other pertinent data will consist of our own experimental results in addition to those available in the literature.

## 3. Experimental

### 3.1. Reagents and materials

Reagent Pluronic P123 triblock copolymer (average M<sub>n</sub> ~5800) from Aldrich was used as a template. The followings were obtained from the corresponding reputable firms: tetraethyl orthosilicate (TEOS) from Merck as a silica source, cetyl trimethylammonium bromide (CTAB) 98% from ABCR GmbH & Co. as a co-surfactant, *n*-BuOH > 99.0% from Fluka as a structure directing agent, HCl fuming 37% p. a. from Aldrich, NH<sub>4</sub>OH 28–30% ACS Reag. from Merck, In addition, TEPA ≥95% from Merck, DETA ≥98% from Merck, APTES ≥98% from BASF and PEI, branched (average M<sub>n</sub> ~ 600 by GPC) from Sigma-Aldrich were used as amine sources. All of the chemicals were used as supplied by the manufacturers without further purification.

### 3.2. Synthesis of mesoporous silica supports and their amine immobilization

The syntheses of MCM-41, SBA-15 and KIT-6 were carried out according to established literature methods and pertinent details

of them are given in Section 4. The wet impregnation method was used to dope the silica supports with TEPA as the amine source according to the procedure described in literature [56,85]. Briefly, the sample with the chosen mass percent of TEPA (that is, 30, 40 and 50%) was dissolved in methanol and mixed with the silica (MCM-41, SBA-15 or KIT-6). Then the mixture was refluxed in methanol at about 65 °C for couple of hours. After complete evaporation of methanol, the residual solid was dried at 60–80 °C for couple of hours under vacuum (700 mmHg).

### 3.3. Characterization of synthesized adsorbents

The structures of the mesoporous silicas were analyzed by powder X-ray diffraction (PXRD) by using a Rigaku Miniflex 600 desktop with Cu K $\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ) at 40 kV, 15 mA. The N<sub>2</sub> adsorption/desorption isotherms were obtained at 77 K by using a Quantachrome Autosorb 1C. Prior to each measurement, the adsorbent was degassed at 100 °C in high vacuum for 3 h. The surface areas were calculated by using the Brunauer–Emmett–Teller (BET) method, and the pore size distributions were obtained from the desorption branch of isotherms based on the Barrett–Joyner–Halenda (BJH) method. The total pore volume was determined as the volume of liquid nitrogen adsorbed at a relative pressure of  $P/P_0 = 0.99$ . Scanning Electron Microscope (SEM) measurements were obtained by using a JEOL 6510LV.

The Perkin Elmer Pyris 1 TGA analyzer was used for adsorption/desorption of CO<sub>2</sub> gas according to following procedure where the gas flow rate, the temperature and the duration time were previously optimized. First, the moisture and the CO<sub>2</sub> on the sample were removed by passing N<sub>2</sub> gas at 100 °C for 1 h at a flowrate of 30 mL/min. Second, after measuring the sample weight, the temperature was decreased from 100 °C to 75 °C (that is, to adsorption temperature) under N<sub>2</sub> flow. Then CO<sub>2</sub> gas (100%) was passed at 75 °C for 5 h. Finally, N<sub>2</sub> gas was passed at 75 °C for 5 h for desorption.

## 4. Support materials for solid amine sorbents

### 4.1. Mesoporous silica

Three well known mesoporous silica, namely, MCM-41, SBA-15 and KIT-6 were chosen as support materials. These supports find also widespread applications in heterogeneous catalysis. They were synthesized and comparatively discussed in this work.

#### 4.1.1. MCM-41

MCM-41 is mesoporous silica which can be synthesized hydrothermally. In this work, four different methods were used and the pertinent details of each one of them can be found elsewhere [44–47]. Tetraethyl orthosilicate (TEOS) is the most common silica source for synthesizing MCM-41-type materials and was used in this study. Various templating micelles must also be used. These micelles can be obtained from cationic organic surfactants such as cetyltrimethylammonium bromide (CTAB). In this work, we have prepared four MCM-41 samples – coded as MCM-41/1 to MCM-41/4 – and Table 1 gives the corresponding reactant compositions as well as conditions for aging and calcination for the synthesized supports.

These four MCM-41 samples were then characterized by standart techniques in order to make meaningful comparisons. First, the BET surface areas, pore volumes and the average pore sizes –by using two different methods– of the samples MCM-41/1 to MCM-41/4 were determined and the experimental results are summarized in Table 2. It is seen that although the sample MCM-41/4 has the largest average pore size, its surface area and pore

**Table 1**

Reactant compositions and preparation conditions of MCM-41 samples according to four different methods [44–47].

Sample		MCM-41/1	MCM-41/2	MCM-41/3	MCM-41/4
Reference		[44]	[45]	[46]	[47]
Mole fractions	TEOS	1	1	1	1
	CTAB	0.152	0.22	0.7	0.137
	NH <sub>3</sub>	2.8	11	–	2.23
	Water	141.2	155	83.2	139
	Ethylene glycol	–	–	46.8	–
	EDA	–	–	13	–
	Sodium acetate	–	0.034	–	–
Aging conditions	Ethyl alcohol	–	1	–	–
	Temperature (°C)	RT	RT	RT	100
Calcination conditions	Time (h)	1	5	24	48
	Temperature (°C)	550	550	550	550
Heating rate (°C/min)	Time (h)	5	5	5	5
	Heating rate (°C/min)	1	1	–	–

volume are the smallest. These results indicate that its porosity is very low [48]. On the other hand, the textural properties of MCM-41/1 are greater than those of the others.

The mesoporous molecular sieve, MCM-41 samples were then characterized by PXRD prior to any modification. Examples of the X-ray diffractograms before and after calcination in air at 550 °C are given in Fig. 1. As a comparison in Fig. 1(a) and b the PXRD peaks become more intense and sharp (crystalline) because of the release of the organics from the silica structure after the calcination step. The diffractogram in Fig. 1(a) shows the presence of a single high intensity peak along with three weak peaks in the low 2 $\theta$  degrees of 2°–7°. The PXRD pattern exhibits four diffraction peaks which could be indexed as (100), (110), (200) and (210) reflections respectively [49]. This is the characteristics of long range ordered hexagonal MCM-41 mesoporous phase. The parent MCM-41 exhibits a narrow and strong peak at 37.19 Å and other three weak peaks at 21.31 Å, 18.55 Å and 14.14 Å are due to the (100), (110), (200) and (210) reflections, respectively.

The X-ray diffraction patterns of MCM-41, prepared by four different methods, are given in Fig. 2. Fig. 2 shows several Bragg peaks at low angles between 2° and 7° 2 $\theta$  deg which are typical for any MCM-41 material. The diffraction patterns of MCM-41/1 are compared with those of the others which were synthesized by using different methods. It is seen that the degree of Bragg diffraction angles are nearly identical indicating that the structure of MCM-41 was preserved in all methods. The slight

**Table 2**

The specific surface areas, pore volumes and the average pore sizes of the synthesized MCM-41 samples.

Sample	Specific surface area <sup>a</sup> (m <sup>2</sup> /g)	Pore volume <sup>b</sup> (mL/g)	Pore diameter <sup>c</sup> (nm)	Pore diameter <sup>d</sup> (nm)
MCM-41/1	1759	1.370	2.51	3.72
MCM-41/2	1875	1.177	2.18	3.43
MCM-41/3	1077	1.333	2.61	3.86
MCM-41/4	922	0.843	3.04	4.17

<sup>a</sup> According to the BET equation ( $P/P_0 = 0.99, 407$ ).

<sup>b</sup> According to the BJH method (Grün, Unger, Matsumoto, & Tsutsumi, 1999).

<sup>c</sup> 4V/A. (Grün, Unger, Matsumoto, & Tsutsumi, 1999).

