Chemical Engineering Science 241 (2021) 116717

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Influence of water on amine loading for ordered mesoporous silica

John-Timothy Anyanwu, Yiren Wang, Ralph T. Yang *

Department of Chemical Engineering, University of Michigan, Ann Arbor, MI, USA

HIGHLIGHTS

- Increase water amount during grafting increases the amine loading without plateauing.
- The mere presence of water can shorten the grafting time to 30 min.
- Polymerization of amines was proven in wet grafting.
- Universality of the influence of water during grafting was demonstrated.

ARTICLE INFO

Article history:
Received 25 November 2020
Received in revised form 21 April 2021
Accepted 23 April 2021
Available online 27 April 2021

Keywords:
CO_2 capture
SBA-15
KIT-6
Silica
Amine grafting
Wet grafting

ABSTRACT

SBA-15, a mesoporous silica, was employed to systematically study the influence of water concentration during amine grafting and also on amine loading. It was found that water as opposed to alcohol was a more effective agent for influencing amine loading. The addition of alcohol did not result in higher amine loadings; however, the addition of water leads to higher amine loading. Under the reported synthesis conditions, further increase in water concentration resulted in further increase in amine loading without plateauing. Additionally, increasing the aminosilane content beyond 2 mL/g (SiO_2) during amine grafting did not yield higher amine loading. Moreover, the mere presence of water during grafting affects the grafting rate of the aminosilanes, resulting in complete grafting of amines to supports in 30 min. The stability of wet grafted materials and the universality of the studied effects for other aminosilanes and mesoporous silica supports (KIT-6 and MCM-48) were also demonstrated.

1. Introduction

One of the major greenhouse gases that poses a significant threat to the environment is carbon dioxide (CO_2). The concentration of atmospheric CO_2 has been increasing at an alarming rate and efforts have been undertaken to develop carbon capture and sequestration technologies to curb emissions (Vitillo et al., 2017). The most mature technology currently used for post-combustion CO_2 capture is liquid solution absorption using amine solutions. However, this technology is energy intensive and therefore, new and promising technology is sorely needed (Li et al., 2014, Sanz-Pérez et al., 2016, Vitillo et al., 2017, Wang and Yang, 2019).

Adsorption using amine grafted porous adsorbents is one of the most promising technologies for mitigating global CO_2 emissions (Anyanwu et al., 2020, Darunte et al., 2016a, 2016b, Fan et al., 2015, Huang et al., 2018, Lee et al., 2017, 2018, Park et al., 2020, Okonkwo et al., 2020, Tumuluri et al., 2014, Wilson et al., 2020, Yoo et al., 2020). Particularly, ordered mesoporous silica supports (e.g. SBA-n, MCM-n, and KIT-n) display unique characteristics such as high surface area, adjustable pore properties and notably, they possess an abundance of silanols (surface hydroxyl groups) (Kleitz et al., 2003, Pang et al., 2017, Schumacher et al., 2000, Zhao et al., 1998). The presence of these silanol groups make ordered mesoporous silicas ideal for amine grafting. Amine grafting involves the covalent tethering of a grafting compound, usually aminosilanes, to silica supports in dry conditions (anhydrous solvents) via a condensation reaction (Moschetta et al., 2015). One of the earliest uses of amine grafted adsorbents for the adsorptive capture of CO_2 was reported by Leal et al. (1995). They studied carbon dioxide adsorption on amine-grafted silica gel and reported an adsorption capacity of 0.2 mmol/g at 1 bar. The low adsorption capacity was due to the low surface area of the silica gel (200 m^2/g). Subsequently, Huang et al. (2003) prepared amine-grafted MCM-48 (surface area of 1400 m^2/g) with high adsorption capacity and high-selectivity for carbon dioxide and hydrogen sulfide. Several groups have followed up the earlier pioneering works on amine grafted porous adsorbents due to their high CO_2 adsorption capacity and selectivity, multicycle and moisture stability, and

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* Corresponding author at: 3074 H.H. Dow, 2300 Hayward Street, Ann Arbor, MI 48109-2136, USA.

E-mail address: yang@umich.edu (R.T. Yang).

https://doi.org/10.1016/j.ces.2021.116717
0009-2509/

fast uptake rates (Chang et al., 2003, Darunte et al., 2019, Sánchez-Zambrano et al., 2018, 2020, Santiago et al., 2020, Yu and Chuang, 2016).

One of the most studied methods of improving the adsorptive capabilities of amine grafted porous adsorbents is by increasing the amine loading (Anyanwu et al., 2020, Chang et al., 2003, Darunte et al., 2016a, 2019, Fan et al., 2015, Huang et al., 2003, Huang et al., 2018, Leal et al., 1995, Lee et al., 2017, 2018, Moschetta et al., 2015, Okonkwo et al., 2020, Sánchez-Zambrano et al., 2018, 2020, Santiago et al., 2020, Tumuluri et al., 2014, Wilson et al., 2020, Yoo et al., 2020, Yu and Chuang, 2016). Typically, an increase in the amine loading of accessible amine results in higher CO_2 adsorption capacity. Thus, the strategy is to maximize the amount of accessible amines on porous adsorbents that will result in the highest CO_2 capture performance. As mentioned earlier, amine grafting involves the condensation reaction between the aminosilanes and the surface silanol groups. Thus, increasing the silanol groups on the silica will yield higher loading of amines and consequently higher CO_2 adsorption capacity (Wang and Yang, 2011, Wang and Yang, 2020, Yuan et al., 2014). Reduction in silanol groups, however, is harmful for further grafting of amines.

