Novel-Doped Zinc Oxide Sorbents for Low Temperature Regenerable Desulfurization Applications

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Eight metal oxide sorbents including transition metal doped ZnO/SiO_2 sorbents and ZnO/SiO_2 were prepared by incipient wetness impregnation for regenerable desulfurization applications at low temperatures (i.e. room temperature). Among them, copper-doped sorbent (Cu-ZnO/SiO_2) demonstrated the highest saturation sulfur capacity of 0.213 g sulfur/g ZnO (54% of the theoretical capacity), which is twice that of ZnO/SiO_2 sorbent. Compared with ZnO/SiO_2, Cu-ZnO/SiO_2 demonstrated superior desulfurization performance in a wide temperature range of 20–400°C. Due to the use of porous SiO_2 support, Cu-ZnO/SiO_2 is highly regenerable. It can be easily regenerated in air at low temperatures, ca. 300–550°C, which are much lower than the typical regeneration temperatures of commercial ZnO sorbents. Cu-ZnO/SiO_2 maintained its sulfur capacity during 10 cycles of regeneration/sulfidation. © 2010 American Institute of Chemical Engineers *AIChE J,* 56: 2898–2904, 2010
Keywords: desulfurization, breakthrough curve, sorbent, zinc oxide, low temperature

Introduction

In logistic fuel cell power systems, precious metals are widely used as catalysts in fuel processing units, such as water gas shift (WGS) and CO preferential oxidation, to produce high purity hydrogen. They are also used as electrode materials in fuel cells. As a result, these systems usually have low sulfur tolerance, i.e. 0.1 part per million by volume (ppmv) total sulfur for Proton Exchange Membrane Fuel Cells (PEMFC) and some tubular Solid Oxide Fuel Cell (SOFC). Sulfur content in fuels varies from ~ 10 parts per million by weight (ppmw) in ultralow commercial gasoline/diesel to several thousand ppmw in military fuels such as JP5 and JP8. After reforming, logistic fuels are converted to reformates, which consists of H_2, CO, CO_2, water and C1–C4 hydrocarbons, and sulfur species mainly hydrogen sulfide (H_2S). Sulfur concentration in reformates is typically in the range of several ppmv to several hundred ppmv. Therefore efficient sulfur removal is required for these fuel cell applications.

Metal oxide based sorbents, such as zinc oxide (ZnO), iron oxide (Fe_2O_3), and copper oxide (CuO) have been developed to remove sulfur compounds from reformates.[1] ZnO has been widely used to remove H_2S at moderate low temperatures (300–500°C) because of its high equilibrium constant and high sulfur capacity in this temperature range. However, it is difficult for ZnO sorbents, especially regenerated sorbents, to remove H_2S below 0.1 ppmv due to the equilibrium limitation at these temperatures in the presence of high concentration water. For example, the equilibrium H_2S concentration was 0.6 ppmv in the presence of 30 vol % water at 400°C. Moreover, in the presence of CO and CO_2, sulfur removal becomes even less efficient due to the formation of carbonyl sulfide (COS), which is difficult to be captured by ZnO sorbents.[2,3] In these cases, a secondary

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desulfurization unit is required to operate at the stack temperatures of PEMFC (ca. room temperature to 100°C) to remove sulfur residuals from reformates leaving the primary desulfurization unit down to the sulfur threshold of PEMFC (ca. 0.1 ppmv). In addition, during the cold startup or transition operations of a fuel cell system, the desulfurization reactor experiences a temperature change from room temperature to several hundred Celsius. This also requires the sulfur sorbents in the reactor performs well at low temperatures. However, the reactions between sulfur species and metal oxide sorbents at room temperature are confined only in the outer layer of the sorbent particles[4]; therefore the sulfur capacity at low temperatures is much lower than that at higher temperatures. As a result, the metal oxide based sorbents need improvements for low temperature applications.