<sup>d</sup> Using the  $d_{100}$ -value and assuming a pore wall thickness of 1.0 nm.

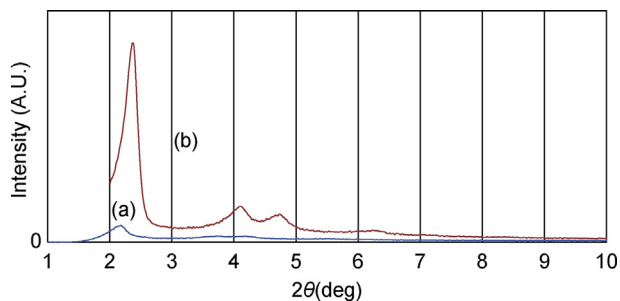


Fig. 1. X-ray diffractograms of MCM-41 before (a) and after calcination (b).

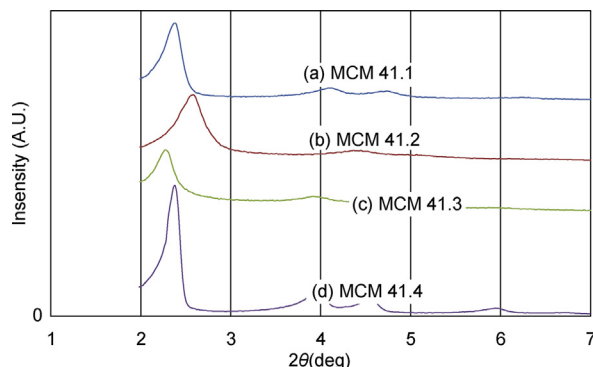


Fig. 2. X-ray diffractograms of MCM-41 spheres synthesized by four different methods (see Table 2 for references).

deviations observed in the  $2\theta$  angles in Fig. 2(a)–(d) may be attributed to the sample preparation methods.

The average pore diameter of the MCM-41/1 sample was determined as 35.3 Å. The nitrogen adsorption-desorption isotherms and BJH pore size distributions which were calculated from the  $N_2$  adsorption data are given in Fig. 3. The BET isotherms of the synthesized materials exhibited a Type IV isotherm [50] where mono dispersed pore size distributions were obtained.

#### 4.1.2. SBA-15

SBA-15, which consists of mesoporous silica nanoparticles, was synthesized by using the method which was described by Mat [51]. The reactants of triblock copolymer P123 (PEO<sub>20</sub>P-PO<sub>70</sub>PEO<sub>20</sub>) and TEOS were used as structure directing agent and silica source respectively. According to this method, the mole ratio of P123:HCl:TEOS:H<sub>2</sub>O is equal to 0.017:50.63:1:41.5 respectively (see Table 3) which was also exactly the case in this study. Five different combinations of stirring, aging temperatures and aging durations were investigated in order to find out the

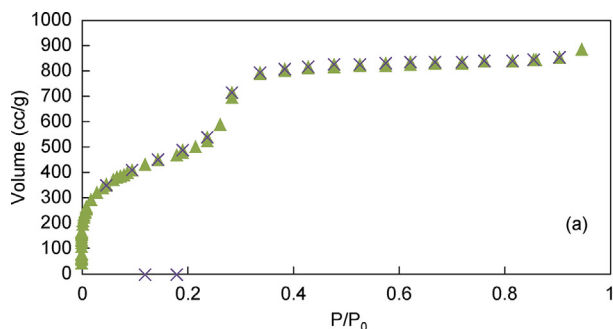


Table 3

The reactants, their mole, weight ratios and roles in the reaction for the SBA-15 synthesis.

Reactant	Role	Mole ratio	Weight ratio
TEOS	Silica source	1	8.5
P123	Structure directing agent (SDA)	0.017	4
HCl (37% in H <sub>2</sub> O)	Acid	50.63	120
H <sub>2</sub> O	Solvent	41.5	30

optimum reaction conditions. Eventually, the solution of P123, HCl and H<sub>2</sub>O was kept at 35–40 °C for about 2 h while stirring before TEOS was added. After the addition of TEOS, the stirring of the solution continued for about 20 h at the constant stirring speed of 120 rpm. Then, the aging process has begun. Finally, the solution was transferred to a PP polypropylene (PP) bottle which was placed in an oven at 80–100 °C for 24–48 h without any stirring.

SBA-15 was synthesized by stirring at 40 °C for 20 h and then aging at 100 °C for 48 h. Fig. 4 shows the PXRD graphs for the synthesized sample before aging, before calcination and after calcination. After the calcination in air at 550 °C for 5 h, the polymer P123 leaves the structure so that the intensity of (100) peak increases where the (110) and (200) peaks become more clear. In Table 4,  $2\theta$ , distance (d) and intensity ratios are compared for the synthesized SBA-15 with the work of Celer et al. [52]. The  $2\theta$  values for the synthesized SBA-15 are smaller and the d values are higher than those of Celer et al. [52]. This finding means that the particle dimensions of the synthesized SBA-15 are bigger than those of Celer et al. [52].

Normally, the mole ratio of TEOS/P123 is 60/1 in the SBA-15 synthesis. If the amount of silica source is more than this ratio, then narrow mesopores are produced leading to clogging. Celer et al. [52] found that the increase in the TEOS/P123 ratio decreases the specific surface area so that the total pore volume decreases by about 45% and the diameter of the mesopores decreases from 10.3 nm to 6.6 nm. For this reason, the mole ratio of TEOS/P123 is kept constant at 60/1 in this work. Five SBA-15 samples were synthesized and they were coded as SBA-15/1 to SBA-15/5.

The PXRD graphs of the calcinated SBA-15 samples at 550 °C in air and their surface properties which were determined by Autosorb are shown in Fig. 5 and Table 5 respectively. PXRD graphs showed that the samples are all crystalline and there was no clear difference in the synthesized materials, for example in SBA-15/4 the peak shifts slightly from  $2\theta$  angles of 0.91°, 1.54° and 1.77° to the right which can be originated from the sample preparation methods. It can be seen from Table 5 that as the synthesis temperature or aging time increases, pore volume and pore diameter increases as well which is consistent with the literature [53–55].

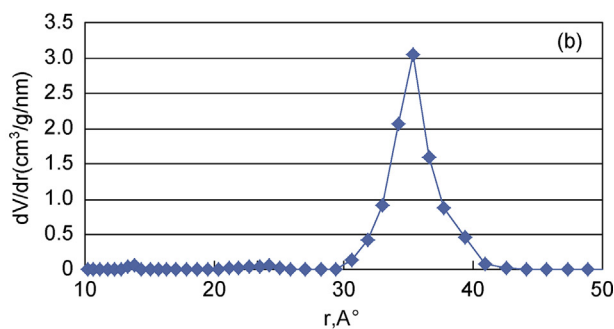
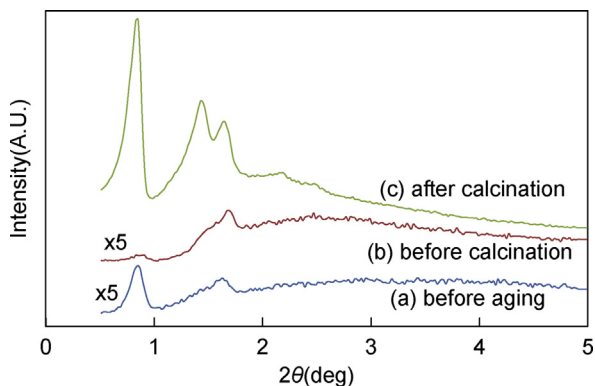


Fig. 3. Nitrogen adsorption-desorption isotherms (a) and BJH pore size distributions (b) of MCM-41/1.



