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

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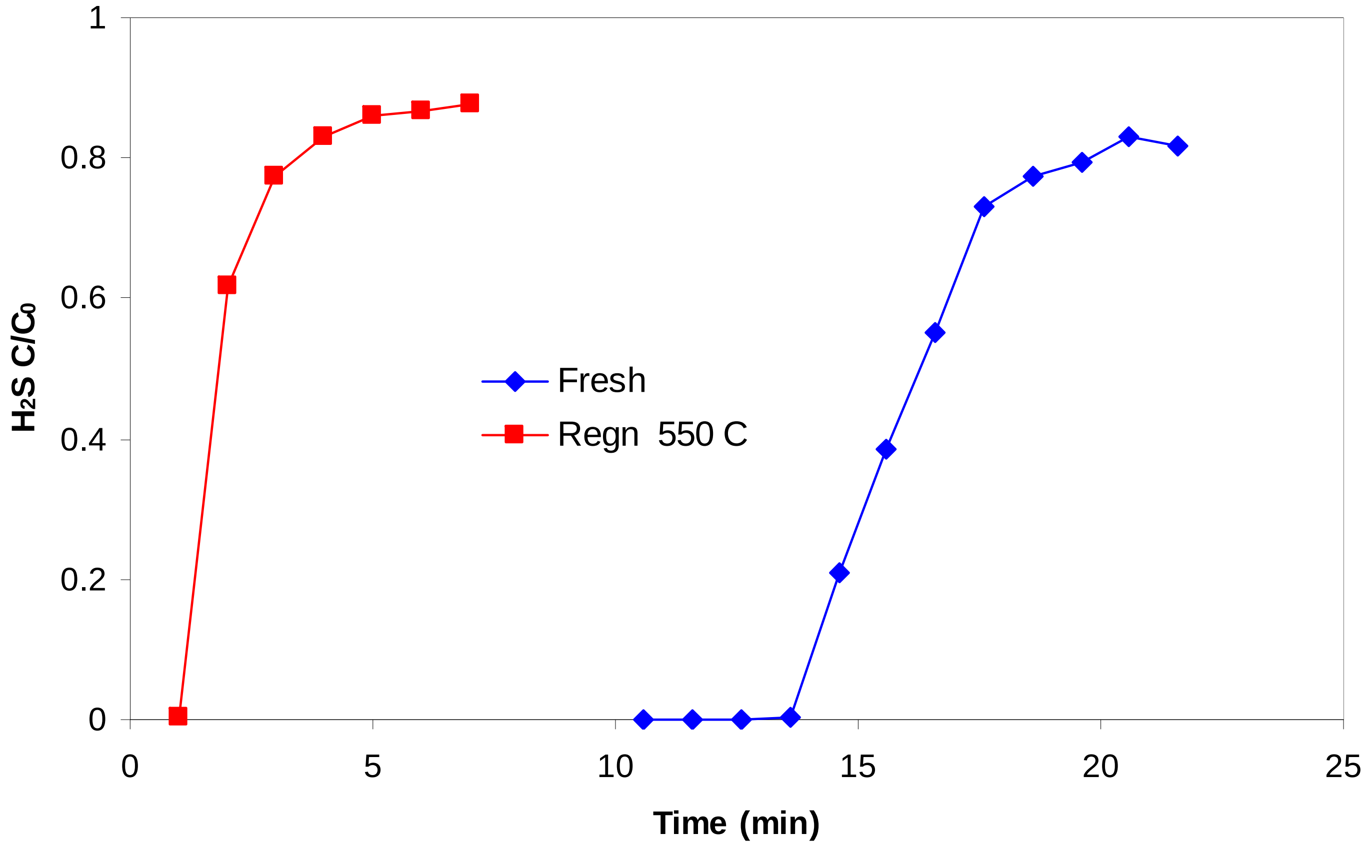
# Objectives

- 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

Oxygen Vacancy

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Ag | Ag | V | O | Ag | Ag | V | O |
| Zn | Zn | O | O | Zn | Zn | O | O |
| Zn | Zn | O | O | Zn | Zn | O | O |
| Zn | Zn | O | O | Zn | Zn | O | O |

