Journal of Thermal Analysis and Calorimetry (2022) 147:135–143
https://doi.org/10.1007/s10973-020-10322-9

# Synthesis and characterization of lithium silicates from organosilicone precursors for carbon dioxide adsorption

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Received: 24 January 2020 / Accepted: 30 September 2020 / Published online: 17 October 2020

**Abstract**

Lithium silicates are ceramic materials known for its high $CO_2$ adsorption capacity and excellent cyclic stability at high temperatures. In the present work, an attempt has been made to use different types of organosilicone precursors viz., methyltrimethoxysilane, triethoxyphenylsilane, polyoligomericsilsesquioxane and polydimethylsiloxane as the silica precursor for the synthesis of lithium silicates for $CO_2$ adsorption. Thermogravimetry and differential scanning calorimetry were used to optimize the thermal decomposition of precursor to lithium silicate. Polydimethylsiloxane could not produce lithium silicate, as it decomposed to form volatile cyclic silicon oligomers at high temperatures. Lithium silicates were obtained from the other three precursors and were characterized for its structure and morphological features using X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron micrography, energy-dispersive X-ray spectrometry, particle size and surface area analysers. The $CO_2$ adsorption/desorption studies using thermogravimetry showed that lithium silicates synthesized from the silica precursor, methyltrimethoxysilane, retained a cyclic adsorption capacity of 31% for 10 cycles. The study reveals that hydrolysable aliphatic organosilicone compounds are better silica precursors for the synthesis of lithium silicates for regenerable $CO_2$ sorption.

**Keywords** Lithium silicate · $CO_2$ adsorption · Organosilicones · Cyclic stability · Thermogravimetry

## Introduction

Considering the anomalous increase in the atmospheric concentration of carbon dioxide ($CO_2$), techniques for its industrial and economical capture are in high demand. Burning of fossil fuels has resulted in the drastic increase in the average $CO_2$ concentration to around 414.7 ppm as on Dec 2019 [1–3]. Flue gas from coal burning power plants constitutes about 10–15% of the $CO_2$. Being the main source of $CO_2$ exit to atmosphere, methods for direct $CO_2$ capture from flue gases at high temperatures are preferred considering the high energy penalty and cost in cooling the flue gas [4–6]. Among the various separation technologies like absorption, adsorption, cryogenic separation, membrane separation and micro-algal bio-fixation adopted for carbon capture and storage, adsorption technique is considered as a competitive solution, considering its ease of regeneration by thermal or pressure modulation [7–9]. The adsorbents available for $CO_2$ separation are alkaline ceramics, zeolites, activated carbons, porous carbon, hydrotalcites, porous silicates, metal oxides, amine functionalized solid sorbents, metal–organic frameworks and metal-based oxides [10–15].

For the separation of $CO_2$ from flue gas at temperatures around 400–800 °C, materials with high thermal stability, high $CO_2$ capture capacity, high $CO_2$ selectivity, excellent regeneration property, stable sorption capacity during cycles and improved kinetic properties are required. Recent researches in this field have shown much attention in using dry solid sorbents for $CO_2$ capture. Lithium ceramics are excellent class of materials for $CO_2$ capture at high temperatures. Among these ceramics, lithium orthosilicates ($Li_4SiO_4$) have received worldwide attention because of their high theoretical $CO_2$ sorption capacity (0.367 g $CO_2$/g sorbent) and excellent cyclic stability. They also possess the advantage of using cheaper and widely available raw material ($SiO_2$) [16–23]. The reversible chemisorption of lithium orthosilicates is shown as

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$$Li_4SiO_4 + CO_2 \leftrightarrow Li_2CO_3 + Li_2SiO_3 \qquad (1)$$

Different methods like solid-state reaction method, sol–gel method, precipitation method, combustion method, etc. were developed for the synthesis of $Li_4SiO_4$ sorbents. In solid-state reaction method, $Li_2CO_3$ and $SiO_2$ are mixed together and calcined at high temperatures to form $Li_4SiO_4$ sorbent. The solid-state reaction method is a facile and the most commonly used technique to synthesize $Li_4SiO_4$ sorbents [24–26]. Sol–gel method includes different steps for the synthesis like uniform mixing of the lithium and silicon precursors in a liquid phase, formation of a gel of a three-dimensional network by the gelatinized particles and finally the drying and calcination of the gel to obtain the $Li_4SiO_4$ sorbent. Sol–gel method facilitates the formation of relatively homogeneous material at lower temperatures [27–29]. In precipitation method, the silicon source is mixed with solution of lithium source and the mixture suspension is stirred, dried and calcined at high temperatures to produce $Li_4SiO_4$ sorbent [25, 29–31]. In combustion method, the silicon source is mixed with the lithium solution and the fuel (i.e., citric acid, urea, glycine) followed by vaporization during which it begins to foam and swell and finally burns itself (autoignition) due to strong exothermic reaction. The charred ash is grinded and calcined at high temperatures to produce $Li_4SiO_4$ sorbents [32, 33]. Other techniques like solvo-plasma synthesis and spray-drying methods are also applied for the synthesis of $Li_4SiO_4$ sorbents [34, 35]. Methods like microstructural modification, utilization of efficient lithium and silicon sources or by doping with transition/alkali metals are also attempted to enhance their sorption capacity [36, 37].

