A Study of Kinetic Effects Using Microfibrous Entrapped ZnO Sorbents for H_2S Removal

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Objectives

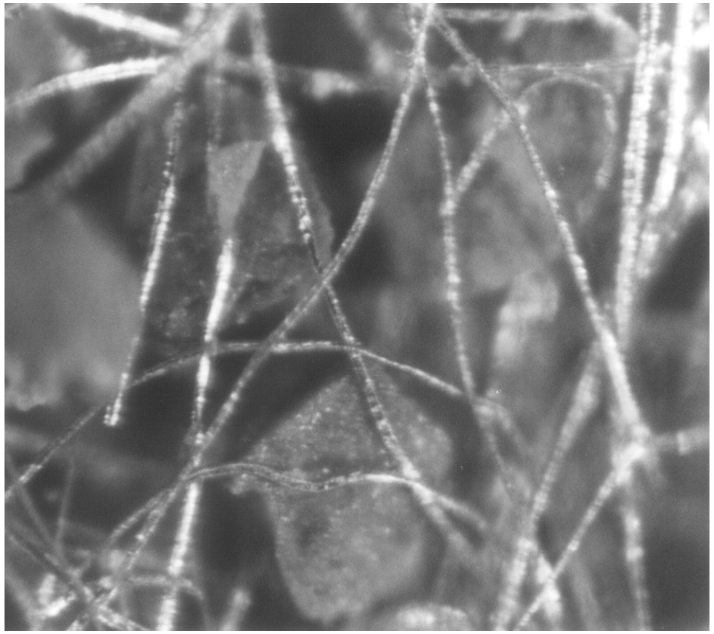
- To establish a mathematic model for adsorption/reaction processes using both packed beds and microfibrous entrapped sorbents.
- To investigate the effects due to using microfibrous media.

Outline

- Microfibrous Entrapped Sorbents/Catalysts
- Model Evaluation
  - Particle size effects
  - The relationship between lumped shape factor (*K*) and apparent reaction rate constant (k_a)
  - The relationship between *K* and challenge concentration (C_{A0})
  - The relationship between *K* and sorebent bed capacity density (ρ_c)
  - Effects of microfibrous media and void
- Composite Bed (Packed Bed+Polisher)
- Conclusions
- Acknowledgements

Microfibrous Entrapped Sorbents/Catalysts

Concept:

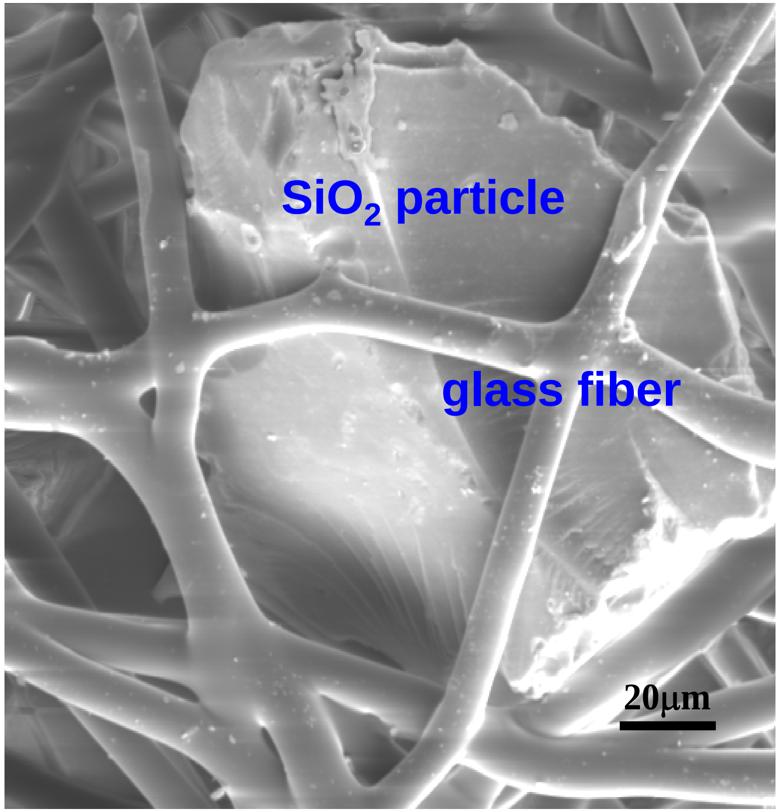


Microfibrous Entrapped
Micro-catalyst/sorbent particles

Properties:

- Unique form factors and thermal integration
- High contacting efficiency
- High intrabed thermal conductivity
- Enhanced mass and heat transfer
- Ease of regeneration
- High voidage (i.e., 75% for glass fiber entrapped sorbents)

Glass Fiber Entrapped Sorbents



Glass fiber entrapped SiO_2 particles

Properties of Glass Fiber Entrapped Sorbent (GFE)