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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2. Davidson,J.M.; Lawrie, C.H.; Sohail, K. *Ind. Eng. Chem. Res.* **1995**,*34*, 2981-2989
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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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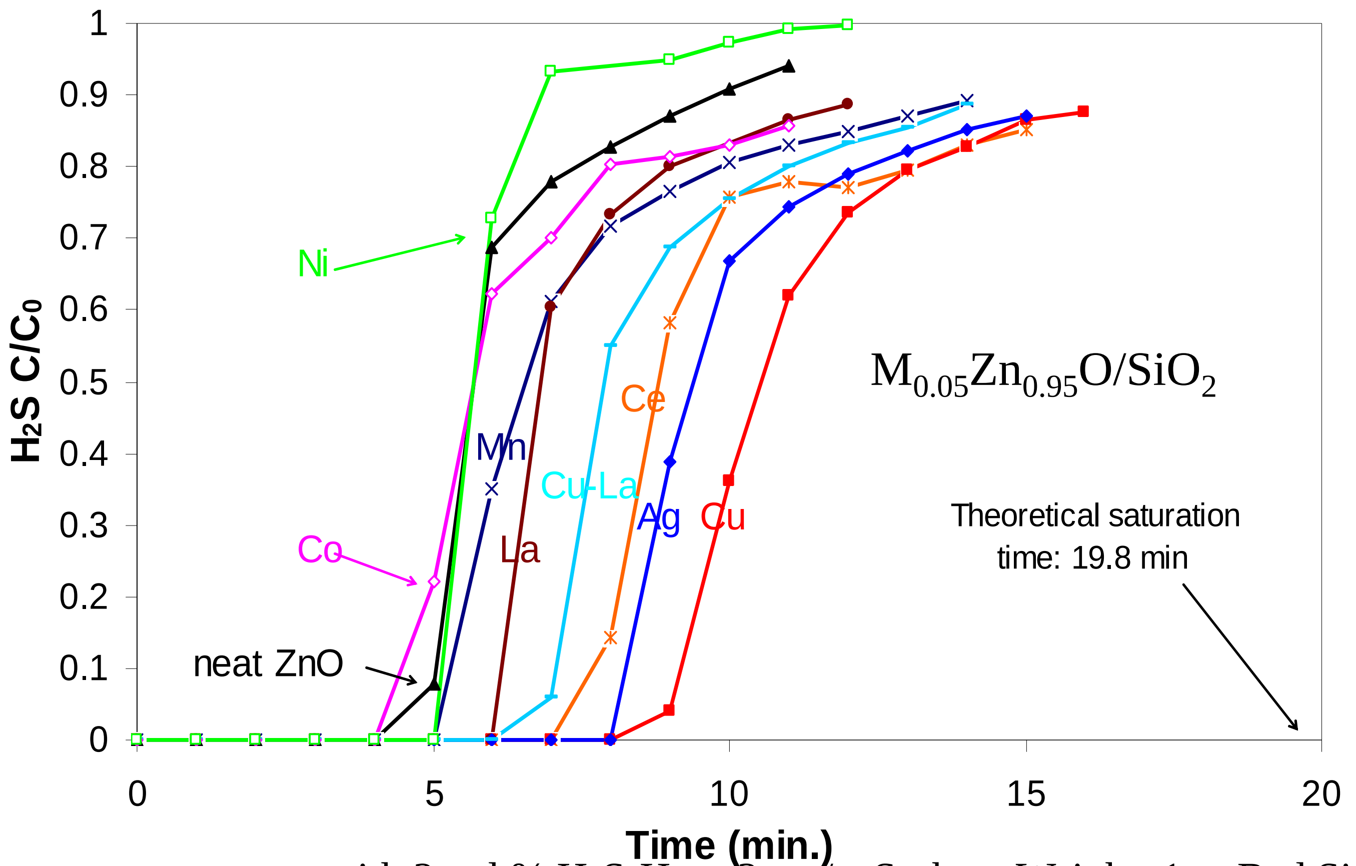
# Desulfurization Performance at Room Temperature




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 |
| $CuO\text{-}La_2O_3$ | 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.