The structure and properties of the synthesized lithium silicates (LS) are wholly dependent on many factors like synthesis method adopted, type of raw material used and the synthesis temperature [25–28]. The lithium sources typically employed are limited to lithium nitrate, lithium carbonate, lithium acetate and lithium hydroxide. In the case of silicon sources, substantial researches have been carried out by using raw materials like natural silicon containing minerals, biomass ashes, fly ashes, zeolite-based materials, organosilicone compounds, silica powder and its different forms like fumed silica, amorphous silica gel, colloidal silica, aerosol silica, silica sol and quartz powder [21, 38–43]. Silica obtained from most of the inorganic routes are contaminated with various impurities which are very difficult to remove and will adversely affect the properties of the final product. Silica produced by the hydrolysis/oxidative decomposition of organosilicone compounds will be of high purity. In addition to that in solid-state synthesis, homogenous mixing of reactants is essential which is not possible in the case of aged silica which is a polymerized form of silica molecules. However, insitu generation of silica and mixing with LiOH before polymerization of silica will produce a homogeneous mixture of reactants at molecular level, which is ideal for the synthesis of $Li_4SiO_4$.

Organosilicone compounds on heating in air decompose and oxidize with the release of gaseous products and ultrafine silica. The fine silica formed then reacts with the lithium precursor at high temperature aiding in the formation of porous LS as compared to other silicon precursors [44, 45]. The controlled thermal decomposition of the organosilicones also helps in the synthesis of silicates at relatively lower temperatures when compared to solid-state methods. The porous LS thus synthesized is expected to have high $CO_2$ adsorption capacity and cyclic stability. The formation of silica from different organosilicone compound depends on its structure, chemical and thermal stability. Considering this, we attempted to synthesize highly active and efficient lithium orthosilicates from $LiOH.H_2O$ and different types of organosilicone precursors viz., an aliphatic $SiO_2$ precursor—methyltrimethoxysilane, an aromatic $SiO_2$ precursor—triethoxyphenylsilane, acyclic, aliphatic $SiO_2$ precursor—polyoligomericsilsesquioxane, and a long chained, high molecular weight $SiO_2$ polymer—polydimethylsiloxane. For the first time, the effect of such types of $SiO_2$ precursor on the structure and morphology of the synthesized lithium silicates is studied. Thermogravimetry is employed for comparing the $CO_2$ adsorption capacities of the synthesized lithium orthosilicate sorbents and also for evaluating the cyclic adsorption capacity [46].

## Experimental

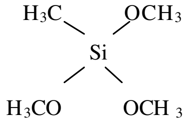
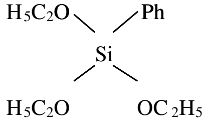
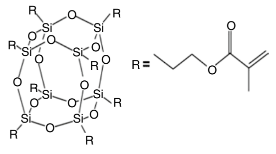
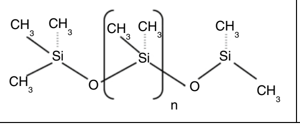
### Materials

Analytical grade lithium hydroxide monohydrate was procured from Supraveni chemical Pvt. Ltd., India and was used as the lithium source. The $SiO_2$ precursors used for the study are Methyltrimethoxysilane (MTMS), Triethoxyphenylsilane (TEPS), Polyoligomericsilsesquioxane (POSS) and Polydimethylsiloxane (PDMS). All the chemicals were of purity > 98% and have been used as such for the study without further purification. The structure and source of the $SiO_2$ precursors used are given in Table 1.

### Preparation of lithium silicate sorbents

Lithium silicate sorbents were prepared from stoichiometric volumes of $LiOH.H_2O$ and organosilicone precursors. The silicone precursor was dissolved in ethanol and was added to the aqueous solution of $LiOH.H_2O$ drop by drop with constant stirring. The stirring was continued for 1 h, followed by ageing in room temperature for 24 h. After adjusting the pH of the solution to 8 using nitric acid, the solution was

**Table 1** Structure and source of the $SiO_2$ precursors used for the study

| Sl no. | $SiO_2$ precursor | Structure | Source |
|---|---|---|---|
| 1. | Methyltrimethoxy silane (MTMS) |  | Source: Sigma Aldrich Chemicals<br>Molecular weight:136 g $mol^{-1}$ |
| 2. | Triethoxyphenylsilane (TEPS) |  | Source: Sigma Aldrich Chemicals<br>Molecular weight:240 g $mol^{-1}$ |
| 3. | Polyoligomericsilsesquioxane (POSS) |  | Source: Hybrid Plastics<br>Molecular weight:1082 g $mol^{-1}$ |
| 4. | Polydimethylsiloxane (PDMS) |  | Source: Sigma Aldrich Chemicals<br>Molecular weight:18000 g $mol^{-1}$ |

carefully heated to a dry mass on a boiling water bath for 10 h.