**Fig. 4.** The PXRD graphs taken at the synthesis steps for SBA-15 (a) before aging (b) before calcination (c) after calcination.

#### 4.1.3. KIT-6

Almost all synthesis methods of KIT-6 in the literature [39,51,53] cite the study of Giersal et al. [58]. Generally the starting molar compositions of the reactants are the same and only the reaction temperatures and aging durations may differ (see Table 6). In this study, the synthesis conditions given in Table 7 were used. However the reaction temperature, aging and calcination durations were optimized. Six different combinations of reaction temperatures and aging durations were performed in order to find out the best reaction condition. The reaction temperatures varied between 35 °C and 40 °C and three aging durations, namely, 24, 48 and 72 h, were used. Six KIT-6 samples were synthesized and they are coded as KIT-6/1–KIT-6/6.

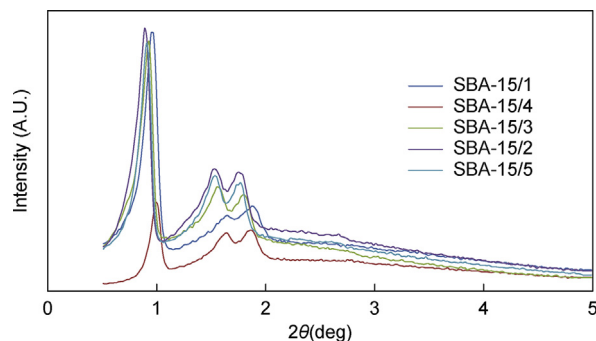
The PXRD graphs of the KIT-6 samples before calcination and after calcination for 2, 4 and 6 h are shown in Fig. 6. It is seen that after calcination the broad amorphous nature of the peak has been converted to a more crystalline behaviour (leaving the inorganics behind) showing the two characteristic peaks of KIT-6 with (211), (420) indices. The peak 2θ degrees are at close to each other where the highest intensity of the (211) peak has been observed in the 4 h calcinated sample. The (hkl) indexes for KIT-6 synthesized in this work were shown in the inside graph which are compatible with the literature. The PXRD data for our KIT-6 samples, corresponding to stirring at 35 °C for 24 h and aged at 100 °C for 24, 48 and 72 h, were compared with those of Gierszal et al. [58] in Table 8. The distances, unit cell parameters and the hkl values are close to the literature values. In addition, increasing the aging duration did not affect the wall thickness to any significant extent. According to these values and the corresponding PXRD graph, 35 °C was selected as the optimum stirring temperature.

The PXRD graphs of the KIT-6 samples are shown in Fig. 7 and it is seen from the matching crystalline peaks that there is no substantiated difference in the synthesized materials. Table 9 shows the textural properties of the KIT-6 samples together with the published data. The BET surface area, pore volume and

**Table 4**

The PXRD data for the synthesized SBA-15 and those of Celer et al. [52].

hkl	Celer [52]		This work	
	2θ (deg)	d (Å)	2θ (deg)	d (Å)
100	0.91	97.0	0.85	104.0
110	1.54	57.4	1.43	61.6
200	1.77	50.0	1.65	53.6
210	2.33	37.9	2.18	40.6
300	2.60	34.0	2.47	35.7
220	2.94	30.0		



**Fig. 5.** The PXRD graphs of the SBA-15 samples synthesized at different reaction temperatures and aging times.

the pore diameter were found to be 753 m<sup>2</sup>/g, 0.92 cm<sup>3</sup>/g and 6.6 nm respectively for the KIT-6/4 sample which was aged at 100 °C for 24 h. On the other hand, the corresponding published data had ranges of 694–800 m<sup>2</sup>/g, 0.95–1.29 cm<sup>3</sup>/g and 6.0–8.5 nm respectively. It was found that as the aging duration increased, the textural properties changed dramatically (see Table 9). For instance, when the aging duration was increased from 24 to 72 h, the surface area and the pore volume increased from 753 m<sup>2</sup>/g to 1398 m<sup>2</sup>/g and 0.92 cm<sup>3</sup>/g to 2.06 cm<sup>3</sup>/g respectively. On the other hand, pore diameter decreased from 6.6 nm to 5.9 nm. Based on these values, it was decided that 48 h aging time would be the most suitable duration for the synthesis of KIT-6 in this study.

The adsorption/desorption isotherms of the synthesized KIT-6/4–KIT-6/6 samples are shown in Fig. 8 which means that they belong to type IV isotherm. The pore dimension distributions of KIT-6/4–KIT-6/6 samples are shown in Fig. 9. KIT-6/5 sample has the smallest pore dimension, ranging between 4.0 and 6.5 nm where it is aged for 48 h at 100 °C. The pore dimensions for KIT-6/4 and KIT-6/6 range between 6–13 nm and 6.5–16 nm where they have aging durations of 24 and 72 h respectively. As a result, the best synthesis conditions for KIT-6 those for KIT-6/5 which corresponds to stirring at 35 °C for 24 h, aging at 100 °C for 48 h and calcination at 550 °C for 6 h.

#### 4.1.4. Comparison of the properties of MCM-41, SBA-15 and KIT-6

Table 10 shows the list of starting materials required for synthesizing MCM-41, SBA-15 and KIT-6. It is seen that the

**Table 5**

The properties of the SBA-15 materials synthesized at different conditions and their comparison with the published data.

Sample	Synthesis conditions			Surface properties		
	T <sub>synthesis</sub> <sup>a</sup> (°C)	T <sub>aging</sub> <sup>b</sup> (°C)	t <sub>aging</sub> <sup>c</sup> (hour)	S <sub>BET</sub> <sup>d</sup> (m <sup>2</sup> /g)	V <sub>p</sub> <sup>e</sup> (cm <sup>3</sup> /g)	r <sub>p</sub> <sup>f</sup> (Å)
SBA-15/1	35	80	24	1177	1.33	45.2
SBA-15/2	35	100	24	980	1.32	53.7
SBA-15/3	35	100	48	1036	1.51	58.4
SBA-15/4	40	100	24	1113	1.51	54.4
SBA-15/5	40	100	48	1151	1.56	54.1
Yue [56]	40	100	24	725	1.12	93.0
Linfang [57]	40	100	48	582	0.95	92.0
Wang [54]	40	90	24	769	1.04	78.0
Hao [55]	40	90	24	502	0.98	64.9

<sup>a</sup> Synthesis temperature.

<sup>b</sup> Aging temperature.

<sup>c</sup> Aging time.

<sup>d</sup> Surface area calculated by BET method.

<sup>e</sup> Pore volume: 4V/A (V: specific pore volume; A: surface area).

<sup>f</sup> Pore diameter.

**Table 6**

The reactants, their mole, weight ratios and roles in the reaction for the KIT-6 synthesis [58].

Reactant	Role	Mole ratio	Weight ratio
TEOS	Silica source	1	8.6
P123	Surface active material	0.017	4
n-Butanol	Structure directing agent (SDA)	1.31	4
HCl (37% in H <sub>2</sub> O)	Acid	1.83	7.7
H <sub>2</sub> O	Solvent	195	144

**Table 7**

The synthesis conditions of KIT-6.

Conditions/Sample	KIT-6/ 1	KIT-6/ 2	KIT-6/ 3	KIT-6/ 4	KIT-6/ 5	KIT-6/ 6
Reaction temperature (°C)	40	40	40	35	35	35
Reaction time (h)	24	24	24	24	24	24
Aging temperature (°C)	100	100	100	100	100	100
Aging time (h)	24	48	72	24	48	72
Calcination temperature (°C)	550	550	550	550	550	550
Calcination time (h)	4	4	4	4	4	4

syntheses of SBA-15 and KIT-6 require an acidic medium. On the other hand, MCM-41 synthesis requires both basic conditions and CTAB whose presence is necessary as the surface active agent. Table 11 compares the surface areas, pore volumes and pore diameters of the samples synthesized in this study with Son et al. [63].