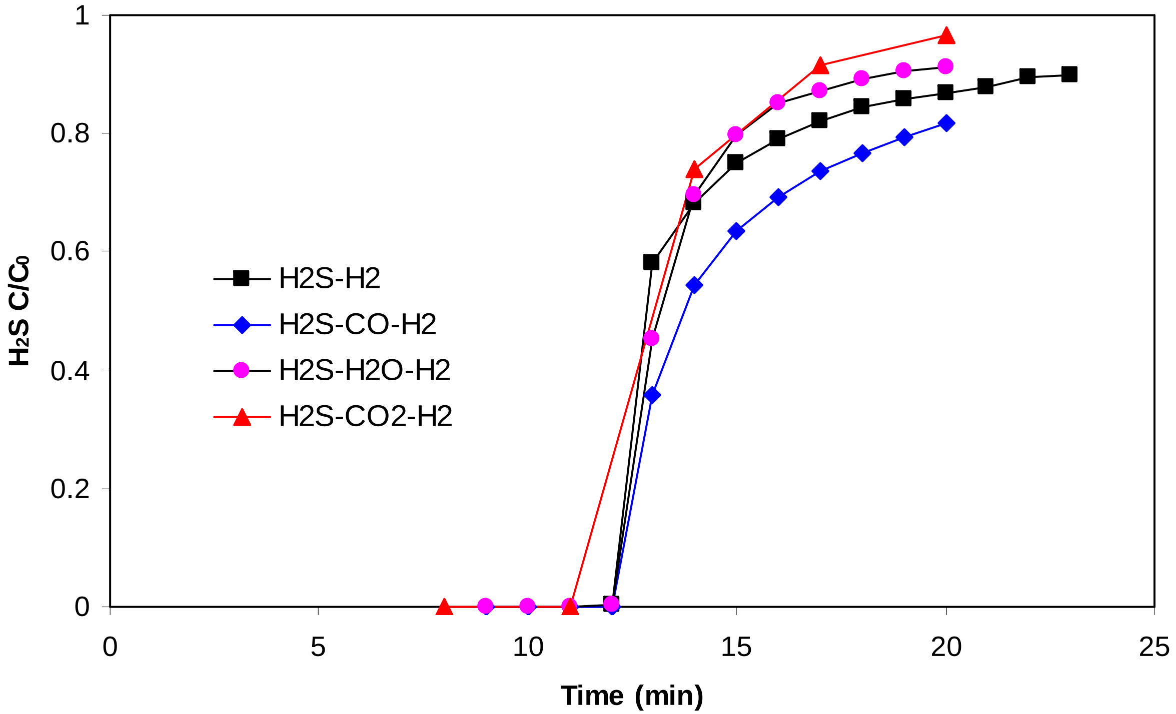
# Low Temperature Cu-ZnO Sorbent

- 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.

