Moderate Temperature H_2S removal over High Specific Surface Area SiO_2 supported ZnO Sorbent: Design and Preparation

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Introduction

Onboard Fuel Cell applications are the focus of current extensive R&D. As an essential process, on-site multi-step reformation technologies utilize high energy density commercial-grade hydrocarbon fuels to generate clean feed gas to power fuel cell. 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 in both reaction and regeneration cycles. 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. Moreover, powdered catalysts/sorbent may clump in a way that leads to fluid bypassing. 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.). Other designs, bare metals and catalysts washcoating have been used to avoid one or more of these problems [1-4], but surface areas per unit reactor volume have remained unacceptably low. It is a dilemma for traditional design appproaches. In this situation, new approaches and new catalysts/sorbents have been developed, for example micorchannel reactors.

Bulk H_2S removal is a key step of the fuel processor in ensuring the activity of various cleanup catalysts and high value membrane electrode assemblies. In this paper, we target our research effort at designing small, efficient, lightweight H_2S removal sorbents based on microfibrous media technologies developed at Auburn University [5-12]. 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 improve contacting efficiency, and promote regenerability while make more effective (cassette type) design of reactor possible [13-15]. To accomplish this goal, a new ZnO based sorbent was designed and prepared.

Experimental

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 househood air was applied to convert ZnS to ZnO at 600 ^{o}C. A Gas Chromatograph (GC S-500, Gow-Mac, USA) was used to analyze the H_2S concentration in outlet gas.

Bulk ZnO pellets test. In this test, the bulk ZnO pellets (1mm diameter ×2mm length, 90 wt% ZnO) was used to reduce the sulfur compounds in reformate from 60ppm down to 1ppm. The bed thickness is 3mm and gas face velocity is 1.3cm/s at 400°C. The breakthrough was defined at 1 ppm, the breakthrough cure was shown in Figure 1, and the breakthrough capacity and stoichoimetric capacity (g S/ g ZnO) were calculated and shown in Table 1. The regenerated sorbents showed even worse performance (regeneration condition; 600°C in air flow). Further calculation indicates that only 8% ZnO was accessed by H_2S in the test, which was only a thin layer with 40μm average thickness on the pellets, if the pellets is considered as dense solid as in unreacted shrinking core model. This low utilization of ZnO in fresh sorbent suggests the severe mass transfer resistance, which blocks the both adsorption and regeneration processes for the same reason.

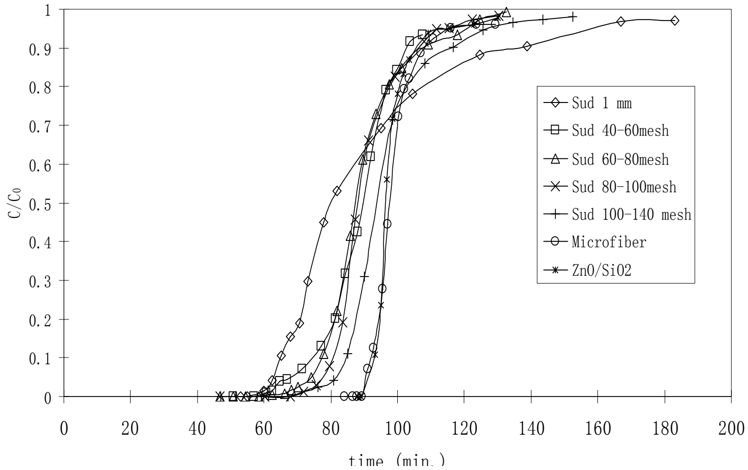


Figure 1. Breakthrough curves of ZnO Sorbents with different size and ZnO/SiO_2 sorbents

