

MASS TRANSFER STUDY ON GLASS FIBER ENTRAPPED H₂S SORBENTS FOR REGENERABLE CONTINUOUS BATCH FUEL PROCESSING IN PEMFC APPLICATIONS

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Introduction

A significant challenge facing Fuel Cell applications is the development of on-site multi-step reformation technologies converting high energy density commercial-grade hydrocarbon fuels into clean gas fuel. Bulk H₂S removal is a key step of the fuel processor in ensuring the activity of various cleanup catalysts and high value membrane electrode assemblies. So far, most designs have adopted packed bed reactors, which do not scale well with the small modular nature of fuel cells. Packed beds of catalyst/sorbent pellets of one to five millimeters in diameter suffer from high intraparticle mass/heat transfer. As result, reactors with huge size are required to remove the H₂S to below 1ppm. Mass transfer may be ameliorated by decreasing the particle size and increasing the face velocity, which in turn causes the high pressure drop and bypassing in packed bed. On the other hand, catalyst/sorbent pellets are not likely to withstand mechanical shaking in many applications (such as portable electric devices, propulsion devices, etc.); powdered catalysts may clump in a way that leads to fluid bypassing. Bare metals and catalysts washcoats have been used to avoid one or more of these problems [1-4], but surface areas per unit reactor volume have remained unacceptably low.

The research effort here was targeted at designing small, efficient, lightweight fuel processors based on microfibrrous media technologies developed at Auburn University [5-12]. Microfibrrous media carrier can be used, with large surface to volume ratios, to entrap micro-sized sorbent and/or catalyst particulates while withstanding considerable shaking and avoiding bypassing. This generic approach can improve contacting efficiency, and promote regenerability while make more effective (cassette type) design of reactor possible [13-15]. A mathematical model, bed depth service time equation, which describes the relationship between the breakthrough curve ($\frac{C}{C_0} \sim t$ curve) and the apparent rate constant (k'), was developed by Dr. Cahela in our group. From the linear regression from the breakthrough curve, the k' can be extrapolated

$$\frac{C}{C_0} = \frac{1}{1 + e^{k'\tau(1-\frac{C}{C_0})}} \quad (1)$$

In this paper, the glass fiber entrapped ZnO/SiO₂ desulfurization sorbents for reformat were prepared and the comparative study of mass transfer has been conducted.

Experimental

Sorbents Preparation. Sintered glass fiber entrapped 150-200 μm (dia.) SiO_2 ($300\text{m}^2/\text{g}$, Grace Davison) support particulates were fabricated by regular wet layer paper-making/sintering procedure [5-12]. ZnO was then placed onto the supports by incipient wetness impregnation. 6g of glass fiber chops, and 0.7g of 30-60 μm (dia.) cellulose (100-1000 μm in length) were added into about 5L water and stirred at 50Hz to uniform suspension. The produced suspension and 12g SiO_2 were added into the headbox of the 6-inch (dia.) circular sheet former under stirring. A 6-inch circular preform was then formed by draining followed by pressing at $\sim 400\text{kNm}^{-2}$ and drying in air at $\sim 110^\circ\text{C}$. The As-prepared perform was directly sintered in air for 30 min at 925°C , while burning off the celluloses. The sintered glass fiber entrapped SiO_2 particulates comprised 3.0 vol% of glass fibers, 45 vol% of 150-200 μm (dia.) SiO_2 particulates, and 52 vol% voidage. To place the ZnO onto the support, the as-prepared microfibrous entrapped SiO_2 paper was immersed into a ZnO sol-gel for 10min. The ZnO sol-gel was prepared by adding 70ml $\text{NH}_3\cdot\text{H}_2\text{O}$, 42g $(\text{NH}_4)_2\text{CO}_3$, and 66g $\text{Zn}(\text{Ac})_2\cdot 6\text{H}_2\text{O}$ in series into 56ml water under vigorously stirring. The paper was subsequently removed from the ZnO sol-gel, drained under vacuum, and calcined in air. The final composite sorbent product had a ZnO loading around 20wt% (including the mass of the glass fibers).

For comparative study, ZnO/ SiO_2 sorbent without microfiber was prepared by the impregnation as mentioned above; commercial ZnO sorbent (3/16" pellet, $25\text{m}^2/\text{g}$, 90wt%ZnO) from Sud Chemie was crushed and sieved into desired particle size for comparative study use.