The morphological differences of MCM-41, SBA-15 and KIT-6 are shown by the SEM pictures in Fig. 10. According to this figure, our synthesized MCM-41 particles are about 5–10 μm in size. These values are similar to those of Tai et al. [64]. On the other hand, our SBA-15 sample has a long stick shape particles whose widths and lengths are about 5 μm and 500–750 μm. These dimensions compare well with similar images of Yu et al. [65]. Finally, KIT-6 is a mesoporous material which has a cubic symmetry. Its image looks like SBA-15 except that it is 3D instead of 2D. That is shown in Fig. 10(c) as long sticks seen for KIT-6. However, they are much wider than SBA-15 particles also their average length (150 μm) is about four times shorter.

## 5. Polymeric supports

Polymer based support materials are often considered to be alternatives of silica based meso-porous support materials. Most common polymeric supports are poly(methyl methacrylate)

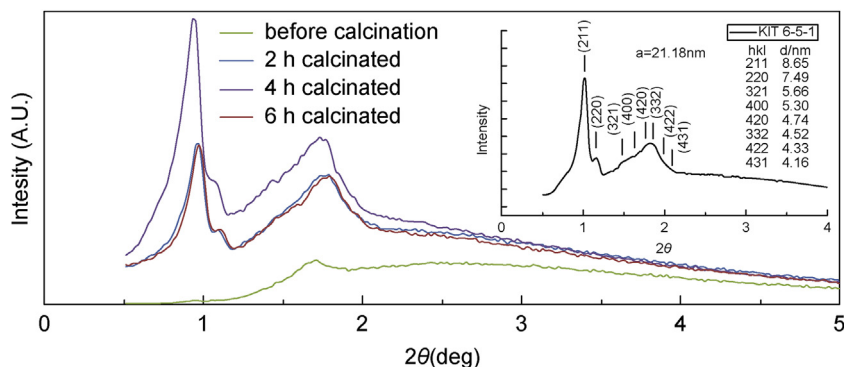


Fig. 6. The PXRD graphs of the KIT-6 samples before calcination and after calcination for 2, 4 and 6 h.

**Table 8**

Comparison of the distances, unit cell parameters and the *hkl* values of the synthesized KIT-6 samples with the literature [58].

Sample	KIT-6/4	KIT-6/5	KIT6/6	Gierszal [58]
Aging duration (hour)	24	48	72	24
a (nm)	21.2	21.7	22.2	22.9
<i>hkl</i>	d (nm)	d (nm)	d (nm)	d (nm)
211	8.65	8.88	9.08	9.35
220	7.49	7.69	7.86	8.16
321	5.66	5.81	5.95	6.12
400	5.30	5.44	5.56	5.74
420	4.74	4.87	4.97	5.12
332	4.52	4.64	4.74	4.91
422	4.33	4.44	4.54	4.68
431	4.16	4.27	4.36	4.49

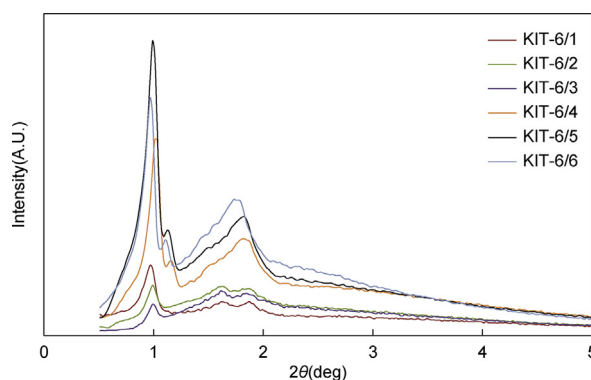


Fig. 7. The PXRD data for the KIT-6 samples which were synthesized at different stirring temperatures and aging durations.

(PMMA) and polystyrene (PS). They have both lower costs and higher stabilities than other polymeric supports. Therefore, this paper will consider only these two polymeric supports.

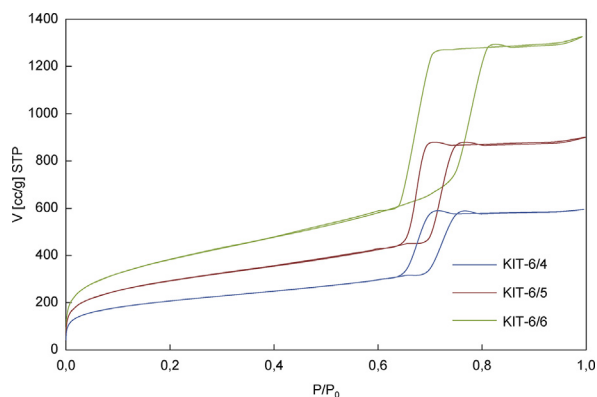
Polymeric amine sorbents have been used for a long time in closed environments where CO<sub>2</sub> capture is the main concern [7]. Polymer structures have quite large specific surface areas and display dominant characterization with their multi-scaled pores. This provides an advantage for developing amine based solid sorbents which are relevant for CO<sub>2</sub> capture [66].

PMMA is a tough, rubbery, and moderately hard polymer with little or no tack at room temperature; superior resistance to degradation and remarkable retention of its original properties under use conditions [67]. On the other hand, PS which is

**Table 9**

The comparison of the textural properties of the KIT-6 samples with the literature values [53,58–62].

Sample	Synthesis conditions			Surface properties		
	T <sub>synthesis</sub> (°C)	T <sub>aging</sub> (°C)	t <sub>aging</sub> (h)	S <sub>BET</sub> (m <sup>2</sup> /g)	V <sub>p</sub> (cm <sup>3</sup> /g)	d <sub>pBJH</sub> (nm)
KIT-6/4	35	100	24	753	0.92	6.6
KIT-6/5	35	100	48	1070	1.4	6.5
KIT-6/6	35	100	72	1398	2.06	5.9
Tüysüz et al. [53]	35	100	24	694	0.95	7.9
Gierszal et al. [58]	35	100	24	740	0.95	–
Kleitz et al. [59]	35	100	24	800	1.05	8.5
Kim et al. [60]	35	100	24	702	0.86	–
Dou et al. [61]	35	100	24	912	1.29	6.3
Liu et al. [62]	40	100	24	943	1.0	6.0

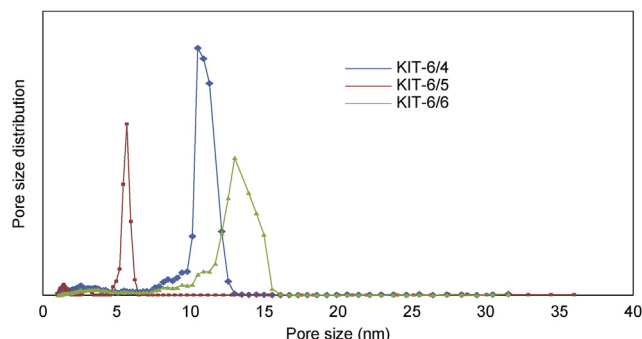


**Fig. 8.** The adsorption and desorption isotherms of the KIT-6 samples synthesized at different aging times.

another polymeric support material for amine immobilization is a crystal clear thermoplastic with hard and rigid structure. It has good thermal stability and excellent thermal and electrical properties [67].

DIAION HP2MG (PMMA) and DIAION HP20 (PS) were purchased from Mitsubishi Chemicals Company and they were used without any treatment. Their properties are given in Table 12.

The textural properties of PMMA and PS supports are both available in the literature [68,69] and they are listed in Table 13 and Table 14, respectively. In general, the BET surface areas and the pore volumes of the samples are similar to the literature ones however the reported pore sizes vary depending on the synthesis conditions.