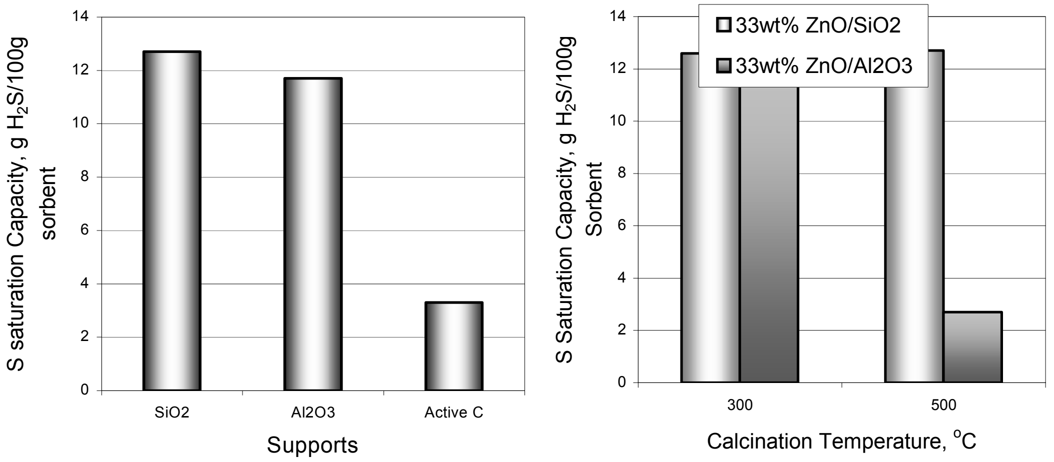
It is not surprise that only tiny amount of ZnO was utilized. The question here is how to improve the ZnO utilization and increase it accessibility. Traditionally, the solution is to decrease the particle size. Another experiment was conducted. The bulk ZnO extraduates were crushed in desired sizes and tested at the same condition as mentioned above. The capacity increased as the size decreased. Even though, the ZnO particles with the 100-200 micron can not achieve even 90% utilization. The breakthrough capacity (time) is much lower than 90% stoichoimetric capacity (time).

New Sorbents design. Since only a thin layer of ZnO can be accessed and inner part is unavailable to gas reactants, the substitution of inner part with inert support will not hurt the performance of sorbents. If the thickness of supported sorbent is thin enough, then all the sorbent should be accessible. Moreover, if the support particles are small in size, the active chemical density (g ZnO/ ml) is still acceptable. So the question here becomes to find the best support to load ZnO on, and how to support the particles in small size without significantly increase the pressure drop. In the following experiments, three widely used supports, activated carbon, alumina, and silica were evaluated.

Supports Screening. Supported-ZnO sorbents were prepared by incipient wet impregnation method using zinc nitrate as precursor and the sorbents were examined by H_2S pulse reaction at 400 °C. H_2S adsorption performance was found to be strongly dependent on the types of support, and calcination temperatures (see Figure 2 a and b). It should be noticed that no detectable adsorption of H_2S was observed over all three neat supports at 400 °C.

Figure 2 shows that H_2S saturation capacity attenuated in the following order: SiO_2>□-Al_2O_3>>AC. The specific surface area of the supports ranks in the order AC($560 m^2/g$) >SiO_2($300 m^2/g$) >γ-Al_2O_3($220 m^2/g$), and their mean pore size ranks in order SiO_2(15nm) > □ γ-Al_2O_3(7nm) > AC. Clearly, H_2S saturation capacity is correlated very well with the mean pore size but not with the specific surface area. We presumed that the most micro-pore was blocked by ZnO particle in the case of AC-supported ZnO sorbent, with the result that it offered low reactivity with H_2S. In contrast, large-pore SiO_2 produced sorbent gave a H_2S saturation capacity as high as 12.7g H_2S per 100g of sorbent (ZnO + support) with a ZnO utility of 90% by taking advantage of both good accessibility of reactive site and nanoscale size of ZnO particles.

Figure 3 shows that H_2S saturation capacity almost remained unchanged for SiO_2-supported ZnO sorbent, but had a dramatic reduction for □-Al_2O_3-supported ZnO sorbent with increase in calcination temperature from 300 ^oC to 500 ^oC. It was well understood that the surface is quite reactive for □-Al_2O_3 but very inert for SiO_2. As a result, strong interaction even solid reaction of ZnO happened easily with □-Al_2O_3 but quite hardly with SiO_2 at temperature higher than 500^oC. Meanwhile, the formation of inactive "$ZnAl_2O_4$-like" compound via the solid reaction was mostly accelerated with increase in calcination temperature. This is the reason for rapid deactivation of □-Al_2O_3-supported ZnO sorbent with increase in calcination temperature.