ZnO and CuO are the two most favored regenerable sorbents. ZnO has a very high theoretical sulfur capacity; CuO has extremely high equilibrium sulfidation constant, which can allow extremely low equilibrium H_2S concentrations even at high steam content and high temperatures.[5] The mixed metal oxide sorbents of ZnO and CuO have been studied extensively for regenerable high temperature desulfurization applications.[6–10] However, Cu-ZnO sorbents also suffer from limitations such as oxide reduction,[1,5] loss in surface area[1,5] and porosity[1,9] and subsequently degrading in their desulfurization performance during the cyclic sulfidation/regeneration tests.[9] At low temperatures (i.e. room temperature), fresh Cu-ZnO sorbents also showed promising performance. Baird et al. found that Cu and Co dopants reduced the ZnO grain size and enhanced the surface area, thus improve the sulfur capacity at room temperature[4]; Xue et al.[11] found ZnO doped with Cu, Mn, and Co demonstrated significant improvement in reactivity. However, applications of Cu-ZnO for regenerable low temperature desulfurization have not been reported yet. In this study, active sorbent compounds (ca. ZnO, and CuO) were loaded onto an inert sorbent support (SiO_2) to improve sorbent regenerability. These support can hold the sorbent grains in their micropores and prevent increase in the grain size and agglomeration,[5,12,13] maintain high sorbent porosity and high surface area,[14] and perhaps stabilize the active metal oxide from metal reduction in the presence of H_2 and CO.[5,14]

The Center for Microfibrous Materials Manufacturing (CM^3) at Auburn University has developed several ZnO based sorbents for gas phase desulfurization at various temperatures. Ni fiber entrapped ZnO/ACP[15] prepared by incipient wetness impregnation demonstrated three-fold longer breakthrough times for H_2S compared to packed beds of several commercial carbon-based sorbents with double the bed thickness. However, this sorbent was not regenerable because of the use of activated carbon.[15] For regenerable desulfurization applications at moderate low temperatures (300–500°C), SiO_2 was found to be a better support than Al_2O_3.[16] Due to the use of highly porous supports, ZnO supported on SiO_2 (ZnO/SiO_2) demonstrated a high sulfur capacity and almost complete ZnO utilization indicating minimized intraparticle mass transfer resistance.[17] In this study, eight sorbents of transition metal doped ZnO supported on SiO_2 particles were evaluated for H_2S removal under various desulfurization conditions.

Experimental

ZnO/SiO_2 developed at CM^3 for PEMFC applications contains 17 wt % of ZnO supported on highly porous and high surface area SiO_2 particles (Selecto Silica gel, Fisher Scientific), which have an average pore size of 60 Å, a pore volume of 1 cc/g, a surface area of 600 m^2/g and a particle size of 100–200 μm. ZnO/SiO_2 was prepared by incipient-wetness impregnation at room temperature using $Zn(NO_3)_2$ (Purum p.a. crystallized, $>$ 99%, Sigma-Aldrich) aqueous solutions as precursor. Following impregnation, the preformed sorbent was dried and calcined. The sorbents had a high surface area of 250 m^2/g and a porosity of 63%. The detailed sorbent preparation procedure was described by Lu et al.[15] Transition metal doped ZnO/SiO_2 sorbents were prepared by the similar procedure using mixed metal nitrates as oxide precursors. The molar ratio of Zn to dopant metal(s) is 19:1, therefore, the general formula of doped ZnO/SiO_2 sorbents is $M_{0.05}Zn_{0.95}O/SiO_2$, where M is the dopant metal. A commercial ZnO sorbent containing 90% of ZnO with a porosity of 53% and a surface area of 25 m^2/g was used for comparison purpose. It was crushed and sifted to the size of 105–250 μm before use.

If not otherwise stated, all gases were ultra-high purity (UHP) gases purchased from Airgas South (Opelika, AL). The sources of H_2S is 2 vol % H_2S-H_2 mixture (Airgas South). Challenge gases containing 8000 ppmv H_2S were prepared by mixing 2 vol % H_2S-H_2 with other gases such as CO, CO_2, H_2, He, and steam. Although this sulfur concentration is higher than these present in typical fuel cell applications, it is a suitable concentration for the preliminary sorbent screening using GC-TCD (Varian GC 3800) as sulfur detector. Water was introduced to the gas stream by passing H_2/He/CO through a vaporizer with a temperature controller. The distilled water in the vaporizer was preheated to 100°C to remove oxygen. The steam was carried in a 1/8″ stainless steel tubing wrapped in a heating tape. The steam-containing gas stream was mixed with the H_2S-containing stream before entering the reactor. All experiments were carried out in a quartz tube with an inner diameter of 1 cm. Breakthrough concentrations was arbitrarily defined at 1% of inlet sulfur concentrations, and breakthrough times were read from breakthrough curves.

Results and Discussion

Desulfurization evaluation at room temperature

Eight metal oxide sorbents including transition metal doped ZnO/SiO_2 sorbents and ZnO/SiO_2 were evaluated for H_2S removal at room temperature (20°C). In each evaluation, a packed bed containing 1 g of sorbent (bed thickness: 2 cm) was tested with 2 vol % H_2S-H_2 at a face velocity of 3 cm/s. The breakthrough curves and calculated capacities are shown in Figure 1 and Table 1.

