Novel Doped Zinc Oxide Sorbents For Regenerable Desulfurization Applications at Low Temperatures

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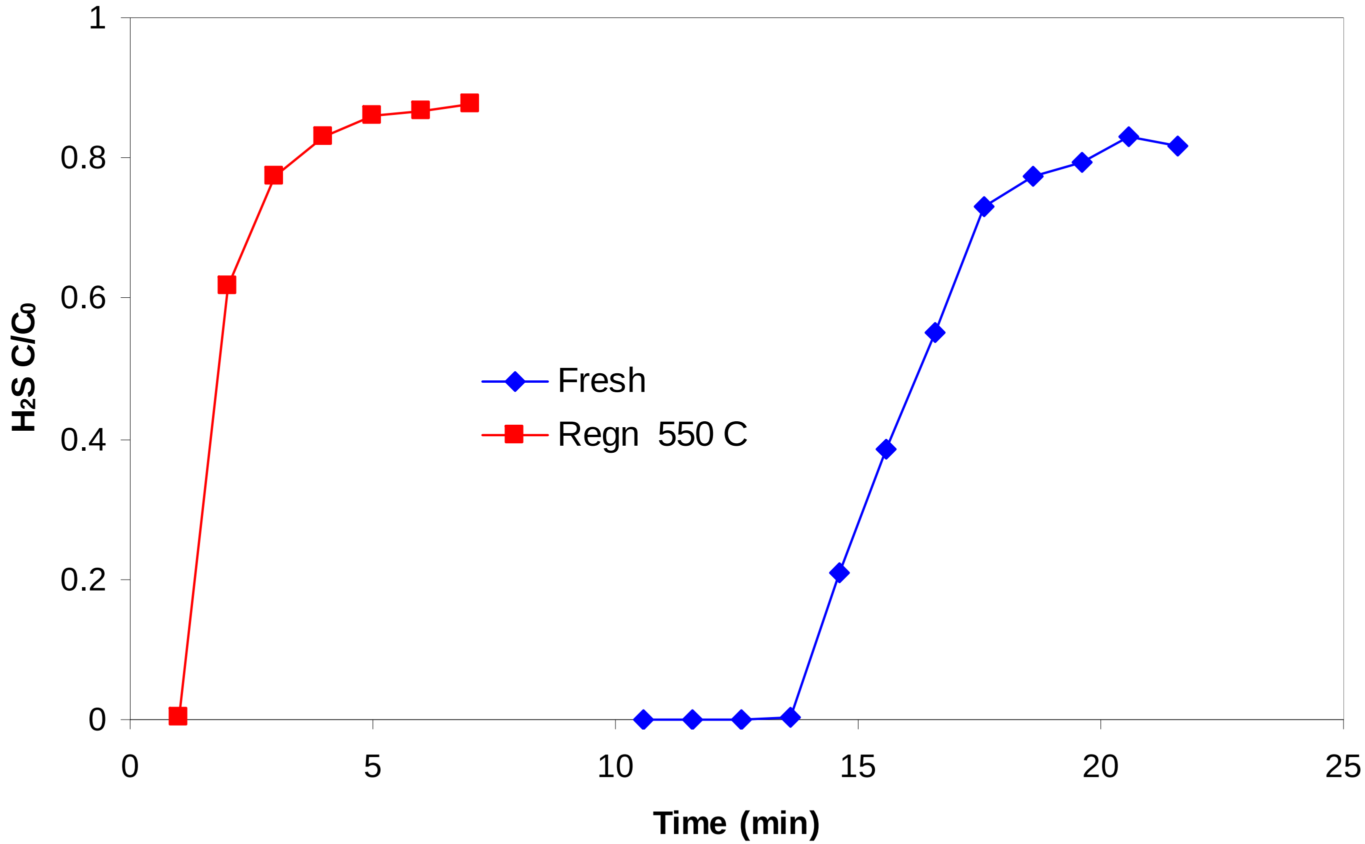
Objectives

- To develop novel H_2S sorbents with high sulfur capacity at low temperatures for quick system startup.
- To evaluate the multicycle performance of the sorbents as a function of temperature and regeneration conditions.

Outline

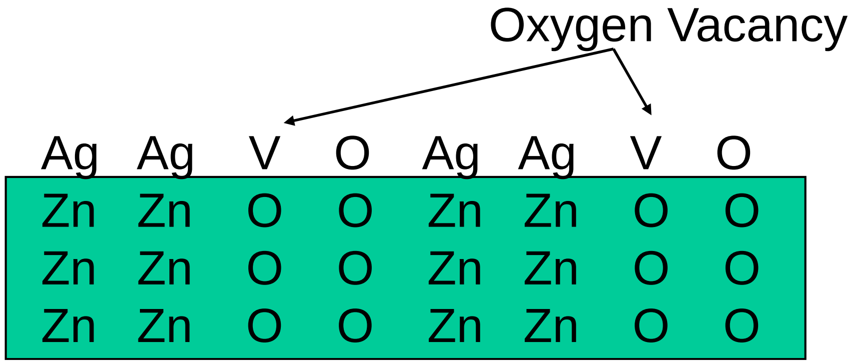
- Performance of Commercial ZnO Sorbents
- Sorbent Screening
- Sorbent Evaluation
  - Water, CO and CO_2 effects
  - Adsorption/reaction temperature
  - Regeneration temperature
  - Multicycle of behavior
  - Aging effects
- Conclusions
- Acknowledgement

Performance of Commercial ZnO Sorbent at Room Temperature



0.5 g of sorbent (105-250 μm, 25 m^2/g) tested at room temperature (20 C) with 8000 ppmv H_2S at a face velocity of 2.3 cm/s. Regn. at 550C for 3 hours.