The dried powder was then heated in an alumina crucible using a muffle furnace from 30 to 700 °C at a heating rate of 3 °C $min^{-1}$ and kept inside the furnace at 700 °C for 3 h. Throughout the heating experiment, air at the rate of 100 mL $min^{-1}$ was passed through the furnace. The heated samples are referred as LS-MTMS, LS-TEPS, LS-POSS and LS-PDMS depending on the precursors used for its synthesis.

## Thermal characterization of adsorbents

Thermal decomposition behaviour of the LS precursors and the $CO_2$ adsorption capacity of the LS adsorbents were studied using TA Instruments Q 600 simultaneous TG-DSC. A sample mass of $5 \pm 1$ mg of precursor samples was taken in a platinum crucible and heated from 30 to 900 °C with a heating rate of 10 °C $min^{-1}$. All analysis was carried out in air atmosphere purged at the rate of 100 mL $min^{-1}$.

The $CO_2$ adsorption capacities of the sorbents were studied using a dynamic TG analysis. About 5 mg of the sorbent was taken in a platinum crucible and was heated from 30 to 900 °C at a heating rate of 20 °C $min^{-1}$ in pure $CO_2$ purged at the rate of 100 mL $min^{-1}$.

The cyclic stability for $CO_2$ adsorption/desorption capacity was evaluated using the thermogravimetric analyser at 700 °C for 10 cycles. For this, the sorbent was initially heated up to 700 °C in pure nitrogen atmosphere. After equilibrating at 700 °C, the purge gas was changed to pure $CO_2$ and the sorption was performed for 30 min. For desorption studies, the purge gas was switched over to pure nitrogen, under the same temperature for 30 min. A flow rate of 100 mL $min^{-1}$ was used for nitrogen and $CO_2$ in all experiments. The sorption capacity of the sorbent was calculated based on the initial sorbent weight.

## Characterization of sorbents

FTIR analysis was carried out using Thermofisher Nicolet iS50 Fourier transform infrared spectrometer in the wave number range of 4000–400 $cm^{-1}$, after pelletising the sample with KBr powder. The XRD patterns of the samples were recorded using a Bruker D8 Discover diffractometer with Cu-Kα radiation ($\lambda = 1.5406$ Å) at scanning rate of 5°/min from 10° to 90°. Surface morphology of the samples was studied using a Carl Zeiss Gemini SEM 500 Field emission scanning electron microscope. The elemental identification was done using Bruker Quantax XFlash Energy Dispersive X-ray Spectrometer. Brunauer–Emmett–Teller (BET) surface area was determined using Quantachrome NOVA 1200 e surface area analyser. Particle size was assessed using Malvern Mastersizer 2000 particle size analyser.

