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Tetraethylenepentamine-modified mesoporous adsorbents for CO_2 capture: effects of preparation methods

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Abstract Tetraethylenepentamine (TEPA)-modified mesocellular silica foams (MSFs) were fabricated via physical impregnation (MSF-T-x) and chemical grafting (MSF-CT-y) methods. The CO_2 adsorption on these TEPA-modified MSFs was measured by using microbalances at 348 K and their adsorption capacities were observed to be 26.4–193.6 mg CO_2/g-sorbent under ambient pressure using dry 15 % CO_2. It was found that the CO_2 adsorption capacities of MSF-CT-y were smaller than those of MSF-T-x sorbents which may be attributed to their higher density of amine groups. On the contrary, MSF-CT-y exhibited enhanced stability during repeated adsorption-desorption cycles compared to MSF-T-x sorbents. This notable enhancement in the durability of CO_2 adsorption-desorption process was probably attributed to the decreased leaching of TEPA which is chemically bonded to the surface of MSF.

Keywords Tetraethylenepentamine · Surface modification · Mesoporous silica · CO_2 capture · Durability

1 Introduction

Climate change and global warming are receiving great attention and considered as the most important and severe challenging issue facing human beings. It is generally known that a main cause for global warming of the earth is the progressive increase of CO_2 concentration in the atmosphere due to the extensive utilization of fossil fuels (Figueroa et al. 2008; Belmabkhout and Sayari 2009; MacDowell et al. 2010). Thus, it is crucial to find ways to efficiently and economically capture CO_2 from large stationary sources, such as coal-fired power plants, cement and steel factories, etc. For post-combustion capture, amine absorption processes has been commonly used. However, this technology is limited by the high capital and operation costs as well as high-energy consumption during regeneration of the absorbents.

Recently, a large amount of studies have reported techniques of physisorption using nanoporous solids for sequestration of CO_2, such as microporous zeolites (Pulido et al. 2009; Sayari et al. 2011; Akhtar et al. 2012), porous carbon materials (Choi et al. 2009; Hao et al. 2010; Fulvio et al. 2011; Sevilla et al. 2011), porous coordination polymers (Navarro et al. 2006; Liu et al. 2012) and organic nanostructures (Serre et al. 2007; D'Alessandro et al. 2010; Krishna and van Baten 2012). Nevertheless, most of above-mentioned materials exhibit low CO_2 adsorption capacity which is typically smaller than the substantial value of ca. 88 $\mathrm{mg\,g^{-1}}$ adsorbent (Hicks et al. 2008) for practical applications. In addition, these materials suffer from problems such as poor selectivity, poor tolerance to water, and high-temperature regeneration or activation.

Ordered mesoporous silicas (OMSs), which possess unique properties including tunable pore size (2–50 nm), narrow pore size distribution, high surface area, large pore volume, and good thermal stability, are widely used for applications as gas adsorbents. In the recent past, further modification of OMSs with amine functional groups were reported to capture CO_2. There are two main methods to prepare amine-modified adsorbents, including (i) liquid amines physically impregnated onto the OMSs and (ii) amines chemically bonded to the OMSs. For the former method,

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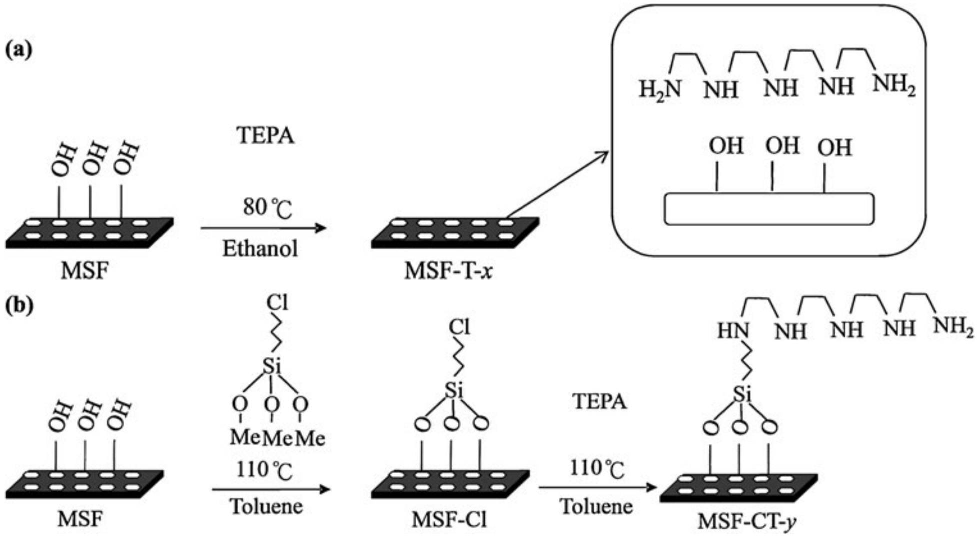