In the synthesis of ordered mesoporous silica, the composites are commonly calcined at 550 °C for >4 h in air to remove the organic template and create porosity. However, the long treatment times and high temperatures associated with air calcination result in reduced silanol groups due to dehydroxylation (Wang and Yang, 2011, Wang and Yang, 2020, Yuan et al., 2014). To conserve the silanol groups of as synthesized ordered mesoporous silicas, new template removal methods at lower temperature and shorter times were developed. One such method is low-temperature extraction using organic solvents (solvent extraction). The pioneering work by the Hitz and Prins (1997) showed that the template of MCM-41 can be extracted with an ethanol solution containing acid or salt at 78 °C. They examined the effects of extraction and determined the extraction conditions were effective in preserving silanol groups. Wang et al followed up on their work and extracted the template of SBA-15 using just an ethanol solution (Wang and Yang, 2011). They confirmed that due to the higher silanol groups of solvent extracted SBA-15 compared to air calcination, more amines were grafted. Consequently, the ethanol extracted SBA-15 achieved a higher CO_2 adsorption capacity (1.84 mmol/g) than the calcined SBA-15 (1.54 mmol/g). Recently, Wang and Yang (2020) highlighted the advantages of using ionic liquids for template removal and achieved a similar CO_2 adsorption capacity (1.8 mmol/g). These methods while effective at increasing the quantity of accessible amines are limited due to the finite amount of silanol groups.

In order to overcome the silanol group limitation of ordered mesoporous silica, a new approach that involves amine grafting in the presence of water to greatly enhance the amount of grafted species was utilized (Feng et al., 1997). This process involves the addition of water (wet grafting) to a toluene solution containing ordered mesoporous silica and stirring the mixture to achieve complete hydration of the silica (Feng et al., 1997, Kim et al., 2005, Liu et al., 1998, Zheng et al., 2005). Subsequently, a desired amount of aminosilanes is added to the mixture and it is refluxed under heat for twelve hours.

In this work, we explored the use of water and an alcohol (n-Butanol) during amine grafting and how it affects the amine loading. Amine grafting conditions such as water and amine concentration and graft reaction time were also examined. Additionally, the stability of the wet grafted adsorbents under multiple CO_2 adsorption/desorption cycles was investigated. The universality of the observed wet grafting effects were studied for other alkoxysilanes and ordered mesoporous silica supports.

2. Experimental

2.1. Materials

N^1-(3-Trimethoxysilylpropyl)diethylenetriamine (Triamine), (3-Aminopropyl)trimethoxysilane (APTMS), Pluronic P123, Hydrochloric Acid (HCl), Ethanol, Aqueous Ammonia and Tetraethylorthosilicate (TEOS) were obtained from Sigma Aldrich. Anhydrous toluene, cetyltrimethylammonium bromide (CTAB) and n-butanol were obtained from Fisher Scientific.

2.2. SBA-15

The synthesis of SBA-15 was performed according to the procedure reported by Wang et al. (2016). 8 g of Pluronic P123 was dissolved in 240 mL H_2O and 40.1 mL of 37% HCl at room temperature. After the complete dissolution of Pluronic P123, the temperature was increased to 35 °C. 18.2 mL of TEOS was then added to the solution dropwise. The mixture was stirred at 35 °C for 24 h, followed by another 24 h at 100 °C. The resulting white solid was collected by filtration, washed with water, and dried at 50 °C overnight. Finally, it was calcined at 550 °C for 6 h under an air flow. It was designated as SBA-15.

2.3. KIT-6

The synthesis of KIT-6 was performed according to the procedure reported by Kim et al. (2005). 4 g of Pluronic P123 was dissolved in 144 mL H_2O and 6.63 mL of 37% HCl at room temperature. After the complete dissolution of Pluronic P123, the temperature was increased to 40 °C and 4.94 mL of n-Butanol was added and stirred for 1 h. 9.14 mL of TEOS was then added to the solution dropwise. The mixture was stirred at 40 °C for 24 h. The mixture was put in a Teflon autoclave and hydrothermally treated for 24 h at 100 °C under static conditions. The resulting white solid was collected by filtration, washed with water, and dried at 50 °C overnight. Finally, it was calcined at 550 °C for 6 h under an air flow. It was designated as KIT-6.

2.4. MCM-48

The MCM-48 type silica was prepared according to the procedure outlined by Schumacher et al. (2000). 5.2 g of CTAB, 240 mL of H_2O, and 100 mL of ethanol were mixed and subsequently stirred at room temperature. 24 mL of aqueous ammonia was then added to the mixture. 7.2 mL of TEOS was subsequently added and the entire mixture was stirred for 10 h. The resulting white solid was collected by filtration, washed with copious amounts of water, and dried at 50 °C overnight. Finally, it was calcined at 550 °C for 6 h under an air flow. It was designated as MCM-48.

2.5. Dry grafting

All supports were dried at 100 °C overnight prior to amine grafting. In a typical synthesis, 100 mL anhydrous toluene was mixed with 10 mL N^1-(3-Trimethoxysilylpropyl)diethylenetriamine (Triamine) in an erlenmeyer flask, and then 1 g of SBA-15 was added. The mixture was stirred and refluxed at 85 °C for 12 h. The grafted silica was filtered and washed with copious amounts of toluene, then dried in a 50 °C oven overnight. Amine-grafted adsorbents were designated as AG-SBA-15-X-Y. X refers to the amine concentration (mL/g SiO_2) used during grafting and Y refers to the grafting reaction time used for amine grafting.

2.6. Wet grafting

All supports were dried at 100 °C overnight prior to amine grafting. In a typical synthesis, a specific amount of H_2O (0.2–0.6 mL) was added dropwise to a solution containing 100 mL anhydrous toluene and 1 g of SBA-15. The mixture was stirred at room temperature for 5 min. 10 mL N^1-(3-Trimethoxysilylpropyl)diethylenetriamine or (3-Aminopropyl)trimethoxysilane (APTMS) was then added. The mixture was stirred and refluxed at 85 °C for the desired amount of time. The grafted adsorbents were filtered and washed with copious amounts of toluene, then dried in a 50 °C oven. This synthesis procedure was also performed for all supports. Wet grafted adsorbents were designated as WG-SBA-15-X-Y-Z. X refers to the amine concentration (mL/g SiO_2) used during grafting, Y refers to the grafting reaction time used for amine grafting and Z refers to the amount of water (mL/g SiO_2) added during wet grafting.