## Results and discussion

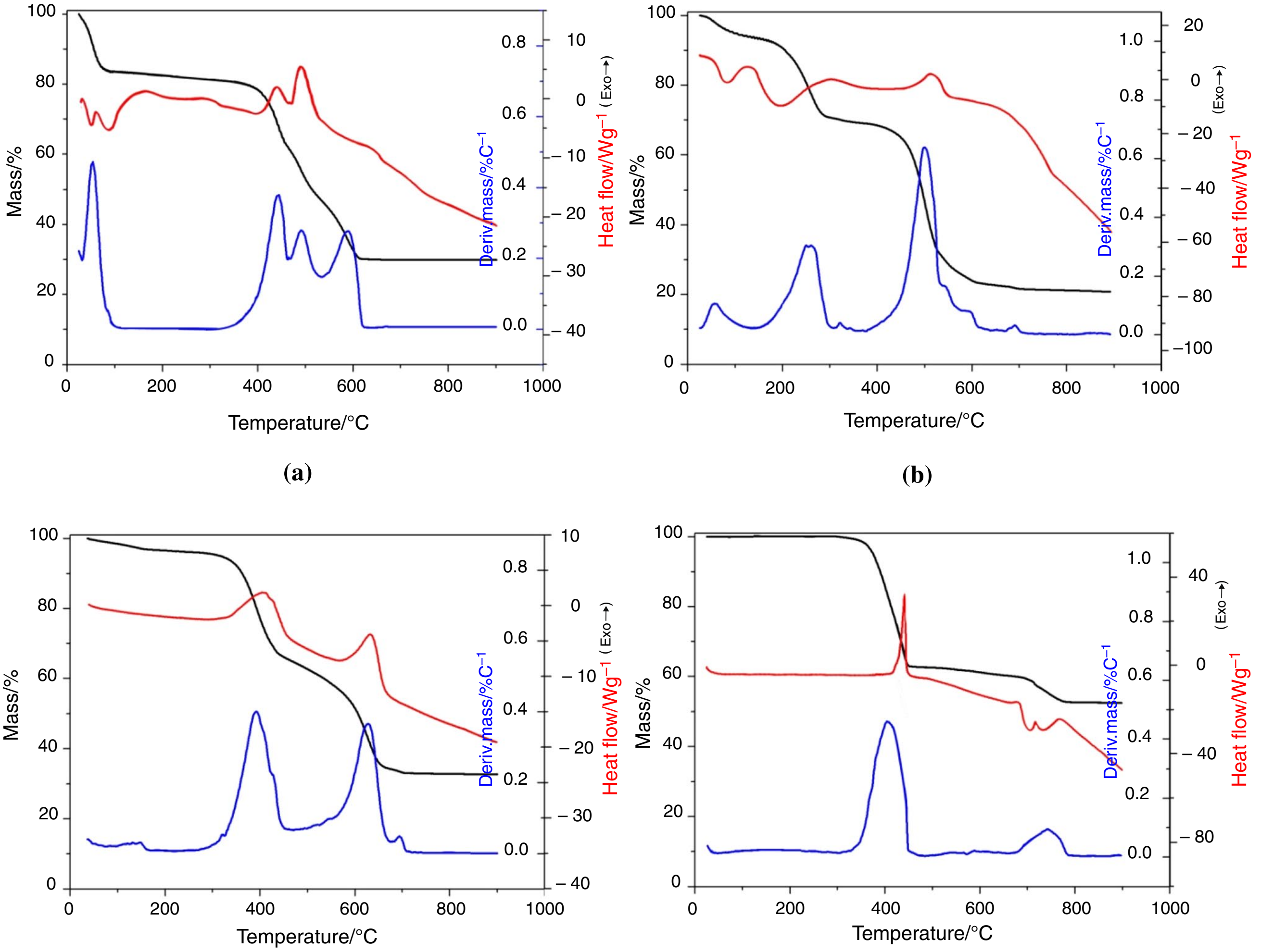
### TG/DSC analysis of lithium silicate precursors

To determine the calcination temperature for the synthesis of the LS sorbents, TG and DSC analysis of the precursors were carried out in air up to 900 °C. The TG/DTG/DSC curves of the four LS precursors are given in Fig. 1.

From the TG-DTG-DSC curves, it is observed that the precursor to LS-MTMS (Fig. 1a), shows an endothermic mass loss of 15% below 100 °C corresponding to the loss of adsorbed water. This is followed by another mass loss in the temperature range of 400–600 °C corresponding to the multistage reactions involving melting and decomposition of LiOH, oxidation of organic moieties and the solid-state reaction between silica and lithium oxide to form $Li_4SiO_4$. The overall reaction is indicated as exothermic by the DSC.

In the case of precursor to LS-TEPS, the TG-DTG-DSC curves show an initial endothermic mass loss of 10% corresponding to the loss of adsorbed water, followed by another endothermic mass loss of 20% due to the hydrolysis of TEPS and the loss of volatile hydrolysis products. Similar to LS-MTMS, an exothermic mass loss stage is observed in the range of 400–600 °C corresponding to the oxidation of organic groups, melting and decomposition of LiOH, and conversion of silica to LS.

TG-DSC curves of precursor to LS-POSS show an initial mass loss in the temperature region of 300–450 °C corresponding to the decomposition and oxidation of POSS molecules with the formation of ultrafine silica particles. The second mass loss stage from 550 to 700 °C indicates the exothermic oxidation of remaining organic residue and the formation of LS. DSC analysis indicates that both



(a)

(b)

(c)

(d)

**Fig. 1** TG/DTG/DSC curves of **a** LS-MTMS, **b** LS-TEPS **c** LS-POSS and **d** LS-PDMS the stages are exothermic in nature. In the case of precursor to LS-PDMS, the TG-DSC curves show an exotherm (350–450 °C), indicating the partial oxidative decomposition of PDMS to its volatile oligomers and decomposition of LiOH [47, 48]. This stage accounts for 40% mass loss and is exothermic in nature. This stage is followed by an endothermic mass loss of 10% in the range of 680–780 °C indicating a partial loss of lithium oxide.

Based on the TG analysis, the temperature selected for calcination was fixed at 700 °C for all the four precursor samples.

## FTIR analysis

The overlaid FTIR curves of LS sorbents are given in Fig. 2.