Most doped ZnO/SiO_2 sorbents demonstrated improvement in both saturation capacity and breakthrough capacity. Among all the doped sorbents, copper doped ZnO/SiO_2 sorbents (Cu-ZnO/SiO_2) showed the highest saturation capacity and breakthrough capacity of 213 mg sulfur/g ZnO and 163 mg sulfur/g ZnO, respectively, which were twice these of ZnO/SiO_2 at 113 mg sulfur/g ZnO and 81 mg sulfur/g ZnO, respectively. The capacity of silver-doped ZnO/SiO_2 (Ag-ZnO/SiO_2) and cerium doped ZnO/SiO_2 (Ce-ZnO/SiO_2) ranked second and third at room temperature. Other metal dopants, such as Ni, Co, Mn, which have oxide states of 2+

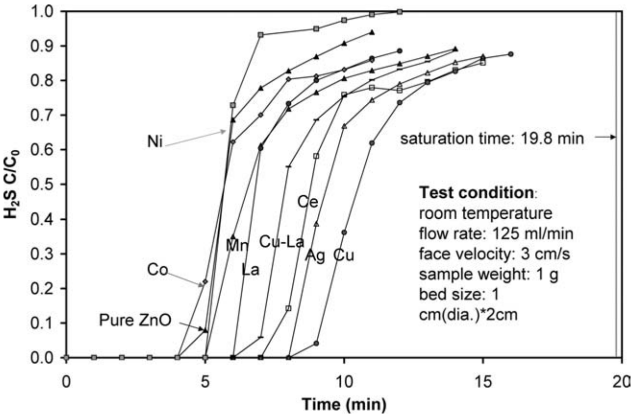

Figure 1. Breakthrough curves of transition metal doped ZnO sorbents tested with 2 vol % H_2S-H_2 at room temperature.

or 3+, did not significantly improved the sulfur capacity. It was also reported that the addition of Al^{3+} and Fe^{3+} did not improve the sulfur capacity.[11,18] A possible explanation is that the addition of copper or silver with 1+ oxide state may introduce more oxygen vacancies in ZnO lattice and therefore enhance the oxygen and sulfur mobility in the oxide lattice.

Effects of water, CO, and CO_2 at 20°C

Water, CO and CO_2 have strong effects on the desulfurization performance even at low temperatures.[2,3] In this section, the effects of water, CO, and CO_2 at room temperature (20°C) were investigated. To determined the effects of water, 3 vol % water was introduced to the packed bed by passing H_2 (60 ml/min) through a vaporizer at 30°C. For the effects of CO and CO_2, 30 vol % CO/CO_2 (30 ml/min) was added to the flow consisting of 40 vol % H_2S-H_2 (40 ml/min) and 30 vol % H_2 (30 ml/min). In each test, the total gas flow rate was maintained at 100 ml/min and the H_2S concentration was maintained at 8000 ppmv. The breakthrough curves are shown in Figure 2. The breakthrough curves tested with H_2S-H_2 is also shown for comparison. Figure 2 suggests H_2S breakthrough took place at almost the same time during all the tests. This suggests that water, CO, and CO_2 have no significant effects on desulfurization performance at room temperature. Moreover, no COS formation was detected in the presence of CO and CO_2. Water did not show any hindering effect on desulfurization performance either.

Temperature effects

Desulfurization temperature has a strong influence on desulfurization performance. The breakthrough curves of Cu-ZnO/SiO_2 and ZnO/SiO_2 at different temperatures are shown in Figures 3 and 4, and their breakthrough capacities at these temperatures were calculated and are shown in Figure 5.

Table 1. Sulfur Capacities of Doped ZnO/SiO_2 Sorbents

	Saturation Capacity*		Breakthrough Capacity‡
Dopant	(g S/g ZnO)	% of theor.†	(g S/g ZnO)
Cu_xO ($1 < x < 2$)	0.213	54	0.163
Ag_2O	0.189	48	0.163
Ce	0.177	45	0.142
CuO-La_2O_3	0.161	41	0.122
La_2O_3	0.140	35	0.122
MnO_x ($1 < x < 1.5$)	0.132	33	0.102
NiO	0.113	29	0.102
CoO_x ($1 < x < 1.5$)	0.113	29	0.081
ZnO	0.113	29	0.081

*Sulfur capacity calculated base on $t_{1/2}$ concept. The sorbents are assumed as pure ZnO.

