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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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In this study, a microfibrous carrier consisting of 3 vol.% of 8 μm (diameter) glass fibers is used to entrap 45 vol.% of 150 to 250 μm (diameter) SiO_2 support particulates. ZnO is then nanodispersed onto the support by impregnation at the loading of 17 wt.%. At equivalent bed volumes, ZnO/SiO_2-entrapped materials provide twofold longer breakthrough times for H_2S (with a 67% reduction in sorbent loading) compared with packed beds of 1 to 2 mm commercial extrudates. Five-log reductions in H_2S concentration with up to 75% ZnO utilization at breakthrough are achieved. H_2S concentrations from 60 to 2000 parts per million in volume (ppmv) can be reduced to as little as 0.6 ppmv at 400 °C in 30% H_2O at a face velocity of 1.7 cm/s for layers as thin as 1.0 mm. At 500 to 600 °C, ZnO/SiO_2-entrapped materials provide much higher regenerability in air than do 1 to 2 mm commercial extrudates. The use of glass fibers permits greater than 50 regeneration cycles.

Keywords fuel cell, glass fiber, H_2S removal, sorbent

1. Introduction

A significant challenge facing fuel cell applications is the development of on-site multistep reformation technologies utilizing high-energy density commercial-grade hydrocarbon fuels (Ref 1-4).

Microfibrous media technology developed at Auburn University (Ref 5-12) provides a novel approach for the more effective design of small, efficient, and lightweight fuel processors. A microfibrous media carrier, with large surface-to-volume ratios, can be used to entrap microsized 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 (Ref 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 two to six times higher specific activities than the conventional packed bed catalysts on a gravimetric basis, while volumetric activities of 40 vol.% composite catalysts were 80% higher than those of conventional extrudates (Ref 13). Bulk H_2S removal is a key step in the fuel processing in ensuring the activity of various cleanup catalysts and high-value membrane electrode assemblies. To accomplish this goal, in the current study a sintered glass fiber carrier, with high contacting efficiency, was used to entrap microsized 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.

2. Experimental

2.1 Fabrication of Glass Fiber-Entrapped ZnO/SiO_2 Sorbent

Sintered glass fiber-entrapped (GFE) 150 to 250 μm (diameter) SiO_2 (300 m^2/g; Grace Davison) support particulates were fabricated by a regular wet layer paper-making/sintering procedure (Ref 5-12). ZnO was then placed onto the supports by incipient wetness impregnation. A total of 6 g of 8 μm (diameter) × 6 mm (length) S-2 glass fiber chops (Advanced Glassfiber Yarns LLC), and 0.7 g of 30 to 60 μm (diameter) cellulose (100–1000 μm in length) were added into 2.5 L of water and stirred vigorously at 50 Hz for 2 min. The produced suspension and 24 g of SiO_2 (which can be increased up to 36 g) were added into the headbox of the 15.2 cm (diameter) circular sheet former and stirred to a uniform suspension. The 15.2 cm circular preform was then formed by draining, pressing at ~400 kN/m, and drying in air at ~110 °C. The as-prepared preform was directly sintered in air for 30 min at 925 °C while burning off the celluloses. The sintered GFE SiO_2 particulates were composed of 3.0 vol.% of 8 μm (diameter) glass fibers, 45 vol.% of 150 to 250 μm (diameter) SiO_2 particulates, and 52 vol.% of voidage. To place the ZnO onto the support, as-prepared microfibrous entrapped SiO_2 paper was immersed

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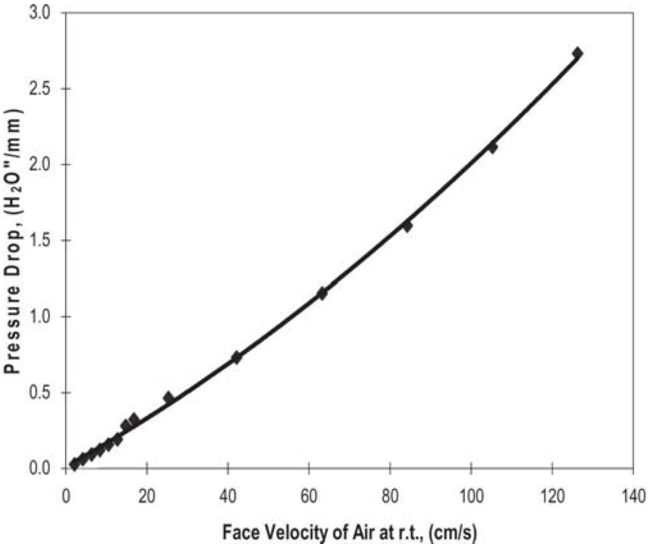