All the four FTIR spectra (Fig. 2) show peaks at 1440 $cm^{-1}$ and 860 $cm^{-1}$ corresponding to $CO_3^{2-}$ ions indicating the formation of $Li_2CO_3$ in all the four compounds [49]. Peaks at 500 $cm^{-1}$ and 700–740 $cm^{-1}$ may be attributed to O-Li–O structure in all the compounds. The IR absorption bands corresponding to $[SiO_4]^{2-}$ tetrahedral arrangements are found at 940–950 (v3), 820(v1), and 520–524(v4) $cm^{-1}$. The vibration bands at 980–1060 $cm^{-1}$ and 620 $cm^{-1}$ are attributed to Si–O-Si and O-Si–O, respectively. Thus, the FTIR spectra confirms the presence of $Li_4SiO_4$ with some $Li_2CO_3$ in LS-MTMS, LS-TEPS and LS-POSS where as the absence of bands due $[SiO_4]^{2-}$ ions in the FTIR spectrum of LS-PDMS indicate the non-formation of $Li_4SiO_4$ in that compound. The FTIR spectrum of LS-PDMS confirms only the formation of hydrated lithium oxide along with some lithium carbonate.

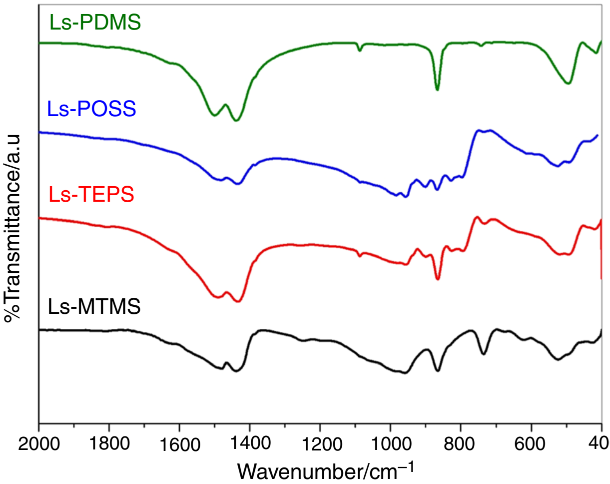


**Fig. 2** FTIR spectra of synthesized lithium silicate sorbents

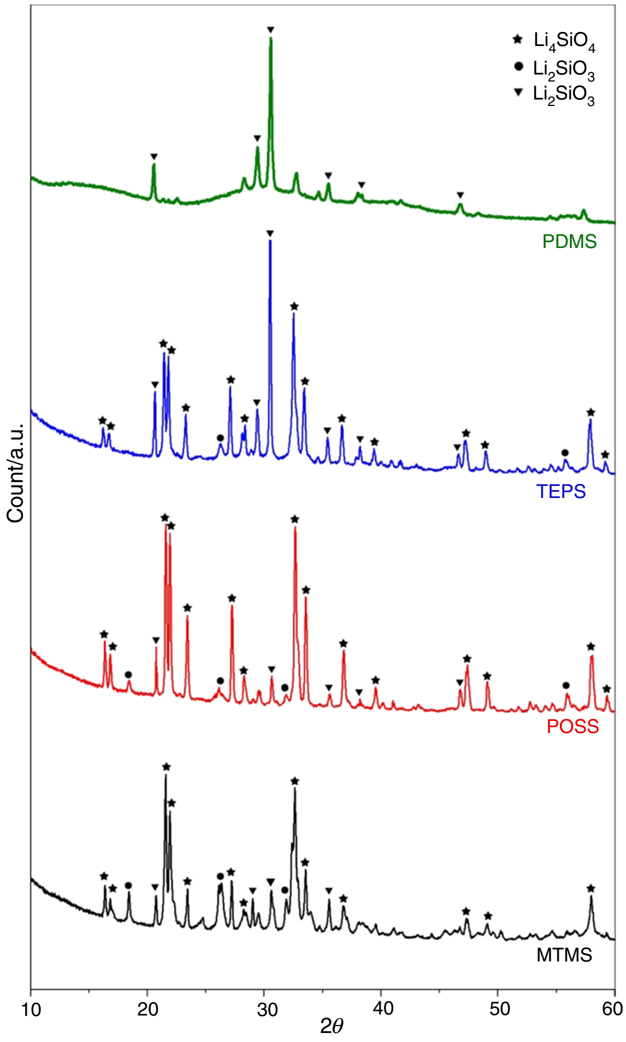


**Fig. 3** XRD pattern of lithium silicate samples

## XRD analysis

The XRD patterns of the samples are given in Fig. 3. From the XRD spectra, it is seen that all the samples were highly crystalline in nature. In the case of LS-MTMS, LS-TEPS and LS-POSS, other than the expected main phase of $Li_4SiO_4$, phases like $Li_2SiO_3$ and $Li_8SiO_6$ were also present in minor quantities. Traces of $LiAlSiO_4$ phase was also identified, which is expected to be formed by the reaction of the alumina crucible with the raw materials at high temperatures.

Some $Li_2CO_3$ is also observed in all the samples, which is formed by the reaction between lithium compound and $CO_2$ from the atmosphere as well as from the $CO_2$ formed by the oxidation of carbonaceous residue in organic precursors. Since aluminium is reported as a promoter for the adsorption of $CO_2$ by $Li_4SiO_4$ and $Li_2CO_3$ is one of the byproduct of $CO_2$ adsorption, these compounds will not affect the $CO_2$

adsorption/desorption capacity of the LS, especially in a cyclic adsorption/desorption process.