(a) (b)

Figure 2 saturation capacities of sorbents with 33wt% ZnO. at 400^oC (a) the effect of support; (b) the calcinations temperature effect

ZnO loading. Sintered-SiO_2-supported ZnO sorbents with different ZnO loading were prepared using zinc nitrate as precursor and examined. The H_2S adsorption performance of sorbents with different ZnO loading is displayed in Figure 3.

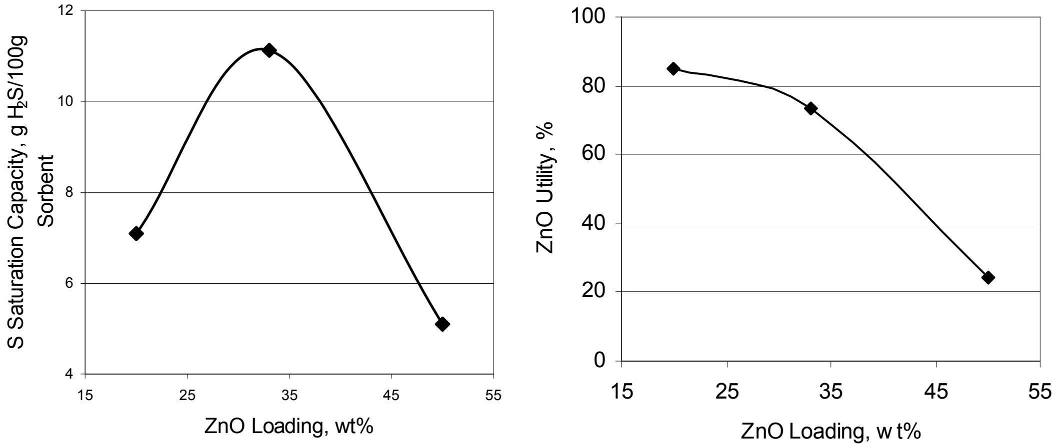


Figure 3. Effect of ZnO loading on H_2S adsorption performance of sintered-SiO_2 -supported ZnO sorbents. Data were derived from H2S pulse reactions at 400^{o}C.

It shows that H_2S adsorption capacity increased obviously with ZnO loading to 33wt% and then dropped dramatically with ZnO loading up to 50wt%. ZnO utilization decreased sharply from 93% to 24% with increase in ZnO loading from 25wt% to 50wt%. The above results indicate that optimal ZnO loading for a sintered-SiO2-supported sorbent with good H_2S adsorption performance is ~33wt% when zinc nitrate is used as precursor. For the stoichiometric adsorption reaction of H_2S with ZnO, however, high ZnO content in the sorbent inventory with high ZnO utilization is pursued to achieve a long breakthrough time (i.e. high H_2S saturation capacity) over per unit weight (or volume) of sorbent. Two-step impregnation method was developed to improve the H_2S adsorption performance of the sorbents especially with high ZnO loading. Table 1 compares the H2S adsorption performance of the sorbents prepared by different preparative methods. It is clear that sintered-SiO_2 supported ZnO sorbents prepared by two-step impregnation method showed much better H2S adsorption performance especially in the case of samples having high ZnO loading. The results indicate that second step impregnation with ZnO sol-gel played a key role in increasing ZnO loading of the sorbents meanwhile sustaining excellent H2S adsorption performance.

Table 1 Comparison of the H2S adsorption performance of the sintered-SiO2 -supported ZnO sorbents prepared by different preparative methods*

Preparation Method	ZnO Loading (wt%)	S Saturation Capacity (g H2S/100g sorbent)	ZnO utilization (%)
One-step impregnation	33	11.7	88
a	43	5.1	30
Two-step impregnation	33	13.0	98
b	45	16.4	96

* Data derived from H2S pulse reactions at 400 ^{o}C; a Using zinc nitrate as precursor

b 25wt% of ZnO was loaded using zinc nitrate as precursor in 1st-step impregnation, and the rest part of ZnO was loaded in 2nd-step impregnation with ZnO sol-gel.

After careful design the ZnO utilization reached above 90%. It means the severe internal mass transfer resistance has been removed successfully by supported sorbent design.