Fig. 1 The pressure drop of the GFE ZnO/SiO_2 as a function of the face velocity of air at room temperature

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 20 min at each of the selected temperatures (80, 100, 120, 140, 160, and 180 °C). The final composite sorbent has a ZnO loading of 17 wt.% (including the mass of the glass fibers). The ZnO sol-gel was prepared by adding 70 mL of $NH_3 \cdot H_2O$, 42 g of $(NH_4)_2CO_3$, and 66 g of $Zn(Ac)_2 \cdot 6H_2O$ into 56 mL of water and stirring vigorously. The pressure drop of the GFE ZnO/SiO_2 as a function of the face velocity of air at room temperature is shown in Fig. 1.

A commercial ZnO sorbent (4.8 mm pellet; 25 m^2/g; 90 wt.% ZnO) from Sud Chemie was crushed and sieved into the desired particle size for comparative studies.

2.2 Characterization

Powder x-ray diffraction (XRD) patterns were recorded using a scanning speed of 4°/min and an accelerating voltage of 40 kV, unless stated otherwise.

The scanning electron microscopy (SEM) micrographs of the GFE ZnO/SiO_2 sorbent were obtained by a Zeiss DSM 940 instrument. As shown in Fig. 2, the micron-sized ZnO/SiO_2 particulates were uniformly entrapped into a well-sinter-locked, three-dimensional network of 8 μm glass fibers.

2.3 Microreactor Evaluation

Absorption and regeneration cycle tests were carried out in a continuous batch mode. The sorbent loading was kept at 0.53 mL (16.5 mm [diameter] × 2.5 mm [thickness]). To avoid the gas bypass, a sample of GFE ZnO/SiO_2 sorbent was cut into a 16.5 mm (diameter) disc and sealed with the inner wall of the tubular quartz reactor by a mixture of α-Al_2O_3 powder and SiO_2 sol-gel (Si-RIG, 40 wt.% SiO_2, Zircar Ceramics). Absorption with an H_2S challenge of 60 ppmv in a model reformate stream (40% CO_2, 10% CO, 9% C1-C3 hydrocarbon, with balance being H_2) was performed at 400 °C in the presence of 30% H_2O at a face velocity of 1.7 cm/s on a dry gas basis (dry gas flow rate 220 mL [at standard temperature and pressure]/min). The H_2O vapor of 30% was added into the model reformate due to the need to perform downstream water-gas shift reaction (WGSR) and to keep the membrane electrolyte assembly from drying in practical operations. Regeneration was performed at 500 to 600 °C in an airflow (50 mL/min) for 1 to 3 h. The breakthrough of H_2S is determined by the rate of color change of the lead acetate strips (H_2S detection limit; 1 ppmv). To prove that the equilibrium H_2S absorption is achieved in the current study, a MultiRAE Plus multigas monitor (PMG-50/5P, H_2S detection limit 0.5 ppmv) was used to monitor the outlet H_2S concentrations continuously. Absorption with H_2S challenges of 60 and 2000 ppmv in He ran at 400 °C in the presence of 30% H_2O. Helium was used in lieu of the model reformate because H_2 and CO are interferential to the H_2S detection of the MultiRAE monitor. When using He, the outlet H_2S concentrations were ~0.5 ppmv before 1 ppmv H_2S breakthrough, consistent with the equilibrium H_2S concentration (~0.6 ppmv) at 400 °C in 30% H_2O.

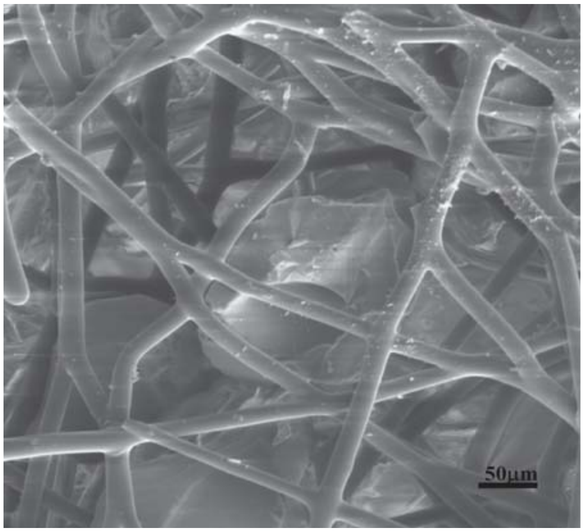

Fig. 2 SEM micrographs of GFE ZnO/SiO_2 sorbents

Table 1 Results of absorption with 60 ppmv H_2S challenge in a model reformate at 400°C and 1.7 cm/s face velocity in the presence of 30% steam over GFE ZnO/SiO_2 sorbents and 1 to 2 mm commercial sorbent extrudates

