Facile Regeneration vitreous microfibrous entrapped supported ZnO sorbent with high contacting efficiency for bulk H_2S removal from reformate streams in fuel cell applications

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Abstract

In this study, a microfibrous carrier consisting of 3vol% of 8 m (dia.) glass fibers is utilized to entrap 45 vol% of 150-250 m (dia.) SiO_2 support particulates. ZnO is then nano-dispersed onto the support by impregnation at the loading of 17 wt%. At equivalent bed volumes, ZnO/SiO_2 entrapped materials provide 2-fold longer breakthrough times for H_2S (with a 67% reduction in sorbent loading) compared to packed beds of 1-2 mm commercial extrudates. 5-log reductions in H_2S concentration with up to 75% ZnO utilization at breakthrough are achieved. H_2S concentrations from 60 to 2,000 ppmv can be reduced to as little as 0.6 ppmv at 400 ^oC in 30% H_2O at a face velocity of 1.7cm/s for layers as thin as 1.0 mm. At 500-600^oC, ZnO/SiO_2 entrapped materials provide much higher regenerability in air than 1-2mm commercial extrudates do. The use of glass fibers permits greater than 50 regeneration cycles.

Key Words: Glass Fiber, Sorbent, H_2S removal, Fuel Cell

Introduction

A significant challenge facing Fuel Cell applications is the development of on-site multi-step reformation technologies utilizing high energy density commercial-grade hydrocarbon fuels.

Microfibrous media technology developed at Auburn University [5-12] provides a novel approach for more effective design of small, efficient, and lightweight fuel processors. Microfibrous 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 also enhance heat/mass transfer, improve contacting efficiency, and promote regenerability [13-15]. The fabrication of the microfibrous media is based on reliable, proven, high-speed, roll-to-roll, papermaking and sintering processes, substantially reducing production costs while improving product quality. Microfibrous entrapped 16% Ni/Al_2O_3 catalysts for toluene hydrogenation in a trickle bed reactor have demonstrated 2-6 times higher specific activities than the conventional packed bed catalysts on a

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gravimetric basis, while volumetric activities of 40 vol% composite catalysts were 80% higher than conventional extrudates [13]. Bulk H_2S removal is a key step of the fuel processing in ensuring the activity of various cleanup catalysts and high value membrane electrode assemblies. To accomplish this goal, in the present study sintered glass fiber carrier was used, with high contacting efficiency, to entrap micro-sized ZnO/SiO_2 sorbent particulates for regenerable continuous batch bulk H_2S removal. Microfibrous media preparation, characterization and evaluation will be discussed as well as the impact of performance behavior on reactor weight, volume, and bed utilization efficiency.

Experimental

Fabrication of glass fiber entrapped (GFE) ZnO/SiO$_2$ sorbent

Sintered glass fiber entrapped 150-250 m (dia.) SiO_2 ($300m^2/g$, 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 8 m(dia.)x6mm(length) S-2 glass fiber chops (Advanced Glassfiber Yarns LLC), and 0.7g of 30-60 m (dia.) cellulose (100-1000 m in length) were added into 2.5L water and stirred vigorously at 50Hz for 2min. The produced suspension and 24g SiO_2 (can be increased up to 36g) were added into a headbox of the six-inch (dia.) circular sheet former and stirred to a uniform suspension. Six-inch circular preform was then formed by draining, pressing at ~ $400kNm^{-1}$, and drying in air at ~110^oC. As-prepared preform was directly sintered in air for 30 min at 925 ^oC while burning off the celluloses. The sintered glass fiber entrapped SiO_2 particulates was comprised of 3.0 vol% of 8 m (dia.) glass fibers, 45 vol% of 150-250 m (dia.) SiO_2 particulates, and 52vol% of voidage. To place the ZnO onto the support, as-prepared microfibrous entrapped SiO_2 paper was immersed into a ZnO sol-gel for 10 min. The paper was subsequently removed from the ZnO sol-gel, drained under vacuum, and calcined in air for 20min at each of selected temperatures (80°, 100°, 120°, 140°, 160°, and 180^oC). The final composite sorbent has a ZnO loading of 17wt% (including the mass of the glass fibers). The ZnO sol-gel was prepared by adding 70ml $NH_3 \cdot H_2O$, 42g $(NH_4)_2CO_3$, and 66g $Zn(Ac)_2 \cdot 6H_2O$ into 56ml of water and was vigorously stirred. Pressure drop of the above GFE ZnO/SiO_2 vs. face velocity of air at room temperature is presented in Figure 1 for reference.