†% of theor. equals to capacity/theoretical saturation capacity ×100%.

‡Adiabatic temperature rise at the test condition was calculated to be 38°C.

A noted phenomenon in the shape of breakthrough curves is the step curb. This was not observed in all ZnO/SiO_2 tests. It suggests new reaction mechanisms such as CuO reduction and grain-cracking were involved during desulfurization at low temperatures. The breakthrough time/saturation time versus temperature ($t_b/t_s\sim$ T) plot of two sorbents (Figure 5) shared some characteristics in common. At low temperatures (from room temperature to 150°C), a slight decrease in capacity was observed for both sorbents as the temperature increased, then the capacity increased with temperature. Both sorbents reached almost 100% ZnO utilization at 400°C. However, the significant differences in the two $t_b/t_s\sim$ T plots occur in the temperature range of 20–250°C. In this temperature range, the breakthrough capacity (time) of Cu-ZnO/SiO_2 is two to three times larger than that of ZnO/SiO_2. Moreover, Cu-ZnO/SiO_2 started to response the temperature changes at 150°C and ZnO/SiO_2 at 200°C. Thus the $t_b/t_s\sim$ T plot of ZnO is much sharper than that of Cu-ZnO/SiO_2. After the desulfurization temperature reached 300°C, the performance of two sorbents reached another stable stage, and their desulfurization performance became less distinct. These results suggest copper dopant significantly improves the low temperature desulfurization performance of ZnO, and enables Cu-ZnO/SiO_2 to work well in a wide temperature window, ca. from room temperature to 400°C.

Regeneration performance

Single Cycle Test Desulfurization sorbents are required to be regenerable for multiple cycles to reduce the operational cost. Therefore, the regenerability of Cu-ZnO/SiO_2,

Table 2. Saturation Capacities of Commercial ZnO Sorbent, ZnO/SiO_2 and Cu-ZnO/SiO_2 After First Regeneration at 550°C

	Saturation Capacity					
	(mg S/g ZnO)		(mg S/g sorbent)		(mg S/cm^3 bed)	
Sorbent	Fresh	Regn.	Fresh	Regn.	Fresh	Regn.
ZnO	37.8	4.73	34.1	4.26	37.5	4.68
ZnO/SiO_2	113	93.1	19.2	14.9	11.5	8.94
Cu-ZnO/SiO_2	213	146	36.2	23.4	21.7	14.0

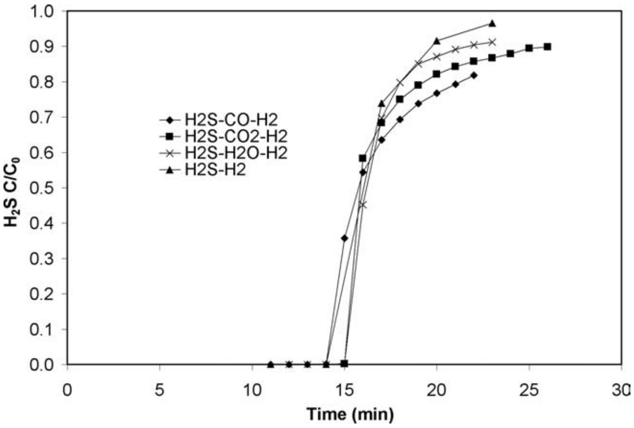

Figure 2. Breakthrough curves of Cu-ZnO/SiO_2 tested at room temperature in the presence of water, CO or CO_2.

In each experiment, 0.5 g of Cu-ZnO/SiO_2 was loaded and tested with 8000 ppmv H_2S at a face velocity of 2.3 cm/s.

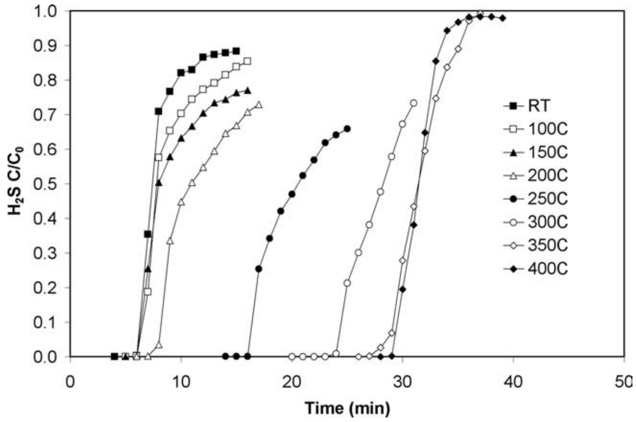

Figure 4. Breakthrough capacity of ZnO/SiO_2 at various desulfurization temperatures.