Oxygen Vacancy in Doped ZnO/SiO_2 Sorbents



Function of dopants [1-5]:

(1) Stabilize sorbents

(2) Reduce the crystal size

(3) Increase the surface area

(4) Introduce crystal defects

Oxygen vacancy

(1) Improve the reaction rate

(2) Enhance the desulfurization reaction rate

(3) Metals in group IB are the best candidates to introduce oxygen vacancies

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4. Baird, T; Campbell, K.C.; Holliman, P.J.; Hoyle, R.W.; Huxam, M.; Stirling, D.; Williams, B.P.; Morris, M. *J. Mater. Chem.* **1999**, 9, 599–605
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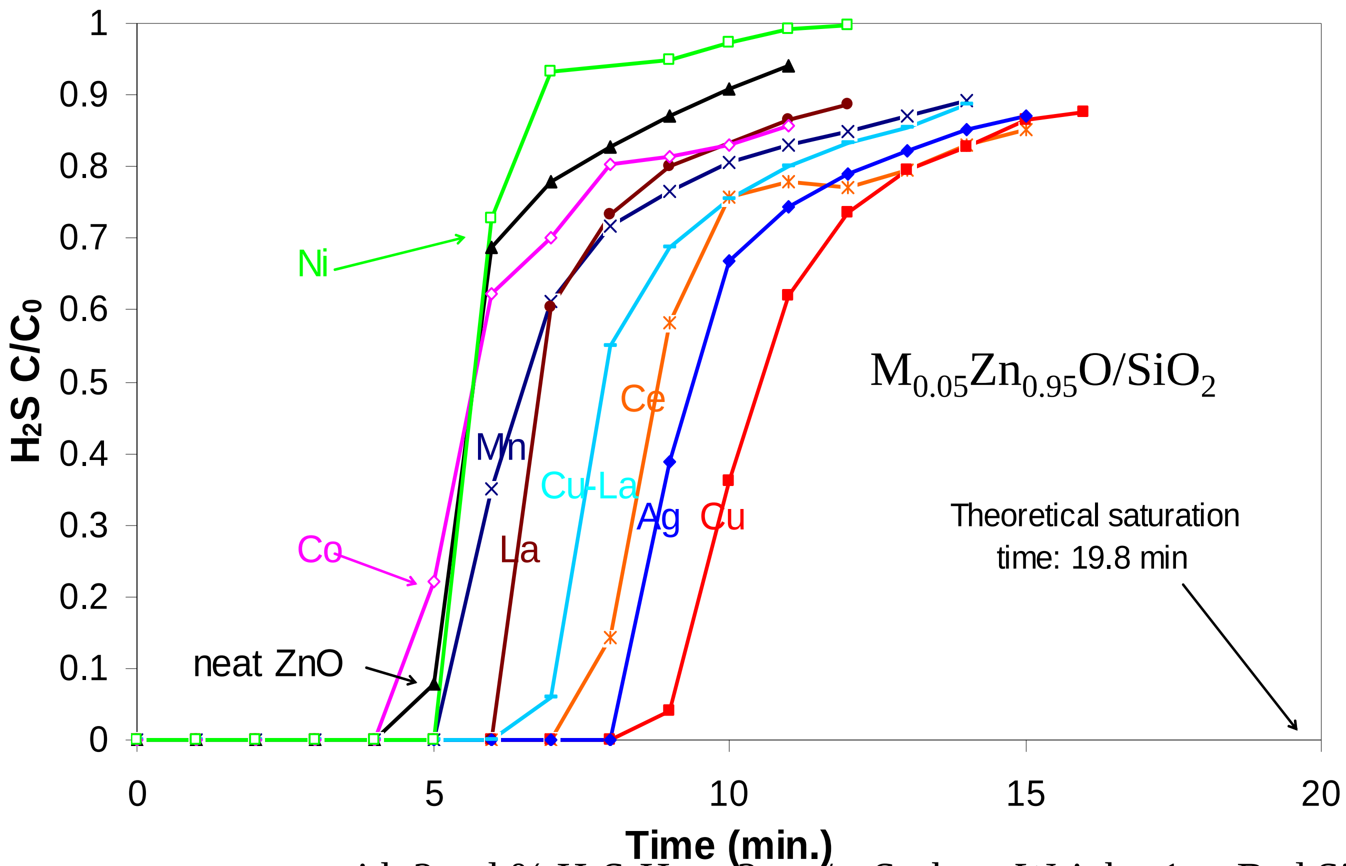
Desulfurization Performance at Room Temperature



Tested at room temperature with 2 vol.% H_2S-H_2 at 3 cm/s; Sorbent Weight: 1 g; Bed Size: 0.97 cm (dia.)× 2 cm (thickness), 100-200 mm SiO_2 support. All sorbents contain the same mole of metal, and all doped sorbents contained the same amount of ZnO.