Apparatus and Equipments. The H_2S removal tests were conducted in a fixed bed quartz reactor (9mm id.).The challenging model reformat gas contains 2% H_2S (balance H_2) (Airgas,USA). In regeneration cycle, the household air was applied to convert ZnS to ZnO at 600°C . A Gas Chromatograph (GC S-500, Gow-Mac, USA) was used to analyze the H_2S concentration in outlet gas.

Results and Discussion

Particle Size Effect. It is believed that sorbent of small size can enhance the intraparticle mass transfer, thus improves the utilization. In this study, Sud Chemie ZnO sorbent pellets were crushed and sieved into desired particle sizes. The comparison between the performance of ZnO/ SiO_2 and Sud Chemie sorbents is shown in **Figure 1**. In each experiment, 0.18 g effective ZnO was loaded. Reactor temperature kept at 400°C and face velocity 1.28 cm/s. The only difference was the particle size. It is clearly illustrated that the breakthrough curves shift right and give sharper breakthrough curves and higher capacities with the decrease in sorbents size. This is because smaller particles offer larger surface, which in turn means more sorbents may be accessible to challenge gas, assuming challenging gas can diffuse through the same distance d in the spherical sorbents particles, where d is less than the size of particles in Sud Chemie cases. If the size of ZnO particles is less than d , then theoretically all ZnO can be consumed by H_2S , which will only demonstrate a step at the theoretical saturation time in the breakthrough curve. Although the particles of this size are impracticable due to the drastic increase in pressure drop, the particulates could

be supported on other particles with reasonable size. This is an idea to get rid of the intraparticles mass transfer resistance that suffers almost all packed beds. Actually, through the impregnation process, nanosized ZnO was dispersed on the silica particles [16]. As expected, the nanosized ZnO impregnated on silica particle demonstrates the sharpest breakthrough curve and the breakthrough capacity is twice that of Sud 40-60mesh, and the breakthrough capacity reached 90% of stoichiometric capacity. For convenience, the breakthrough was defined at the point that the outlet concentration reached 1% inlet concentration (C_0).

External mass transfer study. In this study, the ZnO/SiO₂ sorbent was tested at 400 °C with challenge gas concentration (C_0) of 2%. In the first experiment, 0.1 g ZnO/SiO₂ (ZnO loading ratio 19%) sorbent was loaded and the face velocity was about 1.28 cm/s. In each of the following experiments, the weight of sorbent loaded and face velocity was twice of these in former experiment, thus the resident time was maintained unchanged, so did the theoretical saturation time. The breakthrough curves of ZnO/SiO₂ at different face velocities is shown in **Figure 2**. The breakthrough cure of glass fiber entrapped sorbent (GFE) with 0.019 g ZnO loaded at the face velocity of 1.28 cm/s is also shown for comparison.

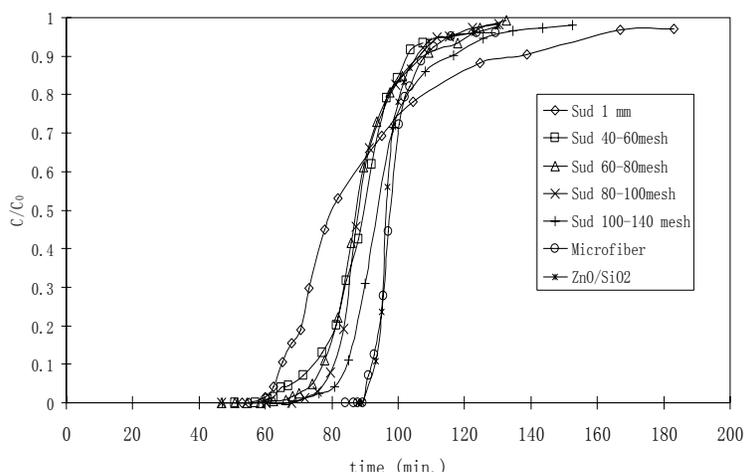


Figure 1. Breakthrough curves of Sud Chemie Sorbents with different size and ZnO/SiO₂ sorbents