In each experiment 0.5 g of ZnO/SiO_2 was loaded and tested with 8000 ppmv H_2S at a flow rate of 100 cm^3/min STP.

ZnO/SiO_2, and the commercial ZnO sorbents was examined and compared in this section. The regenerated sorbents were evaluated for desulfurization at room temperature and their breakthrough curves are shown in Figures 6–8, respectively. Their sulfur capacities before and after the first regeneration are summarized in Table 2. All sorbents were only regenerated once the desulfurization test. Figure 6 suggests that the fresh commercial ZnO sorbent (0.5 g) prepared by crushing ZnO extrudate is an outstanding sorbent even at room temperature; it provided a breakthrough time of 14 min, higher than the breakthrough time of Cu-ZnO/SiO_2 sorbent. It, however, yielded a breakthrough time of 1 min with a corresponding capacity of 2.3 mg sulfur/g sorbent after regeneration. Its saturation sulfur capacity dropped to only 4 mg sulfur/g sorbent. These results indicate that the commercial ZnO was barely regenerated after 1-h regeneration at 550°C. It needs a higher regeneration temperature and a longer regeneration time.

Compared with the commercial ZnO sorbent, both supported sorbents, ZnO/SiO_2, and Cu-ZnO/SiO_2, demonstrated good regenerability as shown in Figures 7 and 8. Their sulfur capacity can be fully recovered after regeneration at 550°C for 1 h. At this regeneration condition, the regenerated Cu-ZnO/SiO_2 demonstrated a saturation capacity of 25 mg sulfur/g sorbent, which is six-times higher than the commercial sorbent. At low regeneration temperatures (i.e. 200°C), the capacity of both ZnO/SiO_2 and Cu-ZnO/SiO_2 cannot be fully recovered, but retained a much longer breakthrough time (capacity) than the commercial as described above. The comparison between the supported sorbents (ca. ZnO/SiO_2, Cu-ZnO/SiO_2) and the commercial ZnO confirms that the highly porous support structure with large surface area is critical to maintain good regenerability.

The regeneration characteristics of two supported sorbents are shown in Figure 9. As shown in Figure 9, the two regenerated sorbents yielded the same breakthrough time after regeneration at of 200°C. The breakthrough times of both regenerated ZnO/SiO_2 and Cu-ZnO/SiO_2 sorbents increased as the regeneration temperature increased, though the breakthrough time of the regenerated ZnO/SiO_2 is rather stable at

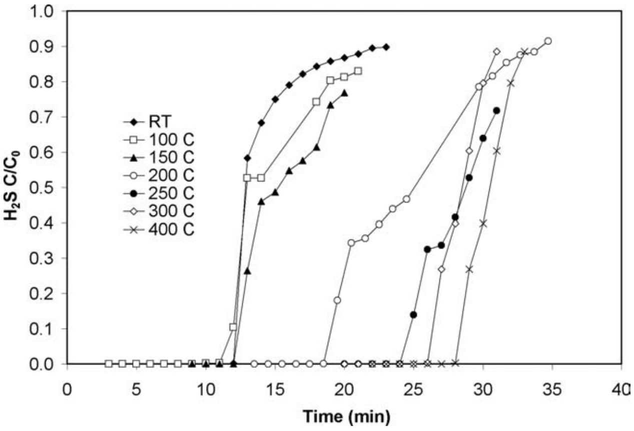

Figure 3. Breakthrough curves of Cu-ZnO at various desulfurization temperatures.

In each experiment 0.5 g of Cu-ZnO/SiO_2 was loaded and tested with 8000 ppmv H_2S at a face velocity of 2.3 cm/s.

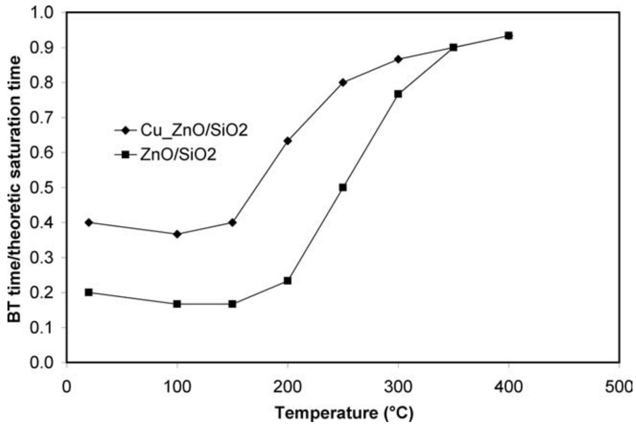

Figure 5. Breakthrough time/theoretic saturation time of ZnO/SiO_2 and Cu-ZnO/SiO_2 at various desulfurization temperatures.