Fig. 1 Scheme of preparation of TEPA-modified adsorbents by (**a**) physical impregnation and (**b**) chemical grafting methods

ca. 50 wt% polyethylenimine (PEI)-incorporated MCM-41 with a high CO_2 adsorption capacity of 246 $mg\,g^{-1}$-PEI is 30 times higher than that of MCM-41 and also ca. 2.3 times that of the pristine PEI (Xu et al. 2002, 2005). Also, different polyamines loaded on various OMSs, such as MCM-48, KIT-6, MSF and SBA-15 have been utilized as adsorbents for CO_2 capture (Yue et al. 2006, 2008; Ichikawa et al. 2010; Qi et al. 2011). For the latter method, primary, secondary and tertiary amine-containing compounds have been functionalized onto the OMSs for CO_2 capture (Zeleňák et al. 2008; Liang et al. 2009; Chang et al. 2009; Tang and Landskron 2010; Lee et al. 2011; Yan et al. 2011; Zhou et al. 2011; Bai et al. 2012; Sharma et al. 2012; Yan et al. 2012; Zhao et al. 2012; Sayari et al. 2012). It was reported that grafting amines into the pore-expanded mesoporous silicas was able to capture CO_2 by greater amount of amine and also more resistant to moisture as compared with other supports such as activated carbon, silica gel, and pristine silica (Harlick and Sayari 2007; Serna-Guerrero et al. 2008, 2010). Cyclic adsorption-desorption process revealed that the above adsorbents have good durability. Hicks et al. (2008) synthesize a covalently tethered hyperbranched aminosilica (HAS) adsorbent which can perform CO_2 adsorption-desorption reversibly with a high capacity of 136.4 $mg\,g^{-1}$ adsorbents at 298 K and cyclic stability. Bhagiyalakshmi et al. (2010) reported a method to stepwise synthesis of amine-containing dendrimers grafted SBA-15 adsorbents which are thermally stable and efficient for CO_2 capture and their adsorption performance can be intact during 7 cycles of adsorption and thermal regeneration.

According to the published literature, different amines supported on various OMSs as adsorbents for CO_2 adsorption were extensively investigated. In particular, tetraethylenepentamine (TEPA) incorporated mesoporous silicas show promising applications due to their high CO_2 adsorption capacities and simple preparation route. Yue et al. (2006, 2008) dispersed TEPA onto as-synthesized mesoporous silica (MCM-41 and SBA-15) and attained the highest capacity of 237.6 $mg\,g^{-1}$ adsorbents at 348 K under pure CO_2 flow. Liu et al. (2010) loaded TEPA into KIT-6 mesoporous silicas by a conventional wet impregnation method and an excellent dynamic CO_2 adsorption capacity of 127.6 $mg\,g^{-1}$ adsorbents at 333 K was observed. Wen et al. (2010) reported an one-pot route to synthesize the TEPA-modified mesostructured monolith adsorbents which exhibited a high capacity of 171 $mg\,g^{-1}$ adsorbents in CO_2 adsorption. The surfactant-promoted adsorbents with TEPA also demonstrated much better CO_2 adsorption performance (Wang et al. 2012). Although the above-mentioned TEPA-modified adsorbents have high CO_2 adsorption capacities, they suffer from the deficiency concerning the instability of cyclic adsorption-desorption process (Hicks et al. 2008; Chen et al. 2009; Goeppert et al. 2010; Qi et al. 2011). In the present study, two different methods have been adopted to prepare TEPA-modified adsorbent materials (as shown in Fig. 1), namely (i) incorporating TEPA onto mesocellular silica foam (MSF) by physical impregnation method and (ii) functionalizing TEPA onto the MSF by chemical grafting method. These TEPA-modified MSFs were characterized by a series of different analytical and spectroscopic techniques, including N_2 adsorption/desorption, Small angle X-ray scattering (SAXS), elemental analysis (EA), and Fourier-transformed infrared (FTIR) spectroscopies. Among them, the adsorbents prepared by the latter method represent a remarkably enhanced durability after repeated adsorption-desorption cycles, revealing some opportunities for future practical and cost-effective applications.