For grafting with n-Butanol, 2 mL of n-Butanol was added dropwise to a solution containing 100 mL anhydrous toluene and 1 g of SBA-15. The mixture was stirred at room temperature for 5 min. 10 mL N^1-(3-Trimethoxysilylpropyl)diethylenetriamine was then added. The mixture was stirred and refluxed at 85 °C for 12 h. The grafted adsorbents were filtered and washed with copious amounts of toluene, then dried in a 50 °C oven. The n-Butanol grafted adsorbents were designated as nBG-SBA-15-10-12. The grafting conditions for different supports are summarized in Table 1.

3. Characterization

Carbon dioxide isotherms were measured at 25 °C and 75 °C and nitrogen adsorption isotherms were measured at −196 °C with a Micromeritics ASAP 2020 Analyzer. All samples were degassed at 105 °C overnight prior to all measurements. The surface area was calculated from the adsorption isotherm using the BET equation. The pore volume was estimated from the single-point amount adsorbed at P/P_0 = 0.99. The pore size was determined by using Barrett, Joyner and Halenda (BJH) analysis. Thermogravimetric analysis was carried out on a Shimadzu TGA-50H. Amine loading analysis was performed by pretreating the sample under a helium flow for 2 h at 100 °C, then heating to 850 °C at a heating rate of 5 °C/min under a helium and airflow. Adsorption rates measurements were performed using a TGA under a dry 70% CO_2 flow (in He) at 25 °C and 75 °C. Multi-cycle stability studies were examined using a TGA under a dry 70% CO_2 flow (in He) at 75 °C. The sample was desorbed at 90 °C in He after each adsorption cycle.

4. Results and discussion

4.1. Effect of water on amine loading

Amine grafting in the presence of water and alcohol were studied to further understand how aqueous solutions, namely water and alcohol, affect the grafting of amines. To this end, the amine loading of adsorbents grafted in the presence of 0.4 mL H_2O/g SiO_2 and adsorbents grafted in the presence of 2.0 mL n-Butanol/g SiO_2 were compared. 0.4 mL H_2O/g SiO_2 and 2 mL n-Butanol/g SiO_2 were used because they are molar equivalents. Additionally, n-Butanol was chosen as the alcohol due to its high boiling point compared to other alcohols (Ndaba et al., 2015). It was determined that 85 °C is the optimal temperature needed to attain the highest amount of grafted silanes and n-Butanol possesses a boiling point above the optimal temperature. To determine the amine loading of dry and wet grafted SBA-15, the adsorbents were analyzed by TGA under air flow and the results are displayed in Fig. 1. Weight loss below 150 °C corresponds to the removal of adsorbed atmospheric CO_2 and water, and therefore it was omitted. The decomposition of the majority of grafted amines occurs between 150 and 600 °C. The amine loading for AG-SBA-15-10-12 was 28.8% and increased to 40.5% for WG-SBA-15-10-12-0.4. The TGA results confirm the presence of water influences the amount of grafted amines. However, for n-Butanol grafted SBA-15 the amine loading was lower than that of dry grafted SBA-15 indicating that the presence of n-Butanol did not result in more grafted amines. This can be attributed to the replacement of the ethoxy groups of N^1-(3-Trimethoxysilylpropyl)diethylenetriamine with butoxy groups resulting in a less hydrolysable and reactive compound (Bernards et al., 1994). Notably, it is possible that alcohols like methanol with less steric bulk would perform better than n-butanol, however, the lower amine grafting temperatures needed for those alcohols would yield lower amine loadings (Arkles et al., 1992, Bernards et al., 1994). Moreover, the amount of alcohol that would need to be added will be in excess when compared to water. The addition of water, on the other hand, results in greater hydrolysis of the N^1-(3-Trimethoxysilylpropyl)diethylenetriamine alkoxy groups. The water hydrolyzed aminosilanes are highly reactive compared to alcohol which results in much higher amine loadings (Arkles et al., 1992).

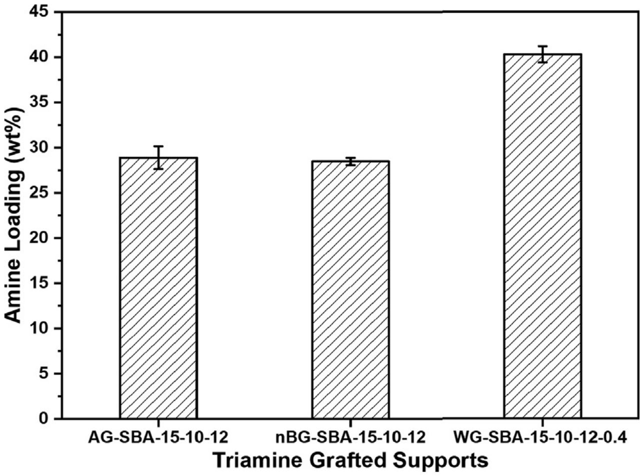

Fig. 1. Amine loading of dry grafted AG-SBA-15-10-12, wet grafted WG-SBA-15-10-12-0.4, and alcohol grafted nBG-SBA-15-10-12.