Sulfur Capacities of Various Dopants at RT

Dopant	Capacity [1]	
	(g S/g ZnO)	% of theor [2]
CuO	0.213	54
Ag_2O	0.189	48
Ce	0.177	45
CuO-La_2O_3	0.161	41
La_2O_3	0.140	35
MnOx (1<x<1.5)	0.132	33
NiO	0.113	29
CoOx (1<x<1.5)	0.113	29
ZnO	0.113	29

1. Sulfur capacity calculated base on $t_{1/2}$ concept. Assume the sorbents are pure ZnO;
2. % of theoretical saturation capacity=capacity/theoretical saturation capacity $\times$100%

Note: tested at room temperature and the adiabatic temperature rise at the test conditions is 38 ^{o}C.

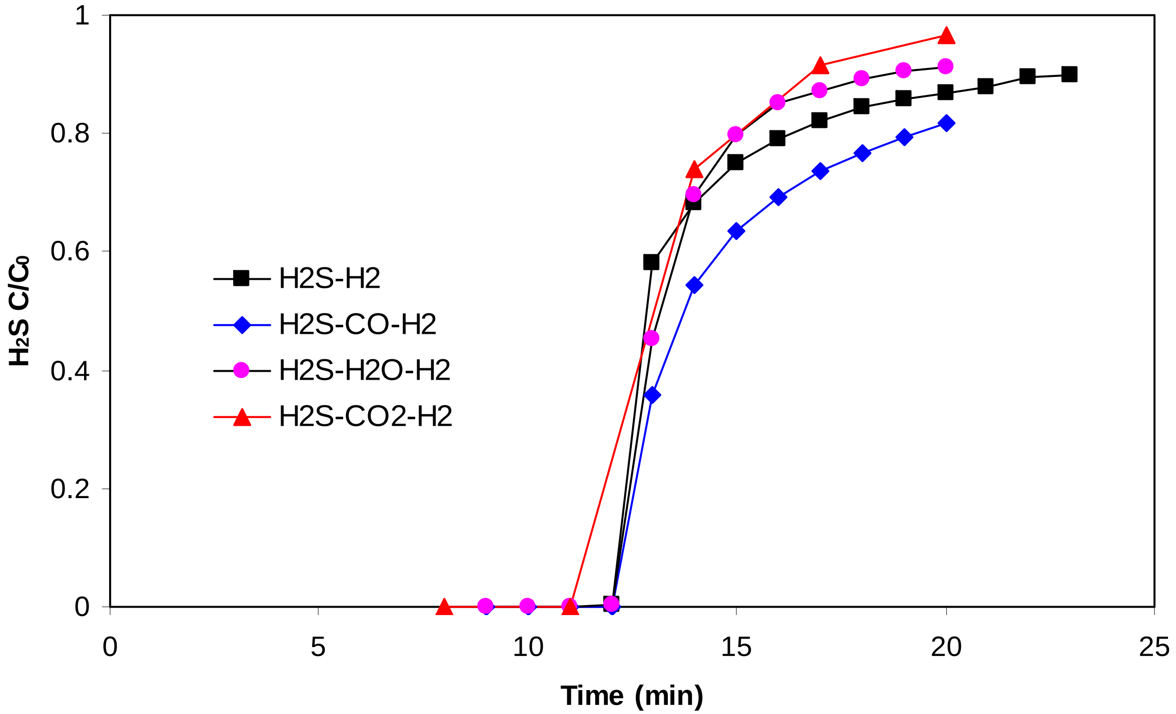
Low Temperature Cu-ZnO Sorbent

- Advantages
  - Low equilibrium H_2S concentration
  - Improved desulfurization capacity
  - Reduced grain size (XRD)
  - No COS formation

Note

Inert supports are necessary to maintained the surface area and porosity.