A commercial ZnO sorbent (3/16" pellet, $25m^2/g$, 90wt%ZnO) from Sud Chemie is crushed and sieved into desired particle size for comparative studies.
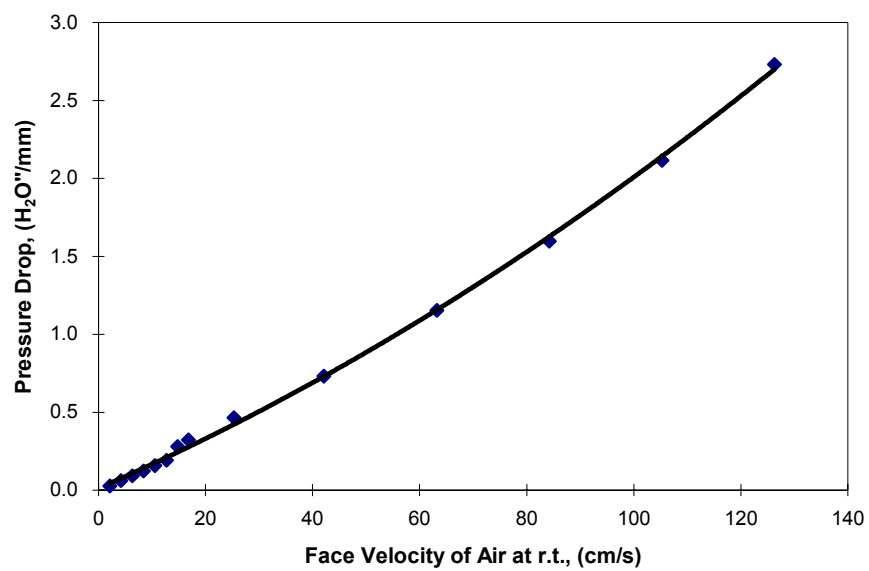
Characterizations

Powder XRD patterns were recorded on Rigaku instrument using a scanning speed of 4°/min and an accelerating voltage of 40kV, unless stated otherwise.

SEM micrographs of the GFE ZnO/SiO_2 sorbent were obtained by a Zeiss DSM 940 instrument. As shown in Figure 2, the micro-sized ZnO/SiO_2 particulates were uniformly entrapped into a well sinter-locked, three-dimensional network of 8 m glass fibers.
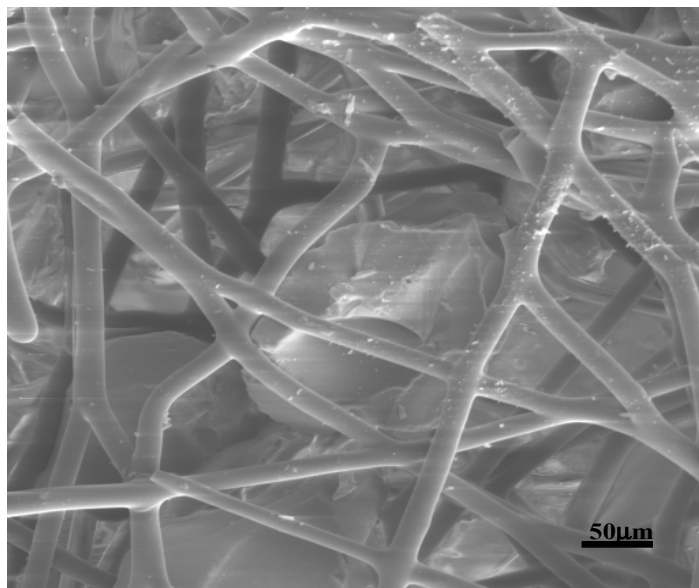

