Utilization of Polymer Cross-Linkers to Improve the Thermal Stability of CO_2 "Molecular Basket" Sorbents

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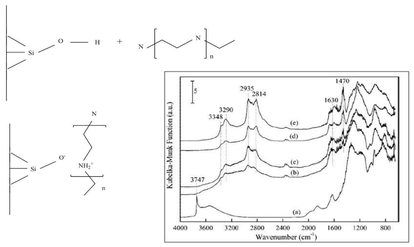
Introduction

Polymeric interactions are important to the thermal stability and long-term regenerability of CO_2 Molecular Basket Sorbents. Polyethylenimine (PEI) interactions are of two types: PEI with the support and PEI with other polymer strands. The polymer/support interactions can be described as follows:



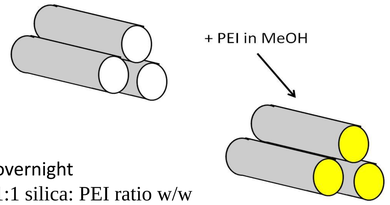
There is a strong interaction between PEI and the silica surface but this also leaves non-surface layers to be bound weakly through hydrogen bonding. Improving the thermal stability of these materials then necessitates strengthening the interactions between attachment sites and the rest of the amines. This can be done in two ways: increasing polymer strand length or enhancing the interactions between shorter polymer strands.

Increasing the molecular weight of PEI increases the stability of the sorbent, but also causes a marked decrease in total sorptive capacity.

Additionally incorporation of a cross-linking agent also has the ability to strengthen the interactions between polymer strands creating a more stable sorbent.

Experimental

Synthesis: MBS-2 standard sample preparation follows the method found in Xu et al.[1]



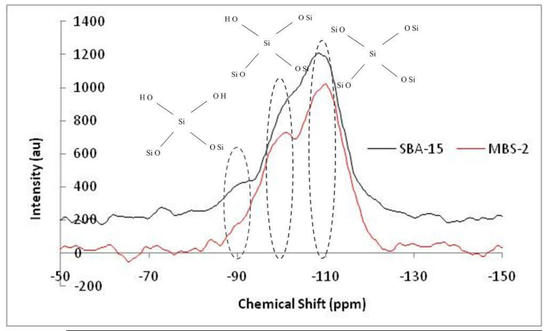
-Dissolve PEI in MeOH
-Stir 15 min
-Add Oxalic Acid*
-Stir 1 hr*
-Add SBA-15
-Stir 4 hrs
-Dry under vacuum at 40°C overnight
-Samples were prepared at 1:1 silica: PEI ratio w/w
-SBA-15 prepared following Zhao et al.[2]
-PEI from Aldrich (~423 Mw) or Polysciences Inc (600, 1200, 1800 Mw)
-Oxalic Acid dihydrate from Aldrich

Characterization: Thermogravimetric analysis was done using SDT Q600 TGA-DSC. Cyclic regeneration was done by first pretreating the sample at 100°C under 100mL/min N2 for 50 min, the temperature was the decreased to 75°C and CO2 passed over for 50 min. The gas was then changed back to N2 and the temperature returned to 100°C and the process was repeated.

Decomposition measurements were made by ramping the temperature from RT to 500°C at 5°C/min and holding for 30 min.

DRIFT were collected using a Nicolet Nexus 470 FTIR using SMART collector attachment. Samples were purged with N_2 and KBr background subtracted.

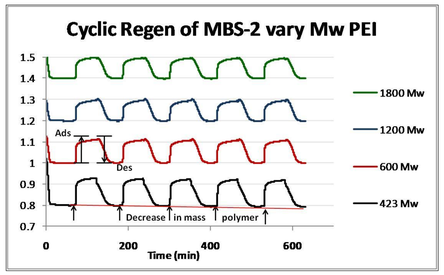
^{29}Si NMR



	SBA-15			MBS-2		
	Chemical Shift	Percent Si	Rel. Pop.	Chemical Shift	Percent Si	Rel. Pop.
Q4	-109.4	54.9	100	-110	56.7	100
Q3	-100.7	41.1	74.9	-99.3	42.5	75
Q2	-89.6	4.0	7.3	-89.6	0.8	1.4

^{29}Si NMR of SBA-15 and MBS-2 shows that amines bind primarily to the Q2 silica sites but with almost no change to the Q3 population. This also indicates that PEI appears to be bound to the surface to only a small percentage of surface sites.