Component	Wt.%	Vol.%
ZnO	12	N.A.
SiO_2	66	22
Fiber	22	3
Void	N.A.	75

Bed Service Time Models

General Equation $t=A'+B'C'$

Term	Yoon's Model	Wheeler Model	Mecklenburg Model
A'	$\frac{W_e}{CF}$	$\frac{W_s W_c}{CF}$	$\frac{W_s AZn'\rho_c}{CF}$
B'	$\frac{W_e}{kCF}$	$\frac{W_s \rho_c}{k_v C}$	$\frac{An'}{a_c}(\frac{dG}{\eta})^{0.41}(\frac{\eta}{\rho_a D})^{0.67}\frac{W_s}{CF}$
C'	$\ln\left(\frac{C_b}{C_{A0}-C_b}\right)$	$\ln\left(\frac{C_b}{C_{A0}}\right)$	$\ln\left(\frac{C_b}{C_{A0}}\right)$

Yoon's model

$$\ln\left(\frac{C_{A0}}{C_A}-1\right)=K(\tau-t)$$

K=?

•Yoon, Y.H., Nelson, J.H., (1984). Application of Gas Adsorption Kinetics: I. "A Theoretical Model for Respirator Cartridge Service Life. American Industrial Hygiene Association Journal, 45, 509-516.

Modified Amundson Model

- For a second order heterogeneous reaction Amundson model

$$\frac{C_{A0}}{C_A} = 1 + \left[\exp\left(-\phi k_2 t C_{A0}\right)\right] \cdot \left[\exp\left(\frac{\phi k_2 \rho_c z_t}{U}\right) - 1\right]$$

- Modified Amundson model

$$\ln\left(\frac{C_{A0}}{C_A} - 1\right) = \phi k_2 C_{A0}(\tau - t) \qquad k_2 = \frac{k_a}{\rho_c}$$

$$\ln\left(\frac{C_{A0}}{C_A} - 1\right) = K(\tau - t)$$

$$K = (\phi \cdot k_a)\frac{C_{A0}}{\rho_c}$$

Apparent reaction rate: $(\phi \cdot k_a)$

Gas reactant: C_{A0}

Solid reactant: ρ_c

ρ_c defined as capacity density, is actually an effective ZnO molar density.

•Amundson, N.R., (1948). A note on the mathematics of adsorption in beds. Journal of Physical Colloid Chemistry, 52, 1153-1157.

Mass Transfer Correlation for Apparent Reaction Rate

$$k_a = \frac{1}{\phi} k_c \alpha \qquad \alpha = \frac{6(1-\phi)}{d_p} \qquad k_c = Sh \frac{D_{AB}}{d_p} \qquad Sh = J_d \,\mathrm{Re}\, Sc^{1/3}$$

$$J_d = 1.24\,\mathrm{Re}''^{-0.39} \qquad \mathrm{Re}'' = \frac{\mathrm{Re}}{(1-\phi)}$$

$$k_a = 7.44 \cdot \frac{(1-\phi)^{1.39}}{\phi} \left(\frac{d_p \rho U}{\mu} \right)^{0.61} Sc^{1/3} \frac{D_{AB}}{d_p^2} \qquad K = 7.44 \cdot (1-\phi)^{1.39} \left(\frac{d_p \rho U}{\mu} \right)^{0.61} Sc^{1/3} \frac{D_{AB}}{d_p^2} \frac{C_{A0}}{\rho_c}$$

