



Carbon dioxide capture using amine-impregnated HMS having textural mesoporosity

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ARTICLE INFO

Article history:

Received 25 September 2009

Received in revised form 6 April 2010

Accepted 12 April 2010

Keywords:

HMS

PEI impregnation

Textural mesoporosity

CO₂ sorption

ABSTRACT

A series of HMS (hexagonal mesoporous silica) materials having different textural mesoporosities was synthesized using dodecylamine as a structure directing agent, which were employed as a host for supporting PEI (polyethylenimine) (PEI/HMS) as a CO₂ capturing agent. The textural properties of the prepared materials were examined by XRD, N₂ adsorption–desorption isotherms, and SEM. CO₂ sorption/desorption measurements were carried out using a TGA unit using high purity (99.999%) CO₂. The as-prepared HMS alone exhibited a moderate sorption capacity of 34 mg_{CO₂}/g_{sorbent} at 25 °C. The PEI/HMS prepared using a HMS having complementary textural mesopores exhibited CO₂ sorption capacity of 128 mg_{CO₂}/g_{sorbent} with a 45 wt% PEI loading at 75 °C, whereas a sorption capacity of 94 mg_{CO₂}/g_{sorbent} only was obtained under the same loading level using a HMS host with negligible textural mesoporosity. In addition, we were able to increase the PEI loading to 60 wt% without losing the capturing efficiency of the former, and achieved a CO₂ sorption capacity of 184 mg_{CO₂}/g_{sorbent}, one of the highest capturing capacities reported in the literature thus far under the given conditions. PEI/HMS exhibited only a minor drop in CO₂ capture capacity during a 4 repeated cyclic sorption–desorption run at 75 °C.

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1. Introduction

Anthropogenic CO₂ emissions, largely caused by fossil fuel combustion, have become a serious concern in relation to global warming, and much effort has been devoted to developing technologies for efficient capture and sequestration of CO₂. Among the various chemical and physical methods available for separation of CO₂ from gas mixtures [1], large-scale separation of CO₂ by liquid phase amine-based absorption is currently in commercial operation throughout the world; during the chemical absorption of CO₂, two molecules of amine species in various capturing sorbents react with one molecule of CO₂ to form a carbamate species (2R-NH₂ + CO₂ → R-NH₃⁺ + R-NHCOO⁻). However, serious drawbacks of these sorbent systems have been also reported, including the requirement of a large amount of energy for regeneration, equipment corrosion, and solvent degradation in the presence of oxygen [2].

Various porous solid materials have been investigated as well for CO₂ capture by means of the adsorption principle, and the zeolite 4A, 13X, and ZSM-5 [3–10], and activated carbons [11–13] have been considered for low temperature applications. However, the adsorption capacities of these materials, generated by physisorp-

tion induced either by ion-quadrupole interaction (zeolites) or van der Waals forces (activated carbons), decrease rapidly at moderately high temperatures. Lower selectivity to CO₂ is another problem of these materials.

More recently, several research groups reported excellent performances of mesoporous silica materials incorporated with an amine-type CO₂ capturing agent for CO₂ removal. These materials can be grouped together depending on the preparation methods: grafting with diverse amine species [14–26] and impregnation using polyethylenimine (PEI), tetraethylenepentamine (TEPA) or diethanolamine (DEA) on mesoporous silicas [27–37]. In both of these amine-supported systems, amine-functionalities are dispersed inside the pores of a mesoporous support material, and thereby produce enhanced CO₂ capturing performance relative to that of the bulk amines.

HMS is a highly porous 3-D channel mesoporous silica material with a disordered wormhole structure. As is well known [38], HMS can be easily synthesized by a sol–gel process using a primary alkylamine, inexpensive and biodegradable, as a structure directing agent at room temperature. After removing surfactant molecules, HMS can be used for impregnation with an amine-type chemical agent with high N group concentrations for CO₂ capture. Since the alkylamine templating agent itself used in the HMS synthesis is expected to have some CO₂ sorption capacity, it will be also interesting to know if the as-prepared HMS can be used without further treatment as a CO₂ capturing sorbent.

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The small crystallite size of primary particles in HMS is known to yield substantial complementary textural mesoporosities [38], which differentiate the material from the other mesoporous materials we have studied earlier (MCM-41, MCM-48, SBA-15, SBA-16, and KIT-6) [31]. These textural mesopores can make very important contributions in sorption process, since they are known to facilitate mass transport to the framework mesopores [39], and thus can promote efficient transport of CO₂ to the capturing sites; meanwhile, this textural mesoporosity in HMS can also make it possible to increase the total amine loading levels in the silica support material.

In this work, we report the CO₂ capturing performances of as-prepared HMS and those of HMS impregnated with PEI (PEI/HMS). Two groups of HMS samples, one with negligible and the other with varying amounts of textural mesopores, were employed as a support material for amine species to study the textural mesopore effect. The effectiveness of PEI/HMS as a CO₂ capturing agent was investigated in terms of sorption capacity and stability. For this purpose, we measured CO₂ sorption capacities gravimetrically under different conditions of temperature and PEI loading levels. Durability tests using selected samples were also conducted.