Improved External Mass Transfer. The intraparticle mass transfer resistance has been removed, the next step is to enhance the external mass transfer and support the particulate. Among traditional approaches, the fluidized beds offer the best mass transfer rate than other fixed beds at the same condition. However, the main drawback is that a high face velocity is required to fluidize the bed. If the particles are supported by some materials with tiny volume, the "fluidized-bed like" matrix may have the same effect to improve the mass transfer. The microfibrous entrapped technology developed at CM3 center offers such an opportunity. Base on this hypothesis, glass fiber entrapped sorbents were prepared. The SiO_2 support was entrapped in the microfiber media and ZnO was loaded by wet impregnation right after. Figure 4 shows some SEM images of prepared microfibrous entrapped sorbents. The integrity structure after 50 reaction-regeneration cycles defenestrates the robust and thermally and chemically stable matrix made of glass media. The comparison between bulk ZnO sorbents with various size and ZnO/SiO_2 and glass fiber entrapped ZnO/SiO2 is shown in Figure 1; the comparison between ZnO/SiO_2 and glass fiber entrapped ZnO/SiO_2 is shown in Figure 5.

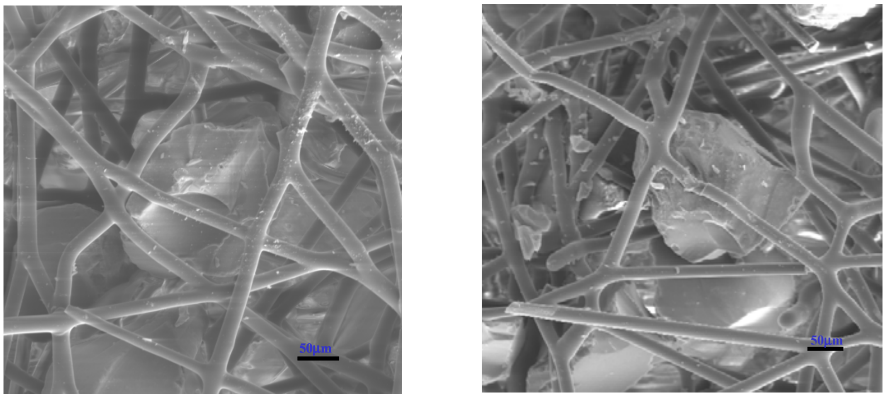


Figure 4. SEM image of fresh sorbent and regenerated sorbent after 50 reaction-regeneration cycles

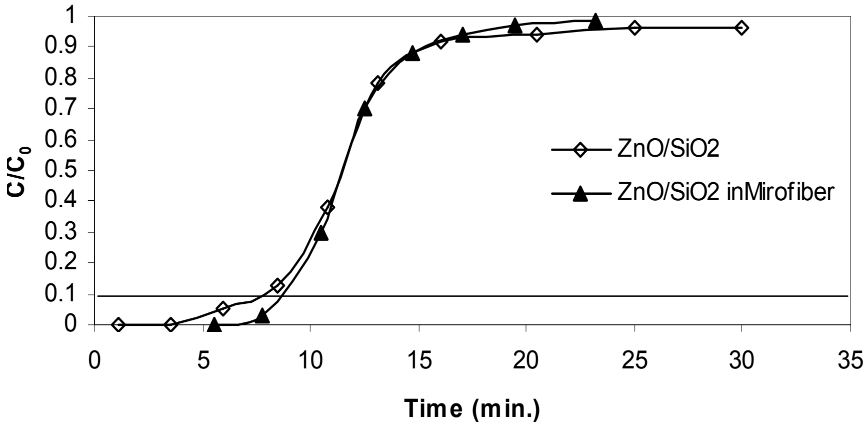


Figure 5. Comparison between Glass Fiber Entrapped (GFE) ZnO/SiO_2 and untrapped ZnO/SiO_2 sorbent

Pressure Drop. The pressure drop values of different beds were measured and test result is shown in Figure 6.