In the case of LS-PDMS, LS was not formed, as PDMS decomposed to form volatile cyclic silicon oligomers, thereby unable to provide silica to react with LiOH at higher temperatures. The XRD spectra showed the presence of $Li_2CO_3$ and traces of $Li_2O$ in the sample.

## FESEM and EDS analysis

The morphology of the synthesised sorbents was studied using FESEM analyses. The SEM images of the sorbents are shown in Fig. 4.

Flake like morphology is observed for LS-MTMS, LS-TEPS and LS-POSS samples indicating the homogenity in the surface composition of the samples. LS-PDMS sample has a dense sheet like structure of lithium carbonate as confirmed from the XRD spectra. The FESEM image also reveals that the particle size of LS-MTMS is much lower than that of LS-POSS and LS-TEPS, which is comparable from the data obtained from the particle size analyser (Refer Table 1). Also, the distribution of particles of LS-MTMS is observed to be more uniform and homogeneous compared LS-TEPS and LS-POSS. The EDS spectra of the LS materials were measured at 10 keV and are shown in Fig. 5.

The EDS spectra of the samples confirmed the presence of silicon, oxygen and carbon in LS-MTMS, LS-TEPS and LS-POSS samples. The EDS spectra of LS-PDMS showed the presence of oxygen and carbon peaks only and no silicon peaks, supporting the absence of silicate formation.

## $CO_2$ adsorption studies

The calcined LS sorbents were evaluated for their $CO_2$ adsorption efficiency using a Thermogravimetric analyser under dynamic conditions in 100% $CO_2$ atmosphere. The overlaid TG curves of LS-MTMS, LS-POSS, LS-TEPS and LS-PDMS in $CO_2$ atmosphere are given in Fig. 6 and their $CO_2$ adsorption capacities are tabulated in Table 2.

From the TG curves, it is observed that LS synthesized from MTMS, POSS and TEPS only could adsorb and desorb $CO_2$. The $CO_2$ adsorption capacities of the sorbents varied with the organosilicone precursor used for the synthesis.

LS-PDMS didn't show any $CO_2$ adsorption. This is due to the inability of PDMS to generate $SiO_2$ at high temperatures for the formation of LS. It is observed from the TG curve of the PDMS precursor (Fig. 1d) that during the heating process, decomposition of the material occurs, leading to unzipping of the polymer chain to form volatile cyclomers. These volatile cyclomers escape with the purge gas, without getting oxidized to silica, making it unavailable for the reaction with $Li_2O$ in the crucible. The absence of silicate in this sample is also confirmed by FTIR spectroscopy and XRD analyses. In addition, the fused lithium oxide (LS-PDMS), as revealed by SEM analysis, has very low surface area to absorb $CO_2$.