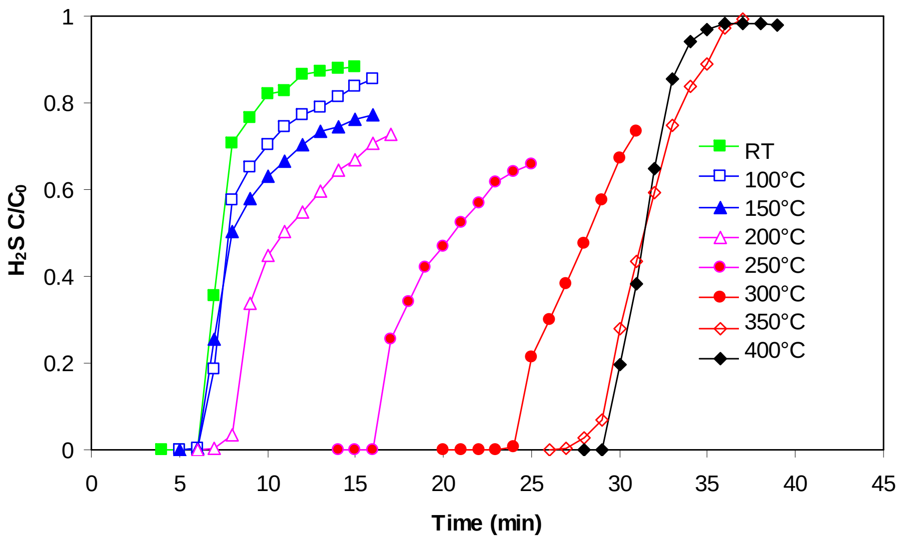
# Water, CO, and $CO_2$ Effects



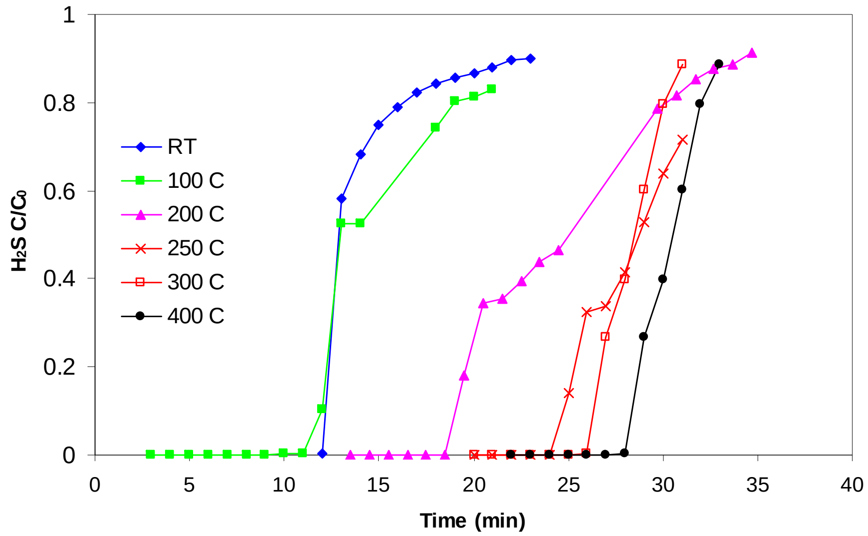

Breakthrough curves of Cu-ZnO/SiO2 tested at room temperature in the presence of water, CO or $CO_2$. In each experiment 0.5 g Cu-ZnO/SiO2 loaded and tested with 8000 ppmv H2S at a face velocity of 2.3 cm/s.

# Desulfurization Performance at Various Temperatures

ZnO/$SiO_2$

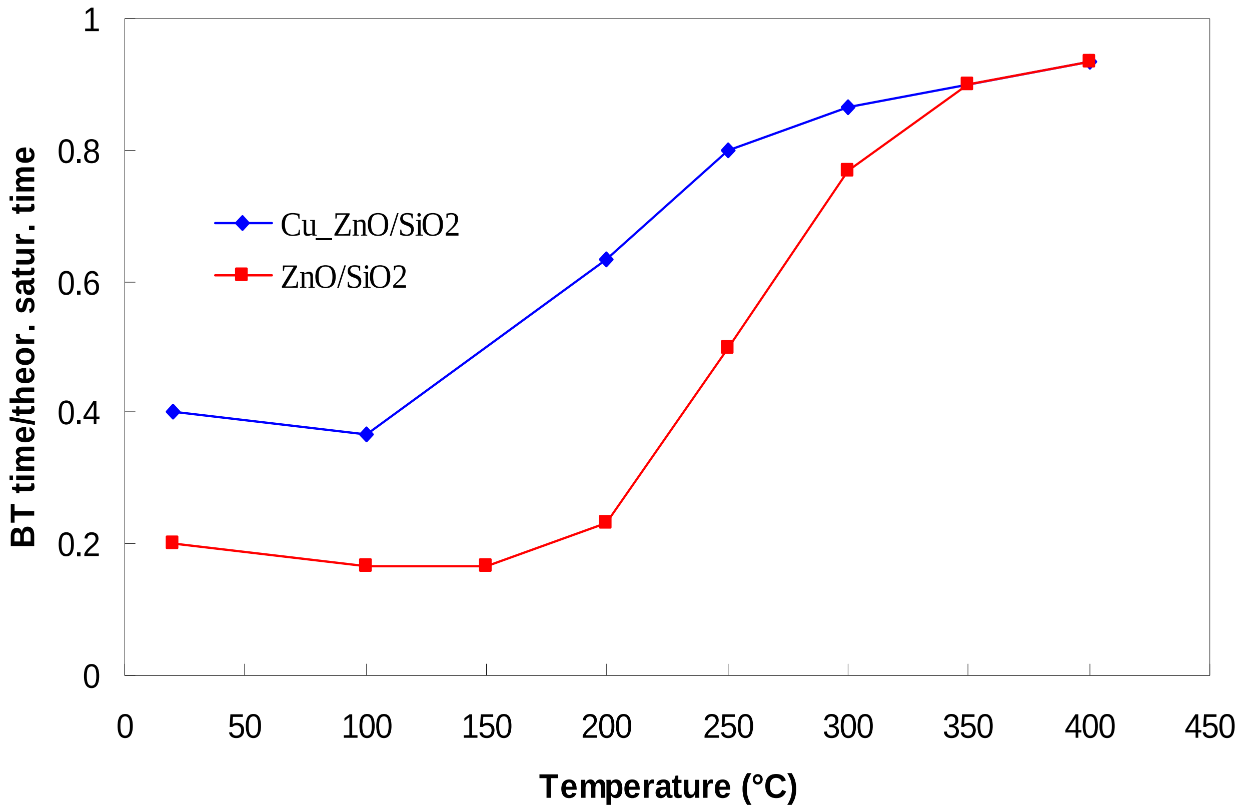



Cu-ZnO/$SiO_2$




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.