2 Experimental section

2.1 Materials preparation

The parent MSF samples were prepared according to the methods reported previously (Lee et al. 2001). Typically, 2 g of neutral tri-block co-polymer surfactant (Pluronic 123; $EO_{20}PO_{70}EO_{20}$, MW = 5800, Aldrich) was dissolved in 75 mL of aqueous 1.6 N HCl at room temperature, then, 12 mg of NH_4F (ACROS) and 1.5 g of trimethylbenzene (TMB; 98 %, ACROS) were added into the mixture. After stirring for 1 h at 313 K, 4.3 g of TEOS was added to the mixture. The resulting reaction mixture was stirred at 313 K for 20 h followed by aging at 373 K for 24 h. The solid products of as-synthesized MSF were recovered by filtration and dried at room temperature overnight followed by removal of organic template by calcination at 823 K. TEPA-modified MSF adsorbents were prepared by two methods: (1) physical impregnation method: typically, calcined MSF (0.5 g) were first dried at 398 K for 6 h in air, then, refluxed in ethanol solution (50 mL) with different weight ratio (x) of TEPA at 383 K for 24 h under an N_2 flow. The products (denoted as MSF-T-x, $x = 0.5$–2) were washed with ethanol and dried at 333 K overnight; (2) chemical grafting method: 0.5 g of calcined MSF was dispersed in 25 mL of dry toluene with 50 mmole (3-Chloropropyl)trimethoxysilane (CPTMS; 98 %, ACROS). The reaction mixture was refluxed at 383 K for 24 h, and the final product was filtered, washed with toluene and then alcohol, and dried under a vacuum at 343 K for 8 h. This resultant sample is denoted MSF-Cl. Subsequently, ca. 0.25 g and 0.5 g of TEPA was added to 0.5 g of MSF-Cl to perform surface functionalization via the above-mentioned procedure developed for CPTMS grafting. The obtained samples are denoted as MSF-CT-y ($y = 0.5$ and 1.0).

2.2 Characterization methods

Small angle X-ray scattering (SAXS) was performed on a Nanostar U system (Bruker, AXS Gmbh). Elemental analyses (EA) were carried out using a CHN elemental analyzer (Heraeus varioIII). Nitrogen adsorption isotherms were measured at 77 K on a Micromeritics ASAP 2020 analyzer. Pore size distribution curves were calculated by the BJH method from the adsorption branch. The Brunauer-Emmett-Teller (BET) specific surface area was calculated from nitrogen adsorption data in the relative pressure (P/P_0) range from 0.05 to 0.2. The total pore volume was estimated from the amount adsorbed at the P/P_0 of 0.99. Fourier transform infrared (FTIR) spectra were obtained on a Bio-rad 165 spectrometer with 4 cm^{-1} resolution using KBr pellets at room temperature.

2.3 CO_2 adsorption

A modified thermogravimetric analyzer (TGA, PerkinElmer Pyris 6) with a H_2O saturator (Liu et al. 2011a) was used to determine the adsorption and desorption properties of various adsorbents. In a typical adsorption/desorption process, ca. 10 mg of adsorbent placed in a sample cell was heated to 373 K under N_2 flow (50 mL min^{-1}), then kept at that temperature for at least 30 min until no weight loss was observed. Then, the sample was cooled down to 348 K, followed by introducing 15 % dry CO_2 into the TGA cell at a flow rate of 50 mL min^{-1}. After 40 min of adsorption process, the gas was changed to pure N_2 flow (50 mL min^{-1}) to perform desorption procedure at the same temperature for 80 min. The sensitivity and accuracy of TGA microbalance are 10 µg and 0.1 %, respectively. The cyclic adsorption/desorption measurements were also studied to evaluate the stability of the adsorbents.