Figure 2 SEM micrographs of GFE ZnO/SiO_2 sorbents

Microreactor evaluation

Absorption and regeneration cycle tests were carried out in a continuous batch mode. The sorbent loading was kept at 0.53mL (16.5mm (dia.)×2.5mm(thick)). To avoid the gas bypass, a sample of GFE ZnO/SiO$_2$ sorbent was cut into a 16.5mm (dia.) disc and sealed with the inner wall of the tubular quartz reactor by a mixture of -Al$_2$O$_3$ powder and SiO$_2$ sol-gel (Si-RIG, 40wt% SiO$_2$, Zircar Ceramics). Absorption with a H$_2$S challenge of 60 ppmv in a model reformate stream (40%CO$_2$, 10%CO, 9%C1-C3 hydrocarbon, balance being H$_2$) was performed at 400°C in the presence of 30% H$_2$O at a face velocity of 1.7cm/s on a dry gas basis (dry gas flow rate: 220mL(STP)/min). The H$_2$O vapor of 30% was added into the model reformate because of the need to perform downstream WGSRs and to keep the membrane electrolyte assembly from drying in practical operations. Regeneration was performed at 500-600 ^{o}C in an air flow (50ml/min) for 1-3h. The breakthrough of H$_2$S is determined by the rate of color change of the lead acetate strips (H$_2$S detection limit: 1ppmv). In order to prove that the equilibrium H$_2$S absorption is achieved in the present study, a MultiRAE Plus multigas monitor (PMG-50/5P, H$_2$S detection limit: 0.5ppmv) was employed to monitor the outlet H$_2$S concentrations continuously. Absorption with H$_2$S challenges of 60 and 2000ppmv in He ran at 400°C in the present of 30% H$_2$O. The He was used in lien of the model reformate since H$_2$ and CO are interferential to the H$_2$S detection of the MultiRAE monitor. When using He, the outlet H$_2$S concentrations were ~0.5ppmv before 1ppmv H$_2$S breakthrough, consistent with the equilibrium H$_2$S concentration (~0.6ppmv) at 400°C in 30% H$_2$O [16].

Results and discussion

The absorption with a H$_2$S challenge of 60 ppmv in a model reformate at 400°C in 30% H$_2$O, was studied over both GFE ZnO/SiO$_2$ and 1-2mm commercial extrudates. The results are summarized in Table 1. At equivalent bed volume, GFE ZnO/SiO$_2$ sorbent provided about 2-fold longer breakthrough times for H$_2$S with 67% reduction of the sorbent loading, compared to packed bed of 1-2mm commercial extrudates. ZnO utilization was 75% for ZnO/SiO$_2$ entrapped materials, 14-fold higher than that of 1-2 mm commercial extrudates.

XRD patterns of GFE ZnO/SiO$_2$ sorbent and commercial extrudates for H$_2$S absorption are presented in Figure 3. The commercial extrudate sample afforded relatively sharp XRD peaks of ZnO crystals, corresponding to a crystal size of 17nm. In addition, commercial extrudate sample has a N$_2$-BET surface area of ~25m^2/g (provided by manufacturer). This suggests that most ZnO crystals were buried inside the bulk, which in turn causes poor accessibility of ZnO. In comparison, very weak and broad XRD peaks of ZnO were observed on the ZnO/SiO$_2$ entrapped materials, corresponding to a crystal size of ~5nm. The N$_2$-BET surface area of the ZnO/SiO$_2$ entrapped materials was determined to be 250m^2/g. This indicates that the nano-sized ZnO was highly dispersed onto the pore surface of entrapped SiO$_2$ supports. It

is well understood that H_2S absorption with large commercial extrudates is a typical process, whose both reaction and regeneration rates are controlled by intra-particle and lattice diffusions [15].
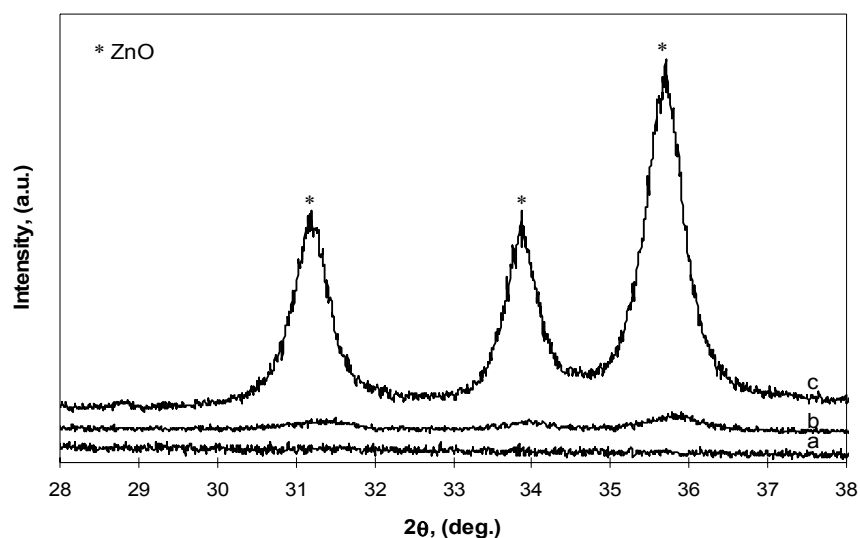

Figure 3 XRD patterns of (a) GFE SiO_2, (b) GFE ZnO/SiO_2, and (c) Sud Chemie extrudates.