**Fig. 9.** The pore dimension distribution for KIT-6 samples.

**Table 10**

The chemicals used in order to synthesize MCM-41, SBA-15 and KIT-6.

Mesoporous silica	MCM-41	SBA-15	KIT-6
Surface active agent	CTAB	P123	P123
Solvent	H <sub>2</sub> O	H <sub>2</sub> O	H <sub>2</sub> O
Silica source	TEOS	TEOS	TEOS
Mineralizing agent	NH <sub>4</sub> OH	HCl	HCl

**Table 11**

Comparison of the general structural properties of MCM-41, SBA-15 and KIT-6 samples synthesized in this work with those published [63].

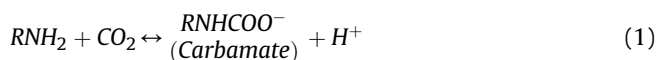
Mesoporous silica	BET surface area (m <sup>2</sup> /g)		Pore volume (cm <sup>3</sup> /g)		BJH pore diameter (nm)	
	This work	Son et al. [63]	This work	Son et al. [63]	This work	Son et al. [63]
MCM-41	1759	1042	1.37	0.85	2.5	2.8
SBA-15	1177	753	1.33	0.94	4.5	5.5
KIT-6	1070	895	1.4	1.22	6.5	6.0

## 6. Solid amine adsorbents

Solid amine adsorbents are extensively used in CO<sub>2</sub> capture. Generally, CO<sub>2</sub> adsorption involves a reaction between the acidic CO<sub>2</sub> molecule and the modified basic active sites. For this reason, amine-based adsorbents are widely studied. Recently, the research in this area has been intensified on enhancing the CO<sub>2</sub> adsorption capacity and selectivity of the solid materials by surface modification. Especially, the studies on basic organic groups (amines) and inorganic metal oxides (alkaline or alkaline earth metals) attract attention [79,80]. The uses of primary and secondary amines are preferred since they can form carbamate upon reaction. Naturally, the widespread use of aqueous solutions of this type of amines for CO<sub>2</sub> capture is the essential hindrance for developing solid amine sorbents [3].

Amine-impregnation is advantageous in many ways. For example, most physical CO<sub>2</sub> adsorbents including mesoporous silicas have less tolerance to water vapor in the gas feed, however if they are amine-impregnated then their tolerance increases. Due to the interactions between amine and CO<sub>2</sub>, the CO<sub>2</sub> uptake increases in the presence of moisture where CO<sub>2</sub>/N ratio increases 2-fold (see Eq. (3) and (4)) [34].

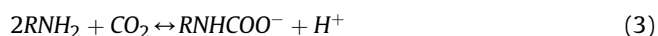
The CO<sub>2</sub> capture by primary or secondary amines proceeds by the formation of carbamate ion according to the following equations:



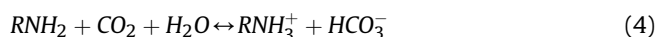
Followed by:



Therefore, the overall reaction is:



If water is present, there exists one additional reaction:



Above reactions will take place in the case of solid amines. However, bicarbonate formation can only take place under humid

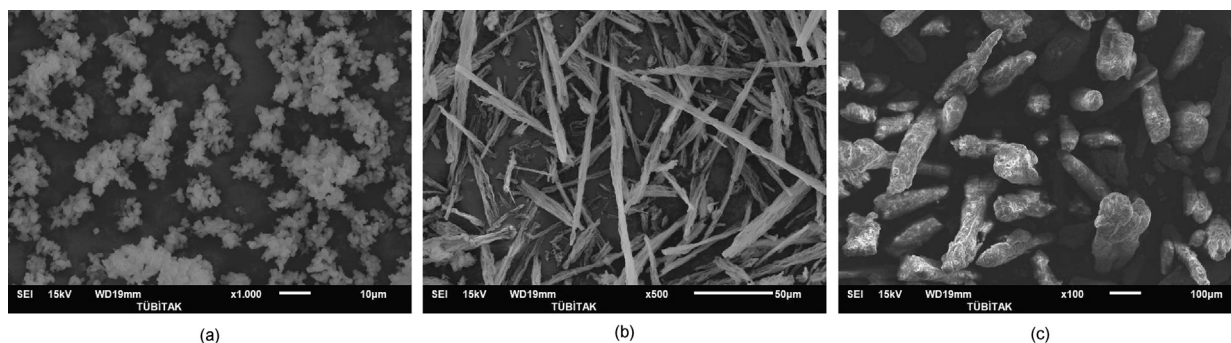


Fig. 10. The SEM images of (a) MCM-41 ( $\times 1000$ ) (b) SBA-15 ( $\times 500$ ) (c) KIT-6 ( $\times 100$ ).

Table 12

Properties of the DIAION HP2MG (PMMA) and DIAION HP20 (PS).

Properties	DIAION HP2MG (PMMA)	DIAION HP20 (PS)
Moisture content (%)	55–65	55–65
Pore volume ( $\text{cm}^3/\text{g}$ )	1,2	1,3
Surface area ( $\text{m}^2/\text{g}$ )	500	600
Pore diameter ( $\text{Å}$ )	150–200	200–300
Particle size ( $\mu\text{m}$ )	0,25–0,6	0,25–0,6

Table 13

The textural properties of PMMA supports.

PMMA support sample	BET surface area ( $\text{m}^2/\text{g}$ )	Pore volume ( $\text{cm}^3/\text{g}$ )	Pore size (nm)
Xie et al. [70]	571	0.97	8
Jung et al. [71]	671	1.26	12
Jo et al. [72]	600	0.97	–
Chen et al. [73]	570	1.30	48
Veneman et al. [74]	500	1.20	17
Gray et al. [75]	579	1.12	10
Gray et al. [76]	470	1.20	–
Diaion HP2MG used in this study	500	1.20	15–20

Table 14

The textural properties of PS supports.

PS support sample	BET surface area ( $\text{m}^2/\text{g}$ )	Pore volume ( $\text{cm}^3/\text{g}$ )	Pore size (nm)
Chen et al. [73]	597	1,42	58
Gray et al. [76]	1000	1.00	–
PS cross-linked with 25% Kaliva et al. [77]	71–83	0.28–0.33	0.59–7.0
PS cross-linked with 65% Kaliva et al. [77]	205	1.10	5.9–6.8
Cross-linked PS Vinodh et al. [78]	224–334	0.19–0.31	3.42–4.08
Diaion HP20 used in this study	600	1.30	20–30

conditions. For solid amines, there are two types of interactions which occur between amine groups and the support. In the first group, weak interactions may occur and in the second type covalently bonded species may be obtained by surface-grafting of aminosilanes [34]. Generally it is claimed that grafted materials exhibit higher rate of adsorption than amine-impregnated adsorbents [81]. In addition, the adsorption rate can even be higher than those of efficient commercial adsorbents, such as 13X [46].

The solid materials have the advantage of low regeneration energy when compared with aqueous amines. However, their

low adsorption capacity and high costs are the main drawbacks in front of their extensive commercialization. Nevertheless, the subject is intensively studied and the recent developments about the amine-based adsorbents include –amongst others– the followings:

- preparation of support materials including high amine contents
- use of amines including high nitrogen contents
- developing effective methods for the amine immobilization [8].

On the other hand, there are several disadvantages of amine impregnated systems which were reported previously by Sayari and Belmabkhout [34]. The disadvantages include –amongst others– high regeneration cost, equipment corrosion, and oxidative degradation of some amines. Therefore, Sayari and Belmabkhout [34], pointed out the importance of the development of recyclable solid sorbents.

Generally, there are two methods for the amine immobilization onto silica surfaces:

- Physical impregnation
- Covalent bonding to the amines including organic chains.