For Packed Bed

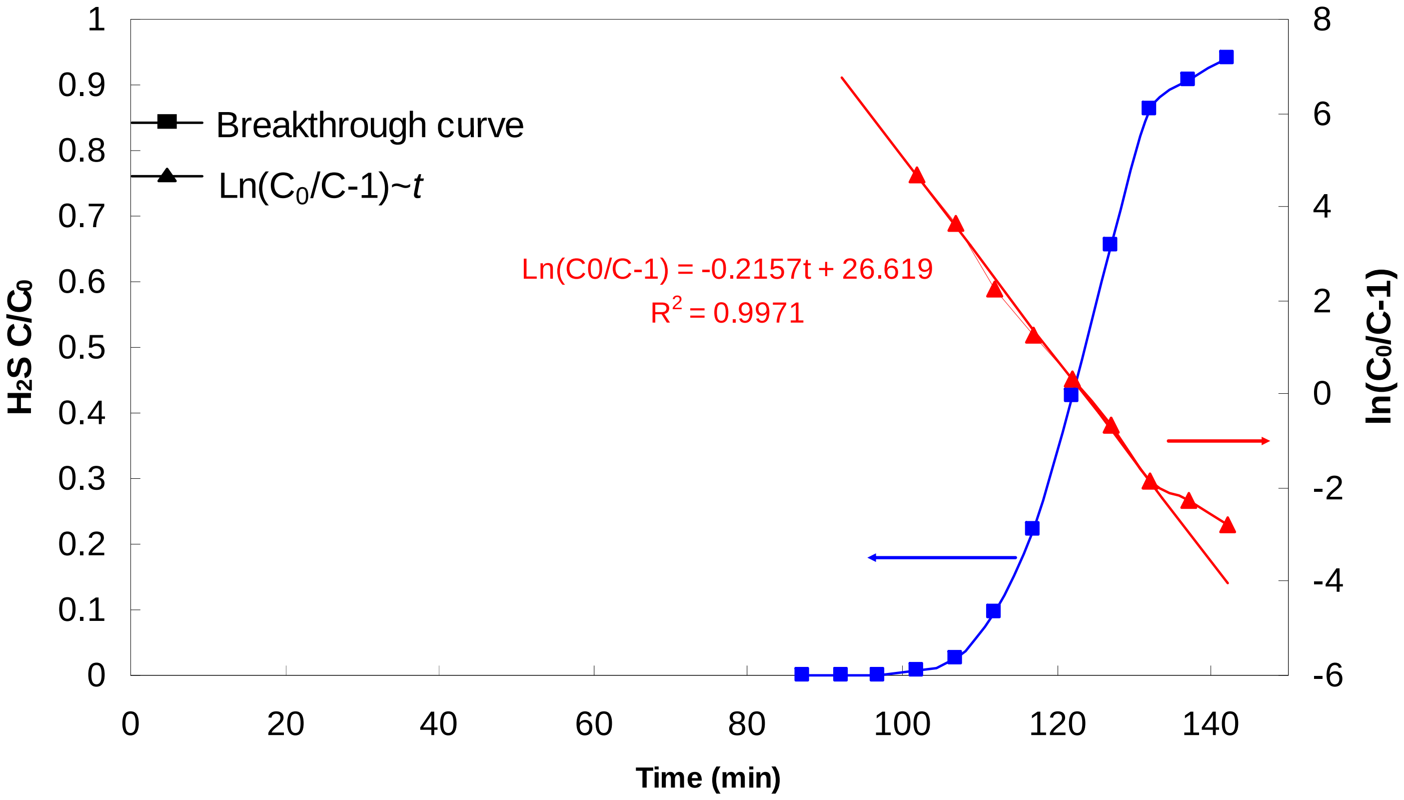
$$\frac{1}{\overline{d}_s} = \frac{a_f}{\varphi_f d_f} + \frac{a_p}{\varphi_p d_p}$$

External surface area based average

$$k_a = 7.44 \cdot \frac{(1-\phi)^{1.39}}{\phi} \left(\frac{\overline{d}_s \rho U}{\mu} \right)^{0.61} Sc^{1/3} \frac{D_{AB}}{\overline{d}_s d_p} \qquad K = 7.44 \cdot (1-\phi)^{1.39} \left(\frac{\overline{d}_s \rho U}{\mu} \right)^{0.61} Sc^{1/3} \frac{D_{AB}}{\overline{d}_s d_p} \frac{C_{A0}}{\rho_c}$$