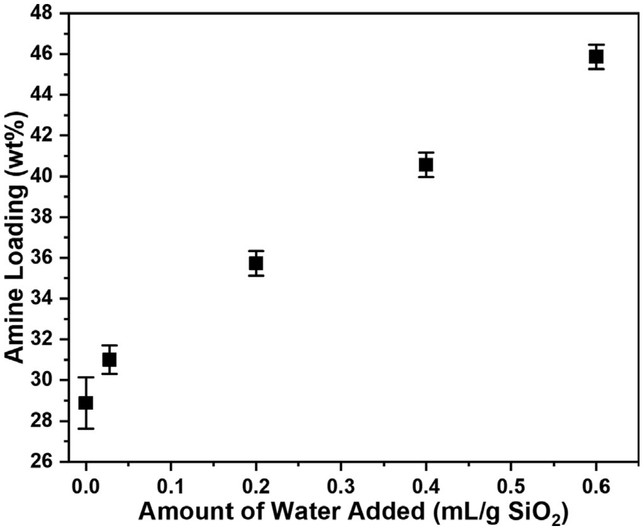

Fig. 2. Amine loading of SBA-15 using 10 mL/g SiO_2 triamine, 12 h grafting reaction time and different amount of water.

Fig. 2 displays the amine loading for dry and wet grafted SBA-15. The TGA thermograms of dry and wet grafted SBA-15 are shown in Fig. S1 of the Supplementary Material. With the addition of small amounts of water (0.03 mL/g SiO_2) while the amount of aminosilane (10 mL/g SiO_2) was kept constant, the amine loading increased. There is a more marked increase in the amine loading when larger amounts of water (>0.03 mL/g SiO_2) are added. The amine loading of SBA-15 increased from 28.8% for dry grafted AG-SBA-15-10-12 to 45.8% for wet grafted WG-SBA-15-10-12-0.6. Notably, under our synthesis conditions, the amount of grafted amines increases with subsequent additions of water without any sign of leveling off. This noticeable increase in amine loading is due to the hydrolysis and condensation of alkoxy groups in the presence of water leading to the aminosilane polymerization. The amount of water present in the solution for alkoxy hydrolysis and condensation determines the degree of polymerization (Arkles et al., 1992, Assink and Kay, 1988). This is further illustrated by examining changes in the textural properties of pristine and wet grafted SBA-15. Fig. 3 shows the N_2 adsorption–desorption isotherms at −196 °C for all calcined supports and isotherms for the amine grafted materials are shown in Fig. S2 of the Supplementary Material. The textural properties of all calcined supports, WG-SBA-15-10-12-0.03, WG-SBA-15-10-12-0.2, WG-SBA-15-10-12-0.4, and WG-SBA-15-10-12-0.6 are summarized in Table 2. Additionally, Fig. 4 illustrates the relative changes in the surface area, pore size and pore volume of dry grafted and wet grafted SBA-15 compared to the amount of water added. In accordance with the N_2 isotherms, the surface area, pore size and pore volume exhibited marked decreases as the amount of added water during amine grafting increases. The surface area, pore size and pore volume decreased by 88.8%, 28.2%, and 84.6% for wet grafted WG-SBA-15-10-12-0.03, 98.7%, 28.2%, and 97.9% for wet grafted WG-SBA-15-10-12-0.2, 99%, 45.6%, and 99% for wet grafted WG-SBA-15-10-12-0.4, and 99%, 60.6%, and 99.2% for wet grafted WG-SBA-15-10-12-0.6 compared to 82.4%, 18.8%, 75.5% for dry grafted AG-SBA-15-10-12. This suggests that the continuous addition of water during grafting which leads to higher amine polymerization has a pore blocking effect. In the pore space, water initiates the hydrolysis and condensation reactions of the alkoxy groups while the aminosilane grafts to the surface hydroxyl groups (Arkles et al., 1992, Assink and Kay, 1988, Wang and Yang, 2011, Wang and Yang, 2020, Yuan et al., 2014). With higher water concentrations in the pore, higher agglomeration of the amine moieties is observed. The presence of the increased agglomeration of amines renders the pores inaccessible for nitrogen molecules, thus resulting in near negligible surface area, pore size and pore volume val-

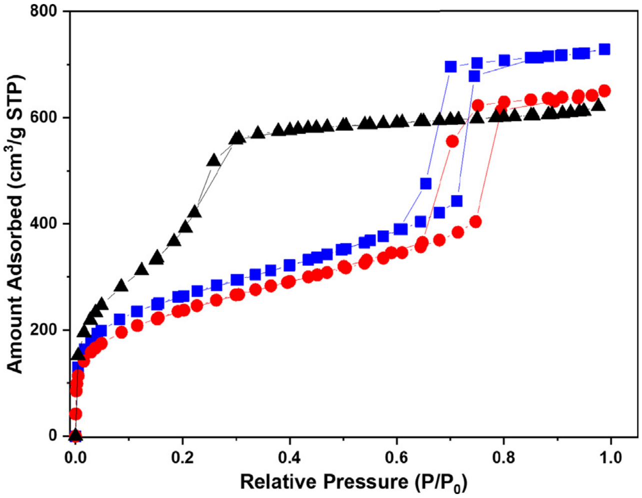

Fig. 3. N_2 adsorption-desorption isotherms at −196 °C for SBA-15 (■), KIT-6 (●), and MCM-48 (▲).

Table 1
Grafting conditions for different supports.