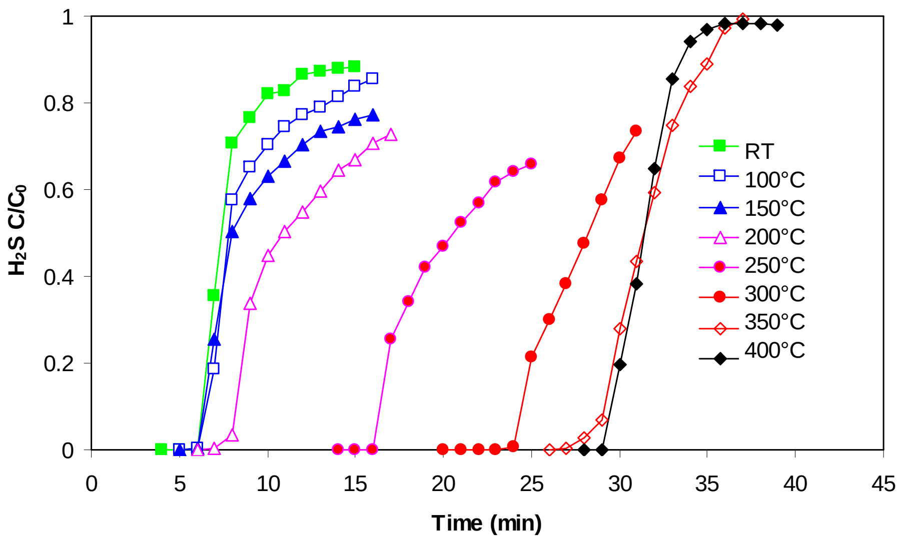
Water, CO, and CO_2 Effects



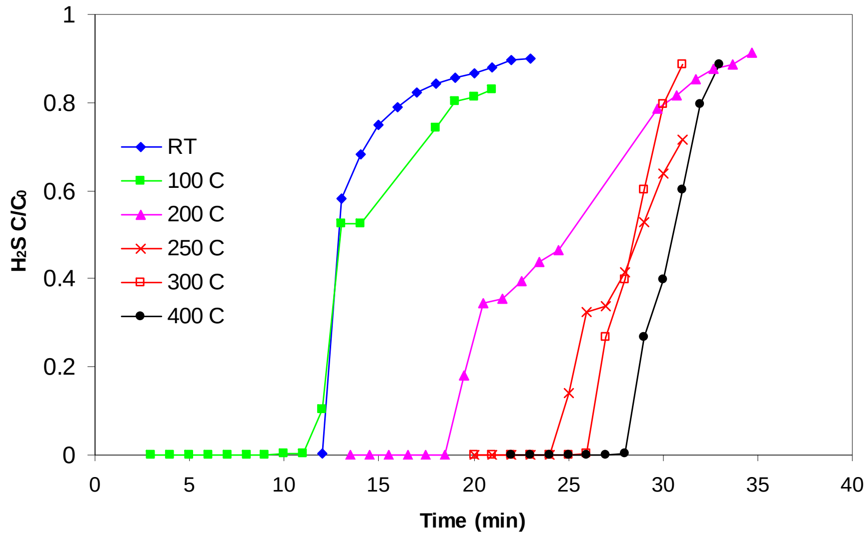
Breakthrough curves of Cu-ZnO/SiO2 tested at room temperature in the presence of water, CO or CO_2. In each experiment 0.5 g Cu-ZnO/SiO2 loaded and tested with 8000 ppmv H2S at a face velocity of 2.3 cm/s.