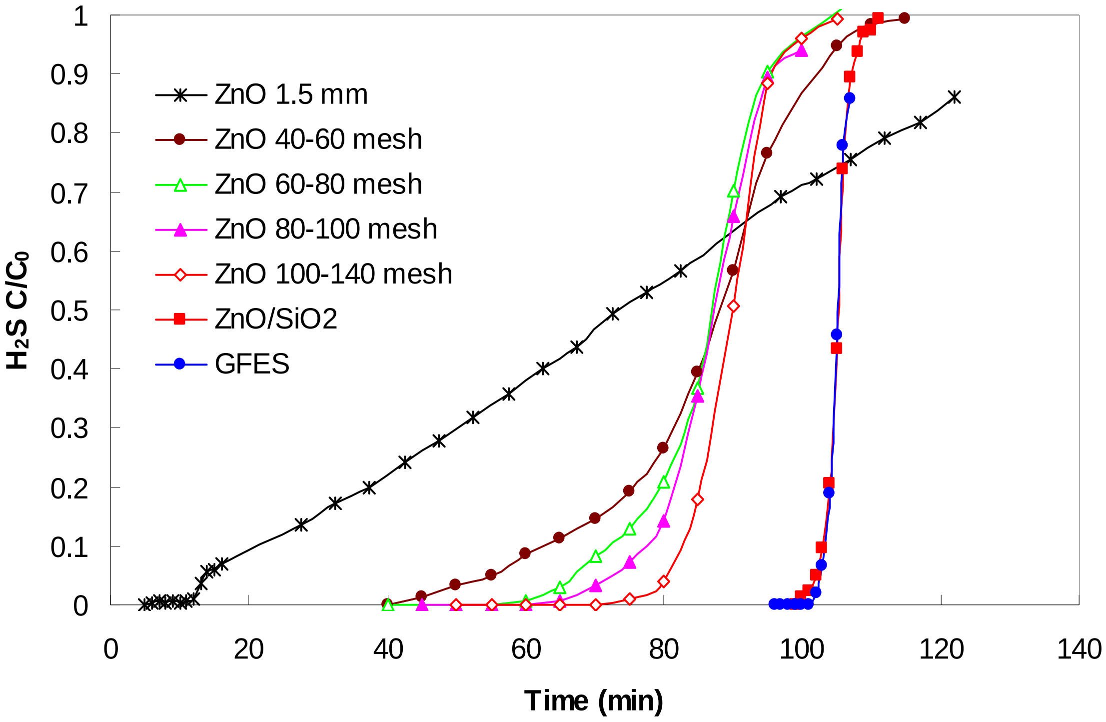
For Microfibrous Media

Model Evaluation



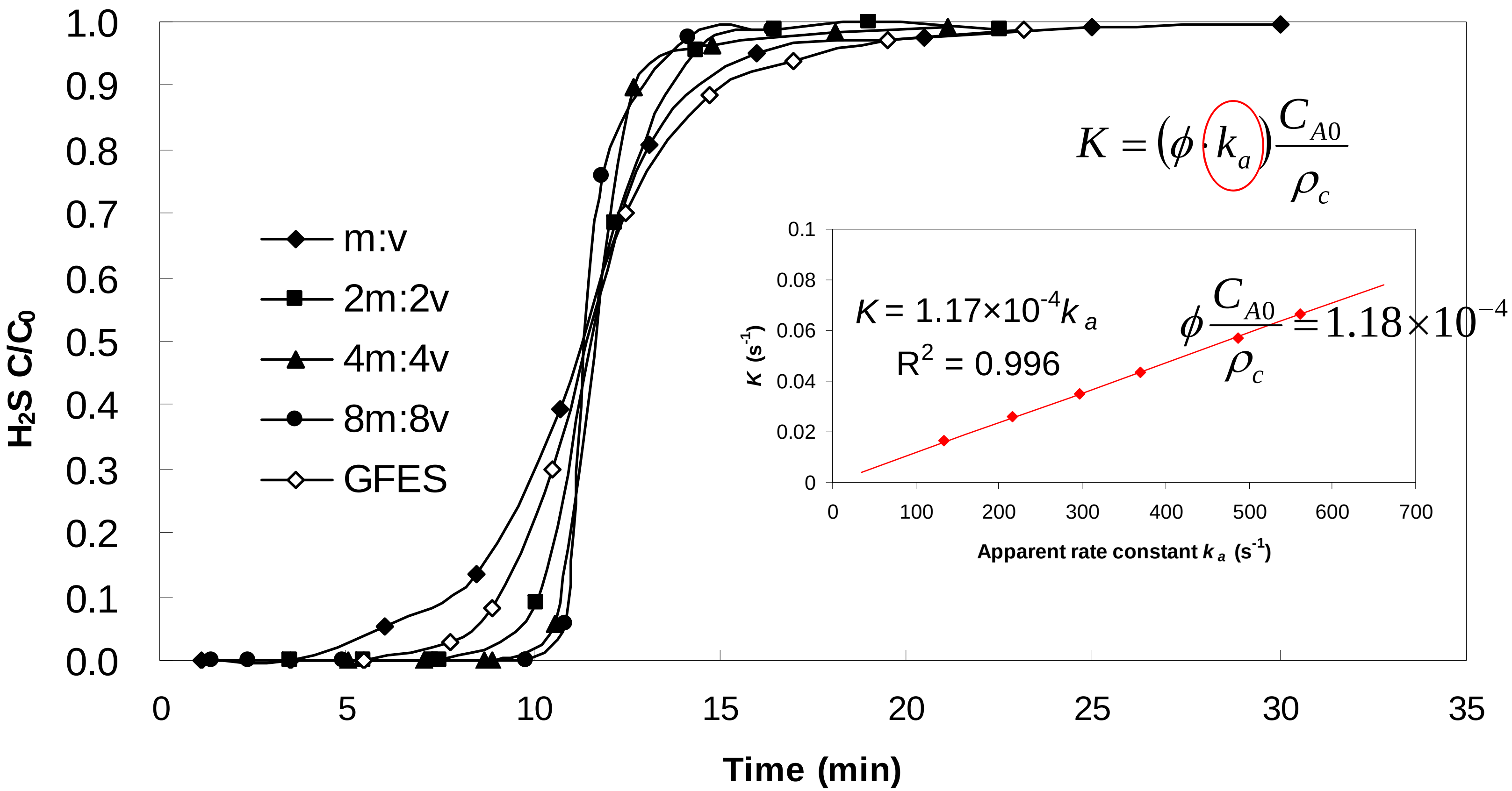
A commercial ZnO sorbent (60-80 mesh, 1 g) was tested with challenge gas concentration of 2 vol. % H_2S in H_2 and flow rate of 100 ml/min STP, at 400 ºC.