Support	Amine concentration (mL/g SiO_2)	Added water (mL/g SiO_2)	Added n-butanol (mL/g SiO_2)	Grafting reaction time (hours)
SBA-15	1–10	0–0.6	–	0.5, 3, & 12
SBA-15	10	–	2.0	12
KIT-6	10	0.4	–	3 & 12
MCM-48	10	0.4	–	3 & 12

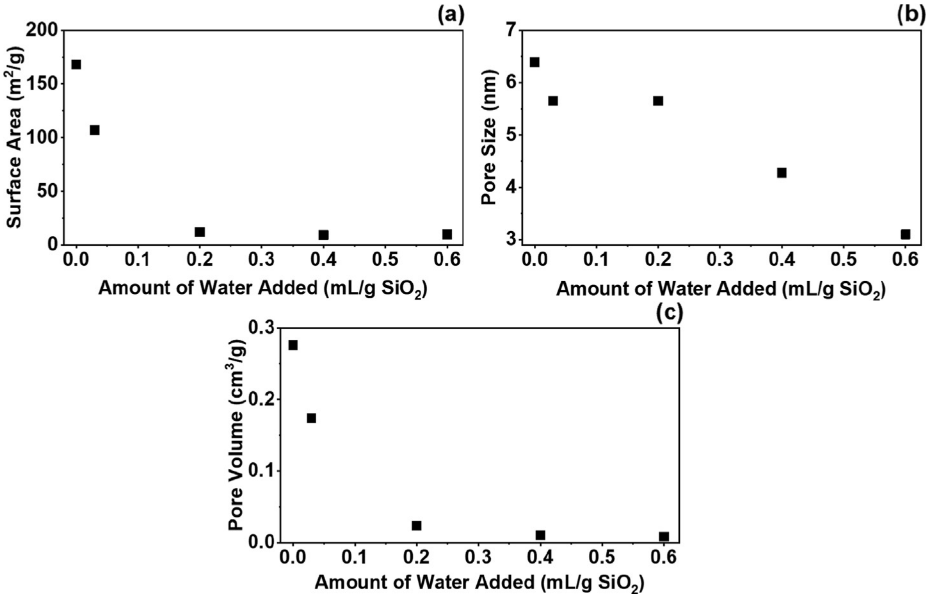

Fig. 4. Surface area (a), pore size (b) and pore volume (c) of dry and wet grafted SBA-15 as a function of the amount of water added.

Table 2
Surface area and pore structure parameters of all prepared materials.

Sample	BET surface area (m^2/g)	Pore diameter (nm)	Total pore volume (cm^3/g)
SBA-15	956	7.87	1.13
AG-SBA-15-10-12	168	6.39	0.276
WG-SBA-15-10-12-0.03	107	5.65	0.174
WG-SBA-15-10-12-0.2	12.1	5.65	0.0236
WG-SBA-15-10-12-0.4	9.25	4.28	0.0104
WG-SBA-15-10-12-0.6	9.7	3.10	0.00823
KIT-6	856	8.54	1
MCM-48	1754	2.08	0.961

ues for wet grafted SBA-15. Lastly, it should be noted that the amount of water added was capped at 0.6 mL/g SiO_2 because further addition resulted in a balling and agglomeration of SBA-15. It is possibly due to inter-particle polymerization of amines after the pore are completely filled (Gartmann et al., 2010).

Typically, wet impregnated silica adsorbents using polymers like polyethyleneimine (PEI) demonstrate pore blocking behavior. Similar to wet grafted SBA-15, PEI polymers are densely packed in the pore channels of silica supports and further loading of PEI leads to the plugging of the pores (Arkles et al., 1992, Bernards et al., 1994, Sanz-Pérez et al., 2016, Sánchez-Zambrano et al., 2020). The CO_2 adsorption capacities of these PEI impregnated silica adsorbents typically achieve their highest capacity within the adsorption temperature range of 50–100 °C. At higher adsorption temperature, polymeric amines become more mobile, facilitating the transport of CO_2 into the bulk of amines in the pores (Anyanwu et al., 2020, Kwon et al., 2019, Sanz-Pérez et al., 2016, Sánchez-Zambrano et al., 2018, 2020, Vilarrasa-García et al., 2014). Therefore, to confirm the polymeric nature of wet grafted amines, CO_2 adsorption capacity and rates were measured for wet grafted SBA-15 to determine if they behave similarly to PEI polymers. Fig. 5 shows the CO_2 equilibrium adsorption isotherms of dry and wet grafted SBA at 25 °C and 75 °C. At 25 °C, the CO_2 adsorption capacity for AG-SBA-15-10-12 is 1.69 mmol/g and after wet grafting the CO_2 adsorption capacity decreases substantially. It went from 0.604 mmol/g for WG-SBA-15-10-12-0.2, to 0.358 mmol/g for WG-SBA-15-10-12-0.4 and 0.290 mmol/g for WG-SBA-15-10-12-0.6. Such a declining trend in adsorption capacity indicates that the increased amine loading (due to higher amounts of water addition) limits the diffusion of CO_2 and reduces the quantity of accessible amines for CO_2 adsorption. However, at 75 °C, the CO_2 adsorption capacity increases as the water concentration increases. The adsorption capacity was 1.26 mmol/g for AG-SBA-15-10-12, 1.91 mmol/g for WG-SBA-15-10-12-0.2, 1.99 mmol/g for WG-SBA-15-10-12-0.4 and 2.24 mmol/g for WG-SBA-15-10-12-0.6. Due to the exothermic nature of adsorption, dry grafted AG-SBA-15 achieved a lower CO_2 adsorption capacity at 75 °C. As previously expressed, the rising trend in adsorption capacity for wet grafted SBA-15 indicates that higher temperatures render the polymer-like amines more mobile and also facilitates the transfer of adsorbed CO_2 from the surface into the bulk of the amines, thereby increasing the quantity of accessible amines (Ma et al., 2009).