For GFE ZnO/SiO_2 sorbents, the nano-dispersed nature of the ZnO combined with the use of small size of support particulates not only attenuates lattice and intra-particle diffusion limits, but also promotes high contacting efficiency and high accessibility of the ZnO. These beneficial properties therefore create high ZnO utilization and high bed utilization efficiency (see Table 1).

Table 1 Results of absorption with 60 ppmv H_2S challenge in a model reformate at 400^oC and 1.7cm/s face velocity in the present of 30% steam over GFE ZnO/SiO_2 sorbents and 1-2mm commercial sorbent extrudates.[a]

Sorbent	GFE ZnO/SiO_2	1-2mm Commercial Extrudates
Total Weight, g	0.2	0.55
ZnO Content, mg	34	495
Bed Volume, mL	0.53	0.53
B.T.*, min	540	180
ZnO Utilization at BT**, %	75	1.8

[a] GHSV = 24,900 h^{-1} (not including the H_2O)

* Breakthrough Time at 1ppmv H_2S breakthrough. ** BT: breakthrough

One other obvious advantage of the nano-dispersed nature of the ZnO and the use of small size support particulates is the great improvement of the

regenerability at 500-600°C in air. Table 2 compares the regenerability of the GFE ZnO/SiO$_2$ sorbents with the 1-2mm commercial ZnO extrudates.

Table 2 Reactivity recovery percentage after regeneration in air at 500-600°C in air.*

Sorbent	GFE ZnO/SiO$_2$		1-2mm Commercial Extrudates	
	B.T.[a], min	Recoverage [b], %	B.T., min	Recoverage, %
Fresh	540	--	180	--
1h Regn.@600°C	400	74	100	56
3h Regn.@500°C	410	76	80	44
1h Regn.@500°C	300	56	10	5.5

* Absorption experiment was carried out at 400°C and 1.7cm/s face velocity in the present of 30% steam, using 60ppmv H$_2$S challenge in a model reformate.
[a] Breakthrough Time at 1ppmv breakthrough for H$_2$S.
[b] Defined as: 100*(B.T. on regenerated sample/B.T. on fresh sample)

Under parallel regeneration conditions, our microfibrous sorbent provided up to 10-fold higher reactivity recovery percentage after regeneration in air from 500 to 600 ^{o}C for 1-3h compared to the packed bed of 1-2mm commercial extrudates. The higher regeneration temperature and longer time period of regeneration made a higher reactivity recovery percentage. To reveal the nature of this large difference in regenerability, XRD analyses were carried out on spent samples before and after regeneration at 500-600°C in air. The spent samples were collected when the outlet H$_2$S concentration reached 60ppmv (the same as inlet concentration).

Conclusion

A highly void, tailorable sintered-glass-fiber carrier has been fabricated via wet layer papermaking/sintering technology [5-12]. This carrier can be utilized, with high surface to volume ratios, to entrap micro-sized catalyst/sorbent particulates while withstanding considerable shaking, avoiding bypassing, maintaining low pressure drop, and achieving excellent corrosion resistance with structural integrity.

A carrier consisting of 3vol% glass fibers was utilized to entrap 45vol% 150-250 micron ZnO/SiO$_2$ H$_2$S sorbent particulates for the regenerable use. The nano-dispersed nature of the ZnO combined with the use of small support particulates not only promotes high ZnO utilization, high contacting efficiency, and high accessibility of ZnO, but facilitates also the regeneration in air at 500-600°C, compared to the packed bed of 1-2mm commercial extrudates. In addition, the use of glass fibers permits a large number of absorption/regeneration cycles due to their high corrosion resistance and thermal stability. The above noted approach allows the continuous batch H$_2$S

removal from reformate streams while significantly increasing bed utilization efficiency and reducing overall system weight and volume.

Acknowledgements

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