3 Results and discussion

Figure 2 shows the small-angle XRD patterns of the pure and TEPA-modified MSF samples (MSF-T-x and MSF-CT-y). The pristine MSF exhibited one main intensive (100) peak at 2θ of ca. 0.35° and two weak (110) and (200) diffraction peaks, indicating the existence of well-ordered hexagonal arrays and two-dimensional (2D) channel structure. However, upon incorporating TEPA into the pristine

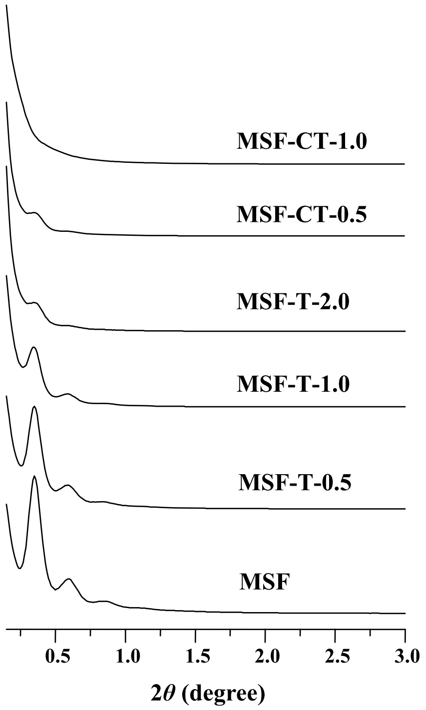

Fig. 2 Small-angle XRD patterns of pure MSF, various MSF-T-x and MSF-CT-y samples

matrix, notable decreases in diffraction peak intensities were observed, especially for the MSF-CT-1.0 in which the characteristic peaks for reflections at 100, 110, and 200 planes were disappeared. Instead of instability of the support itself, a decrease in the reflection at low 2θ angles of all samples could be explained by the successful incorporation of TEPA compounds, resulting in less order of hexagonal structure and/or partial collapse of the wall of mesostructured silica (Liu and Chen 2011; Liu et al. 2011b). As shown in Fig. 3, the N_2 adsorption/desorption curve of the pristine MSF samples showed typical type IV isotherms with an evident hysteresis loop, revealing the existence of ordered mesopores in the frameworks, in agreement with XRD results. Nevertheless, the diminishing of hysteresis loops upon incorporating a substantial amount of TEPA functional groups in the MSF-T-x and MSF-CT-y samples may be due to the blockage of mesopore channels. As displayed in Table 1, remarkable decreases in total porevolume (V_{tot}), BET surface area (S_{BET}) and BJH pore size (D_{BJH}) were observed for TEPA-modified samples compared to the pristine MSF samples, again indicating the successive functionalization of TEPA and/or CPTMS onto MSF. The presence of CPTMS and TEPA functional groups in the surface-modified MSF samples was also confirmed by FTIR spectroscopy. As can been seen in Fig. 4a, the FTIR spectrum of the parent MSF shows its characteristic peaks at 1079 and 968 cm^{-1} due to Si–O–Si and Si–OH stretching, respectively. Upon incorporation of TEPA, the peak at 968 cm^{-1} disappeared, and three weak peaks appear at 1567 cm^{-1} ($\delta_{\text{N–H}}$), 2931 cm^{-1} (–CH$_2$ ν_{as}), and 2818 cm^{-1} (–CH$_2$ ν_s) which indicated the presence of amine groups in TEPA. These results confirm the successful impregnation of TEPA onto MSF. In Fig. 4b, a band at ca. 968 cm^{-1} attributed to the Si–O stretching of the Si–OH groups was observed for MSF samples. However, the decreased absorption intensity of the peak at 968 cm^{-1} was evident for MSF-Cl sample, implying that the pore surface of MSF was functionalized with CPTMS. Compared to MSF-Cl samples, the weak bands at 1567 cm^{-1}, 2931 cm^{-1}, and 2818 cm^{-1} attributed to the NH_2 scissoring vibration and CH stretching vibration in the amine functional groups, respectively, were observed for MSF-CT-y samples, indicating that the MSF surfaces have been functionalized with

