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Regenerable Sorbent for Natural Gas Desulfurization

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Sulfur-containing odorants are normally added to propane and natural gas supplies to facilitate leak detection. The sulfur in these fuels can poison the catalysts used in fuel-cell fuel-processing systems, thereby inactivating the surfaces of the fuel-cell anodes and resulting in degraded power generation performance. The sulfur content of natural gas or any hydrocarbon fuel needs to be reduced to very low levels to ensure long-term stable electrochemical performance for both high- and low-temperature fuel cells. This paper presents the development and test results of a new physical adsorbent for natural gas desulfurization. The sorbent effectively removes all sulfur-bearing compounds at ambient temperature with very high capacity. The new sorbent can also be fully regenerated by the temperature swing. In a series of tests, the sulfur adsorption capacity of the new material is compared with other commercially available and specially prepared sorbents. The results of the comparison tests are also summarized in this paper.

Keywords dimethyl sulfide (DMS), fuel cells, hydrogen sulfide (H_2S), mercaptans, natural gas desulfurization, odorants, physical adsorption, regeneration, solid oxide fuel cell (SOFC), sorbent, SulfaTrap, sulfur, tetrahydrothiophene (THT), *tert*-butyl mercaptan (TBM)

1. Introduction

Advances in fuel-cell technologies have the potential to revolutionize the way the power is produced and distributed. Distributed power generation using fuel cells has the potential of becoming a viable alternative to buying power from a central grid. However, some technical and economical obstacles still limit the commercial potential of these technologies. One issue is the ability to provide an ample supply of low-sulfur fuel for the fuel cells in a cost-effective manner.

Pipeline natural gas is the primary fuel of choice for distributed fuel cell-based power-generation systems due to its abundant supply and well-developed infrastructure. Natural gas is composed of low boiling hydrocarbons (mostly methane) and much smaller amounts of nitrogen, carbon dioxide, water vapor, and sulfur compounds. Although processing of natural gas to remove sulfur is usually carried out close to the point of extraction (e.g., amine absorption), the processing leaves residual hydrogen sulfide (H_2S) as a contaminant at low concentrations (typically 1-2 mg/m^3). In addition to the naturally occurring H_2S, pipeline natural gas also contains other organic sulfur species that have been intentionally added as odorants. Because natural gas often has no distinct odor, for safety reasons pipeline companies are required by law to odorize natural gas as it enters the transmission lines or local distribution facilities. These odorants allows olfactory detection of minute leaks in the gas lines and hence minimize the potential for explosions and fire hazards. Common odorants include mercaptans (e.g., ethyl, isopropyl, and tertiary butyl), thiols (e.g., tetrahydrothiophene), and sulfides (e.g., dimethyl, diethyl). The concentration of sulfur in odorized natural gas is normally a couple of ppm on a volume basis (ppmv) but can be as high as 15-20 ppmv.

Fuel cells require clean feed streams with very low levels of sulfur and other impurities. Sulfur impurities can reduce the effectiveness of fuel-processor catalysts and can poison the anode catalysts of both high- and low-temperature fuel cells. The problem is most severe in polymer electrolyte fuel cells (PEMFC), both because they operate at low temperature and their Pt group catalysts are susceptible to sulfur poisoning. Uribe and Zawodzinski (Ref 1) assessed the effect of fuel impurities on PEMFC performance using a Pt/C electrode and reported severe deterioration of fuel-cell performance in the presence of sulfur. Taking account of the dilution in the fuel processor, a feed containing 5 ppmv of organic sulfur would lead to ~1-2 ppmv of H_2S in the fuel cell when no sulfur is removed in the fuel processor. In the work of De Wild (Ref 2), it was shown that the presence of 2 ppmv H_2S in the fuel drastically decreases the performance of the 1:1 Pt/Ru containing anode catalyst. The poisoning effects of sulfur are irreversible. Regardless of initial H_2S concentration, subsequent replacement of the contaminated fuel stream with pure H_2 does not allow full recovery. Sulfur also degrades the performance of the high-temperature solid oxide fuel cells (SOFC). A recent study by Siemens Westinghouse Power Corporation (Ref 3) showed the performance of their SOFC drops about 15% in the presence of 1 ppmv sulfur. The cell voltage increases, and performance is recovered once the sulfur flow is stopped. Although this poisoning effect is reversible in SOFCs, long-term stable electrochemical performance of both high- and low-temperature fuel cells requires that the sulfur concentration to be reduced to sub-ppmv levels.

In high-volume natural gas processing, the most cost-effective sulfur removal is carried out with a two-step process consisting of hydrodesulfurization of organic sulfur species to H_2S, and subsequent, H_2S removal with a sorbent. This method is not economically practical in small-scale residential fuel-cell units. Due to cost advantages related to system complexity, most developers of the small-scale fuel-cell systems have

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chosen to remove sulfur from feed gases using ambient-temperature adsorbents (most commonly, activated carbon).