Desulfurization Performance at Various Temperatures

ZnO/SiO$_2$

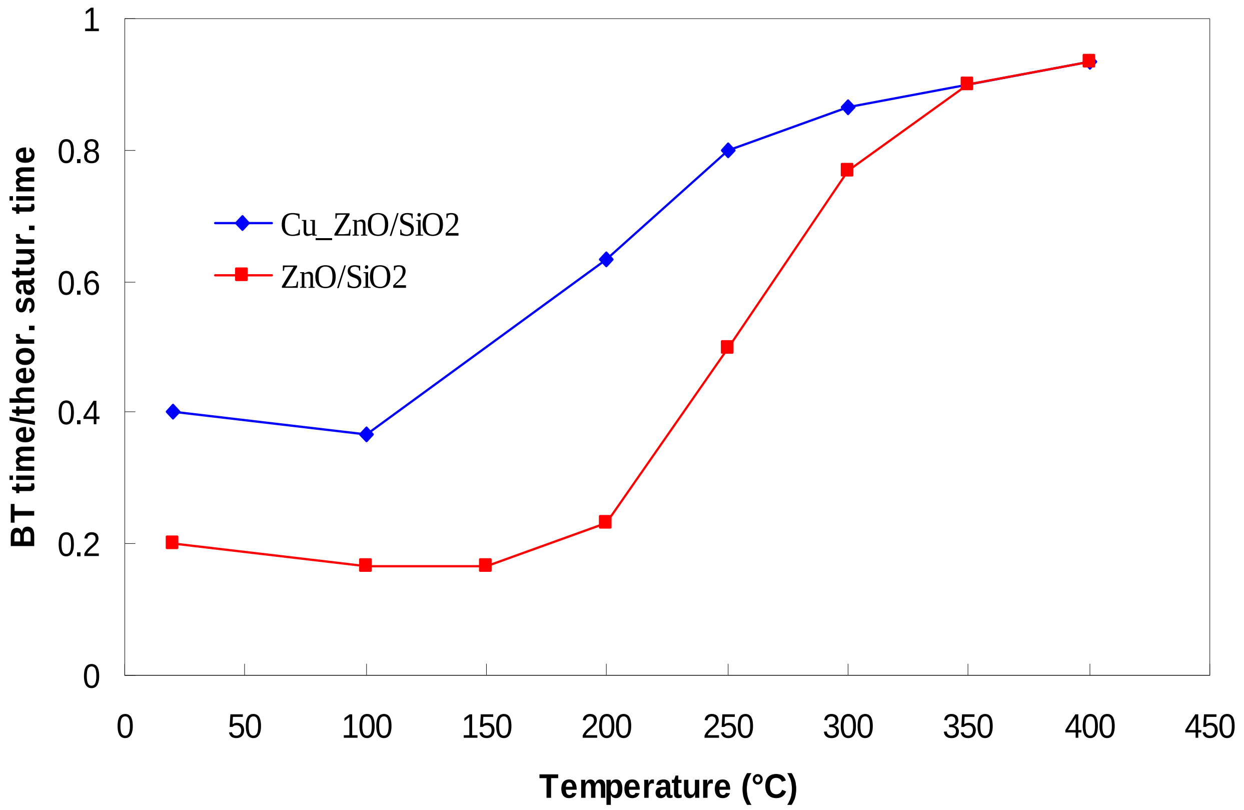


Cu-ZnO/SiO$_2$



Breakthrough curves of ZnO/SiO$_2$ and Cu-ZnO/SiO$_2$ at various desulfurization temperatures. In each experiment 0.5 g Cu-ZnO/SiO2 loaded and tested with 8000 ppmv H_2S at a face velocity of 2.3 cm/s.

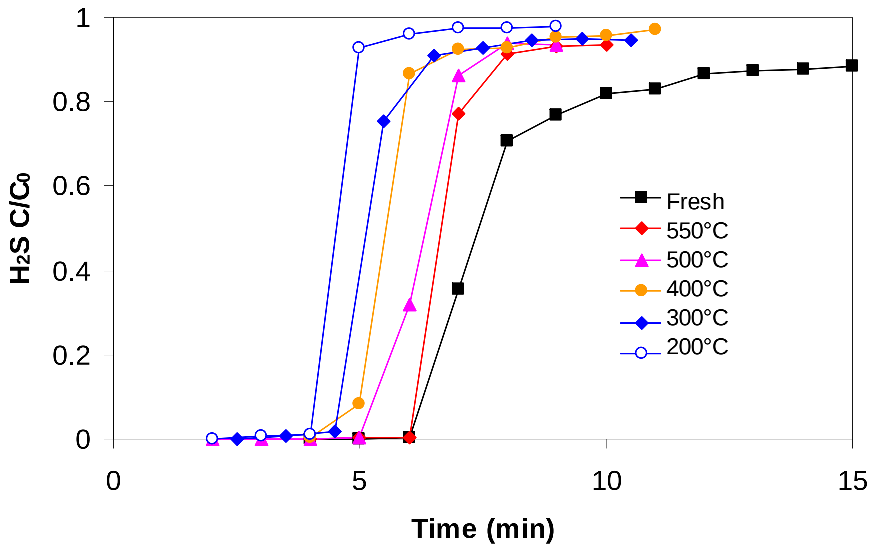
Desulfurization Performance Analysis



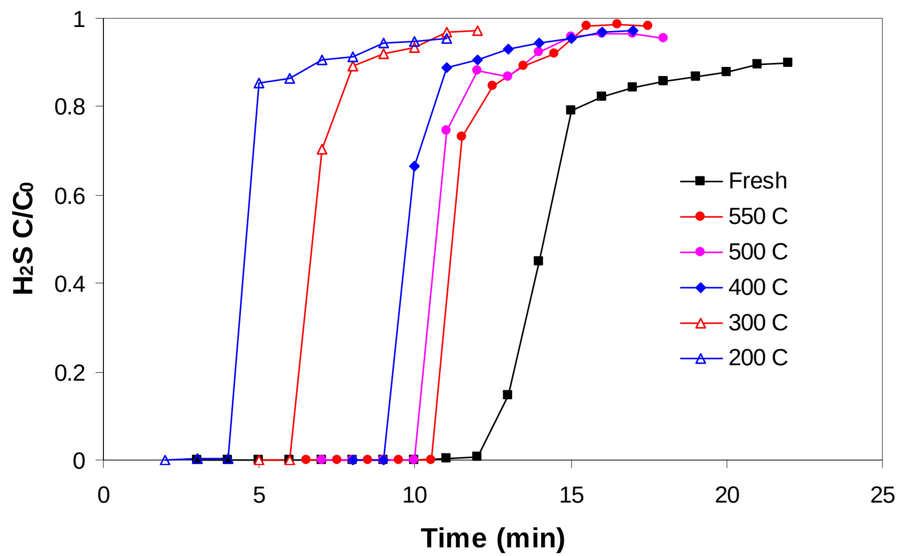
0.5 g ZnO/SiO2 loaded and tested with 8000 ppmv H_2S at a flow rate of 100 cm^3/min STP.