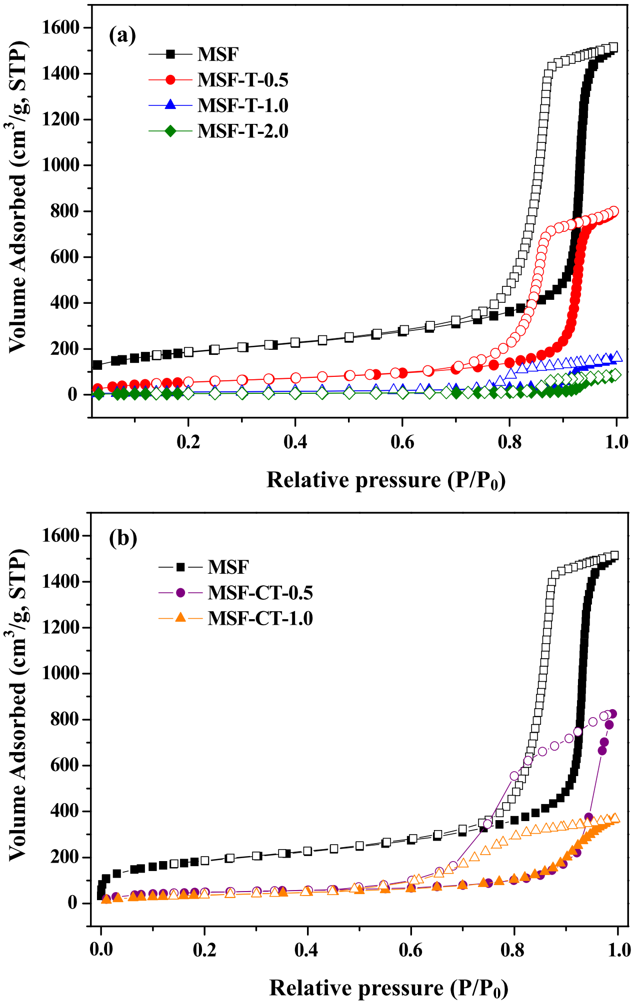

Fig. 3 N_2 adsorption-desorption isotherms of (**a**) pure MSF and various MSF-T-x and (**b**) MSF-CT-y samples

Table 1 Physicochemical properties and CO_2 adsorption performances of parent MSF, various MSF-T-x and MSF-CT-y samples

Sample	N (wt%)	V_{tot} (cm^3 g^{-1})	S_{BET} (m^2 g^{-1})	D_{BJH} (nm)	CO_2 uptake (mg g^{-1})	CO_2/N (mmol mmol^{-1})
MSF	–	2.34	634	29	–	–
MSF-T-0.5	8.0	1.46	249	28	57.2	0.23
MSF-T-1.0	10.4	1.24	206	27	82.5	0.27
MSF-T-2.0	16.1	0.24	42	23	193.6	0.38
MSF-CT-0.5	6.4	1.35	220	26	26.4	0.13
MSF-CT-1.0	9.2	1.11	141	21	58.0	0.19

N Nitrogen content measured by elemental analysis; V_{tot} Total pore volumes calculated as the amount of N_2 adsorbed at $P/P_0 = 0.99$; S_{BET} Brunauer-Emmet-Teller (BET) surface areas; D_{BJH} Pore diameters calculated by the Barrett–Joyner–Halenda (BJH) method using the adsorption branches