Particle Size Effects



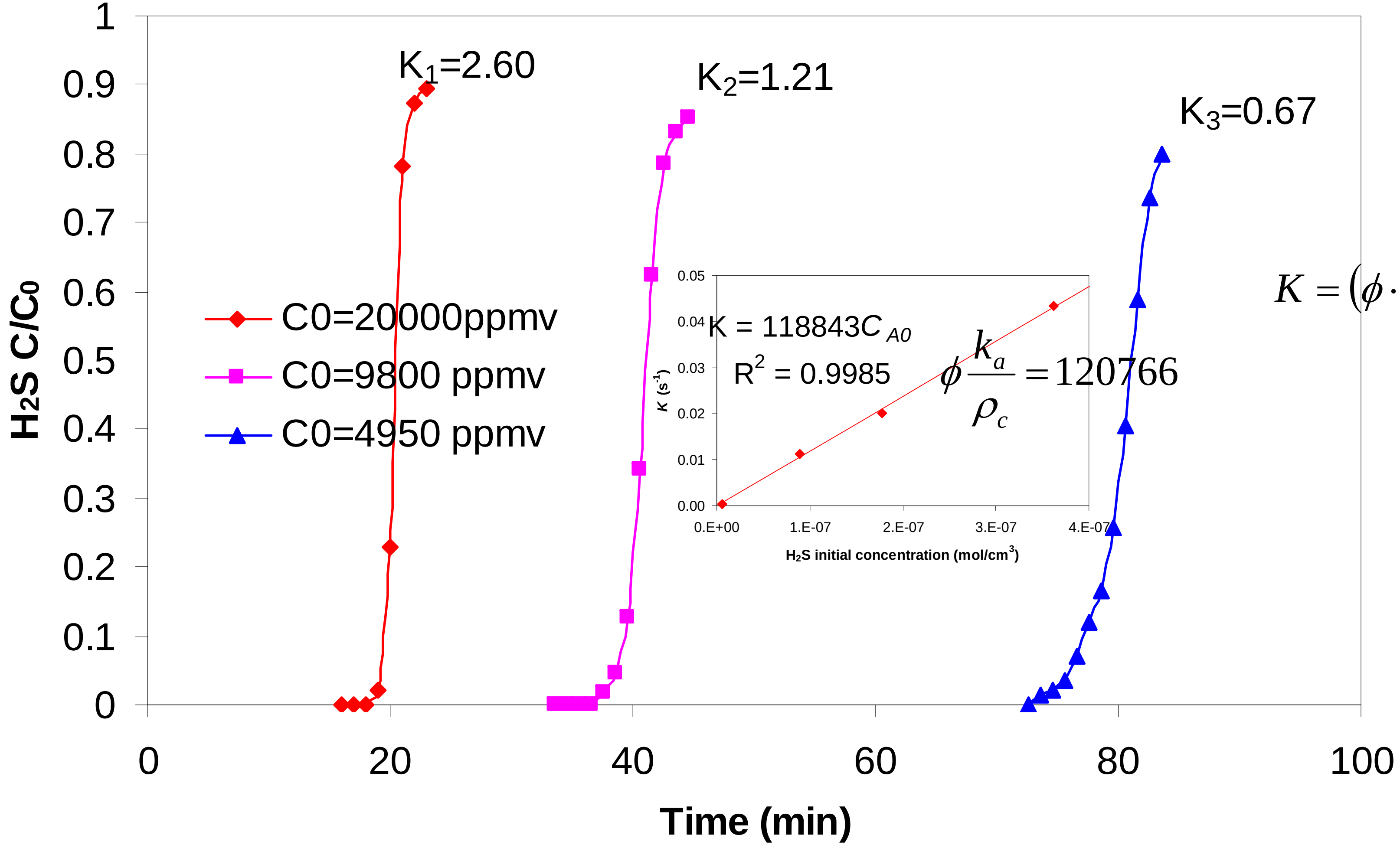
Breakthrough curves of the commercial ZnO sorbent particles (0.2 g, 0.18 g ZnO) with different sizes, and these of ZnO/SiO2 sorbent and glass fiber entrapped ZnO/SiO2 sorbent (GFES). Tested with challenge gas of 2 vol. % H_2S in H_2 at a face velocity of 1.2 cm/s at 400 ºC.

Lumped K vs. k_a



Breakthrough curves of ZnO/SiO_2 sorbent at different face velocities (m=0.1g, v=1.24 cm/s). Tested with challenge gas of 2 vol. % H_2S in H_2 at 400 ºC.