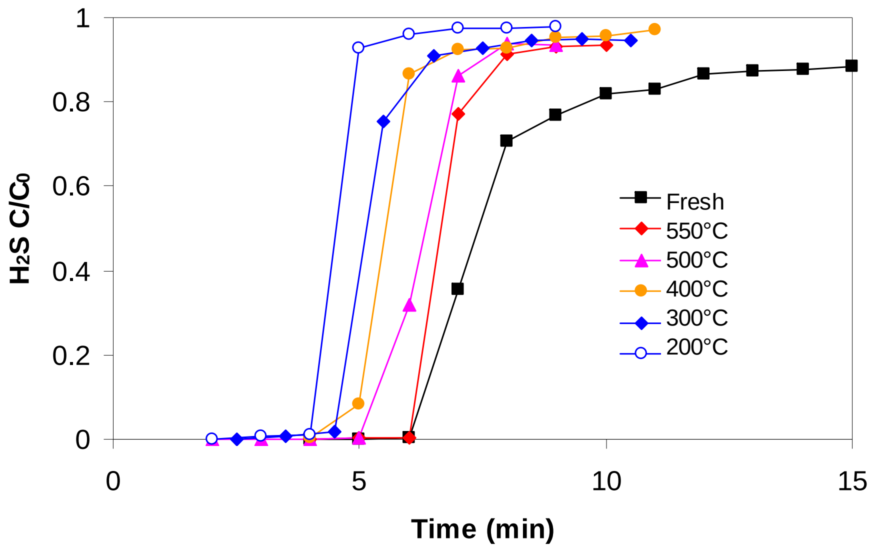
# Desulfurization Performance Analysis



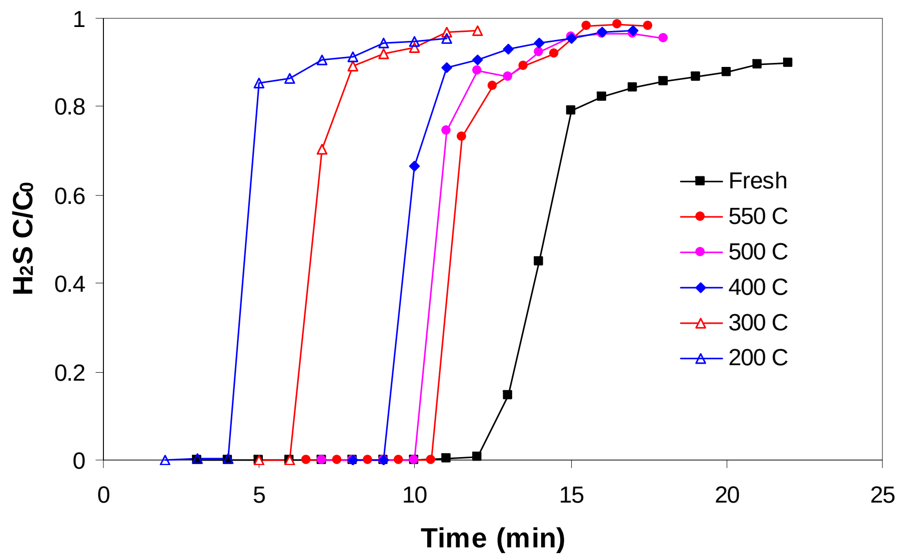

0.5 g ZnO/SiO2 loaded and tested with 8000 ppmv $H_2S$ at a flow rate of 100 $cm^3$/min STP.