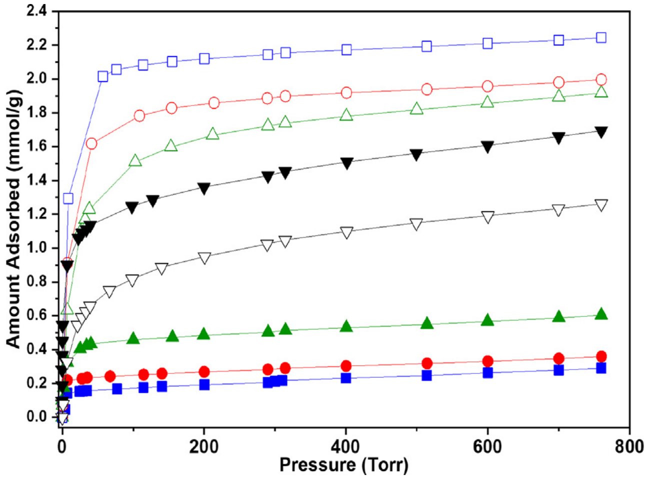

Fig. 5. CO_2 adsorption isotherms at 25 °C (closed symbols) and 75 °C (open symbols) for AG-SBA-15-10-12 (▼), WG-SBA-15-10-12-0.2 (▲), WG-SBA-15-10-12-0.4 (●), & WG-SBA-15-10-12-0.6 (■).

Another factor to examine that confirms the polymerization of grafted amines in the presence of water are the uptake rates. The diffusion time constant (D/R^2, where D is pore diffusivity and R is the radius of the particle) is employed to express uptake rates (Anyanwu et al., 2020, Epiepang et al., 2016, Wang and Yang, 2019). Data obtained from gravimetric adsorption experiments were used to calculate the diffusion time constant. Table 3 portrays the calculated D/R^2 values. The adsorption rate decreased in the following order: AG-SBA-15-10-12 > WG-SBA-15-10-12-0.2 > WG-SBA-15-10-12-0.4 > WG-SBA-15-10-12-0.6. Higher loading of grafted amines (i.e. higher polymerization) results in higher diffusional resistances. From Table 2, it is apparent that higher amine loadings result in lower pore size and pore volume, which significantly increased the diffusion barrier of CO_2 and reduced the diffusion time constant (D/R^2) (Gelles and Rezaei, 2020, Kwon et al., 2019, Wang et al., 2008). Notably, while WG-SBA-15-10-12-0.6 exhibited the highest equilibrium CO_2 adsorption capacity (2.24 mmol/g), it also achieved the lowest uptake rates. This confirms the formation of densely polymerized amine moieties in the pores with subsequent additions of water leading to higher CO_2 adsorption capacities as well as greater diffusional limitations.

4.2. Effect of water on amine grafting

It is important to understand how the presence of water during synthesis affects amine-grafting outcomes. Systematic experiments varying the water and aminosilane concentration as well as amine grafting time were carried out to determine their effects. The resulting amine grafting outcomes were estimated and discussed based on thermal analysis.

At the amine grafting temperature of 85 °C, the water concentration was kept constant at 0.4 mL/g SiO_2, while the aminosilane concentration was varied. Fig. 6 reveals the amine loading of wet grafted WG-SBA-15-X-12-0.4 is not meaningfully affected by the aminosilane concentration passed 2 mL/g SiO_2. However, when the aminosilane concentration was reduced to 1 mL/g SiO_2 the amine loading reduced by approximately 19%. Notably, this trend was not displayed for dry grafted AG-SBA-15-1-12. This observed deviation for wet grafted WG-SBA-15-1-12-0.4 is explained by the amine loading being dependent on the addition of sufficient amounts of aminosilane. Namely, for WG-SBA-15-1-12-0.4, when the silane concentration is insufficient (below 2 mL/g SiO_2), the added water is not completely consumed. When the aminosilane concentration is sufficient (greater than or equal to 2 mL/g SiO_2), the added water is likely completely consumed by the unreacted

Table 3
Diffusion Time Constants (D/R^2) for dry and wet grafted SBA-15 at 75 °C.

Sample	D/R^2 (1×10^{-5}), s^{-1}
AG-SBA-15-10-12	110
WG-SBA-15-10-12-0.2	7.05
WG-SBA-15-10-12-0.4	4.9
WG-SBA-15-10-12-0.6	3.6

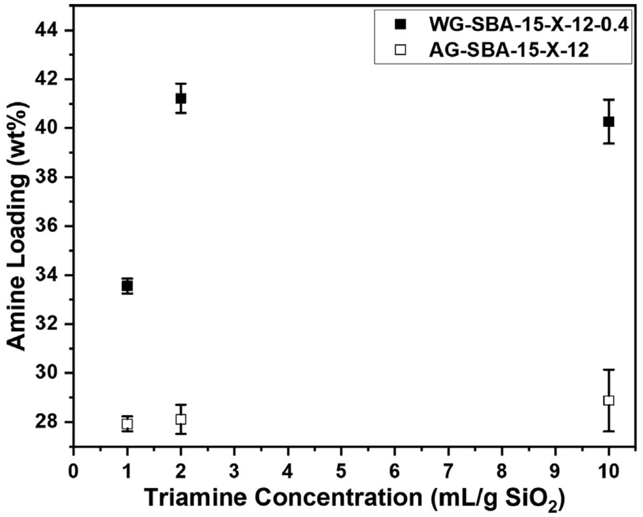

Fig. 6. Amine loading of AG-SBA-15-X-12 and WG-SBA-15-X-12-0.4 using different amounts of Triamine.

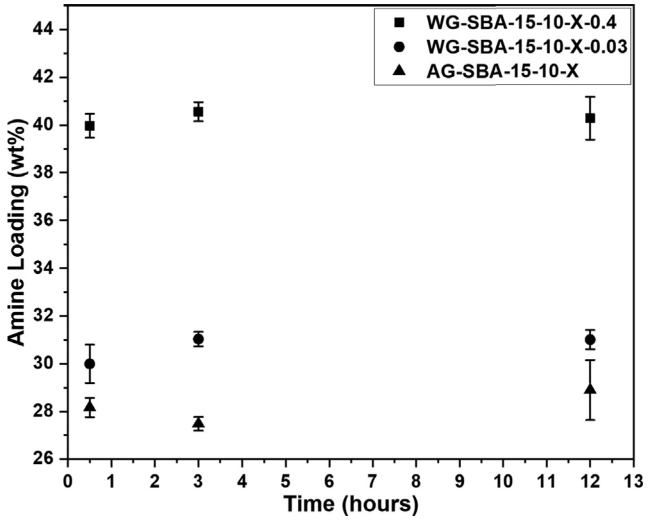

Fig. 7. Amine loading of AG-SBA-15-10-X, WG-SBA-15-10-X-0.03, and WG-SBA-15-10-X-0.4 using different grafting reaction times.

alkoxy groups leading to higher amine loadings. Dry grafting, in comparison, is constrained by the availability of surface silanols groups for covalent tethering with the aminosilanes (Wang and Yang, 2011, Wang and Yang, 2020,Yuan et al., 2014). Thus, further addition of aminosilanes into the solution will not necessarily result in greater amounts of grafted amines unless the silanol group density is increased.