The chemically bonded adsorbents have higher adsorption rates and higher stabilities during their adsorption-desorption cycles [34].

### 6.1. Amine-impregnated adsorbents

There are two basic amine impregnation methods on the adsorbents. One of them is the wet impregnation method which is the easiest way of placing amines onto the solid surfaces. In this method, amines are mixed with the support material by the help of a solvent. The excess solvent is then removed by evaporation of the diluted solution [82].

The advantages of wet impregnation over grafting method are mainly its practical preparation, high amine capacity and decreased corrosion behaviour. The amine source used for wet impregnation method is usually PEI. However there are several other amines ranging from simple monoamines to large amino polymers. Fig. 11 shows schematically some of these amines.

Among the various amines, PEI, methyl-diethanolamine (MDEA), triethanolamine (TEA) diethanolamine (DEA) and monoethanolamine (MEA) are often adsorbed onto MCM-41. However, use of tertiary amines, such as MDEA and TEA are not logical as they cannot react directly with  $\text{CO}_2$  to form carbamates.



On the other hand, MCM-41-MEA and MCM-41-DEA have relatively high CO<sub>2</sub> adsorption capacities of around 40 mg/g at ambient temperatures. The surface area of MCM-41 changes after the amination [83–85]. The CO<sub>2</sub> adsorption capacities of the MCM-41 aminated by diethylenetriamine (DETA), triethylenetetramine (TETA) and 2-amino-2-methyl-1-propanol (AMP) are given in Table 15 [86]. It is seen that amination decreases the surface area considerably which can be explained by the filled or plugged pores. However, the CO<sub>2</sub> adsorption capacity of aminated MCM-41 is higher than the original MCM-41 prior to any amination and the increase depends on the type of the amine.

### 6.1.1. PEI-based adsorbents

CO<sub>2</sub> adsorption properties of PEI-immobilized mesoporous materials –also known as “molecular basket”- were first studied by Xu et al. [84]. The maximum adsorption capacity of 75 wt % PEI-impregnated MCM-41 was found to be 3.02 mmol/g under pure CO<sub>2</sub> stream at 75 °C. There exists a maximum for amine loading beyond which the adsorption efficiency decreases slowly.

It is interesting to note that the adsorption capacity of PEI loaded MCM-41 increases as the temperature increases. This behaviour, which seems to be contradictory at first glance, could be explained. That is, at low temperatures PEI is present as bulk-like states inside the pores which results in a diffusion-limited process [34]. Adsorption capacity is also affected by the pertaining humidity. This is due to the reaction between amine, CO<sub>2</sub> and water resulting in a bicarbonate formation (see, Eq. (4)) in addition to carbamate formation (see Eq. (2)). Therefore, adsorption capacity increases accordingly for humid conditions. Due to larger pore sizes, this phenomenon is more apparent for a PEI-SBA-15 support -when compared with a PEI-MCM-41 support [34,42].

Changing the support material affects the CO<sub>2</sub> adsorption capacity as well. The adsorption process depends strongly on the size of the pore diameter of the support [63,87]. For example, KIT-6 type silica has larger (6 nm) pore sizes than MCM-41 (2.8 nm) resulting in a higher adsorption capacity for the latter.

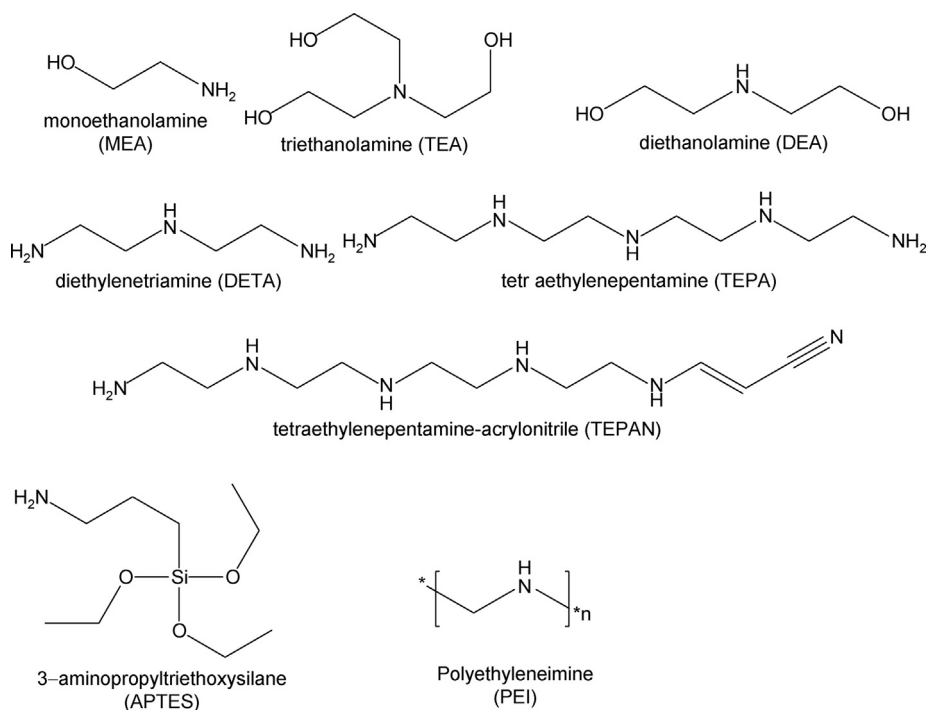
**Table 15**

The CO<sub>2</sub> adsorption capacities of the aminated MCM-41.

Sample	BET surface area (m <sup>2</sup> /g)	Pore volume (mL/g)	CO <sub>2</sub> adsorption capacity (mmol/g)
MCM-41	669.7	0.6	–
MCM-41-DETA	8.1	0.012	1.87
MCM-41-TETA	3.4	0.0048	2.2
MCM-41-AMP	2.2	0.0029	1.14

The size of the pores affects the adsorption rate in the following order: KIT-6 < SBA-16-SBA-15 < MCM-48 < MCM-41. For example, MCM-41 loaded with 65 wt % PEI loading has the adsorption capacity of 3.75 mmol/g in 5% CO<sub>2</sub>/95% N<sub>2</sub> flow at 75 °C. This value is much higher than that of MCM-41 without any amine loading.

Gray et al. [76] reported the immobilization of 40 wt % PEI on three different supports, namely, PS, SiO<sub>2</sub> and PMMA. CO<sub>2</sub> adsorption capacities were obtained from TGA analysis found to be in the range of 2.5–3.5 mmol CO<sub>2</sub>/kg of sorbent. They also examined the adsorption/desorption cycles which were carried out at 25 °C and 105 °C. At the end of 10 cycles, they observed that the sorbents were still stable. Vinodh et al. [78] examined the hyper cross-linked PS and characterized it by different techniques including CO<sub>2</sub> sorption. They used TGA with high purity CO<sub>2</sub> and showed that hyper cross-linked PS is a better adsorbent for CO<sub>2</sub> than the other existing hypercross-linked polymers. Kaliva et al. [77] studied CO<sub>2</sub> adsorption of microporous PS in a gas stream consisting of 5% CO<sub>2</sub> and the rest is methane. They showed that microporous PS exhibit a good separation performance of CO<sub>2</sub> over CH<sub>4</sub>, with separation factors in the range of 7–13 at 268 K indicating that it is an attractive adsorbent for CO<sub>2</sub> separation. Chen et al. [73] loaded 50 wt % PEI on polymeric support PS (HP20). They examined both flue gas (pure and 15% CO<sub>2</sub>) and ambient air environment (400 ppm CO<sub>2</sub>)



**Fig. 11.** Most common amine sources used in solid adsorbents.

to capture CO<sub>2</sub>. HP20/PEI-50 sorbent performed higher adsorption capacity than other PEI-modified materials they studied, namely PMMA, PS and PS-cyanoethylene. They found that the CO<sub>2</sub> loading capacity at 25 °C and 90 °C were 4.11 and 3.2 mmol/g respectively. The cyclic adsorption/desorption performance was measured at 75 °C in a gas environment containing 15% CO<sub>2</sub> and was found that after 5 cycles, loading dropped from 2.95 to 2.9 mmol/g which showed that their sorbent could be considered as stable.