2. Experimental

2.1. Synthesis of HMS

HMS with negligible textural mesoporosity was prepared according to the recipe reported by Pinnavaia et al. [38]. Tetraethyl orthosilicate (TEOS, 0.1 mol) was added under vigorous stirring to a solution of dodecylamine (DDA, 0.027 mol) in ethanol (0.909 mol) and de-ionized water (2.96 mol). The substrate mixture was aged at ambient temperature for 18 h and the resulting precipitate was air-dried on a glass plate. The as-prepared HMS (HMS-A) was calcined at 630 °C for 4 h to remove the surfactant molecules (HMS-C).

HMS samples having different portions of textural mesoporosity were prepared according to the recipe reported by Zhang et al. [39]. In a typical synthesis, TEOS was added under stirring to a solution containing DDA in an ethanol/water mixture (10/90, v/v). The mixture was subjected to vigorous stirring for 20 min in an open vessel. It was then placed in a closed Teflon vessel and stirred for 20 h at different temperatures ranging from 50 to 90 °C. The solid product obtained was filtered, washed with distilled water, dried at 40 °C, and calcined in air at 600 °C (2 °C/min) for 4 h. The molar composition of the synthesis mixture was: TEOS/DDA/ethanol/H₂O = 1/0.25/4.4/128. The samples obtained are denoted as HMS-Tx (x = synthesis temperature in °C).

A sample of different kind of HMS having textural mesoporosity was also prepared using mesitylene as an additive (HMS-M). The synthesis procedure is identical to that for HMS-A described above except for the addition of 0.036 mol of mesitylene to 0.027 mol of DDA template. The substrate mixture was aged at ambient temperature for 18 h and the resulting precipitate was air-dried on a glass plate. The as-prepared material was calcined at 630 °C for 4 h to remove the surfactant molecules.

2.2. PEI impregnation on HMS

PEI in varying quantities was introduced into HMS-C according to the procedure reported by Xu et al. [27,28] and the corresponding samples were designated as XPEI/HMS-C, X being the quantity of PEI introduced in weight percentage. In a typical preparation, PEI (Aldrich, average molecular weight of 600 by GPC, linear type, b.p of 250 °C) was dissolved in methanol under stirring for about 15 min, after which HMS-C was added to the PEI/methanol solution in a glove box. The resultant slurry was continuously stirred for about 30 min and then dried at 70 °C for 16 h under reduced pressure

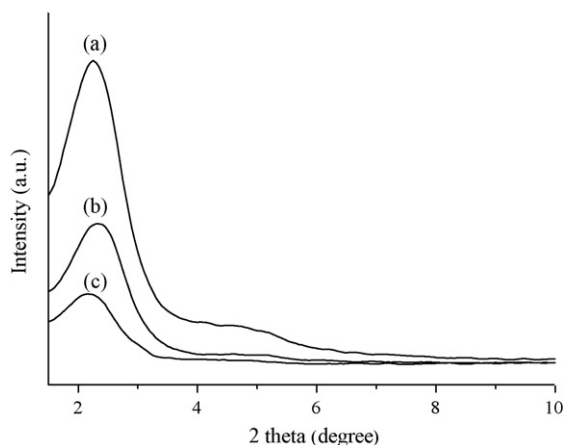


Fig. 1. XRD patterns of the HMS samples prepared: (a) HMS-C, (b) HMS-A, and (c) 45PEI/HMS-C.

(700 mmHg). The samples prepared using HMS-Tx and HMS-M as host materials were designated as XPEI/HMS-Tx and XPEI/HMS-M, respectively.

2.3. Characterization of the HMS materials prepared

Textural properties of all the HMS samples before and after PEI impregnation were characterized by X-ray diffraction (XRD) and N₂ adsorption-desorption. The XRD patterns were obtained on a Rigaku diffractometer using Cu K α ($\lambda = 1.54 \text{ \AA}$) radiation. Nitrogen adsorption-desorption isotherms were obtained on a Micromeritics ASAP-2000 sorptometer at liquid nitrogen temperature. The specific surface areas of these samples were calculated by the BET method, and the pore volumes and pore diameters were evaluated from the desorption branch of the isotherm based on the BJH (Barrett-Joyner-Halenda) model. The amounts of PEI introduced to the mesoporous silica samples were measured by a thermogravimetric analysis (TGA, SCINCO thermal gravimeter S-1000); PEI-impregnated samples were heated at 5 °C/min to 600 °C under airflow (50 mL/min). N amounts in all these samples were measured by EA (elemental analysis). SEM investigation of morphological features was carried out using a Hitachi S-4200 instrument.

2.4. CO₂ sorption-desorption measurement

The same TGA unit (SCINCO thermal gravimeter S-1000) was connected to a flow panel and used for CO₂ sorption/desorption measurement. A sample having a weight of ca. 10 mg was loaded into an alumina sample pan and subjected to CO₂ sorption studies. The initial activation of the samples was carried out at 100 °C for 1 h in N₂ (ultra high purity, U-Sung). The sorption run was carried out using high purity CO₂ (99.999%) gas. N₂ (ultra high purity, U-Sung) was used as a purge gas. A feed flow rate of 30 mL/min to the sample chamber was controlled with a MFC.