# Performance of Sorbent Regenerated at Various Temperatures

ZnO/$SiO_2$

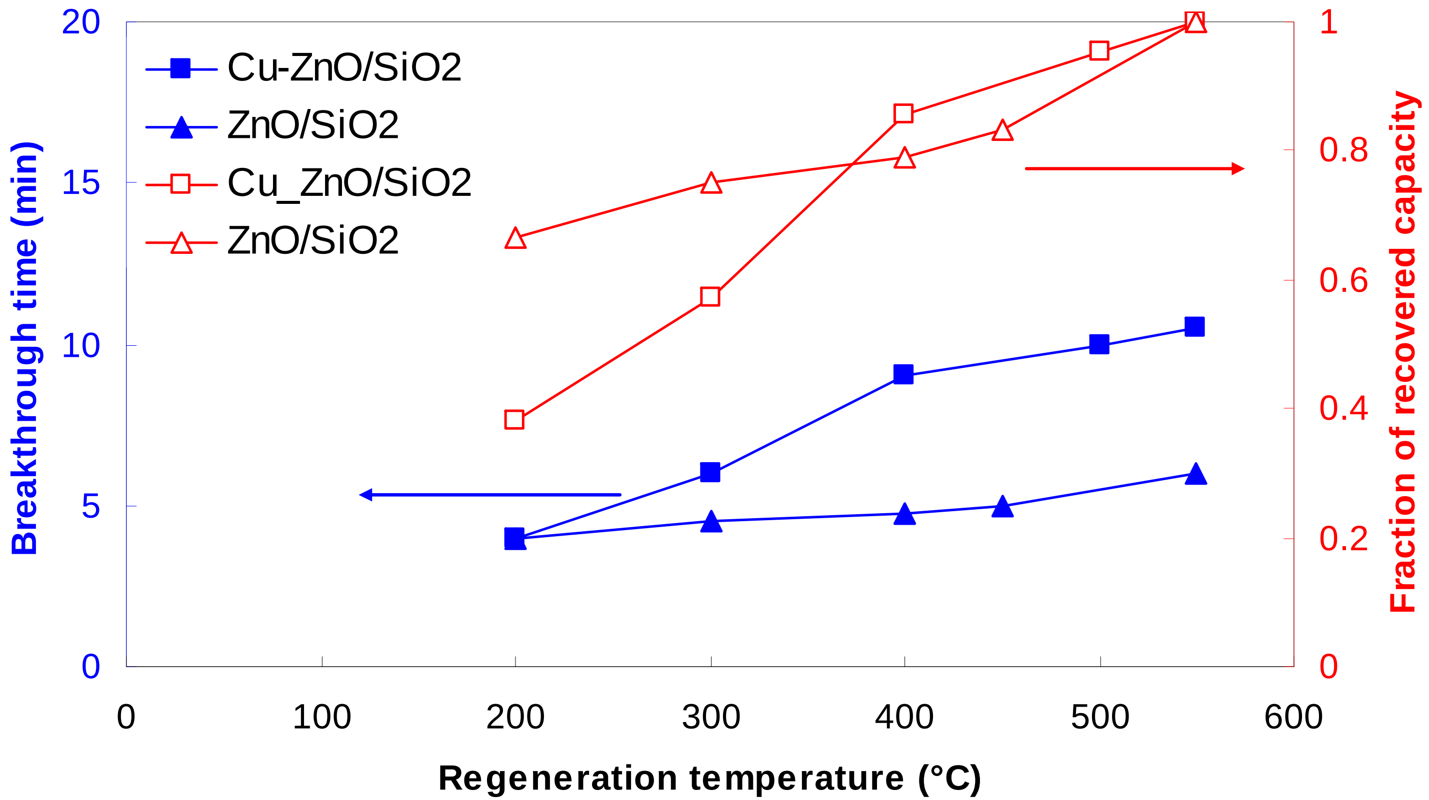



Cu-ZnO/$SiO_2$

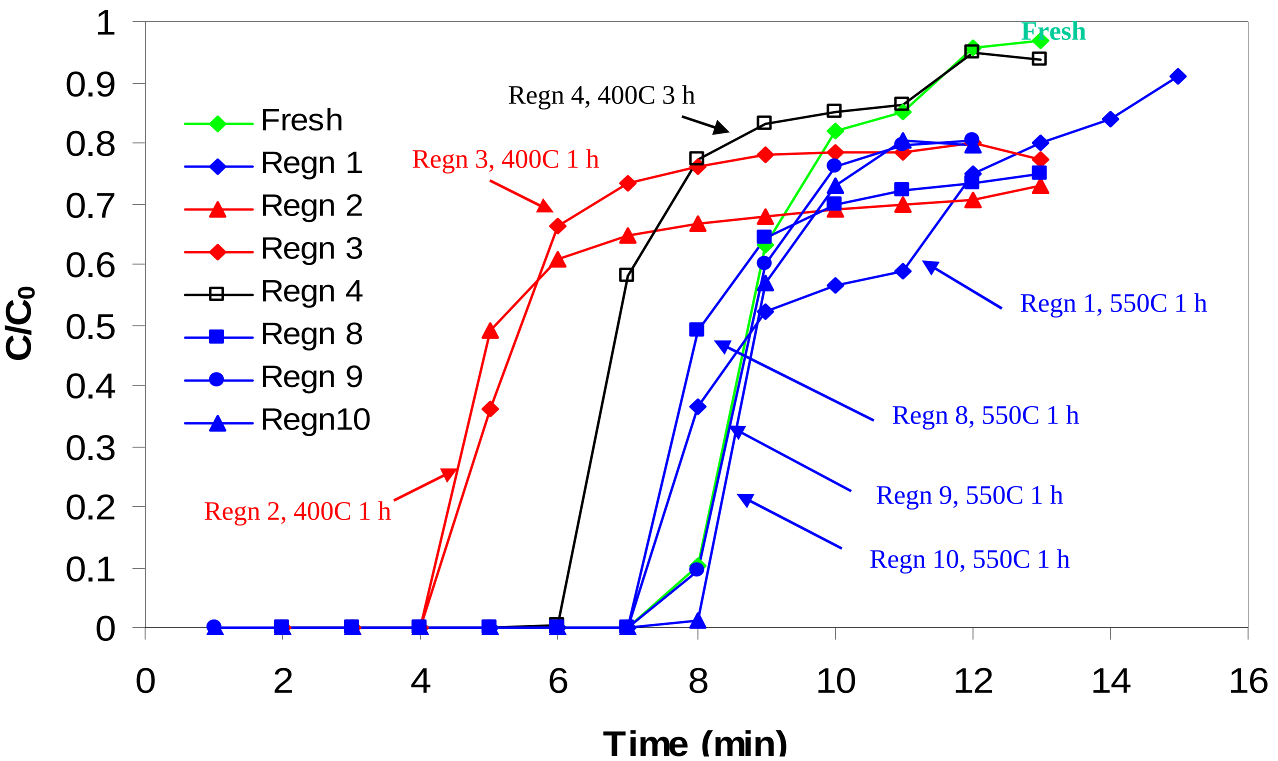



Breakthrough curves of regenerated ZnO/$SiO_2$ and Cu-ZnO/$SiO_2$ at various regeneration temperatures. Sorbent tested at room temperature (20 ° C) with 8000 ppmv $H_2S$ at a face velocity of 2.3 cm/s