Fig. 7 displays the effects of water concentration on the amine grafting reaction time. The grafting temperature and water concentration were kept constant at 85 °C and 0.4 mL/g SiO_2, respectively. However, the grafting reaction time for dry grafted and wet grafted SBA-15 were varied. As can be seen, the amine loading for dry grafted AG-SBA-15-10-X is 28.1% after 30 min, 27.4% after 3 h and 28.8% after 12 h. The amine loading stays relatively constant as the grafting reaction time increases, meaning the surface hydroxyl groups are consumed and further amine grafting is not possible. For wet grafted WG-SBA-15-10-X-0.4, the amine loading is essentially unchanged from 30 min to 12 h. It was then hypothesized that water concentration affects grafting rate, and so the water concentration was varied from 0.03 (1 drop) to 0.4 mL/g SiO_2. Fig. 7 reveals that the grafting rate is possibly affected by the mere addition of water. Furthermore, since the grafting reaction time did not affect the amine loading for dry grafted SBA-15, it is therefore possible that adsorbed moisture is capable of influencing the grafting rate (Zhai et al., 2019). This phenomenon is explained by the reactivity of silanol functional groups. For grafting in the presence of water, the aminosilane alkoxy groups are transformed into highly reactive silanol functional groups. These highly reactive silanol functional groups of the aminosilanes and on the support, condense rapidly to form Si-O-Si (siloxane) linkages (Arkles et al., 1992, Assink and Kay, 1988). In contrast, for amine grafting in purely dry conditions, the condensation reaction occurring between the unhydrolyzed alkoxy groups of aminosilanes and silanol functional groups of the support would be slower resulting in lower amounts of grafted amines at shorter times (Arkles et al., 1992, Assink and Kay, 1988).

4.3. Universality of the observed effects

As previously mentioned, amine grafting involves the reaction between aminosilanes and the silanols on porous supports. Furthermore, the addition of water during amine grafting leads to the polymerization of amines and influences the hydrolysis and condensation rate of the aminosilanes. As such, it is important to test if the observed phenomenon is universal for different supports and different aminosilanes.

In Fig. 8, the amine loading of SBA-15, KIT-6 and MCM-48 at different amine grafting times were compared. The textural properties of the calcined supports are summarized in Table 2. For all supports, a specific amount of water (0.4 mL/g SiO_2) and amine (10 mL/g SiO_2) was used during the grafting process. As expected, the amine loading for all adsorbents at grafting reaction times of 3 and 12 h are essentially the same for each respective support, further demonstrating the effects of water addition. It also reveals that the effects are independent of the support. The effects of water addition at different grafting reaction times were also investigated using another aminosilane (3-aminopropyltrimethoxysilane, APTMS). As shown in Fig. 8, a specific amount of water (0.4 mL/g SiO_2) was used and the grafting reaction times were 3 and 12 h. As anticipated the amine loading for SBA-15, KIT-6 and MCM-48 at the investigated grafting times were the same for each respective adsorbent. This reveals the universality of the effects associated with wet grafting for different kinds of suitable supports. However, it is notable that the amine loading of SBA-15, KIT-6 and MCM-48 were slightly different at the same grafting conditions as well as with different aminosilanes. No strong correlation between amine loading and BET surface area, pore size, or pore volume of their corresponding supports was found. KIT-6 and MCM-48 possess similar bicontinous 3D cubic structure, however, they possess different textural properties. It may be the case that the reactions that occur are affected by the surface geometry of the supports. Typically, amine loading is dependent on the availability of surface silanol groups for covalent tethering to aminosilanes. As such, the differing amounts of available silanol groups on each respective support would affect the amount of grafted amines. Further investigation is needed to reach a conclusion, nonetheless, these results suggest the effects of water addition are ubiquitous for different types of silanes and mesoporous silicas.

4.4. Stability of grafted amines

For practical applications, it is crucial to determine the stability after multiple adsorption/desorption cycles of short time wet grafted adsorbents. These adsorbents grafted at short times compared to conventionally grafted adsorbents should retain their CO_2 adsorption performance. To assess the cyclic stability of WG-SBA-15-10-0.5-0.03, adsorption was carried out at 75 °C and