Several materials have been tested for desulfurization of liquid and gaseous fuels, including a range of commercial sorbents (i.e., zeolites, activated carbon, activated alumina). These ambient temperature processes offer a great deal of simplicity compared with elevated-temperature technology. However, an important drawback of ambient temperature adsorbents is the fact that, for most sorbents, sulfur uptake capacity is low. The result is that relatively large quantities of sorbent are required. For instance, for a typical American family home, approximately 1200 m^3 of natural gas has to be desulfurized annually to power a 1 kW_e fuel-cell-based power generator. The sorbent requirement will be at least 22 L to achieve the desired level of sulfur removal with Cu-exchanged zeolite-Y based sorbents (Ref 4) and 300 L with activated C-based sorbents (Ref 3). The problem of desulfurizer bed size and cost becomes even worse when the amount of sorbent needs to last for several years. The typical homeowner is not qualified to service the equipment for safety reasons, and sorbent replacement must be carried out by a well-trained service technician.

The objective of this study is to develop a passive adsorbent for the ambient temperature desulfurization of natural gas.

2. Materials and Methods

2.1 Sorbent Preparation

As part of an extensive screening process, various sorbent formulations were prepared by TDA Research, Inc. (Wheat Ridge, CO) using different sources of active materials, inert substrates, and additives. The new formulations were first screened according to their physical properties, including porosity, surface area, crush strength of the pellet, and active material content. In the selection of proper active material and support, the material costs were also taken into consideration. The choice of substrate materials included conventional supports, and all of these materials satisfied the criteria of low-cost and high surface area (150-580 m^2/g measured by the manufacturers). Only the best formulations with acceptable physical properties were tested to determine their sulfur removal performance.

2.2 Testing Apparatus

The sorbent performance was measured in an automated test unit. In this setup, the reactor cell consists of a quartz tube that contains a frit in the middle to support the pellets. Different size reactors were used to test different sample sizes ranging from 0.5 to 20 g (Fig. 1). The reactor was inserted in a tube furnace that provided the heating needed for regenerability studies. Streams of uncontaminated natural gas and gas containing sulfur odorants were introduced to the system using electronic mass flow controllers. Certified gas cylinders were used as the source of odorants. The sulfur-contaminated gas was metered into a manifold and mixed with uncontaminated natural gas to achieve desired gas composition. A valve system allowed directing gases to a reactor bypass line for accurate analysis of the feed gas. All system components (tubes, unions, fittings, etc.) were made of quartz, Teflon, or Silcosteel (Restek Corporation, Bellefonte, PA) to minimize the sulfur holdup or interaction with system components. All testing was done near ambient pressure (135.8 kPa).

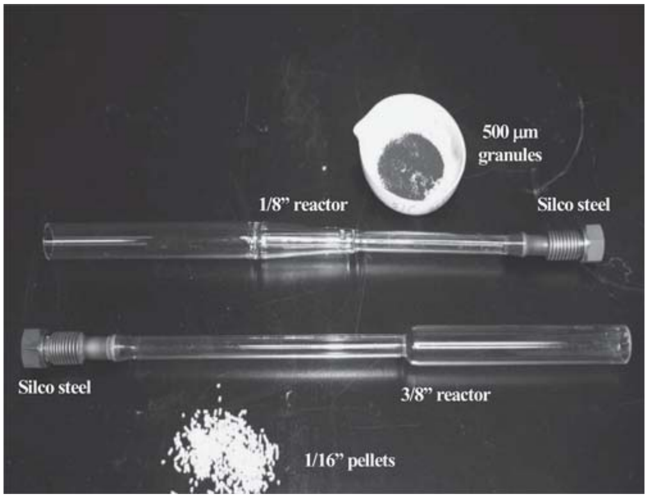

Fig. 1 Test reactors

2.3 Sulfur Analysis

A gas chromatograph equipped with a flame photoionization detector (FPD) was used for analysis of sulfur compounds. FPD is selective to sulfur species only and operates on the principle that the combustion process ionizes sulfur, which subsequently emits light at a wavelength of 393 nm. A photomultiplier tube and an optical band-pass filter allow only the sulfur light emission to be detected. For separation of the odorant species, a Restek Corp. RTX-1 capillary column was used (30 m; 0.53 mm ID with 7.0 μm film thickness). The detection limit of the gas chromatograph was 50 ppbv. Figure 2 shows the separation of the peaks for hydrogen sulfide (H_2S), dimethyl sulfide (DMS), *tert*-butyl mercaptan (TBM), and tetrahydrothiophene (THT) and their retention times (in min). The correlation between the amount of sulfur-bearing gases passed over the sorbent and the amount of sulfur accumulated in the bed allowed the effectiveness of the sorbent to be assessed.

