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Facile synthesis of silica aerogel supported K_2CO_3 sorbents with enhanced CO_2 capture capacity for ultra-dilute flue gas treatment

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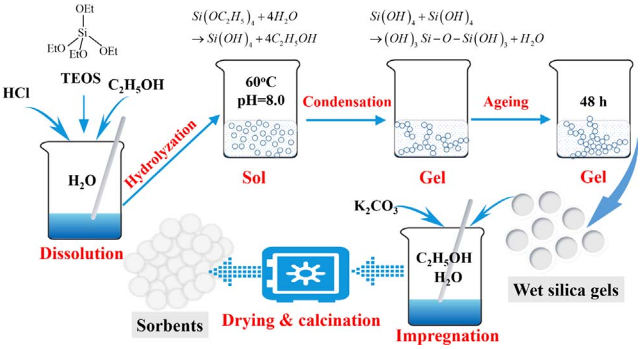
GRAPHICAL ABSTRACT



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ABSTRACT

Silica aerogel supported K_2CO_3 sorbents with different K_2CO_3 loadings were synthesized by sol-gel and wet impregnation processes. The sorbents were characterized by N_2 adsorption-desorption, X-ray diffraction (XRD), and field emission scanning electron microscopy (FESEM) techniques. CO_2 capture performances of the sorbents were tested in a simulated ultra-dilute flue gas stream of 1.0%CO_2 and 2.0%H_2O at 20 °C, using a fixed-bed reactor coupled with an online infrared gas analyzer. Sorbent regeneration performances of the samples were evaluated in a pure N_2 atmosphere at 200 °C with a heating rate of 10 °C/min. CO_2 capture capacity and K_2CO_3 utilization efficiency increased first and then decreased with the increase in K_2CO_3 loading. The desired sorbent with 20 wt% K_2CO_3 was screened for investigating the effects of acid impurities. The presence of 500 ppm SO_2 and 500 ppm NO in the simulated flue gas stream was found to adversely affect the CO_2 capture, sorbent regeneration and multiple cyclic performances. Detailed mechanisms of the irreversible sorbent deactivation process were discussed. SO_2 could be chemically absorbed by K_2CO_3 under a moist condition to form byproduct of $K_2SO_3{\cdot}H_2O$, and the byproduct was stable and would be accumulated in the sorbent during the repeated cycles. This further attenuated the physical properties and K_2CO_3 utilization efficiency of the sorbent. These results would lay a solid foundation for further application of the sorbent in ultra-dilute flue gas treatment.

1. Introduction

Massive CO_2 emitting from fuel combustion process is considered as the major contributor to global warming and climate change. Post-combustion CO_2 capture, oxy-fuel combustion technology, and the integrated gasification combined cycle and carbon capture and storage

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Table 1
A summary of CO_2 capture capacities of several silica aerogel supported sorbents reported in literatures.

Sorbents	Raw materials	Synthesis method	Testing conditions	CO_2 capture capacity (mmol CO_2/g sorbent)	Refs.
A-SCD-acetone[a] A-SCD-ethanol A-SCD-methanol A-SCD-isopropanol	APTES, TEOS, EtOH, H_2O, acetone, ethanol, methanol, isopropanol	One-step sol-gel process and SCD[b]	Fixed-bed reactor, 25–75 °C, 1%CO_2 + 1% H_2O, 300 mL/min	5.55 4.46 3.96 4.24	[18]
AH-RFSA [c]	Resorcinol, formaldehyde APTES, H_2O	Hydrothermal sol-gel process	Fixed-bed reactor, 30–50 °C, 1%CO_2 (+1% H_2O), 300 mL/min	3.57 (4.43)	[19]
AHSA [d]	APTES, TEOS, EtOH, H_2O	One-step sol-gel process and SCD	Fixed-bed reactor, 50 °C, 1%CO_2, 300–700 mL/min	2.42-3.04	[20]
AMSA[e]	APTES, TEOS, EtOH, HCl, H_2O	One-step sol-gel process and SCD	Quartz tubular reactor, 25–50 °C, 10%CO_2 (+10%H_2O)	1.19–1.95 (3.81–6.97)	[21]
M-APTMS [f] T-APTMS [g]	TMOS, EtOH, HCl, H_2O	Two-step hydrolysis-condensation process	Adsorption column, 20 °C, 0.25%CO_2 + 30% RH, 0–2 L/min	1.40 1.62	[22]
P-30-85 [h] W-30-80[i]	TEPA, methanol, n-hexane, $NaIO_4$, $RuO_2{\cdot}2H_2O$, PA [j]	Solvent evaporative precipitation, wet impregnation	Electro-microbalance, 75 °C, 100%CO_2, 100 mL/min	1.6-6.1 0.9-5.8	[23]
SA-I-40-90 [k] SA-O-50-85 [l]	TEPA, PA	Wet impregnation	Electro-microbalance, 75 °C, 100%CO_2, 100 mL/min	2.3-6.1 1.3-3.5	[24]
SiO_2 SiO_2-5%PEI SiO_2-15%PEI SiO_2-2%APTMS	Sodium silicate solution, acetic acid, TEOS, APTMS, EtOH, PEI	Hydrolyzation and polycondensation, wet impregnation	TGA, 50 °C, 100%CO_2, 50 mL/min	0.21 0.88 1.16 0.67	[25]
FS-DETA-0-40 [m]	Silica gel, DETA, methanol	Wet impregnation	TGA, 25 °C, 100%CO_2, 60 mL/min	0.56-0.92	[26]
K_2CO_3/SG[n]	Silica gel, K_2CO_3, H_2O	Wet impregnation	TGA, 60 °C, 15%CO_2 + 15%H_2O, 500 mL/min (fluidized-bed reactor, 1.8 m^3/h)	Carbonation conversion of 34.5% (18.8%)	[11]
K_2CO_3/SG	Silica gel, K_2CO_3, H_2O	Wet impregnation	Fixed-bed reactor, 20 °C, 0.5%CO_2 + 1·.8H_2O, 0.05 m^3/h	0.15	[27]
K_2CO_3/SG	Silica gel, K_2CO_3, ethanol	Wet impregnation	TGA, 20–60 °C, 1.0%CO_2 + 2.0%H_2O, 500 mL/min	0.53	[28]