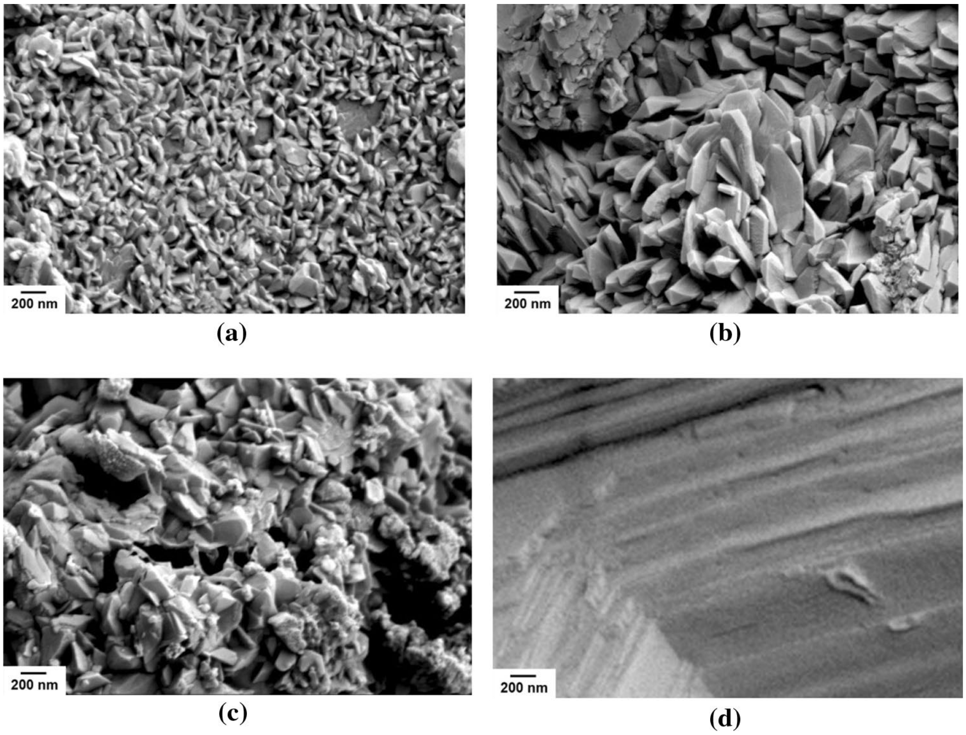
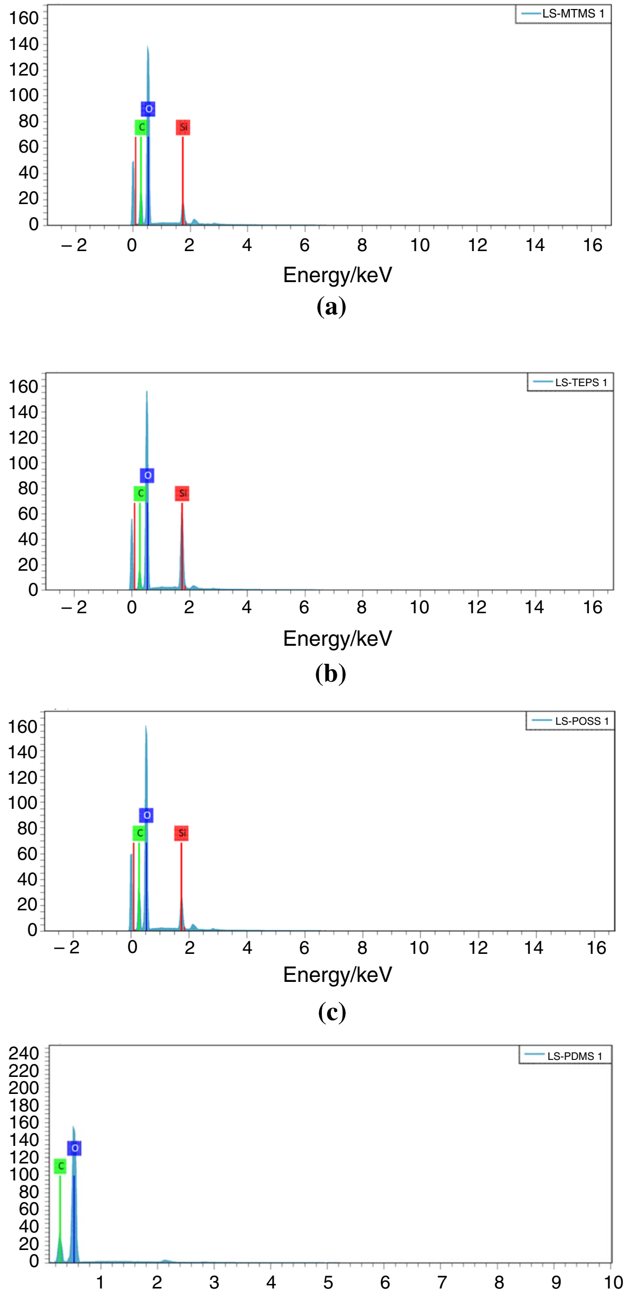


**Fig. 4** FESEM images of **a** LS-MTMS, **b** LS-TEPS **c** LS-POSS and **d** LS-PDMS



(a)

(b)

(c)

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**Fig. 5** EDS spectra of **a** LS-MTMS, **b** LS-TEPS **c** LS-POSS and **d** LS-PDMS

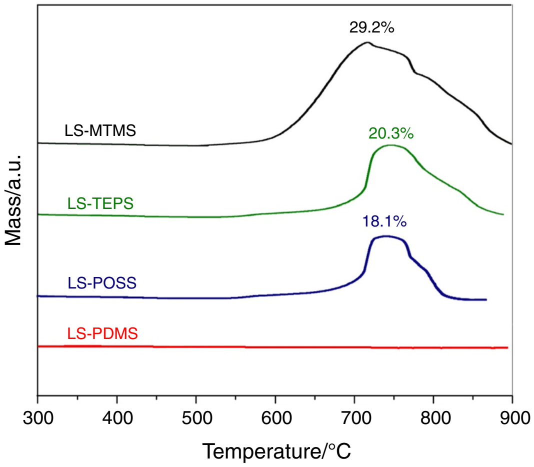

**Fig. 6** $CO_2$ adsorption curves of LS-MTMS, LS-POSS, LS-TEPS and LS-PDMS

**Table 2** Surface area and the particle size of the synthesised lithium silicate sorbents

| Sorbent | Particle size/μm | Surface area/ $m^2\ g^{-1}$ | $CO_2$ adsorption efficiency/% |
|---|---|---|---|
| LS-MTMS | 108 | 7.2 | 29.2 |
| LS-TEPS | 239 | 1.3 | 20.3 |
| LS-POSS | 217 | 1.4 | 18.1 |

The $CO_2$ adsorption of LS-MTMS, LS-POSS and LS-TEPS started at 550 °C, with a peak adsorption at 700 °C for LS-MTMS and around 750 °C for LS-POSS and LS-TEPS. LS-MTMS showed the highest $CO_2$ adsorption efficiency of around 29.2% compared to 20.3% for LS-TEPS and 18.1% for LS-POSS.