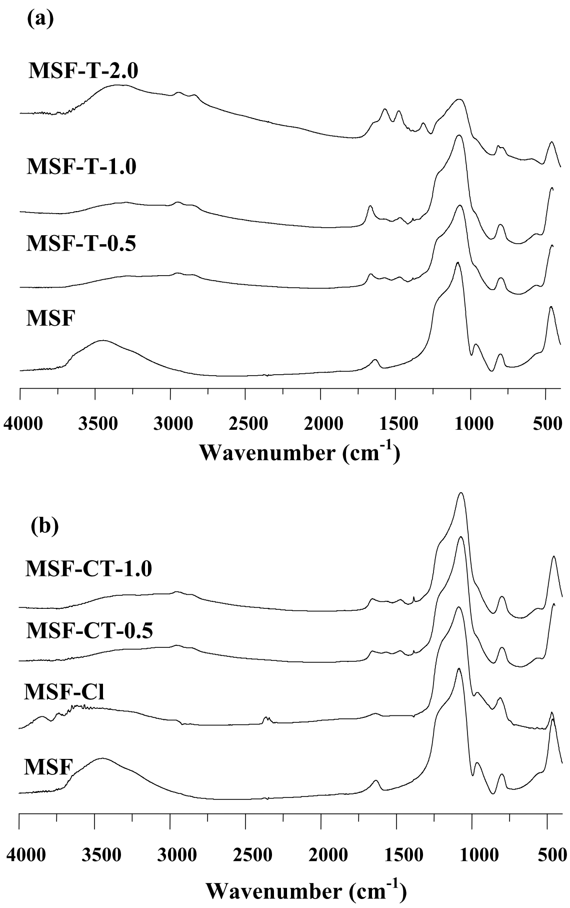

Fig. 4 FTIR spectra of (**a**) pure MSF and various MSF-T-*x* and (**b**) MSF-Cl and MSF-CT-*y* samples

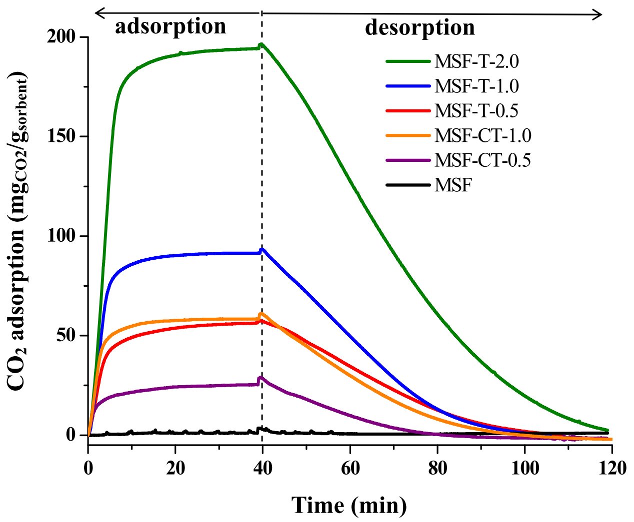

Fig. 5 CO_2 adsorption on pure MSF, various MSF-T-*x* and MSF-CT-*y* samples

TEPA via a reaction between MSF-Cl and amine groups of TEPA (see Fig. 1b). Additional measurements of nitrogen contents by EA were found to vary from 6.4 to 16.1 wt% in the MSF-T-*x* and MSF-CT-*y* samples (Table 1). Moreover, the impregnation/grafting efficiencies of MSF-T-*x* samples were higher than those of MSF-CT-*y* samples based on the N contents (see Table 1) in samples as a function of the same amount of TEPA added.

CO_2 adsorption/desorption measurements of MSF-T-*x* and MSF-CT-*y* at 348 K were carried out using TGA under atmospheric pressure and their corresponding curves are shown in Fig. 5. The CO_2 adsorption capacities of various MSF-T-*x* and MSF-CT-*y* are also summarized in Table 1. It can be seen that a small increase of CO_2 adsorption at ca. 40 min was observed, which may be due to the sudden switch of gas flow. Unlike the pristine MSF samples, which showed almost none CO_2 uptake, MSF-T-*x* and MSF-CT-*y* samples possessed the adsorption capacities of ca. 57.2–193.6 and 26.4–58.0 mg CO_2/g-sorbent, respectively. The mechanism of chemical adsorption pathway between amine active sites and CO_2 in anhydrous conditions is based on the formation of ammonium carbamate (Hiyoshi et al. 2005; Sayari and Belmabkhout 2010). Thus, the isolated amine groups are ineffective in CO_2 capture due to the stoichiometric CO_2/N ratio of 0.5. Among MSF-T-*x* and MSF-CT-*y* samples, amine efficiency (CO_2/N) for MSF-T-0.5, MSF-T-1.0 and MSF-T-2.0 samples were 0.23, 0.27 and 0.38 mmol mmol^{-1}, respectively, which are greater than those for MSF-CT-0.5 and MSF-CT-1.0 samples. This may be due to the fact that partial primary amino groups of TEPA were reacted with Si–Cl in the MSF-Cl samples, leading to the lower surface density of primary amines in the MSF-CT-*y* sorbents which possess lower CO_2 adsorption capacities than those of MSF-T-*x*. It was reported (Ko et al. 2011) that primary amine had the maximum CO_2 adsorption capacity among primary, secondary and tertiary amines. It is worthy to note that the slow desorption kinetics of MSF-T-*x* and MSF-CT-*y* adsorbents were observed. These results may be due to the tightly binding CO_2 molecules with TEPA (Goeppert et al. 2010; Ko et al. 2011), which is in agreement with an enhanced interaction potential between the adsorbate and adsorbent molecules in the confined mesopores of MSF-T-*x* and MSF-CT-*y*.