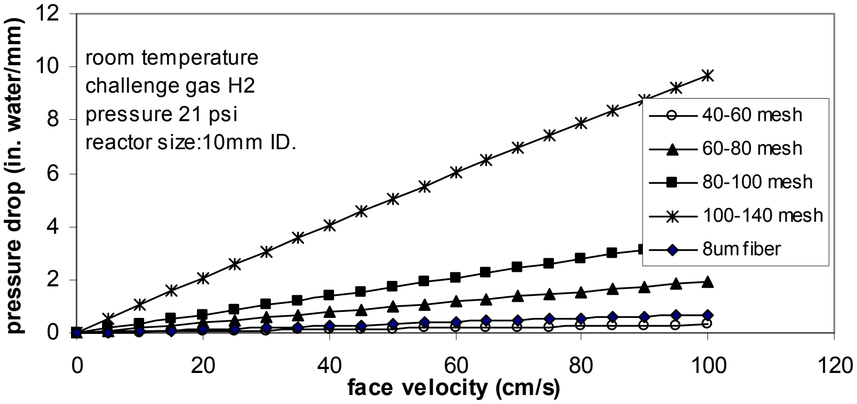


Figure 6. Pressure Drop for different beds

It is clear that with the increase of particulate size the pressure drop decrease. While, even the particle used in glass fiber entrapped media is 100-200 μm (75-140 mesh), its pressure drop is far lower than that of un-entrapped particulates with larger size, i.e. 80-100mesh and 60-80 mesh, and it is very close to that of 40-60 mesh extraduates. The reason behind this is that more than 50 vol % of the glass fiber entrapped sorbent is void.

From the discussion above, it is now known that the glass fiber entrapped media offers an integrity solution to improving external mass transfer, lowering pressure for small particulate and a stable matrix for multi-cycle applications

Figure Extended Application Area. Based the same design approach, microfibrous entrapped sorbents are able to find application in some similar area. It has find application at room temperature as final fuel protector, the last protection before the clean H_2 coming to the PEMFC. Figure is the performance of designed sorbents. Another proposed area is liquid phase desulfurization. Supported Zn and other metal oxide based the sorbents. Based on the enhanced the mass transfer, it is hoped to improve the sulfur capacity of current desulfurization sorbents for liquid fuels.

References

1. McCreedy, T. Trends Anal. Chem., 2000, 19, 396.
2. Srinivasan, S.; Hsing, I.M.; Berger, P.E.; Jensen, K.F.; Firebaugh, S.L.; Schmit, M.A.; Harrold, M.P.; Lerou, J.J.; Ryley, J.F. AIChE J., 1997, 43, 3059.
3. Watanabe, K.; Sakairi, M.; Takahashi, H.; Takahiro, K.; Nagata, S.; Hirai, S. J. Electrochem. Soc., 2001, 148, B473.
4. Wu, X.; Weng, D.; Xu, L.; Li, H. Surf. Coat. Technol., 2001, 145, 226.
5. Tatarchuk, B. J.; Rose, M. F.; Krishnagopalan, A.; Zabasajja, J.N.; Kohler, D. US Patent 5,304,330, 1994; US Patent 5,080,963, 1992.
6. Overbeek, R. A.; Khonsari, A. M.; Chang, Y.-F.; Murrell, L. L.; Tatarchuk, B. J.; Meffert, M. W. US Patent 6,231,792, 2001.
7. Tatarchuk, B. J. US Patent 5,096,663, 1992; US Patent 5,102,745, 1992.
8. Cahela D. R.; Tatarchuk B. J. Catal. Today, 2001, 69, 33-39.
9. Marrion, C. J.; Cahela, D. R.; Ahn, S.; Tatarchuk, B. J. J. Power Sources 1994, 47, 297-302.

10. Kohler, D. A.; Zabasajja, J. N.; Krishnagopalan, A.; Tatarchuk, B. J. J. Electrochem. Soc. 1990, 137(1), 136-141.

11. Ahn, S.; Tatarchuk, B. J. J. Appl. Electrochem. 1997, 27, 9-17.

12. Meffert; M. W. Ph.D. thesis, Auburn University, Auburn, AL, 1998.

13. Harris, D. K.; Cahela, D. R.; Tatarchuk, B. J. Composites, Part A: Applied Science and Manufacturing 2001, 32A(8), 1117-1126.

14. Lu, Yong; Tatarchuk, B. J. 226th ACS National Meeting, New York, NY, Sept. 7-11, 2003, CATL-042.

15. Lu, Yong; Tatarchuk, B. J. AIChE 2003 National meeting, San Francisco, CA, November 16-21, 2003, 331b.

16. Lu, Yong, Chang, B.-K., Yang, H.Y. Tatarchuk, Bruce J., ASM International, Columbus, OH, October 19, 2004 - 10:30 AM FUEL 4.5