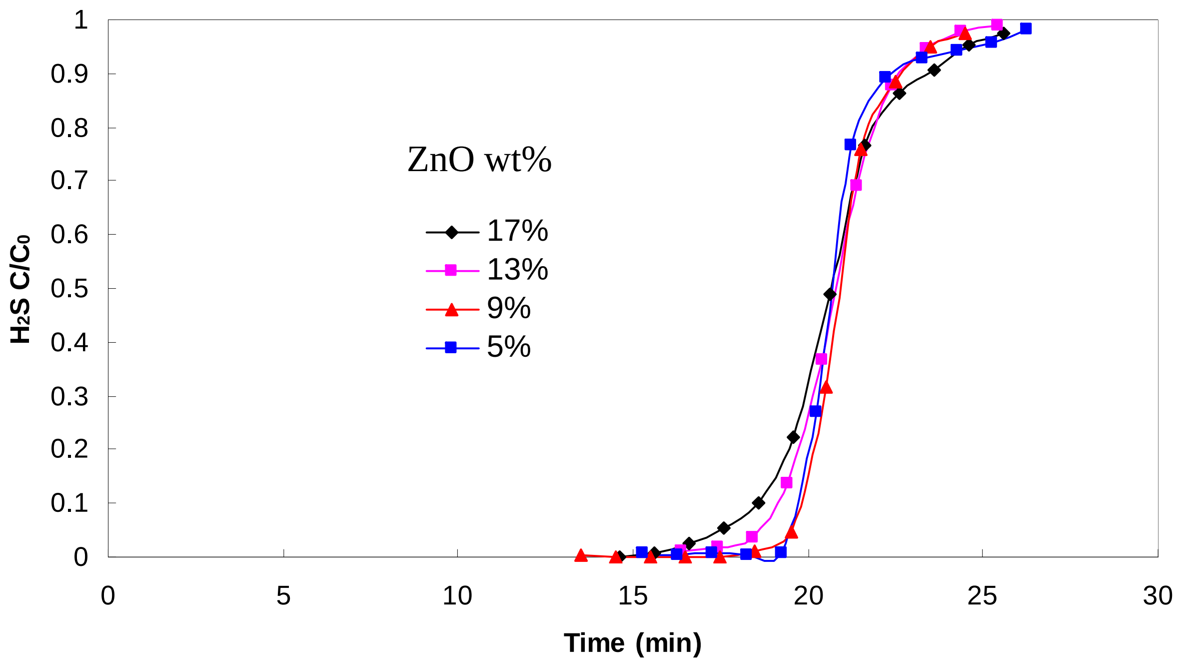
Lumped K vs. C_0



$$K = (\phi \cdot k_a)\frac{C_{A0}}{\rho_c}$$

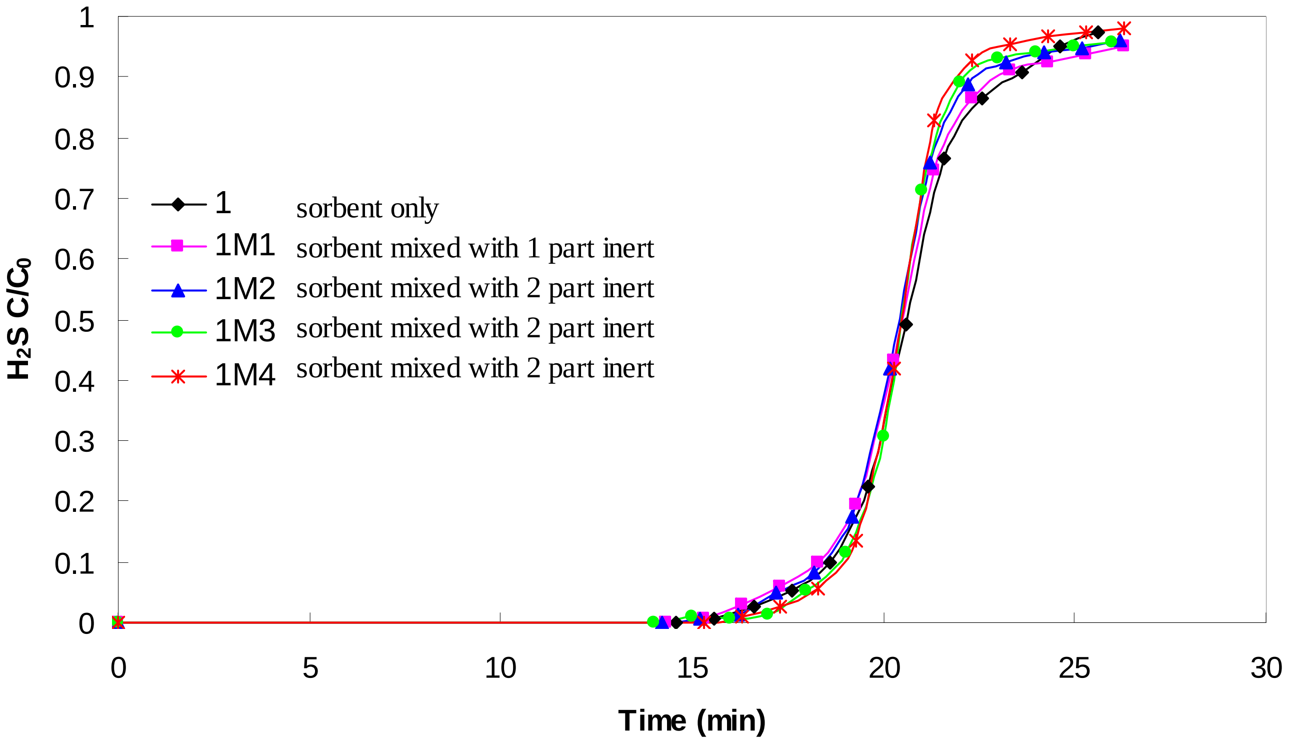
In each experiment, 0.8 g ZnO/SiO_2 was tested at face velocity of 5.0 cm/s at 400ºC.