For practical industrial applications in CO_2 capture, solid adsorbents should possess stable cyclic adsorption-desorption performance during long-term operation. It should be noted that CO_2 adsorption capacity of MSF-T-1.0 showed a steady decrease in the tenth adsorption-desorption cycle (i.e., total operation period of ca. 25 h, Fig. 6) at 348 K under dry 15 % CO_2 concentration. On the other hand, the MSF-CT-1.0 exhibited a stable and reversible performance during ten repeated runs of adsorption-desorption cycles. This result is most likely due to the decreased leaching of TEPA which is chemically bonded to the surface of MSF via chemical grafting method. However, while the cyclic adsorption-desorption tests were extended to 50 cycles, the

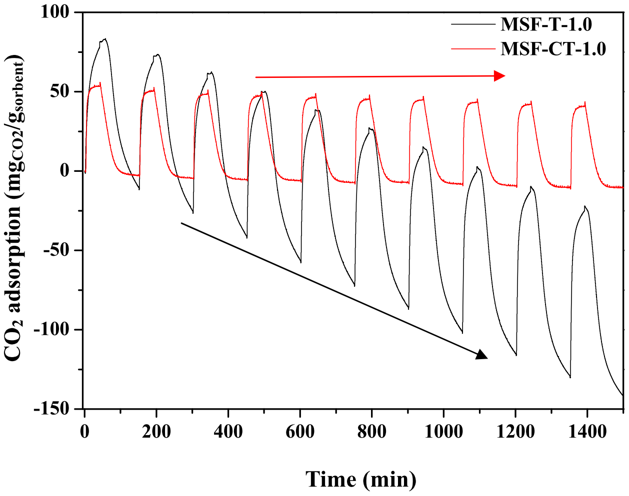

Fig. 6 Cyclic runs of CO_2 adsorption tests on MSF-T-1.0 and MSF-CT-1.0 samples at 348 K

adsorption capacities of MSF-CT-1.0 sample were found to have a decline trend after ca. 26 cycles. Moreover, a capacity loss of approximately 23 % was observed after 50 cycles. The above-mentioned result may be due to the fact that TEPA in the MSF-CT-1.0 possessed primary amines that showed unstable in the presence of dry CO_2, which is consistent with the reports by Sayari and Belmabkhout (2010) and Sayari et al. (2012).

4 Conclusion

CO_2 adsorption on TEPA-modified mesocellular silica foams (MSFs), prepared by physical impregnation (MSF-T-*x*) and chemical grafting (MSF-CT-*y*) methods, indicating their CO_2 uptake capacities of ca. 57.2–193.6 and 26.3–58.0 mg CO_2/g-sorbent, respectively at 348 K under ambient pressure using dry 15 % CO_2. The CO_2 adsorption capacities of MSF-T-*x* were greater than those of MSF-CT-*y*, which may be due to the higher surface density of amine groups in the MSF-T-*x* adsorbents. Nonetheless, the MSF-CT-*y* adsorbents possess enhanced stabilities during repeated adsorption-desorption cycles compared to MSF-T-*x* sorbents. This significant enhancement of durability in CO_2 uptake is possibly ascribed to the decreased leaching of TEPA which is chemically bonded to the surface of MSF. These MSF-CT-*y* sorbents exhibit reversible and stable properties, revealing a promising CO_2 sorbent for the use in a cyclic adsorption process.

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