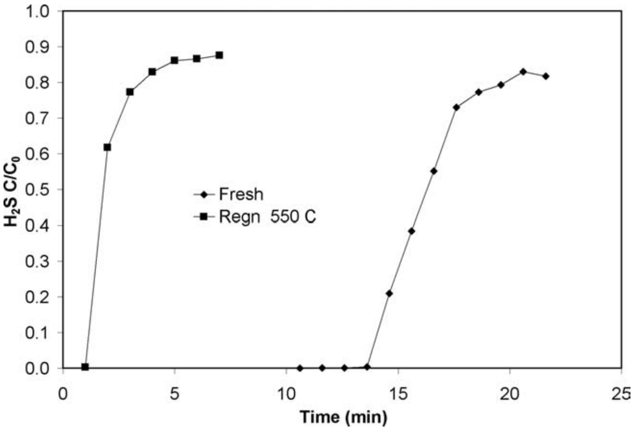

Figure 6. Breakthrough curves of fresh and regenerated commercial ZnO particles (105–250 μm, 25 m^2/g).

0.5 g of such sorbent was tested at room temperature (20°C) with 8000 ppmv H_2S at a face velocity of 2.3 cm/s.

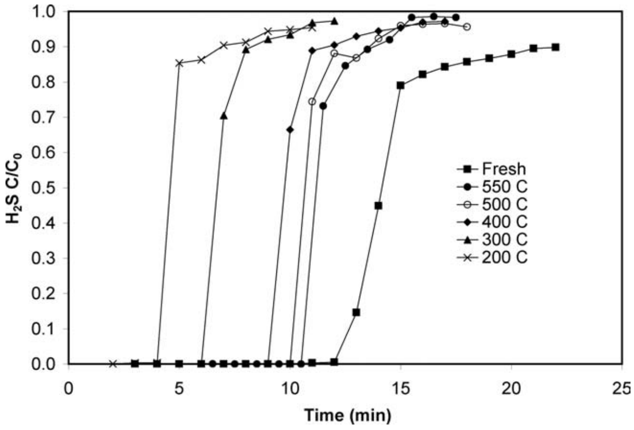

Figure 8. Breakthrough curves of regenerated Cu-ZnO/SiO_2 (0.5 g) at various regeneration temperatures.

Sorbents were tested at room temperature (20°C) with 8000 ppmv H_2S at a face velocity of 2.3 cm/s.

a low level. As ZnO/SiO_2 can be fully regenerated at high temperatures (ca. 550°C),[19] its low breakthrough time after regenerated at 550°C suggests that its breakthrough time (capacity) is determined by slow solid diffusion, which only allows the surface metal oxide accessible to H_2S.[4] Cu-ZnO/SiO_2 demonstrated longer breakthrough times than ZnO/SiO_2 especially after they both were regenerated at high temperatures. This result implies that copper dopant facilitate both regeneration and desulfurization: it makes more spent sorbent (ZnS) accessible to oxygen during regeneration and more metal oxide accessible to H_2S during desulfurization.

Multiple Cycle Tests In this section, Cu-ZnO/SiO_2 sorbent is examined for multiple cycles of desulfurization and regeneration. Cu-ZnO/SiO_2 (1 g) was evaluated for H_2S removal multiple cycles of desulfurization and regeneration, and the breakthrough curves as shown in Figure 10. All the desulfurization tests were carried out at the same conditions. Regeneration was carried out at various conditions. Regenerations 2 and 3 were regenerated at 400°C for 1 h, and Regeneration 4 at 400°C for 3 h. The rest regenerations were carried out at 550°C for 1 h. Breakthrough patterns of Cu-ZnO/SiO_2 after 10 cycles and fresh Cu-ZnO/SiO_2 are almost the same as shown in Figure 10. Figure 10 indicates that Cu-ZnO/SiO_2 is highly regenerable for multiple cyclic applications, and the best regeneration condition is at 550°C for 1 h.