3. Results and discussion

3.1. PEI impregnated onto HMS with negligible textural mesoporosity

Fig. 1 shows the XRD patterns of HMS-A, HMS-C, and 45PEI/HMS-C. HMS-A exhibited a single diffraction peak (at 2 theta of 2.4°) corresponding to the well-known disordered pore structure of the material. The peak intensity increased after the surfactant removal in HMS-C [38]. The location of the characteristic Bragg diffraction peak of HMS remained nearly constant after loading of

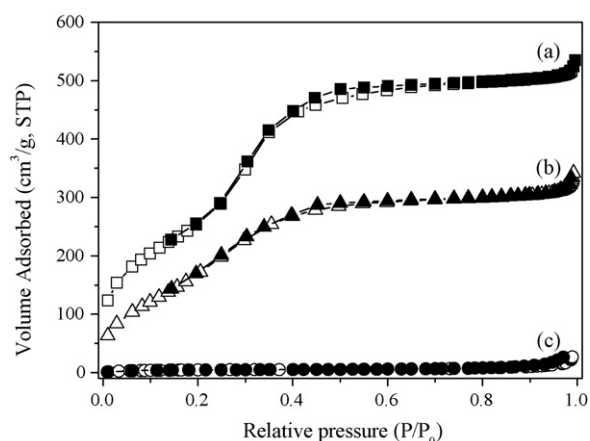


Fig. 2. Nitrogen adsorption-desorption isotherms: (a) HMS-C, (b) 20PEI/HMS-C, and (c) 45PEI/HMS-C.

PEI, but the intensity of the diffraction peak decreased substantially, indicating that PEI was successfully loaded into the channels of the silica support [28].

Fig. 2 shows representative N_2 adsorption-desorption isotherms of HMS-C and PEI/HMS-C with different PEI loading amounts, and Table 1 summarizes the textural properties of all the samples prepared in this work with or without amine loadings. The nitrogen adsorption-desorption isotherm of the HMS-C measured at 77 K shows typical type IV adsorption behavior corresponding to the mesostructure of the materials. Capillary condensation reflecting uniform distribution of mesopores is clearly detected in the region of $0.2 < P/P_0 < 0.5$. Textural mesoporosity in the isotherm, given by the increment in N_2 volume adsorbed at high relative pressure values of $P/P_0 > 0.9$, was minor as shown in Table 1; the suppression of textural mesoporosity in HMS is due to the relatively large amount of ethanol added during the synthesis [39]. The measured BET surface area for HMS-C was $952 \text{ m}^2/\text{g}$ and the distribution of structural mesopore diameters was centered at 2.8 nm. At a loading amount

of 20 wt% PEI on HMS-C, the adsorption branch of the N_2 isotherm shifted to a lower pressure range and the pore volume concurrently decreased, confirming that PEI was successfully loaded into the channels of the support [28]. Above 45 wt% PEI, most of the mesopores are filled up with PEI, resulting in a type II isotherm [27]. As summarized in Table 1, pore volumes and BET surface areas decreased as the loading amount of PEI was increased in HMS-C.

Fig. 3 shows SEM pictures of HMS-C, 45PEI/HMS-C, and 50PEI/HMS-C. The hybrid material still retained the original morphology of HMS-C with PEI loading up to 45 wt% (b). In 50PEI/HMS-C (c), on the other hand, the loading amount of PEI was in excess of the maximum accommodation capacity of HMS-C, i.e., 45% based on the pore volume and density of PEI (ca. $1.0 \text{ g}/\text{cm}^3$), and PEI coated on the external surface of the mesoporous material was clearly observed.

At the outset, we measured the CO_2 sorption capacities of HMS-A at different temperatures. CO_2 sorption capacity of $34 \text{ mg}_{\text{CO}_2}/\text{g}_{\text{sorbent}}$ was obtained at 25°C . This result is encouraging, since we can use the as-syn HMS as a sorbent for CO_2 at ambient temperature; for comparison, monoamine surface-bonded silica gel was reported to have a capacity of $18\text{--}39 \text{ mg}_{\text{CO}_2}/\text{g}_{\text{sorbent}}$ [22]. The CO_2 sorption by HMS-A is apparently due to the surfactant DDA, which not only functions as a structure directing agent for HMS but can provide active sites for capturing CO_2 via formation of a carbamate complex. The N amount in HMS-A was measured by EA, and CO_2/N was calculated to be 0.37 (Table 1). This value is comparable to those exhibited by the amine-grafted systems [15]. When the temperature was increased to 45 and 65°C , the amount of adsorbed CO_2 decreased continuously to 25 and $19 \text{ mg}_{\text{CO}_2}/\text{g}_{\text{sorbent}}$, respectively. CO_2 sorption capacity for HMS-C was only $9.6 \text{ mg}_{\text{CO}_2}/\text{g}_{\text{sorbent}}$ at 25°C .