Jung et al. [71] studied PMMA with 55 wt % PEI loading and observed that the maximum CO<sub>2</sub> adsorption capacity were 4.26 and 4.88 mmol/g at 75 °C and 25 °C respectively. In cyclic tests, by using both TGA and a fixed bed reactor, the adsorption capacity of the sorbents decreased. In TGA under dry gas condition, degradation to urea at high temperatures may be the main reason for the observed performance loss. PEI impregnated adsorbents have been studied extensively and the CO<sub>2</sub> adsorption properties of some of the PEI-immobilized adsorbents are listed in Table 16 for comparison.

### 6.1.2. TEPA-based adsorbents

The TEPA/SBA-15 and TEPA/MCM-41 adsorbents were studied by Zhu et al. without template removal [87]. They found that CO<sub>2</sub> adsorption capacities of TEPA (70%)/as-SBA-15 and TEPA (60%)/as-MCM-41 were 3.93 and 5.39 mmol/g respectively at ambient temperatures. The adsorption capacities of these materials showed 10% better performances with respect to calcinated support materials. This shows that it is not always necessary to remove the template. The reason for this result might be the inhibition of the coagulation of the TEPA by the template. Zhu et al. prepared adsorbents by impregnation of the TEPA-DEA mixture to as-SBA-15 support. The highest CO<sub>2</sub> adsorption capacity under the nonaqueous conditions were 4 mmol/g for TEPA (35%)/DEA (15%) and the highest CO<sub>2</sub>/N ratio with TEPA (30%)/DEA (20%) mixture ratios [91]. In addition, they observed that the adsorption capacity decreased from 3.77 mmol/g to 3.61 mmol/g after 6 adsorption/desorption cycles under dry 5% CO<sub>2</sub> flow. Several other examples can be found in the literature. For example, Filburn et al. impregnated various amine groups of MEA, DETA, TEA, PEI, TEPA, etilenamin (E100), TEPAN and E-100AN to PMMA support [40,92,93]. Among these adsorbents TEPA/PMMA has an adsorption capacity of 21.45 mmol/g at 23 °C with the flow of N<sub>2</sub> gas including 2.6% H<sub>2</sub>O and 15% CO<sub>2</sub>. It is observed that as the temperature increases the CO<sub>2</sub> adsorption capacity decreases as normally expected.

Veneman et al. [74] prepared supported amine sorbents by physical impregnation of PMMA with TEPA and studied post-combustion of CO<sub>2</sub> capture in a laboratory scale circulating fluidized bed reactor. They were able to improve the sorbent capacity to 3–5 mmol/g by tuning the amine loading and pore volume properties. They also compared silica based support sorbents (Cariact Q-3, Cariact Q-10 and Davisil grade 646) with a polymer based sorbent for CO<sub>2</sub> capture performances and found that PMMA supported sorbents achieved a superior CO<sub>2</sub> capture capacity.

Jo et al. [72] impregnated PMMA support by TEPA alone and by a mixture of TEPA and acrylonitrile (which is known as TEPAN) at 1, 2 and 3 M ratios then investigated the cyclic adsorption/desorption performances of both. In cyclic tests they observed a staggering decrease in CO<sub>2</sub> adsorption capacity of sorbent which was impregnated by TEPAN, where TEPA-impregnated sorbent was relatively stable. This behaviour was attributed both to the TEPA loss during desorption as well as the formation of isocyanates. Xie and co-workers [70] studied also several supports -including PMMA, MCM-41, a commercial silica gel (SG) and titanium dioxide (P25, T500) - which were all impregnated by TEPA. They found that 30 wt % was the most effective TEPA loading at 35 °C. They also found that the PMMA supported sorbent showed superior performances, especially at low temperatures. 30 wt % TEPA-PMMA sorbent has a CO<sub>2</sub> adsorption capacity of 0.17 g/g sorbent at 50 °C in a gas stream of 10 vol % CO<sub>2</sub> and 90 vol % helium. Cyclic adsorption/desorption tests of this sorbent showed that its stability was high and after six cycles it maintained 94% of its initial adsorption capacity.

In another study, Gray et al. [92] performed Michael addition reaction of ethylenediamine (ED) and TEPA with acrylonitrile. These amine derivatives were immobilized onto a PMMA support and adsorption capacities for their sorbents after 4 adsorption/desorption cycles ranged from 3.4 to 6.6 mol of CO<sub>2</sub>/kg sorbent.

Often properties of amines -such as their kinetics or reaction enthalpy-in homogeneous liquid form are indicative about their prospects as solid amine sorbent. For instance, noting growing interest in using amidine and guanidine superbases in liquid form for CO<sub>2</sub> capture [97,98], Gray et al. [22] immobilized DBU (1,8 Diazabicyclo-[5.4.0]-undec-7-ene) - which is an amidine [97] - onto a PMMA support. Under simulated flue gas environment (10% CO<sub>2</sub> and 2% water), the sorbent which was prepared at 2.5 wt ratio (bead/DBU) exhibits a 3.02 mol CO<sub>2</sub>/kg sorbent

**Table 16**  
Adsorption/desorption and stability properties of PEI-immobilized adsorbents.

Amine source	Support material	Method	flue gas %	Amine content (wt %)	Adsorption			Desorption			Stability		Ref
					T (°C)	T (min)	Capacity (mmol CO <sub>2</sub> /g adsorbent)	T (°C)	T (min)	Capacity %	No of cycle	Capacity loss (%)	
PEI, branched MW = 1800	Silica	TGA	15%CO <sub>2</sub> , 85% N <sub>2</sub>	40	75	0.5	2.5	120	0.5	2.25	3	8–10	[27]
PEI	MCM-41	TGA	99.8% bone-dry CO <sub>2</sub>	75	75	150	2.54	75	150	99.8		10	[85]
PEI, linear MW = 423	SBA-15	Fixed-bed flow system	15 v % CO <sub>2</sub> , 4.5 v % O <sub>2</sub> , 80.5 v % N <sub>2</sub>	50	75	2	3.14						[88]
PEI	SBA-15		pure CO <sub>2</sub>	26	45		1.49				2	5	[33]
PEI	Mesoporous multilamellar silica vesicle (MMSV)	TGA	pure and dry CO <sub>2</sub>	60	90	60	4.73	110			10	3.7	[5]
PEI	SBA-15	TGA	15% CO <sub>2</sub> in N <sub>2</sub>	49.06	75	420	2.49	100	60		10	11	[89]
PEI	SBA-15	TGA	15% CO <sub>2</sub> in N <sub>2</sub>	53.66	95	60	2.68						
PEI, MW = 25,000 Da	KIT-6	high pressure adsorption setup	Ultra-pure CO <sub>2</sub> (99.99%) and N <sub>2</sub> (99.99%)	50	90		2.45	100			20	5.5	[90]

**Table 17**  
Adsorption/desorption and stability properties of APTES grafted adsorbents.

Support material	Amine content (mmol/g)	Adsorption		Ref
		T (°C)	Capacity (mmol/g)	
Silica gel	1.27	23	0.6	[94]
MCM-41	2.48	30	1.15	[95]
SBA-15	2.56	25	1.20	[96]

adsorption capacity at 25 °C, then the capacity decreased to 2.34 mol/kg as the temperature increased to 65 °C.