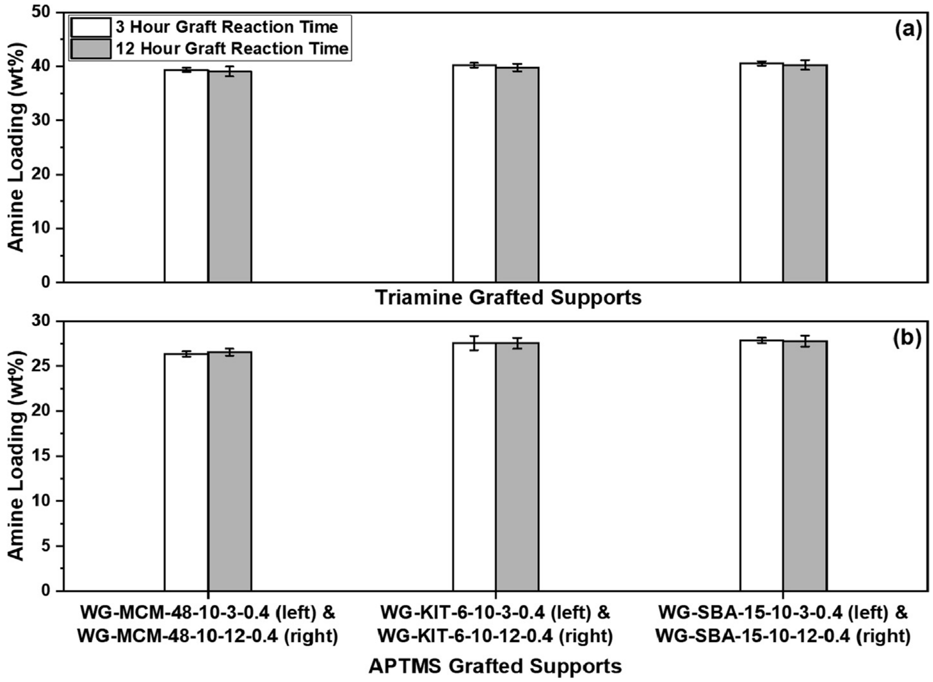

Fig. 8. Amine loading of wet grafted (Triamine) MCM-48, KIT-6 and SBA-15 (a) and amine loading of wet grafted (APTMS) MCM-48, KIT-6 and SBA-15 (b) using 3 and 12 grafting reaction times.

1 bar and the sample was regenerated at 90 °C in He after each adsorption measurement. Full regeneration of WG-SBA-15-10-0.5-0.03 took approximately 3 min. The adsorption/desorption cycle of WG-SBA-15-10-0.5-0.03 after ten cycles is shown in Fig. 9. There is no meaningful loss exhibited after 10 cycles indicating these adsorbents are stable after multiple adsorption/desorption cycles. The observed stability of WG-SBA-15-10-0.5-0.03 shows the effects associated with grafting in the presence of water did not affect the grafted amines.

Furthermore, as mentioned earlier, PEI polymers are deposited within the pore or the external surface of silica supports and held by weak physical forces. The absence of covalent bonding leads to PEI functionalized adsorbents displaying poor multi-cycle stability. The factors that contribute to the decreased CO_2 adsorption capacity of PEI impregnated adsorbents are the degradation and leaching of amines. Conversely, the polymer-like amines observed in wet grafted adsorbent are due to the amines being covalently tethered to the supports and other amines. Under dry adsorption conditions and further cycles (>100), the stability of amine-functionalized adsorbents worsens (Sujan et al., 2019). Each successive adsorption/desorption cycle at high temperatures causes the formation of stable urea groups, which deactivates functionalized amines (Sayari and Belmabkhout, 2010). The formation of urea groups, however, can be greatly inhibited when CO_2 adsorption is carried out in wet conditions (Sayari and Belmabkhout, 2010, Yu and Chuang, 2017). Sayari and Belmabkhout (2010) measured the adsorption capacity of amine grafted MCM-41 under wet conditions (0.4% R.H., 70 °C) for 700 cycles and there was negligible loss in the CO_2 adsorption capacity. It can be concluded that this phenomenon will be seen in other amine-functionalized silica.

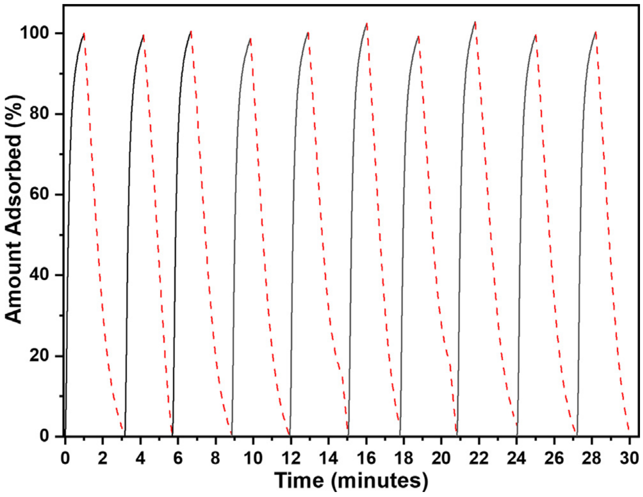

Fig. 9. Cyclic stability studies (70% CO_2 (in He) flow; desorption in He at 90 °C (dashed line)) of wet-grafted WG-SBA-15-10-0.5-0.03 at 75 °C and 1 bar.

5. Conclusion

In this work, the effect of water on amine grafted adsorbents was investigated. The results indicate that presence of water as opposed to alcohol has a positive effect on the amine loading of SBA-15 and other adsorbents. Continued increase of the water concentration results in more polymerization and higher amine loading with no signs of plateauing. The short time wet grafted adsorbents exhibited excellent stability under flue gas conditions. Moreover, the effects of wet grafting were observed for other silanes as well other mesoporous silica materials.

CRediT authorship contribution statement

John-Timothy Anyanwu: Conceptualization, Investigation, Methodology, Software, Validation, Formal analysis, Data curation, Writing - original draft, Writing - review & editing, Visualization. **Yiren Wang:** Conceptualization, Investigation, Methodology, Software, Validation, Formal analysis, Data curation, Writing - original draft, Writing - review & editing, Visualization. **Ralph T. Yang:** Conceptualization, Investigation, Methodology, Software, Validation, Formal analysis, Data curation, Writing - original draft, Writing - review & editing, Visualization, Supervision, Funding acquisition, Project administration, Resources.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by NSF Grant CBET-1826621, the Global CO$_2$ Initiative at the University of Michigan and the Blue Sky program of the College of Engineering at the University of Michigan.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ces.2021.116717.

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