Initially, we investigated the effect of PEI loadings on the CO_2 capturing capacity of the HMS materials prepared. CO_2 sorption runs were conducted at 75°C , selection of which is based upon previously reported optimization studies [28,31]. As shown in Table 1, the CO_2 sorption capacity was $26 \text{ mg}_{\text{CO}_2}/\text{g}_{\text{sorbent}}$ ($130 \text{ mg}_{\text{CO}_2}/\text{g}_{\text{PEI}}$) when the PEI loading was 20 wt%, and as the PEI loading was increased further, the total sorption capacity increased accordingly.

Table 1
Textural properties and CO_2 sorption capacities of PEI-impregnated HMS samples.

Samples	S_{BET} (m^2/g)	V_t^a (cm^3/g)	V_r^b (cm^3/g)	V_{tx}^c (cm^3/g)	Average structural mesopore size (nm)	Sorption capacity ^d		
						$\text{mg}_{\text{CO}_2}/\text{g}_{\text{sorbent}}$	$\text{mg}_{\text{CO}_2}/\text{g}_{\text{PEI}}$	CO_2/N molar ratio
HMS-C	952	0.82	0.77	0.05	2.8	9.6	–	–
HMS-A	–	–	–	–	–	34	–	0.37
20PEI/HMS-C	769	0.39	–	–	2.5	26	130	0.13
40PEI/HMS-C	21	0.07	–	–	–	80	200	0.2
45PEI/HMS-C	4	0.04	–	–	–	94	209	0.21
50PEI/HMS-C	–	–	–	–	–	101	202	0.2
60PEI/HMS-C	–	–	–	–	–	115	192	0.19
70PEI/HMS-C	–	–	–	–	–	108	154	0.15
HMS-T50	759	0.92	0.63	0.29	3.0	–	–	–
HMS-T75	767	1.15	0.90	0.25	3.7	–	–	–
HMS-T90	561	1.44	1.13	0.31	9.8	–	–	–
HMS-M	1123	1.37	0.96	0.41	2.8	–	–	–
45PEI/HMS-T50	17	0.13	–	–	–	113	251	0.25
45PEI/HMS-T75	20	0.23	–	–	–	119	265	0.26
45PEI/HMS-T90	54	0.39	–	–	–	128	285	0.28
45PEI/HMS-M	22	0.3	–	–	–	120	267	0.26
60PEI/HMS-T90	13	0.19	–	–	–	184	307	0.3
65PEI/HMS-T90	7	0.08	–	–	–	183	282	0.28
70PEI/HMS-T90	2	0.04	–	–	–	165	236	0.23

^a Total pore volume by N_2 adsorption to $P/P_0 = 0.99$.

^b Framework pore volume.

^c Textural pore volume.

^d CO_2 sorption capacities for PEI-impregnated samples were measured at 75°C , while CO_2 adsorption capacities for HMS-C and HMS-A were measured at 25°C .

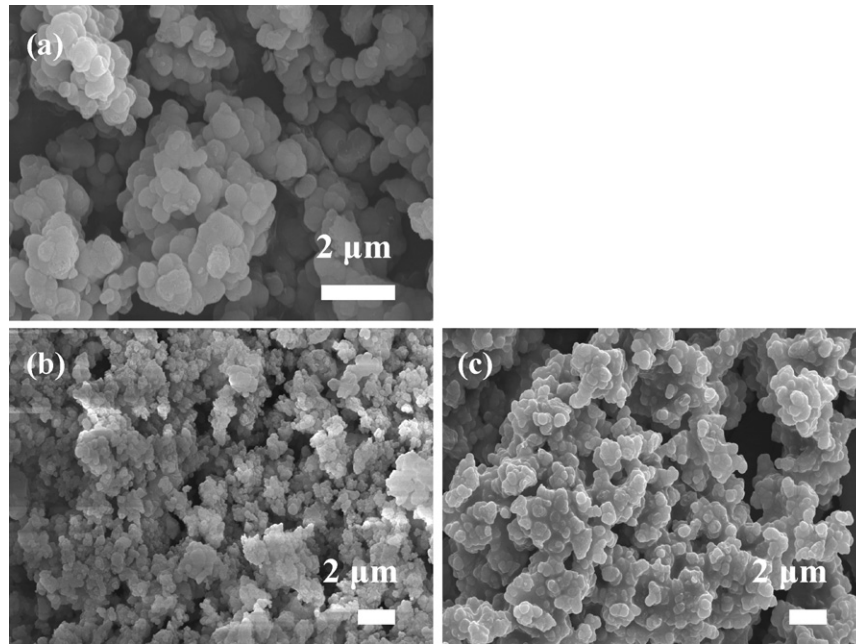


Fig. 3. SEM pictures of (a) HMS-C, (b) 45PEI/HMS-C, and (c) 50PEI/HMS-C.