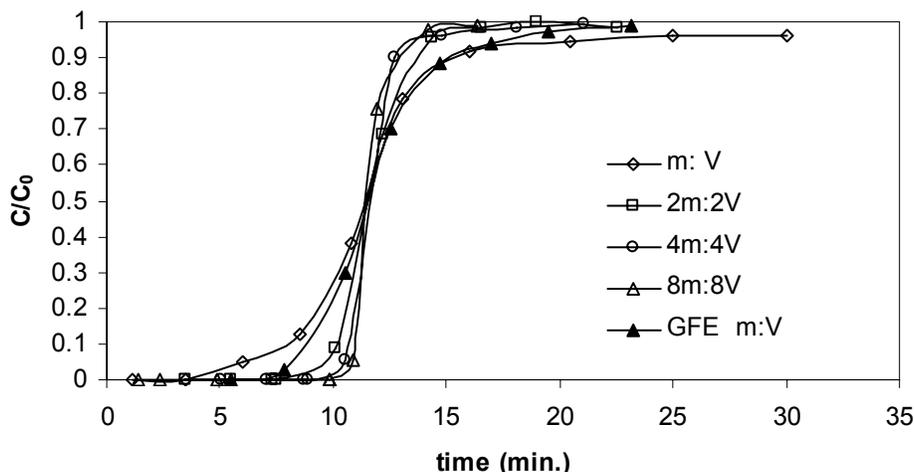


Figure 2. The breakthrough curves of ZnO/SiO₂ at different face velocities ($C_0=2\%$, reactor temperature 400 °C).

All the breakthrough curves pass around the same point, which indicates the consistency of the theoretical capacity. It is a clear trend that the breakthrough curves become sharper with the increase in face velocity of challenge gas. For convenience, the breakthrough point was defined at 1% of inlet concentration. It is clear that the breakthrough curve became sharper as the face velocity increases, thus offers the higher capacity at breakthrough. Glass fiber entrapped sorbent offered a sharper breakthrough compared with ZnO/SiO₂ packed bed sorbent. The apparent rate constants, defined as k' in bed depth service time equation (1), were calculated by regression and shown in Figure 3. In the external mass transfer region, the apparent rate constant increase slowly with the increase of face velocity at a power of 2/3. At the same velocity, same amount of ZnO, after entrapped in the glass fiber media, demonstrated about 50% increase in apparent rate constant (compare GFE and the first data point in the k' - v curve). The only explanation for this improvement is that glass fiber entrapped media make the entrapped sorbent like the sorbent in a fluidized bed, which means the improved external mass transfer rate.

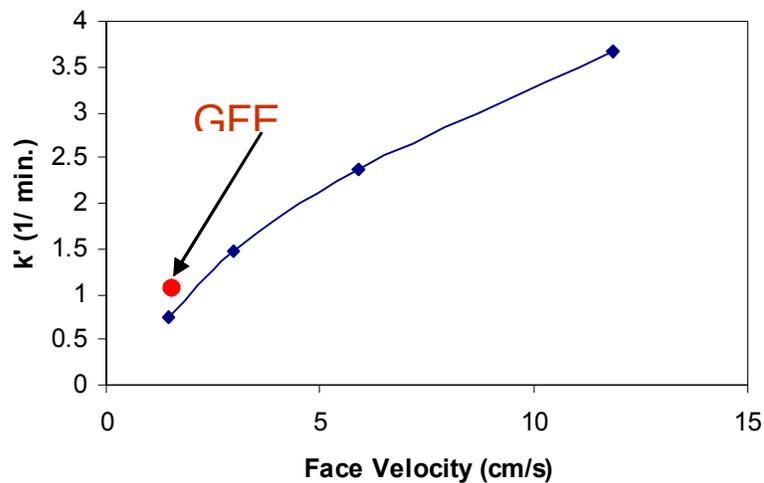


Figure 3. The apparent rate constants at different face velocities.