Performance of Sorbent Regenerated at Various Temperatures

ZnO/SiO_2

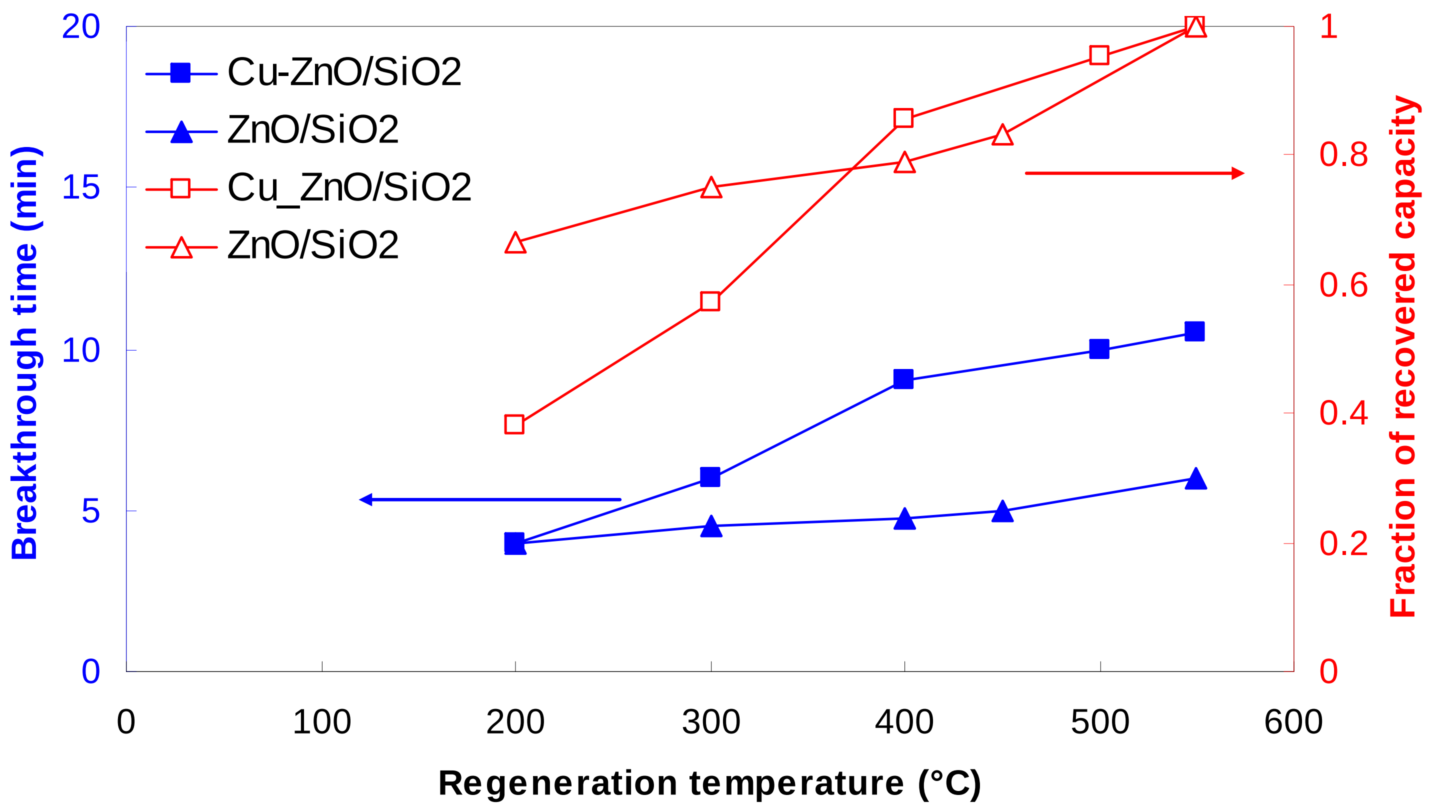


Cu-ZnO/SiO_2

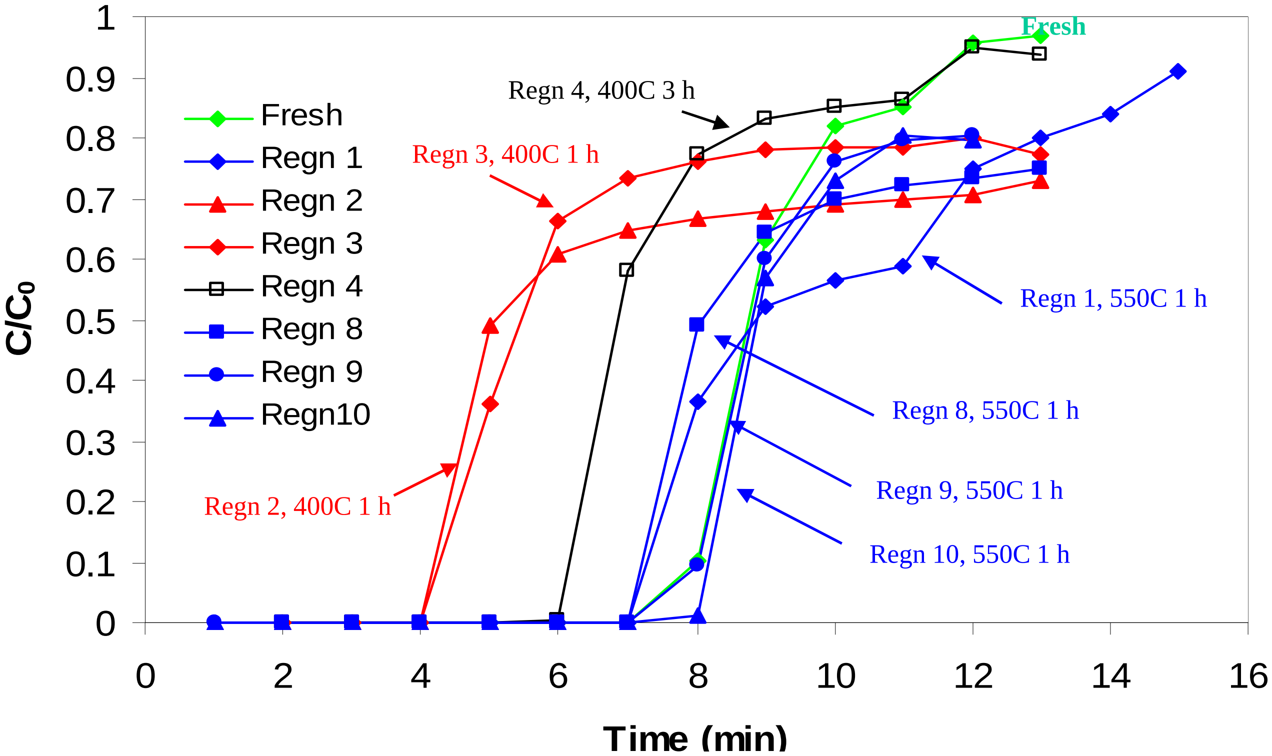


Breakthrough curves of regenerated ZnO/SiO_2 and Cu-ZnO/SiO_2 at various regeneration temperatures. Sorbent tested at room temperature (20 ° C) with 8000 ppmv H_2S at a face velocity of 2.3 cm/s