A maximum of $115 \text{ mg}_{\text{CO}_2}/\text{g}_{\text{sorbent}}$ was measured with 60PEI/HMS-C and the CO_2 sorption capacity decreased at 70 wt% loading. In terms of CO_2 sorption capacity based on impregnated PEI and CO_2/N molar ratio, however, 45PEI/HMS-C exhibited the best performance ($209 \text{ mg}_{\text{CO}_2}/\text{g}_{\text{PEI}}$, $\text{CO}_2/\text{N}=0.21$). Since the pore volume of HMS-C is $0.82 \text{ cm}^3/\text{g}$ and the density of PEI is about $1.0 \text{ cm}^3/\text{g}$, the maximum PEI loading expected to reside inside the pores of HMS is about 45 wt%. At higher PEI loadings on HMS-C, the sorption capacity per gram PEI decreased, indicating that PEI has lower sorption efficiency when PEI is coated on its outer surface than when it is located inside the HMS-C pores [27,28].

Fig. 4 shows the effect of sorption temperature on the CO_2 sorption capacities. The CO_2 capturing capacity increased with temperature and the highest CO_2 sorption capacity ($117 \text{ mg}_{\text{CO}_2}/\text{g}_{\text{sorbent}}$) was obtained in the case of 45PEI/HMS-C at 90°C . As the temperature is increased, PEI becomes more flexible and more CO_2 -affinity sites are exposed to the CO_2 ; the available pore space for CO_2 would also increase to some extent, leading to faster diffusion of CO_2 in the channels [28]. Once efficient contact between CO_2 and sorption sites is established, the sorption process is dictated by thermody-

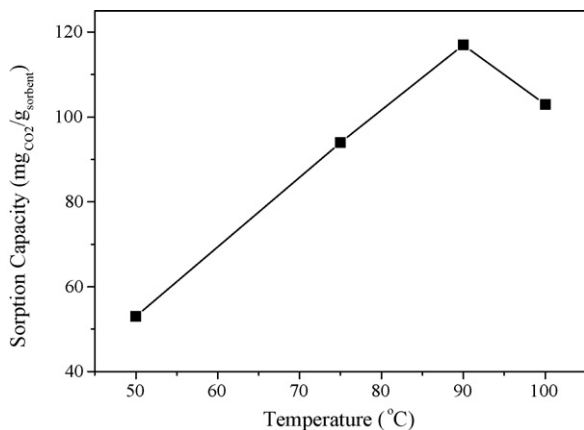


Fig. 4. CO_2 sorption performances of 45PEI/HMS-C at different temperatures.

namics; above 90°C the equilibrium shifts to the reverse direction and desorption is favored.

The performance of 45PEI/HMS-C in 4 consecutive sorption–desorption runs was firstly tested for stability at 90°C , since the highest CO_2 sorption capacity was obtained at 90°C . When the temperature for both sorption and desorption was maintained at 90°C , following the experimental protocol by Xu et al. [28], however, the CO_2 sorption capacities decreased continuously after each cycle of sorption–desorption (not shown), which indicates that PEI/HMS-C is not sufficiently stable at 90°C for prolonged operation. Since PEI is introduced into the support by impregnation, the risk of PEI evaporation from the support would increase with increased temperature. Whilst the highest CO_2 sorption capacity occurred at 90°C as a result of rendering the amine species soft and flexible—and thereby exposing more CO_2 -affinity sites to CO_2 —prolonged operation at 90°C appears to gradually evaporate a small amount of PEI. Therefore, we repeated the same cyclic experiments at a more moderate temperature of 75°C . As shown in Fig. 5, only a minor decrease in sorption capacity is detected with 45PEI/HMS-C; $94 \text{ mg}_{\text{CO}_2}/\text{g}_{\text{sorbent}}$ in the 1st run while $92 \text{ mg}_{\text{CO}_2}/\text{g}_{\text{sorbent}}$ in the 4th run during the sorption–desorption cycle for a total duration of 700 min.

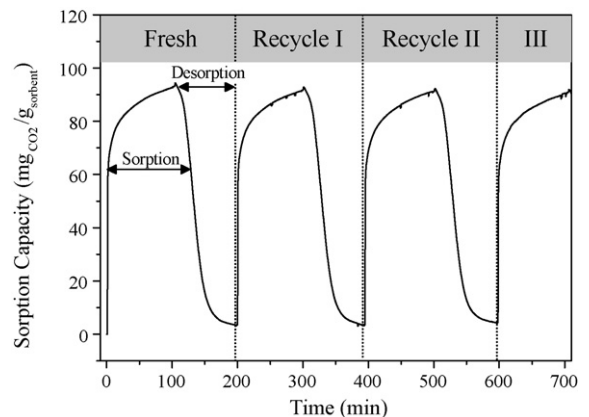


Fig. 5. Recycle runs of CO_2 at 75°C for 45PEI/HMS-C.