Another series of cyclic tests of Cu-ZnO/SiO_2 were carried out, in which the spent Cu-ZnO/SiO_2 were regenerated at 300°C for 1 h, as shown in Figure 11. The degradation in the sorbent capacity was observed during first few desulfurization/regeneration cycles, and the breakthrough time (capacity) finally stabilized around 6 min, which is 20% of theoretical saturation time under the test conditions. As shown in Figures 10 and 11, the sorbent can be regenerated

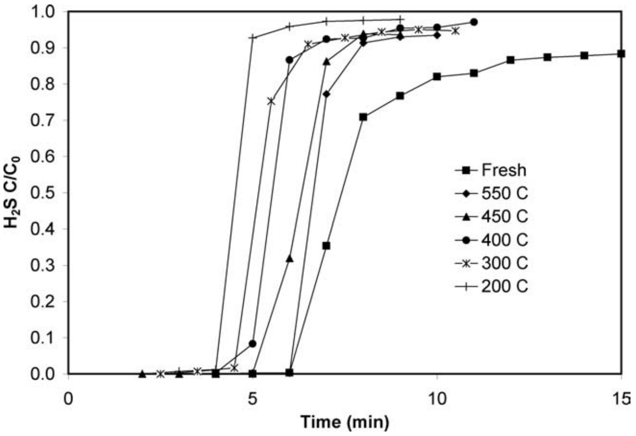

Figure 7. Breakthrough curves of regenerated ZnO/SiO_2 (0.5 g) at various regeneration temperatures.

Sorbents were tested at room temperature (20°C) with 8000 ppmv H_2S at a face velocity of 2.3 cm/s.

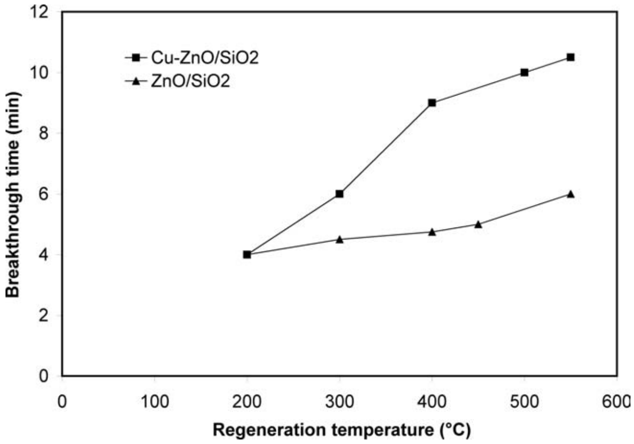

Figure 9. Comparison of regeneration characteristics of ZnO/SiO_2 and Cu-ZnO/SiO_2 sorbents.

Sorbents were tested at room temperature (20°C). Recovery ratio is defined as the breakthrough time of regenerated sorbent/breakthrough time of the fresh sorbent.

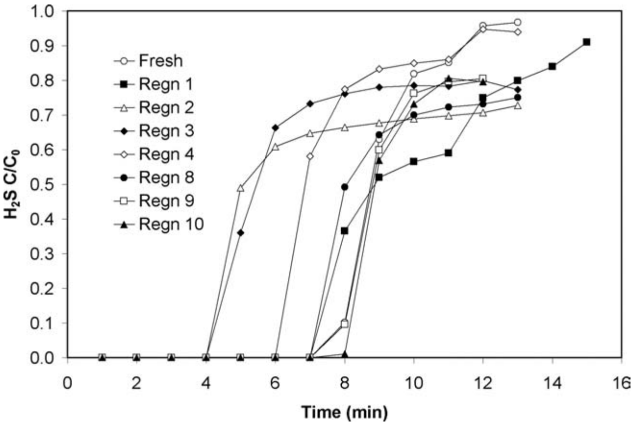

Figure 10. Breakthrough curves of multiple adsorption/desulfurization cycle tests of Cu-ZnO/SiO$_2$.

Cu-ZnO/SiO$_2$ sorbent (1 g) was tested at room temperature with 2 vol % H$_2$S-H$_2$ at a face velocity of 3 cm/s at room temperature.

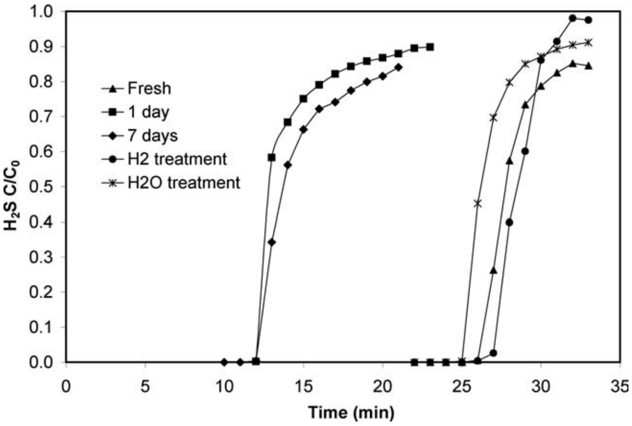

Figure 12. Aging effect of Cu-ZnO sorbent.