Vary MW of PEI



Increasing Mw of PEI decreases sorptive capacity. There is also observed a small decrease in capacity each consecutive regeneration cycle.

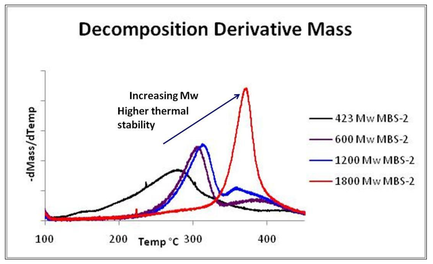
	Molecular Weight PEI			
Cycle	423 amu	600 amu	1200 amu	1800 amu
First	128.6	113.8	102.7	97.8
Second	125.9	110.8	101.8	96.0
Third	123.7	109.3	99.3	94.3
Fourth	123.8	108.7	98.9	93.1
Fifth	122.6	106.2	99.3	92.9

* mgCO2/g sorbent

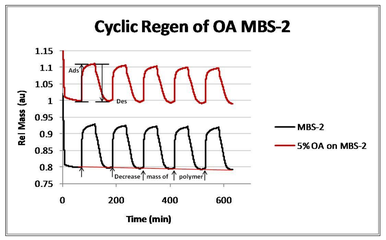
	Molecular Weight PEI			
Cycle	423 amu	600 amu	1200 amu	1800 amu
1 to 2	0.01	0.00	-0.01	0.01
2 to 3	-0.18	0.00	0.15	0.06
3 to 4	-0.10	0.00	-0.05	0.02
4 to 5	-0.21	0.00	-0.10	0.02
Net	-0.49	0.00	-0.01	0.11

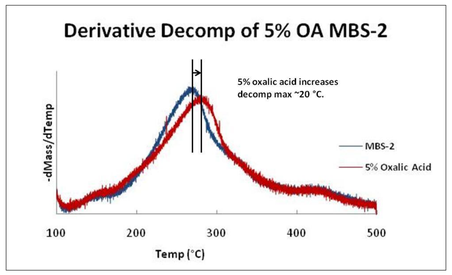
* percent mass lost

Low Mw PEI tends to decompose at lower temperatures than larger Mw PEI. Additionally, there is a loss of mass of polymer as has been observed elsewhere.[3]



Oxalic Acid Incorporation



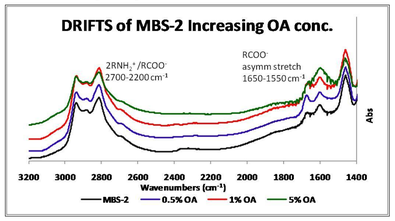


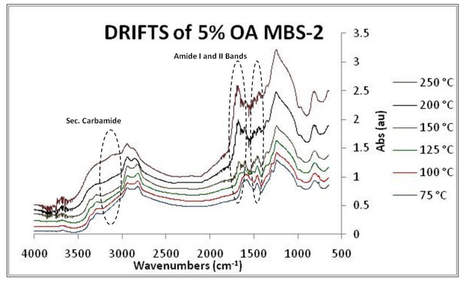
Oxalic acid gives a small increase to thermal stability by forming carbamates between PEI strands at a small cost to capacity.

	Molecular Weight PEI	
Cycle	MBS-2	5% OA
First	128.6	109.9
Second	125.9	106.6
Third	123.7	104.4
Fourth	123.8	103.7
Fifth	122.6	101.2

* mgCO2/g sorb

Carbamates formed may be dehydrated at elevated temperatures resulting in carbamide formation.





Conclusions

-Increasing Mw of PEI increases the thermal stability of MBS-2 while acid provides a small increase in overall thermal stabilitydecreasing the sorptive capacity
-Incorporation of oxalic with minor decrease in sorptive capacity
-PEI binds preferentially to Q2 silanol sites

Acknowledgements

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Reference

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