Lumped K vs. ρ_c



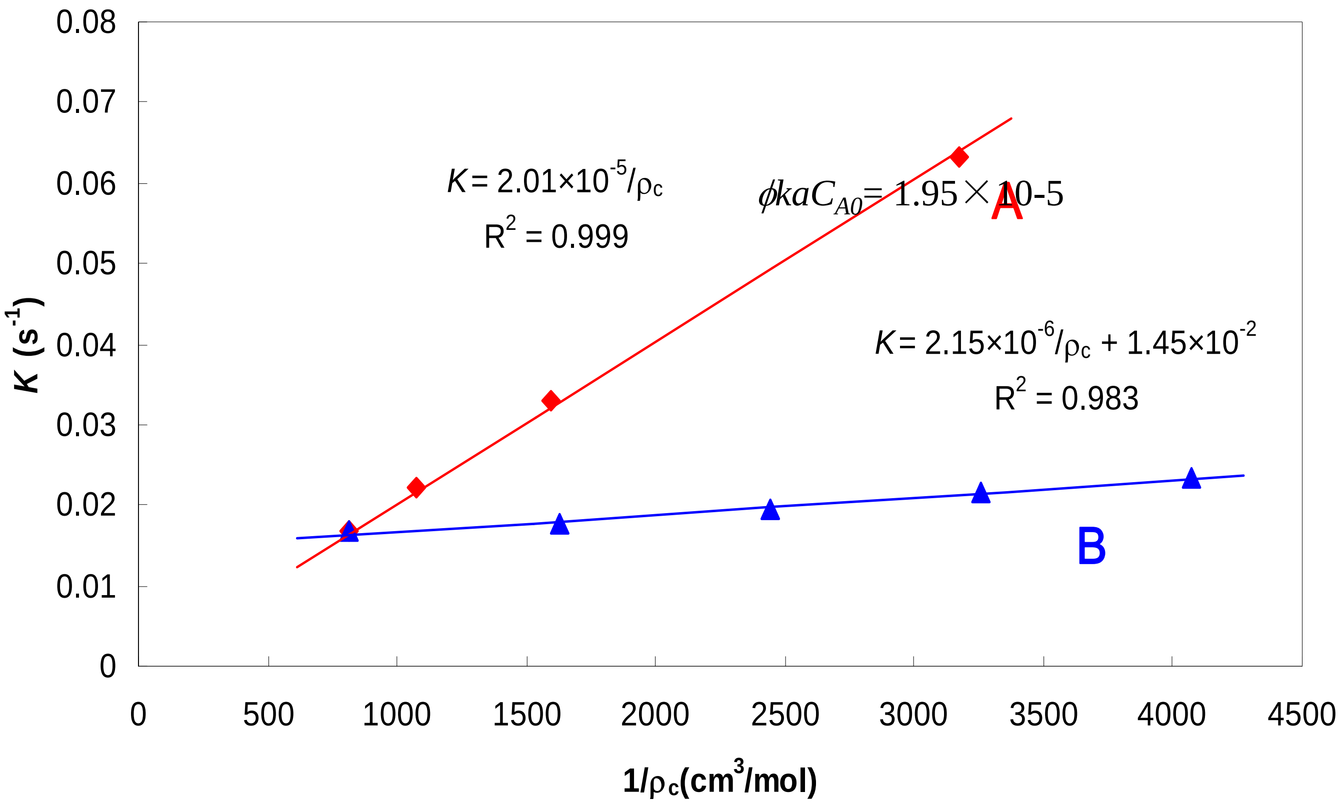
Breakthrough curves of ZnO/SiO_2 sorbents at various ZnO loadings and the same amount of ZnO of 0.034 g. Sorbents tested with challenge gas of 2 vol. % H_2S in H_2 at a face velocity of 1.2 cm/s at 400 ºC.

Lumped K vs. ρ_c –Cont'd



Breakthrough curves of ZnO/SiO_2 sorbents (0.2g ZnO/SiO_2 with ZnO loading at 17 wt.%) diluted by various amount of SiO_2 particles. Tested with challenge gas of 2 vol. % H_2S in H_2 at a face velocity of 1.2 cm/s at 400 ºC.

Lumped K vs. ρ_c -Cont'd



$$K = (\phi \cdot k_a)\frac{C_{A0}}{\rho_c}$$

Tested at a face velocity of 1.2 cm/s at 400 C with 2 vol. % H_2S -H_2.