Cu-ZnO/SiO$_2$ sorbent (0.5 g) was tested at room temperature with 2 vol % H$_2$S-H$_2$ at face velocity of 2.3 cm/s.

at a low temperature, however, a long regeneration time are required to completely recover its sulfur capacity.

Aging effect

Some catalysts and sorbents have shelf life issues. After kept in containers, the catalytic activities or capacities drop as time last. Cu-ZnO/SiO$_2$ sorbent has been examined after 1 month and even 1 year and still provided stable performance as described before. This indicated that Cu-ZnO/SiO$_2$ does not have shelf life issues: However, the outstanding desulfurization performance of Cu-ZnO/SiO$_2$ sorbent as shown in earlier sections is not the best performance that has been observed during this study. As shown in Figure 12, the ''fresh'' sorbent, which in this section means the sorbent right after sorbent preparation rather than the sorbent after aging for 1–3 days, demonstrated a long breakthrough time (26 min) and a high sulfur capacity (355 mg sulfur/g ZnO or 59 mg sulfur/g sorbent). The ZnO utilization of this ''fresh'' sorbent was about 90%, which is much higher than the ZnO utilization of 50% in the earlier sections. The presence of H$_2$ slightly benefited the H$_2$S removal, and H$_2$O had a slight negative effect on desulfurization using the ''fresh'' sorbent. However, this high sulfur capacity was not su, even the sorbent particles were kept well in sealed sample containers. This high capacity is also not regenerable. The aging effects on the Cu-ZnO/SiO$_2$ are not clear yet. Further surface science and solid physics is being conducted to reveal the secrets and perhaps provide a solution to maintain this high sulfur capacity.

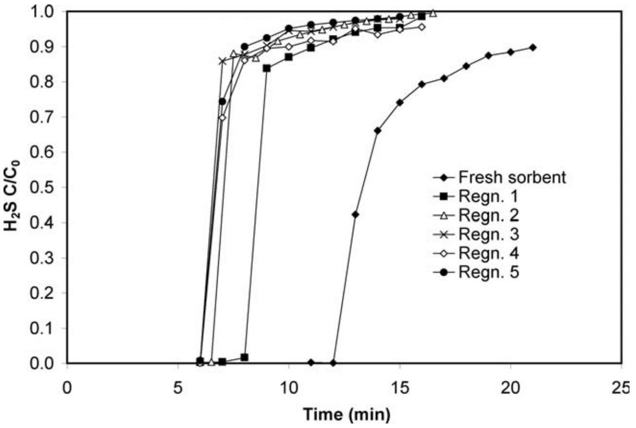

Figure 11. Breakthrough curves of multiple adsorption/desulfurization cycle tests.

Regenerated at 300°C for 1 h. Cu-ZnO/SiO$_2$ sorbent (0.5 g) was tested at room temperature with 8000 ppmv H$_2$S-H$_2$ at face velocity of 2.3 cm/s at room temperature.

Summary

Low temperature desulfurization performance is necessary to protect fuel cell from sulfur poisoning during cold-start up and transition operations. Copper doped ZnO/SiO$_2$ is a promising regenerable sorbent at low temperatures. It demonstrated a high sulfur capacity of 25 mg sulfur/g sorbent. Further sorbent optimization is necessary to achieve higher sulfur capacities. This can be done by using support particles with higher pore volume and high surface area, and varying the copper dopant level and metal oxide loading. Besides its outstanding low temperature desulfurization performance, Cu-ZnO/SiO$_2$ also demonstrated the superior desulfurization performance at higher temperatures (ca. 250–400°C). Therefore, Cu-ZnO/SiO$_2$ has a wide desulfurization temperature window from room temperature to 400°C. Moreover, the sorbent are highly regenerable. Its sulfur capacity can be fully recovered after regeneration at 550°C for 1 h. No capacity loss was observed during 10 desulfurization-regeneration cycles. Due to the use of copper dopant, this sorbent requires a lower regeneration temperature than ZnO/SiO$_2$ sorbent does. As a result, Cu-ZnO/SiO$_2$ is a promising regenerable sorbent for low temperature applications, such as inline gas filters at stack temperatures. Cu-ZnO/SiO$_2$ can also be used as a protective layer in the desulfurizer of logistic fuel system during transitional operations such as system startup/shutdown.

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