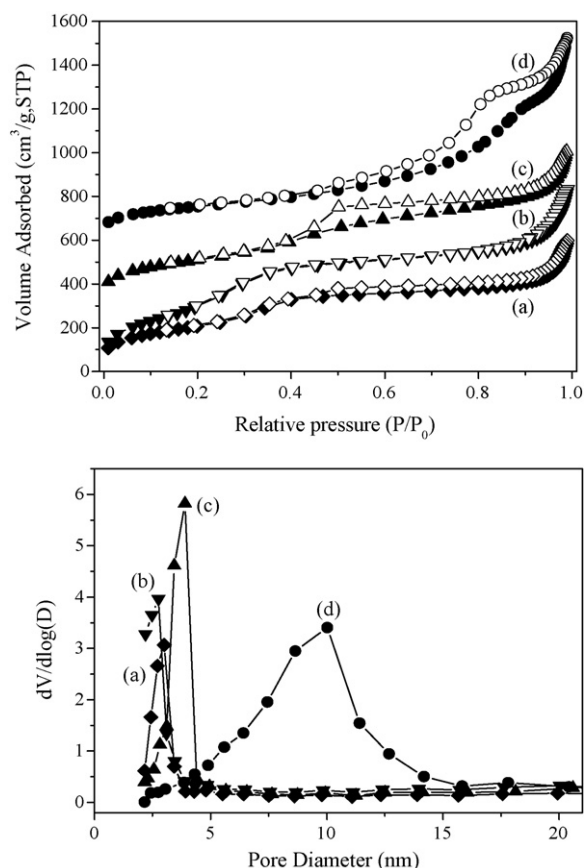


Fig. 6. Nitrogen adsorption isotherms and pore size distributions of HMS samples: (a) HMS-T50, (b) HMS-M, (c) HMS-T75, and (d) HMS-T90. Isotherms of HMS-T75 and HMS-T90 are vertically shifted by 300 and 600 cm³/g respectively, for clarity.

3.2. PEI impregnated onto HMS having textural mesoporosity

After studying the fundamental CO₂ capturing behaviors of PEI-impregnated HMS-C samples, the potential contribution of the complementary textural mesoporosity in HMS to the CO₂ capturing capacity was investigated. To this end, HMS materials with textural mesoporosity (HMS-T and HMS-M) were prepared under low ethanol concentration at synthesis temperatures of 50, 75, and 90 °C [39] and were subsequently tested as a matrix for PEI impregnation.

All the XRD patterns of the HMS-T samples prepared at different synthesis temperatures (not shown) again exhibited a single XRD peak. This is typical of silica materials with a wormhole structure, and the characteristic peak shifts to lower angles in accordance with an increase in structural mesopore size from 3.0 to 9.8 nm as the synthesis temperature is changed from 50 to 90 °C. The corresponding nitrogen sorption isotherms and pore size distribution curves of the HMS-T50, -T75, and -T90 samples are shown in Fig. 6, and the corresponding textural parameters are listed in Table 1. All the samples exhibit typical type IV isotherms with pronounced capillary condensation corresponding to the framework-confined mesopores (structural). For high relative pressure values (i.e. $P/P_0 > 0.9$), another pronounced condensation steps appear, which are ascribed to the inter-particle voids between the primary particles (textural mesoporosity). Compared to HMS-C, these HMS-T and HMS-M samples created much higher textural pore volumes. The average structural mesopore diameter increased from 3.0 to 9.8 nm and the PSD became broader, and the sample pore volume measured by N₂ adsorption increased from 0.92 to 1.44 cm³/g, as the synthesis temperature was increased from 50 to 90 °C. The nitrogen

adsorption–desorption isotherm and pore size distribution curve of HMS-M prepared by the addition of mesitylene at 25 °C are also included in Fig. 6. The average structural mesopore size of HMS-M remains at 2.8 nm, as in HMS-C, but a significant degree of textural mesoporosity was created.

Initially, a CO₂ sorption test was conducted at 75 °C, and sorption capacities of PEI/HMS-T samples were measured and compared against PEI/HMS-C at 45 wt% PEI loading. As summarized in Table 1, the CO₂ sorption capacity increased from 113 to 128 mg_{CO₂}/g_{sorbent} from 45PEI/HMS-T50 to -T90 without any loss in CO₂ capture efficiency of PEI (251 to 285 mg_{CO₂}/g_{PEI}, and CO₂/N in the range of 0.25–0.28). These values are significantly higher than those corresponding to 45PEI/HMS-C (94 mg_{CO₂}/g_{sorbent}, 209 mg_{CO₂}/g_{PEI}, and CO₂/N ratio was 0.21) having negligible complementary textural mesoporosity. HMS-T50, which has a close average structural mesopore diameter to that of HMS-C (3.0 and 2.8 nm, respectively) exhibited ca. 20% (19 mg_{CO₂}/g_{sorbent}) higher CO₂ sorption capacity under the same conditions. This is attributed to the contribution of the textural mesoporosity in HMS-T50. HMS-T75 and HMS-T90 also have much larger average structural mesopore diameters (3.7 and 9.8 nm), and the CO₂ sorption capacity was further increased, consistent with our earlier results [31]. Interestingly enough, 45PEI/HMS-M having large textural mesoporosity but the same structural pore size as HMS-C produced 120 mg_{CO₂}/g_{sorbent}, which is even higher than that of 45PEI/HMS-T75. The high CO₂ capturing efficiency of the HMS-T and HMS-M samples must be attributed to the complementary textural mesoporosity, which can facilitate the effective transport of CO₂ inside the 3-D channels of HMS as expected.