(A) packed beds of ZnO/SiO_2 sorbents (100-200 μm) with various ZnO loadings

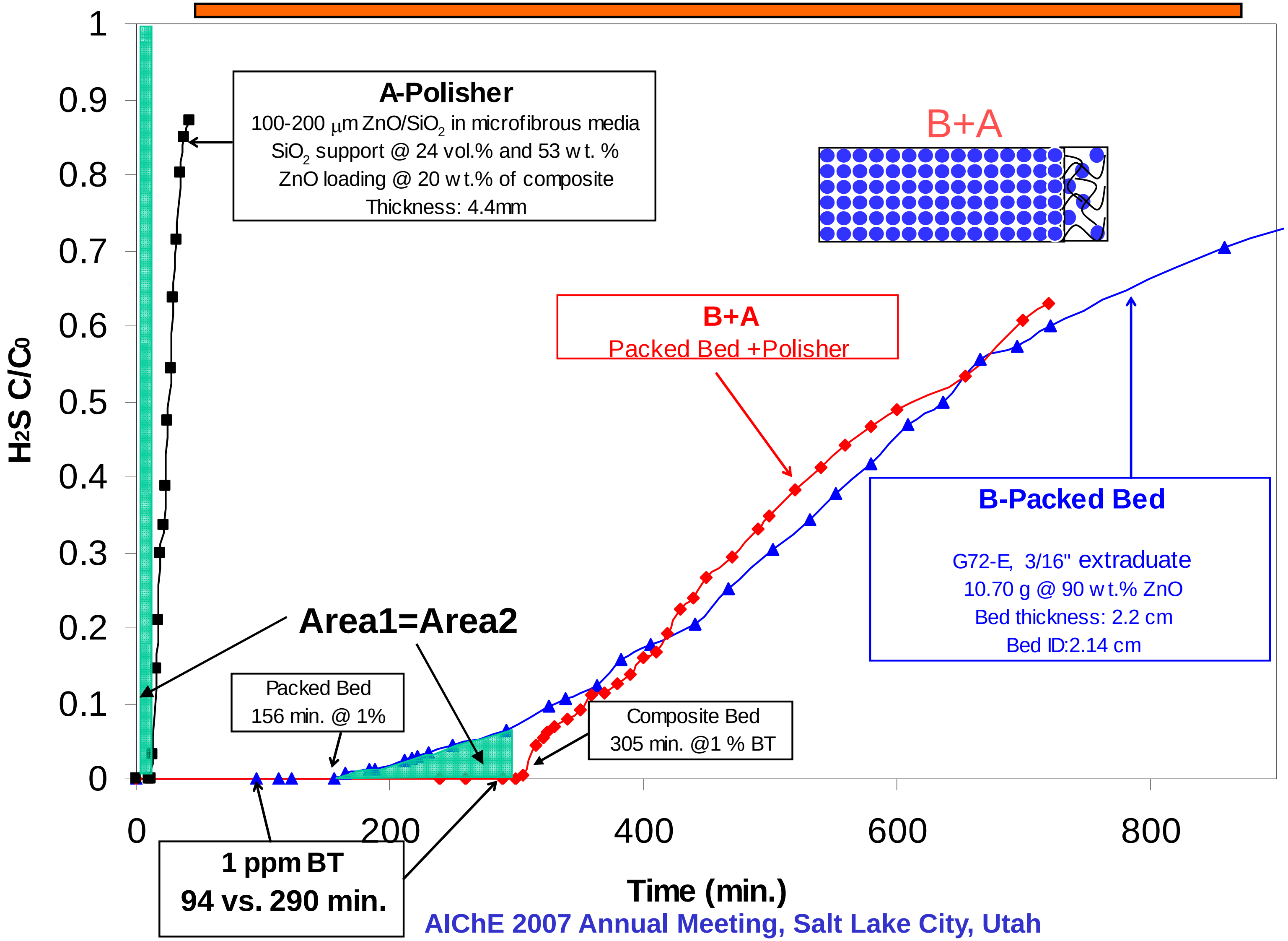
(B) diluted packed beds of ZnO/SiO_2 sorbents (100-200 μm).

Effects of Void and Microfibrous Media

	Packed bed	Packed bed (void diluted)	Microfibrous entrapped sorbents*
ϕ	0.4	0.75	0.75
ρ_c (mol/cm^3)	0.0012	0.00042	0.00042
d_p (μm)	150	150	150
$\bar{d}_s$ (μm)	150	150	**63**
k_c/k_{cp}	1	0.67	0.99
k_d/k_{ap}	1	0.16	0.22
K/K_p	1	0.67	1.13
K/K_p (experimental)	1	-	1.32

*Contains 3 vol.% 8um glass fiber

Kinetics in Composite Bed



Performance of Polishing Sorbent and Packed Bed + Polishing Sorbent @4816 ppm H_2S in H_2, 400°C, 8.05 cm/s.

Kinetics in Composite Bed

Test	K (s^{-1})		τ (min.)		z_c (cm)	
	initial	final	initial	final	(1 ppmv)	(0.1 ppmv)*
Polishing layer	1.33×10^{-2}	-	18.3	-	0.149	0.189
Packed bed	4.08×10^{-4}	1.10×10^{-4}	370	630	1.84	4.03
Composite bed	4.03×10^{-3}	1.15×10^{-4}	327	595	1.36	2.17

Conclusions

- A modified Amundson model successfully characterized the adsorption process taking place in fixed bed reactors;
- Lumped K is introduced to describe the breakthrough curves. K is a function of apparent reaction rate, challenge gas concentration, and sorbent capacity density;
- High voidage decreased the apparent reaction rate; the micron-sized fibers reduce the characteristic dimension.
- The low capacity density increase the lumped K;
- Microfibrous entrapped sorbents have low capacity but high sorbent utilization.
- Composite bed (a packed bed followed by microfibrous entrapped sorbent polisher) synergistically combines the high volume loading of packed beds and the overall contacting efficiency of small particulates.

Acknowledgements

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Thank you for your attention