Sorbent	GFE ZnO/SiO_2	1-2 mm commercial extrudates
Total mass, g	0.2	0.55
ZnO content, mg	34	495
Bed volume, mL	0.53	0.53
BT, min(a)	540	180
ZnO utilization at BT, %	75	1.8

GHSV = 24,900 h (not including the H_2O). (a) Breakthrough time at 1 ppmv H_2S breakthrough

3. Results and Discussion

The absorption with a H_2S challenge of 60 ppmv in a model reformate at 400 °C in 30% H_2O was studied over both GFE ZnO/SiO_2 and 1 to 2 mm commercial extrudates. The results are summarized in Table 1. At an equivalent bed volume, GFE ZnO/SiO_2 sorbent provided about twofold longer breakthrough

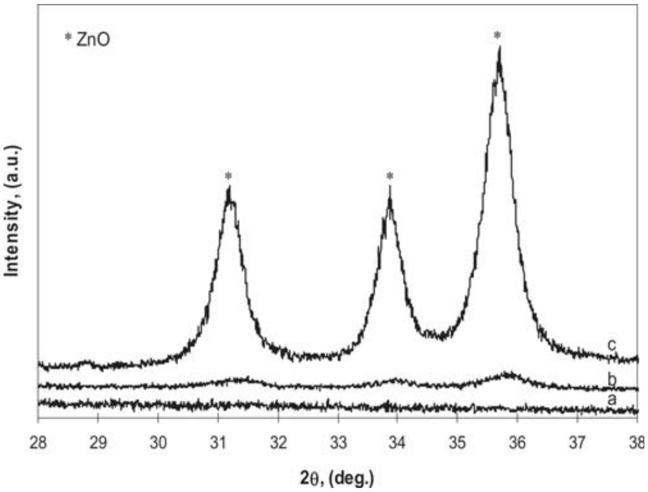

Fig. 3 XRD patterns of (a) GFE SiO_2, (b) GFE ZnO/SiO_2, and (c) Sud Chemie extrudates

times for H_2S with 67% reduction of the sorbent loading, compared with a packed bed of 1 to 2 mm commercial extrudates. ZnO utilization was 75% for ZnO/SiO_2 entrapped materials, which is 14-fold higher than that of 1 to 2 mm commercial extrudates.

The XRD patterns of GFE ZnO/SiO_2 sorbent and commercial extrudates for H_2S absorption are presented in Fig. 3. The commercial extrudate sample afforded relatively sharp XRD peaks of ZnO crystals, corresponding to a crystal size of 17 nm. In addition, the commercial extrudate sample has a N_2-BET surface area of ~25 m^2/g (provided by manufacturer). This suggests that most ZnO crystals were buried inside the bulk, which in turn causes the 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 ~5 nm. The N_2-BET surface area of the ZnO/SiO_2-entrapped materials was determined to be 250 m^2/g. This indicates that the nanosized 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, in which both the reaction and regeneration rates are controlled by intraparticle and lattice diffusions (Ref 15).

For GFE ZnO/SiO_2 sorbents, the nanodispersed nature of the ZnO combined with the use of small-sized support particulates not only attenuates lattice and intraparticle 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 (Table 1).

One other obvious advantage of the nanodispersed nature of the ZnO and the use of small-sized support particulates is the great improvement of the regenerability at 500 to 600 °C in air.

Under parallel regeneration conditions, the microfibrous sorbent provided up to 10-fold higher reactivity recovery percentage after regeneration in air from 500 to 600 °C for 1 to 3 h compared with the packed bed of 1 to 2 mm 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 to 600 °C in air. The spent samples were collected when the outlet H_2S concentration reached 60 ppmv (the same as inlet concentration).

4. Conclusions

A highly void, tailorable sintered glass-fiber carrier has been fabricated via wet-layer papermaking/sintering technology (Ref 5-12). This carrier can be used, with high surface-to-volume ratios, to entrap microsized 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 3 vol.% glass fibers was used to entrap 45 vol.% 150 to 250 μm ZnO/SiO_2 H_2S sorbent particulates for the regenerable use. The nanodispersed 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 also facilitates the regeneration in air at 500 to 600 °C, compared with the packed bed of 1 to 2 mm 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_2S removal from reformate streams while significantly increasing the bed utilization efficiency and reducing overall system weight and volume.

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