We then further increased the PEI loading on HMS-T90 systematically from 45 to 70 wt% in an effort to produce a PEI-impregnated HMS with further enhanced CO₂ capturing capacity. We examined the textural properties of these materials first, and Fig. 7 shows the N₂ adsorption–desorption isotherm of HMS-T90 before and after PEI impregnation. As shown, some free pore volume remained for 45PEI/HMS-T90 after PEI impregnation, but beyond 60 wt% PEI loading, most of the mesopores are filled up with PEI, resulting in type II isotherms, which is consistent with the case of PEI/HMS-C earlier (Fig. 2). The corresponding SEM images of the PEI/HMS-T90 samples are shown in Fig. 8. Whilst agglomeration of PEI on 45PEI/HMS-T90 and 60PEI/HMS-T90 was not observed, HMS particles partly PEI-coated on the external surface were observed for 65PEI/HMS-T90. 70PEI/HMS-T90 produced excessively agglomerated HMS particles covered with PEI.

When we measured the CO₂ capturing performance of these PEI-loaded materials, a CO₂ sorption capacity of 184 mg_{CO₂}/g_{adsorbent}

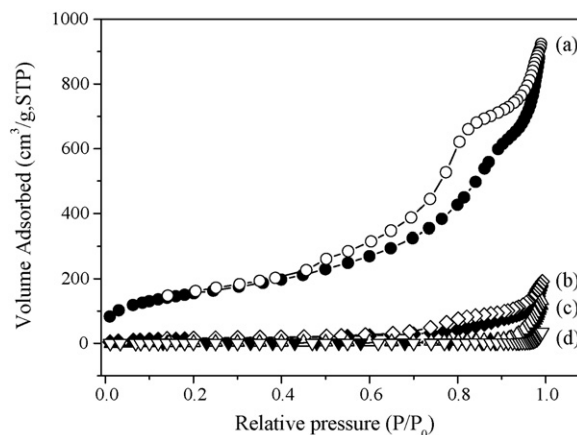


Fig. 7. Nitrogen adsorption–desorption isotherms: (a) HMS-T90, (b) 45PEI/HMS-T90, (c) 60PEI/HMS-T90, and (d) 65PEI/HMS-T90.

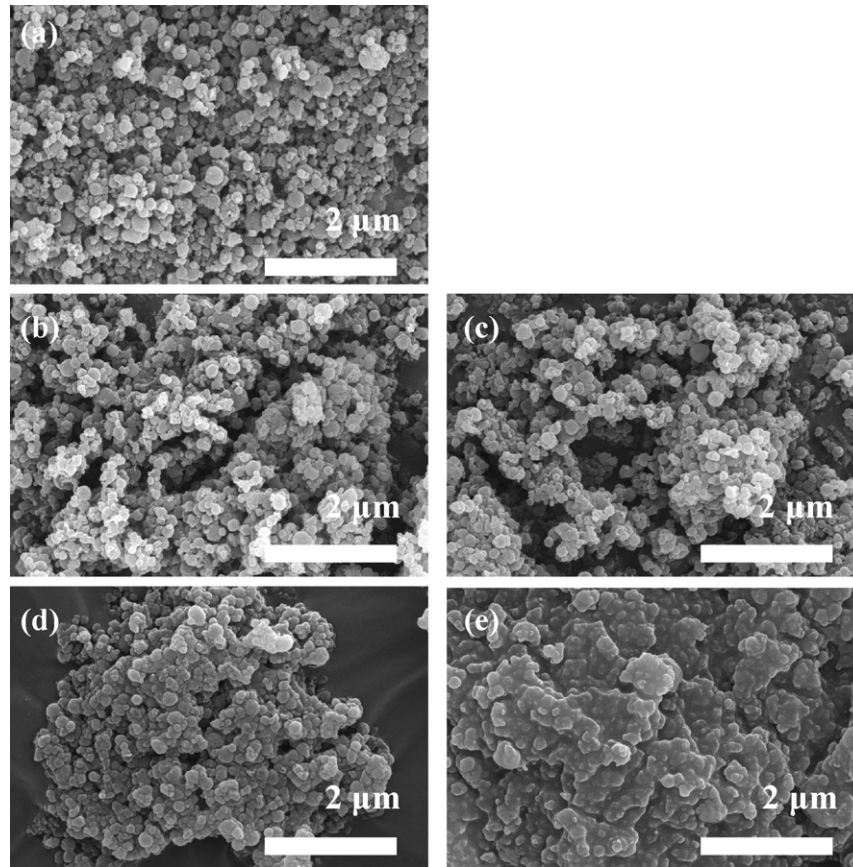


Fig. 8. SEM pictures of (a) HMS-T90, (b) 45PEI/HMS-T90, (c) 60PEI/HMS-T90, (d) 65PEI/HMS-T90, and (e) 70PEI/HMS-T90.