Regeneration Test

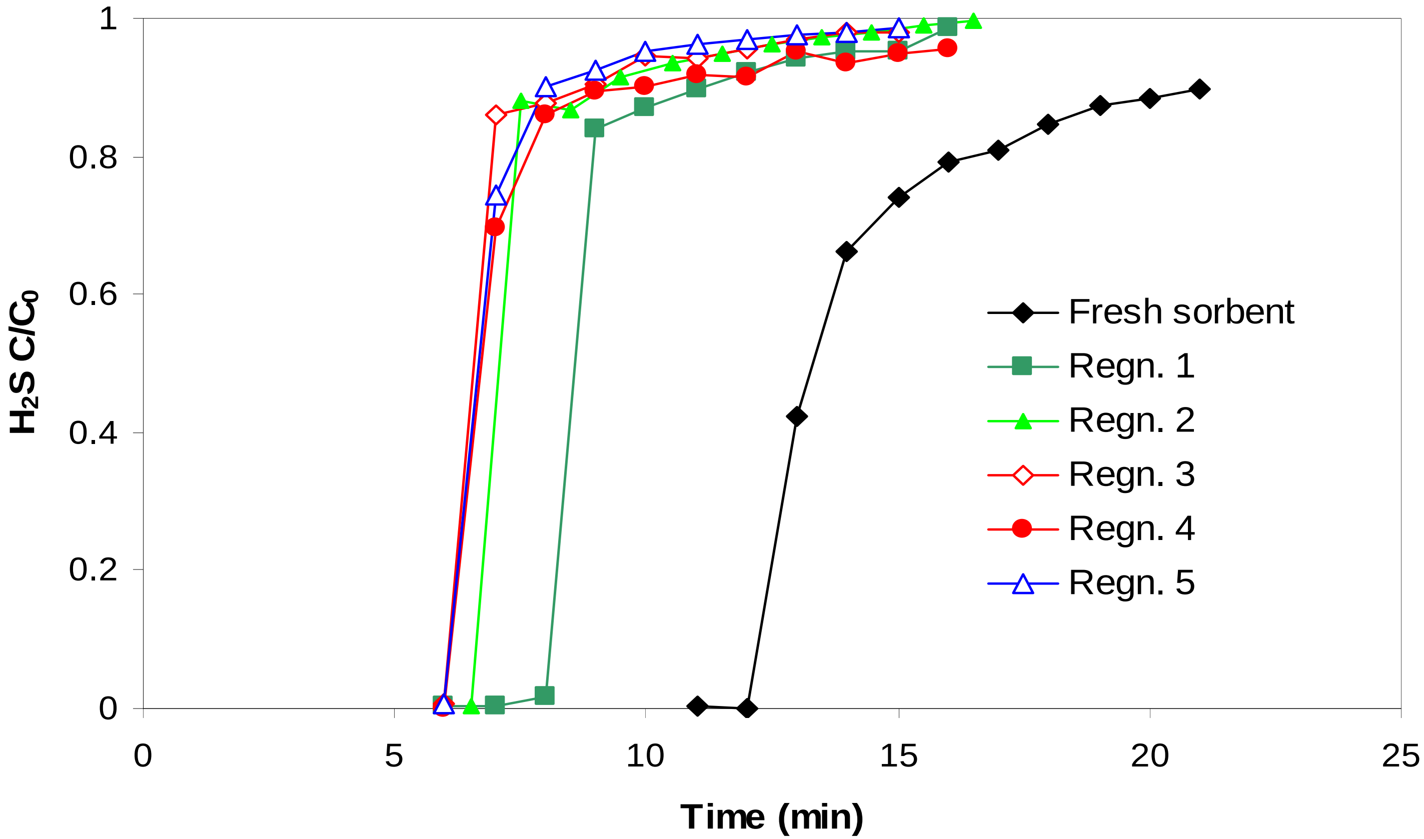


Multi-cycle Test



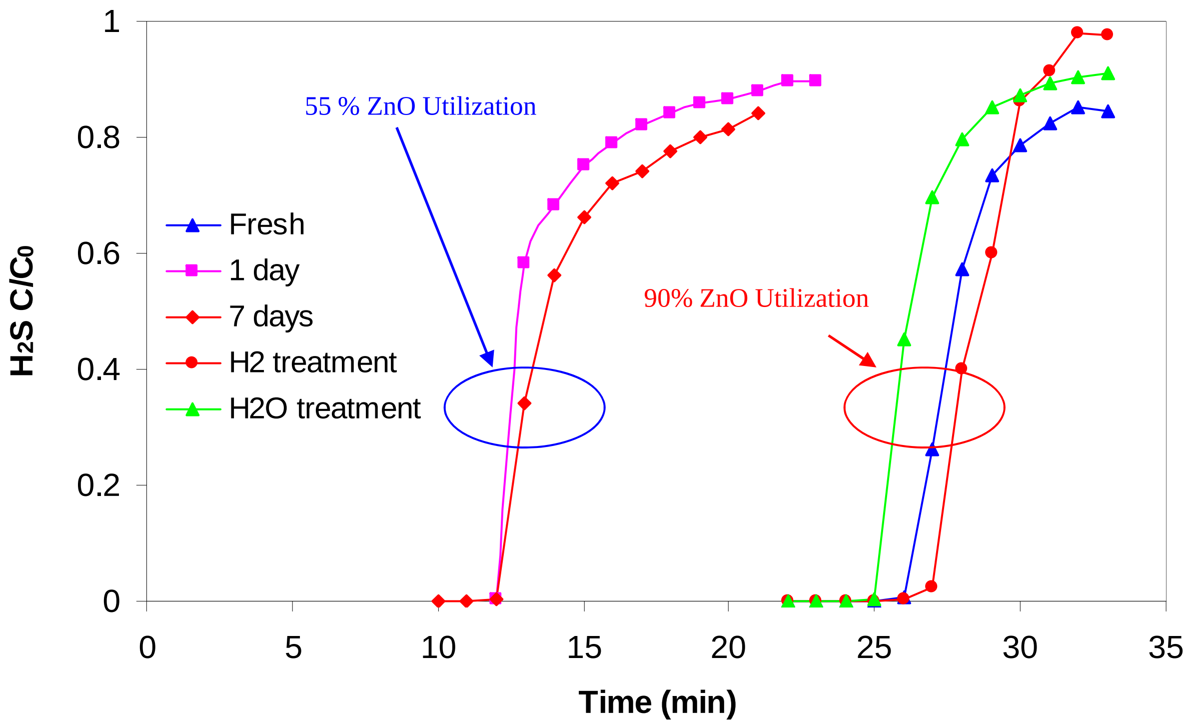
Default regeneration conditions: regenerated in house-hood air flow (20 cm/s) at 550ºC for 1 hour; regn. 2 and regn. 3 were regenerated at 400ºC for 1 hour and regn. 4 was regenerated at 400ºC for 3 hours. Different color indicates different regeneration condition. The regenerated sorbent (1 g of) was tested with 2% H_2S-H_2 at room temperature.

Multi-cycle Test
Regn. at 300° C



1. Sorbents were regenerated at 300 ºC;
2. Desulfurization tests were conducted at room temperature 20 ºC using 0.5 g ZnO/SiO_2 tested with 8000 ppmv H_2S at a flow rate of 100 cm^3/min STP.

Aging Effects



Aging effect of Cu-ZnO sorbent. Cu-ZnO/SiO_2 sorbent (0.5 g) was tested at room temperature with 2 vol % H_2S-H_2 at face velocity of 2.3 cm/s.

Summary/Conclusions

- Copper and silver dopants significantly enhance the desulfurization performance at room temperature. Cu-ZnO/SiO_2 demonstrated the highest sulfur capacity, which is twice that of ZnO/SiO_2 at room temperature.
- Copper dopant also reduced the regeneration temperatures.
- Water, CO, and CO_2 do not influence desulfurization behaviors of Cu-ZnO/SiO_2 sorbent at room temperature. No COS formation was detected.
- The above mentioned Cu-ZnO/SiO_2 sorbent particles are small in size, they are the ideal candidate to be entrapped in microfibrous media.
- The sorbent can be used in packed beds to protect fuel cells at ambient temperatures or during cold startup.

Acknowledgements

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Thank you for your attention