# Regeneration Test

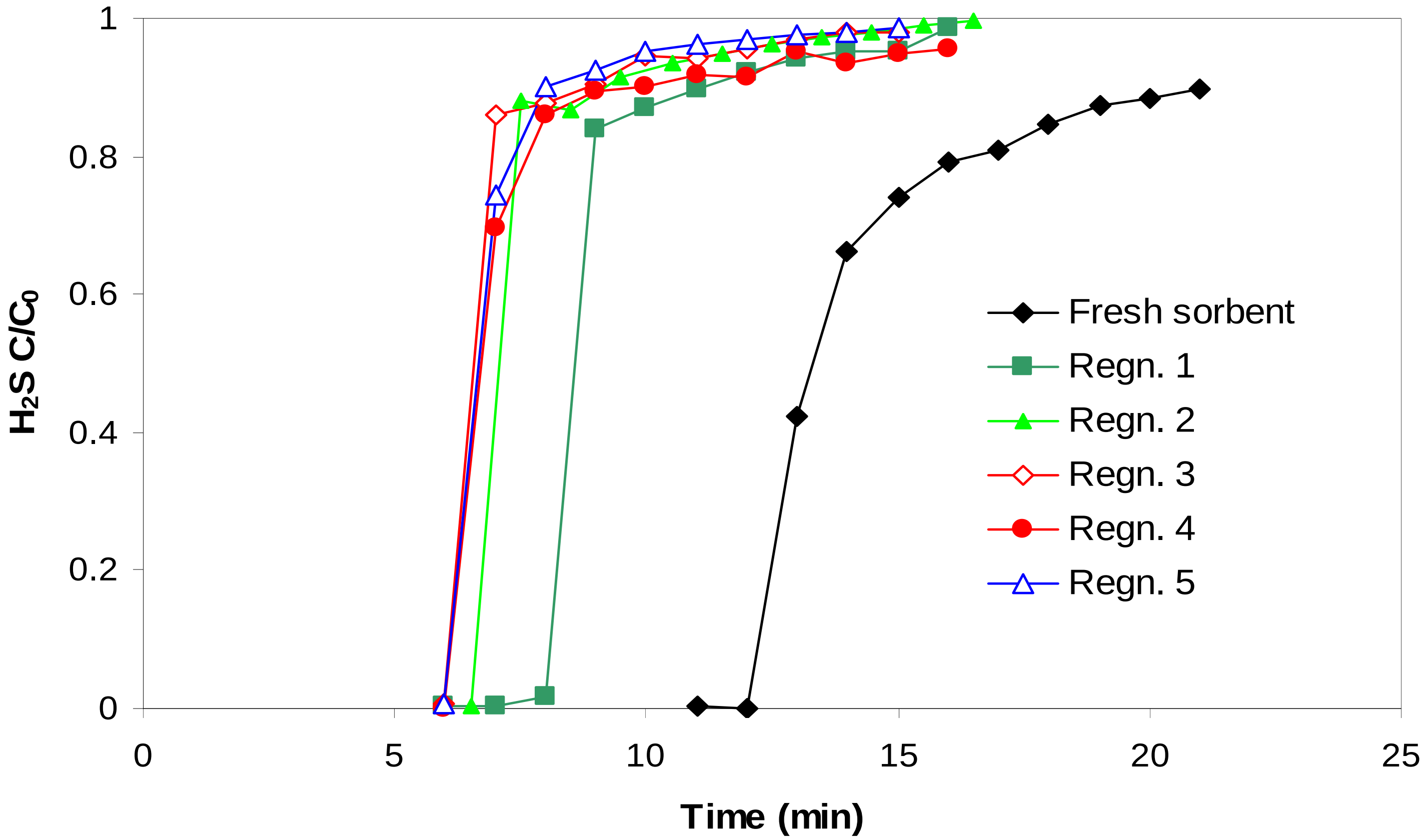


# Multi-cycle Test



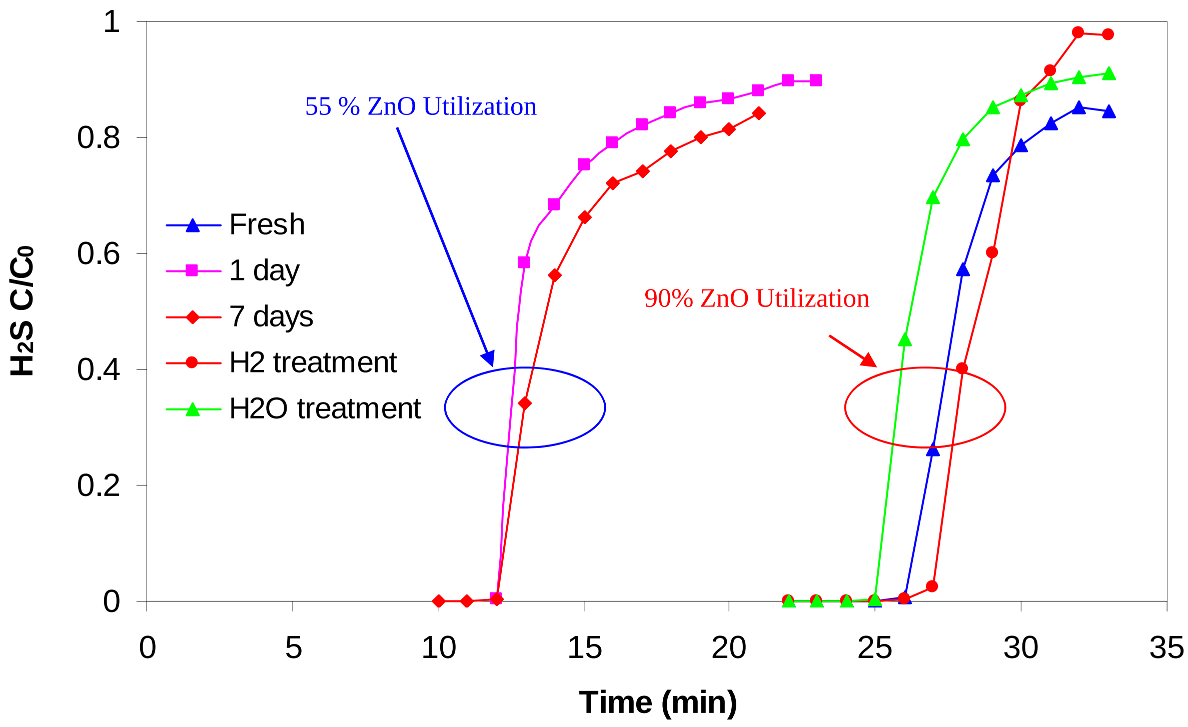

Default regeneration conditions: regenerated in house-hood air flow (20 cm/s) at 550ºC for 1 hour; regn. 2 and regn. 3 were regenerated at 400ºC for 1 hour and regn. 4 was regenerated at 400ºC for 3 hours. Different color indicates different regeneration condition. The regenerated sorbent (1 g of ) was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