Using data of amines in liquid form intuitively suggest that a new amine named 1-diethylamino-2-propanol (1DEA2P) may find applications also in solid form via impregnation. Detailed kinetics of 1DEA2P was recently published by Liu et al., [99]. In this respect, a recent study by Numagichi et al. [100] proposes an interesting amine screening method for solid sorbents. Methodology involves theoretical DFT calculations of reaction enthalpies and plotting them as function of Gibbs energy of carbamate formation. They then compared original polyamine with polyamines modified with alkyl groups which destabilize their carbamates, and found that their reaction enthalpies are decreased. This trend suggest that CO<sub>2</sub> can be desorbed more easily from solid sorbent of these amines. On the other hand, the polyamines modified with alkanol groups exhibit high Gibbs energy and reaction enthalpy, indicating that the carbamate is highly stabilized and thus larger regeneration energy is required.

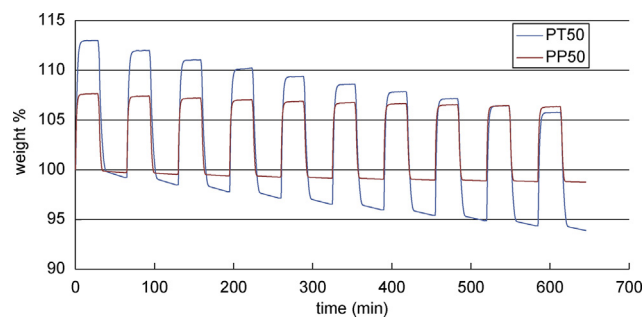
## 6.2. Amine grafted adsorbents

In the grafting method, an amine is covalently bonded to the groups on the silica surface. The reaction between the silanol groups on the silica surface and the aminosilane is a widely used method. A covalent bond is formed between the amine chains and the surfaces formed by the reaction of the silanol groups with the silanes on the chain. In this method, the amount of amine that can be doped into the support material is dependent on the density of the appropriate silanol groups. In grafting method, the strong chemical bond of the amines is advantageous so that they cannot leave the structure easily and a significant temperature increase is required to break the bonds.

Although high CO<sub>2</sub> adsorption capacities are observed for the materials impregnated with amines, their thermal stabilities are low [6]. In order to overcome this problem the aminosilanes are grafted to the interior surfaces of the mesoporous silicas. Generally there are two preparation methods named as direct synthesis and modification after the synthesis.

**Table 18**  
The CO<sub>2</sub> adsorption capacities of the solid amine adsorbents analyzed with TGA (100% CO<sub>2</sub> feed at 75 °C).

Amine source	Support material	Amine content (w/w %)	Adsorption capacity (mmol/g)
DETA	MCM-41	50	1.24
	SBA-15	66	0.96
TEPA	MCM-41	47	1.64
	SBA-15	52	3.01
	KIT-6	50	2.90
	PMMA	50	2.65
PEI	MCM-41	50	2.06
	SBA-15	50	2.17
	KIT-6	52	1.40
	PMMA	50	1.62
	PS	50	1.66
APTES	SBA-15	65	1.73



**Fig. 12.** The cycle stabilities (weight % vs time) of PMMA adsorbent immobilized with 50% w/w TEPA (PT50) and 50% PEI (PP50) (adsorption with 100% CO<sub>2</sub> feed at 75 °C and desorption with 100% N<sub>2</sub> feed at 75 °C).

The research about the covalent bonded amines are based on understanding the interactions between CO<sub>2</sub>, functional chains and silica surfaces. The most used bonding agent is (3-aminopropyl)triethoxysilane (APTES) for the modifications of silica surfaces. Leal et al. studied the CO<sub>2</sub> adsorption on the silica gel grafted by APTES [94]. The adsorption capacity at 1 bar and 23 °C was found to be 0.6 mmol CO<sub>2</sub>/g when the grafting was 1.27 mmol amine/g. Certain properties of APTES grafted adsorbents are compared in Table 17.

## 7. Comparison of the properties of solid amine sorbents

Table 18 shows the CO<sub>2</sub> adsorption capacities of the solid amine adsorbents which were obtained by us from TGA measurements (100% CO<sub>2</sub> feed at 75 °C). According to Table 18, CO<sub>2</sub> adsorption capacities of TEPA based adsorbents are comparatively higher than those based on DETA, PEI or APTES. It is envisaged that this behaviour is due to the high number of amine groups that are present in TEPA.

According to Yue et al. [56], the CO<sub>2</sub> adsorption capacity of SBA-15/TEPA70 (70% TEPA by weight) at 100% CO<sub>2</sub> feed at 75 °C was found to be 3.93 mmol/g adsorbent by the TPD-TCD analysis. However in this study, a CO<sub>2</sub> adsorption capacity of 4.69 mmol/g adsorbent by TGA was obtained which is much higher than those reported in the literature.

The patent WO 2004/054708 claims a CO<sub>2</sub> adsorption capacity of 1.14 mmol/g adsorbent for SBA-15/APTES (20% CO<sub>2</sub> feed at 75 °C) obtained by TGA analysis. However, Sayeri et al. reached to a value of 1.73 mmol/g of adsorbent for the same solid amine system [101].

Our results show that, although the CO<sub>2</sub> adsorption capacity of TEPA based adsorbents are higher than the PEI-based solid amines (see Table 18), the cyclic stabilities of PEI based adsorbents (with 3% capacity lost at 10th cycle) are much higher than the TEPA based adsorbents (with 12% capacity lost at 10th cycle) (see Fig. 12). We believe that this behaviour is due to better hold of a polymeric structure (PEI) in the mesopores of the silicas and easy release or escape of low molecular weight (TEPA) from the silica surfaces.

## 8. Conclusions

For the current situation of CO<sub>2</sub> capture process through a chemical adsorption onto solid amine sorbents, the amine-based systems are the most advanced and inexpensive technologies in terms of postcombustion of CO<sub>2</sub>. Despite its advantageous and advanced stage of development, separation of CO<sub>2</sub> from flue gas by aqueous amine solutions remains very costly. On the other

hand, solid amine sorbents have the potential to obtain some of the advantages of aqueous amines while eliminating the disadvantages such as the high energy requirement for regeneration. In this respect, modifying original amines with various alkyl groups is likely to decrease reaction enthalpy leading to lower energy for regeneration.

A number of solids can be used to react with CO<sub>2</sub> to form stable compounds at one set of operating conditions and then, at another set of conditions, be regenerated to liberate the adsorbed CO<sub>2</sub> to reform the original compound. However solids are inherently more difficult to work with than liquids, and no solid sorbent system for large scale recovery of CO<sub>2</sub> from flue gas has yet been commercialized, although molecular sieve systems are currently used to remove impurities from a number of industrial streams, such as in the production of pure H<sub>2</sub>.

Therefore, CO<sub>2</sub> capture using solid amine sorbents is much less developed and substantial research has to be done on aspects, such as, adsorption capacity and stability of high molecular amines or polyamines impregnated or grafted onto mesoporous silica or polymeric supports. Therefore, there is an urgent need for improvement in terms of working adsorption capacity, cycle lifetime, and multicycle durability.

For understanding the challenges and opportunities as a near or long-term promising technology for CO<sub>2</sub> capture, the literature is certain that research into solid amine sorbents is at a much less-developed stage compared to the aqueous amines. Recent research has been dominated by the development and characterization of new efficient adsorbents, synthetic gases which are not currently addressing the envisaged problems associated with real flue gases and measuring the capacity of the sorbents. While each study often performs a qualitative study of sorption and desorption kinetics, so the results are difficult to compare from one paper to the next. As a result, more research has to be performed on the field of process design and optimization with solid sorbents before this technology can be industrialized. The issues of increasing the sorbent stability and capacity must be enlightened deeply in the current date.

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