(see Table 1) was achieved for 60PEI/HMS-T90: the highest amount of adsorbed CO₂ reported thus far among the PEI-impregnated systems. In addition to the increase in the CO₂ sorption capacity, the capturing efficiency calculated by CO₂ sorption capacity per gram of PEI and CO₂/N ratio was also increased to 307 mg and 0.3, respectively. When the PEI loading amount was further increased to 65 wt%, a sorption capacity of 183 mg_{CO₂}/g_{sorbent} was achieved with a slight drop in the PEI capturing efficiency. 70PEI/HMS-90, on the other hand, achieved only 165 mg_{CO₂}/g_{sorbent}; obviously the CO₂ capturing efficiency was adversely affected by pore blockage of textural mesopores and by PEI coated on the outer surface.

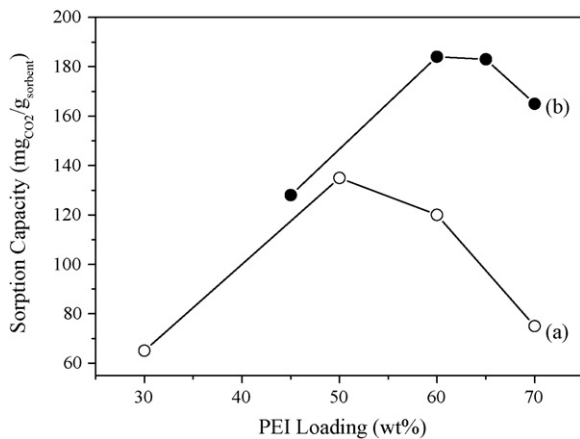


Fig. 9. CO₂ sorption capacities at different PEI loadings: (a) PEI/KIT-6 [31] and (b) PEI/HMS-T90.

Fig. 9 presents a comparison of the CO₂ capturing performance as a function of PEI loading between PEI/KIT-6 and PEI/HMS-T90; KIT-6 was the best support material for the PEI impregnation system reported previously by the present authors [31]. For PEI/KIT-6, a CO₂ sorption capacity of 135 mg_{CO₂}/g_{sorbent} was measured for 50 wt% PEI/KIT-6 and the CO₂ sorption capacity decreased as the PEI loading was increased to 60 wt%. Since KIT-6 can hold up to ca. 55 wt% PEI inside its pores according to the pore volume, some portion of PEI is coated on the outer surface when 60 wt% PEI was introduced, leading to a decreased CO₂ sorption capacity. For the PEI/HMS-T90 system, on the other hand, the maximum CO₂ sorption capacity was measured at 60 wt% PEI loading (184 mg_{CO₂}/g_{sorbent}). HMS-T90 has a larger pore volume, which can hold a greater amount of PEI inside the pores without overflow. At

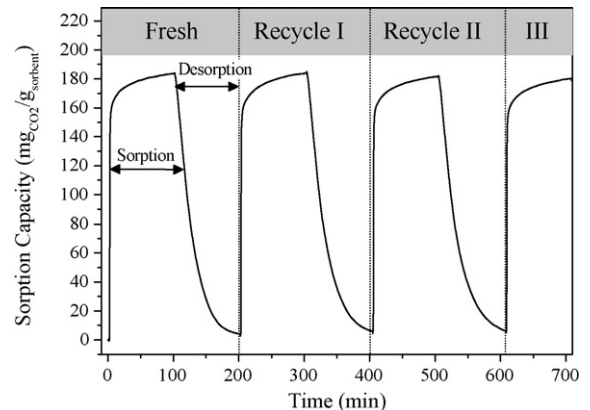


Fig. 10. Recycle runs of 60PEI/HMS-T90 at 75 °C.

the same time, its textural mesoporosity facilitates CO₂ diffusion inside the pores, thereby providing easier access to the active sites. This comparison between HMS-T90 and KIT-6 clearly shows the advantages of the HMS having textural mesopores as a PEI impregnation support material for CO₂ capture.

Finally, the performance of 60PEI/HMS-T90 in 4 consecutive sorption–desorption runs was measured. As shown in Fig. 10, the sample exhibited a stable cyclic sorption–desorption performance for a 700 min cycle with only a minor drop in its capturing capacity (the total sorption capacity in the 1st run was 184 mg CO₂/g sorbent, and the 4th run produced a capacity of 181 mg CO₂/g sorbent, there was only 1.6% drop in the capacity during 4 runs).

4. Conclusions

CO₂ sorption by various HMS silica materials impregnated with PEI (PEI/HMS) was investigated. CO₂ sorption capacity increased remarkably after PEI was loaded onto HMS samples with complementary textural mesopores, and a sample with 60 wt% PEI loaded onto HMS having textural mesopores achieved a very high CO₂ sorption capacity of 184 mg CO₂/g sorbent at 75 °C and also performed well in a cyclic sorption–desorption run for 700 min.

Acknowledgment

This study was supported by the Energy Resources Technology Development Program of Ministry of Knowledge Economy in Korea (2009).

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