[a] A-SCD-acetone = amine hybrid silica aerogel synthesized using acetone for solvent exchange.
[b] SCD = supercritical drying.
[c] AH-RFSA = amine hybrid resorcinol-formaldehyde/silica.
[d] AHSA = amine hybrid silsesquioxane aerogel.
[e] AMSA = amine-modified SiO_2 aerogel.
[f] M-APTMS = ((3-aminopropyl)trimethoxysilane.
[g] T-APTMS = (3-trimethoxysilylpropyl)diethylenetriamine.
[h] P-30–85 = TEPA modified silica aerogel synthesized by precipitation method with amine loading in the 30–85 wt% range.
[i] W-30-80 = TEPA modified silica aerogel synthesized by wet impregnation method with amine loading in the 30–80 wt% range.
[j] PA = particulate aerogel.
[k] SA-I-40-90 = TEPA impregnated hydrophilic silica aerogel with amine loading in the 40–90 wt% range.
[l] SA-O-50-85 = TEPA impregnated hydrophobic silica aerogel with amine loading in the 50–85 wt% range.
[m] FS-DETA-0-40 = DETA impregnated commercial silica gel with amine loading in the 0–40 wt% range.
[n] K_2CO_3/SG = K_2CO_3 modified commercial silica gel.

(IGCC) are regarded as potential strategies for CO_2 emission reduction [1–3]. Amongst these mitigation technologies, post-combustion CO_2 capture through chemical absorption shows particular promise for large-scale application [4–6].

Chemical absorption of CO_2 using dry regenerable potassium-based sorbents is suitable for fossil fuel sector with broad prospects, considering the advantages of high storage capacity, facile regeneration, low cost and energy consumption, and high availability [6–10]. Although considerable efforts have been spent on further improving the CO_2 capture capacities and global reaction rates of potassium-based sorbents, high cost of the supporting materials and sorbent deactivation in acid impurities could be the two major challenges to overcome before cosmically commercial applications [11–17].

To achieve a cost-effective CO_2 capture process, low-cost silica aerogel materials with open pore structure, high porosity and high surface area have been extensively employed as excellent supports for synthesizing solid CO_2 sorbents [18–29]. Table 1 summarizes the CO_2 capture capacities of several silica aerogel supported amine or K_2CO_3 sorbents. Amine functionalization has been widely accepted as a promising route to improve CO_2 capture capacity of silica aerogel. It was found that CO_2 uptakes of the investigated amine-modified silica aerogel sorbents were comparable to or even greater than some commercially available sorbents (higher than 2.0 mmol CO_2/g sorbent) [18–21,23,24]. Particularly, a novel amine-modified SiO_2 aerogel sorbent (AMSA) synthesized by sol-gel process with supercritical drying (SCD) technique possessed an extremely high CO_2 storage capacity of 6.97 mmol CO_2/g sorbent [21]. Reports concerning the modification of silica aerogel with K_2CO_3 for enhanced CO_2 capture capacity are limited. Compared to amine-functionalized silica aerogel sorbents, K_2CO_3-modified silica aerogel (K_2CO_3/SG) prepared by one-step wet impregnation method presented rather poor CO_2 capture performances, as indicated by the low carbonation conversion (34.5% in TGA and 18.8% in fluidized-bed reactor) and CO_2 uptake (0.15 mmol CO_2/g sorbent) [11,27]. Microscopic structure blockage in silica aerogel support and non-uniform distribution of K_2CO_3 thereon were observed during the one-step wet impregnation procedure using deionized water as solvent, and these were responsible for the weak CO_2 capture performances. Overall capture capacity could be enhanced to 0.53 mmol CO_2/g sorbent, when ethanol was used as solvent in the one-step wet impregnation process [28]. Whereas, the K_2CO_3 utilization efficiencies of the K_2CO_3/SG sorbents prepared by the one-step wet impregnation method using deionized water and ethanol as solvents are only 5.5% and 35.6%, which are far from those reported for K_2CO_3/Al_2O_3 sorbents (> 90%) [14,15,30,31]. Hence, there is still room for improvement in CO_2 capture capacity and K_2CO_3 utilization of the K_2CO_3-modified silica aerogel sorbents by further optimizing the synthesis method.

Deactivation in the presence of potential impurities such as SO_2 and NO*x* could be another issue for CO_2 solid sorbents. To date, there are