Glass fiber entrapped sorbents are also applied in final filters to protect the fuel cell. Therefore, it is necessary to discuss the sorbent performance at room temperature. In these experiments, the challenge gas was fed at the same rate 23 ml/min, while the face velocity was about 0.51 cm/s. In each experiment, 0.019 g ZnO was loaded. The comparison between the performance of ZnO/SiO₂ and ZnO/SiO₂ entrapped in glass fibers or glass mixtures of different fiber diameters was shown in **Figure 4**. Here there is a clear distinction in the performance of ZnO/SiO₂ particles and GFE. The hump in the breakthrough curve of former indicates that is a mass transfer dominated process, since the same sorbents entrapped in microfibers demonstrated much sharper breakthrough curves. Moreover, the fiber diameter also affected the mass transfer. The breakthrough curve of sorbents entrapped in the fiber with larger size, say 14 μ m, is not as sharp as that of smaller size, though this difference becomes not significant especially when the fiber diameter is less than 14 μ m. Based on the bed depth equation, the apparent rate constants were calculated. The change of k' is numerically clear. It has a maximum value in the matrix of the mixture of 10 μ m and 6 μ m glass fibers, is 3.5 times greater than the lowest value, the k' of packed ZnO/SiO₂. This

result indicates that the matrix of 10 μ m and 6 μ m glass fibers improve the external mass transfer most.

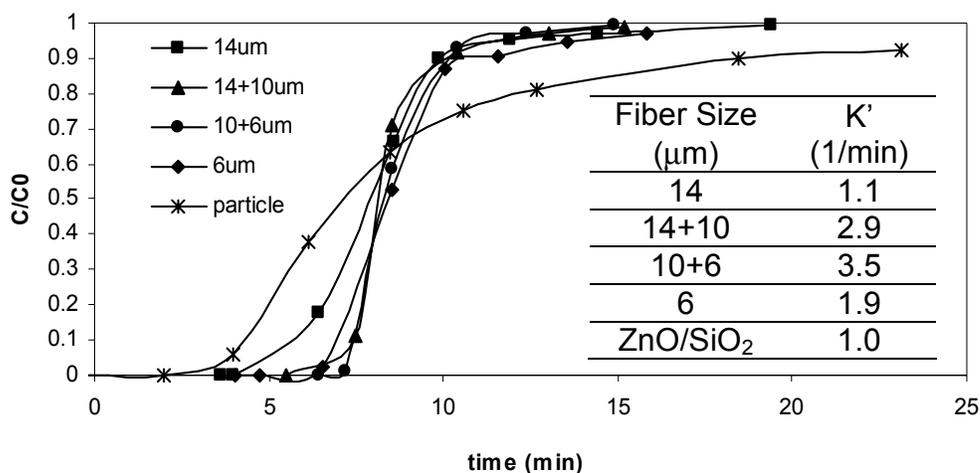


Figure 4. the performance of ZnO/SiO₂ and ZnO/SiO₂ entrapped in glass fibers of different diameters at room temperature.

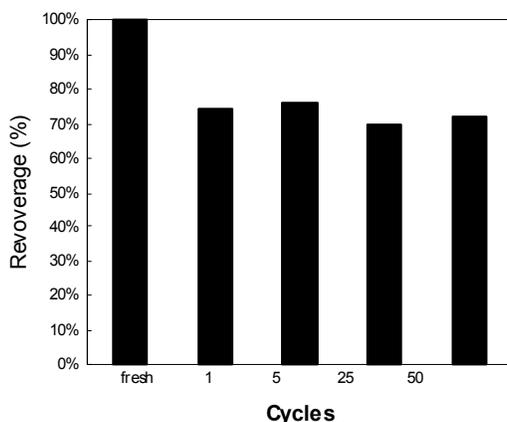


Figure 5. absorption/regeneration cycle test results over the GFE ZnO/SiO₂ sorbents (absorption temperature 400 °C, regeneration at temperature 600 °C for 1 hour; define revoverage as the ratio of capacity of regenerated sorbent to that of fresh sorbent).

Regeneration. It is clear that the microfiber media are able to enhance the external mass transfer thus improve the sorbents performance in the low concentration H₂S removal; ZnO nanosized particulates supported by SiO₂ can minimized the intraparticle mass transfer resistance. It is undoubted that it will also demonstrate outstanding performance in regeneration cycles, where oxygen, instead of H₂S in absorption case, diffuses in the sorbents. As shown in **Figure 5**, the regenerated sorbents have steady capacities which are around 75% of the capacity of fresh ones. From the mass transfer study of glass fiber entrapped ZnO/SiO₂ sorbents, it is clear that the combination of these microfiber media nano-dispersed ZnO on SiO₂ has offered a nice solution to the low concentration H₂S removal in onsite fuel processor.

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