LS-MTMS is an aliphatic $SiO_2$ precursor with low molecular weight. Due to the presence of relatively simple $–OCH_3$ groups attached to the silicon atom, it is easily getting hydrolysed to $CH_3OH$ and $SiO_2$ to react with LiOH for the formation of LS. In the case of TEPS, the phenyl group and the ethoxy groups restrict the easy hydrolysis to generate $SiO_2$. POSS is a cyclo-aliphatic $SiO_2$ precursor with bulky alkyl groups present in the polymer. The presence of bulkier groups always hinders the hydrolysis reaction and hence easy generation of $SiO_2$. This suggests that the easiness to generate $SiO_2$ enhances the silicate formation and hence the increase in their $CO_2$ adsorption capacity. All the three sorbent showed regeneration on heating at high temperatures. Regeneration of the sorbents LS-MTMS, LS-POSS and LS-TEPS was completed by 900 °C even in $CO_2$ atmosphere, indicating their application for use of sorbent for cyclic purposes.

## Particle size and surface area analysis

The particle size and the surface area of the synthesised sorbents, which adsorbed $CO_2$ are tabulated in Table 2.

LS-MTMS is having the lowest particle size and highest surface area among the three samples, which may be the reason for its high $CO_2$ sorption capacity. The easy hydrolysis of MTMS with controlled thermal decomposition has led

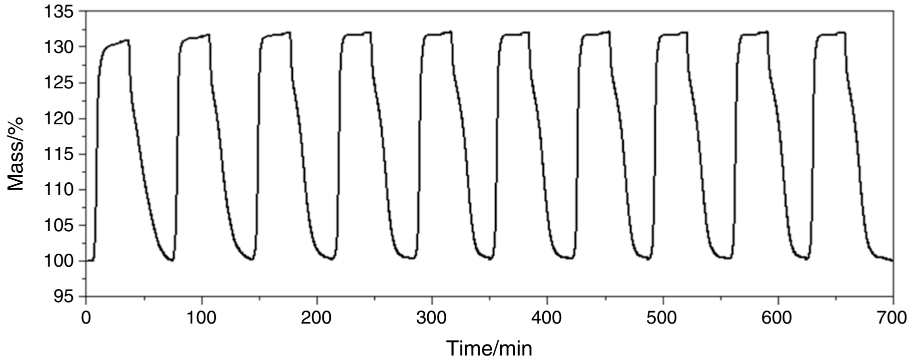

**Fig. 7** Cyclic sorption of the LS-MTMS for 10 cycles at 700 °C

to the formation of particles with comparatively lower size and higher surface area than the other LS precursors. The particle size and surface area of LS-TEPS and LS-POSS were almost the same and show comparable $CO_2$ adsorption capacity.

## Cyclic $CO_2$ adsorption studies

Considering the high $CO_2$ adsorption efficiency and regeneration capability of LS-MTMS sorbent amongst the others, the cyclic performance of the sorbent was studied under isothermal TG conditions at 700 °C as per the procedure in 2.3 and the cyclic sorption plot is given in Fig. 7. The adsorption/desorption cycle was repeated 10 times to ascertain the recyclability of the material.

From the TG curve, it was observed that LS-MTMS showed an adsorption capacity of 31%, higher than that obtained during the dynamic TG process. This is due to the increased diffusion of $CO_2$ molecules on retaining at high temperatures. The cyclic efficiency of the sorbent was retained even after 10 cycles, suggesting its suitability for high temperature $CO_2$ capture. The graph also shows a constant rate of adsorption and desorption throughout the cycles.

## Conclusions

A comparative study of different types of organosilicone polymers were made for the synthesis of lithium silicate for $CO_2$ adsorption. LS were synthesized from lithium hydroxide and silicone precursors viz., MTMS, TEPS and POSS. LS could not be produced form PDMS as it could not generate $SiO_2$ at high temperatures to react with LiOH. The $CO_2$ adsorption capacity of the LS varied with the silicone precursor. LS-MTMS showed the highest $CO_2$ adsorption of 29.2% compared to 20.3% for LS-TEPS and 18.1% for LS-POSS in dynamic TG analysis. LS-MTMS retained a cyclic adsorption capacity of 31% for 10 cycles and is a promising candidate for regenerable $CO_2$ capture at high temperatures. The study concludes that hydrolysable aliphatic organosilicone compounds are better silica precursors for the synthesis of lithium silicates for regenerable $CO_2$ sorption.

**Acknowledgements** The authors thank Director, Vikram Sarabhai Space Centre for permission to publish this work and colleagues in Analytical and Spectroscopy Division, Vikram Sarabhai Space Centre for their analytical support.

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