2.4 Natural Gas Analysis

A simulated natural gas was used in these tests for simplicity and consistency. Table 1 shows the gas composition of two certified cylinders of synthetic natural gas. The composition closely simulates typical pipeline gas composition, including lower alkanes from methane to hexane. Methane is the chief constituent, and some branched hydrocarbons such as isobutane and neopentane exist at representative concentrations. The gas also contained some nitrogen and carbon dioxide. A gas chromatograph equipped with a thermal conductivity detector was used to measure the concentration of the hydrocarbon species during testing.

2.5 Test Profile

Each test started with an analysis of the feed gas (Fig. 3). Once a stable inlet odorant concentration was established, the gas flow was directed into the sorbent bed. Throughout the test, the odorant concentration coming off the reactor was continuously monitored. Most of the tests ended when the sulfur breakthrough was observed at the reactor exit (the breakthrough defined as 0.1 ppmv) and the adsorption capacity of the sorbent was calculated on a pre-breakthrough basis. In

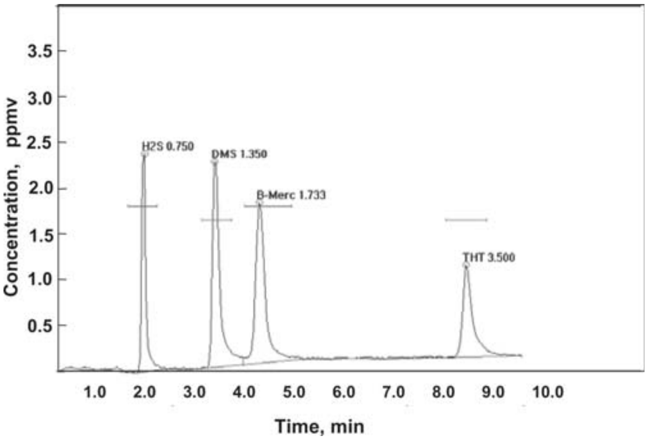

Fig. 2 Sample gas chromatogram for sulfur species

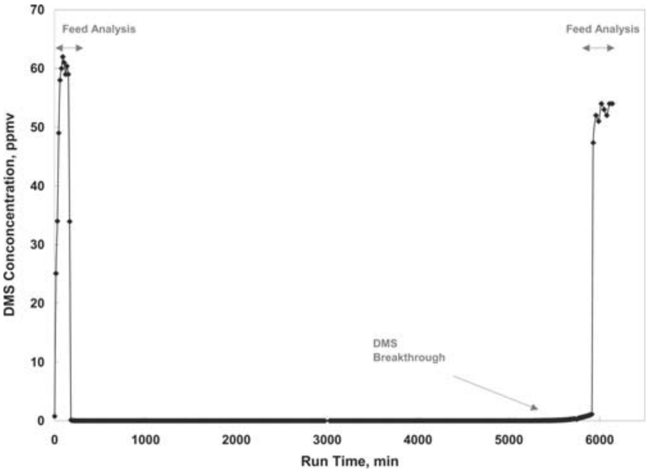

Fig. 3 Test profile from the large-scale reactor: $T = 22$ °C, $p = 50$ psig, DMS inlet = 60 ppmv, GHSV = 1,500 h^{-1}

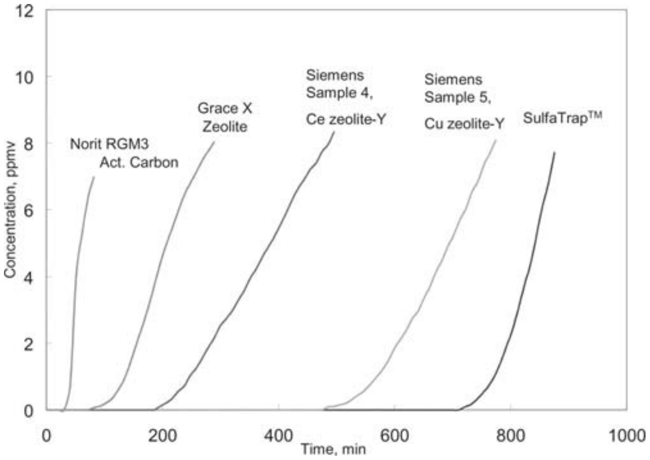

Fig. 4 Comparison of TDA's SulfaTrap sorbent with other adsorbents. All samples were tested at 60,000 h^{-1} in a natural gas mixture containing 12.3 ppmv DMS, 8.9 ppmv TBM, and 8.9 ppmv THT at 5 psig.

Table 1 Typical natural gas mixtures used during testing

	Vol.%	
Component	**Jan. 2004 sample**	**Oct. 2004 sample**
Methane	92.39	92.86
Ethane	3.42	3.31
Propane	0.56	0.60
Butane	0.11	0.10
Isobutane	0.12	0.12
Pentane	0.11	0.10
Isopentane	0.10	0.10
Neopentane	0.10	0.10
Hexane	280 ppmv	251 ppmv
Carbon dioxide	0.81	0.70
Nitrogen	2.08	2.01

some selected experiments, the saturation capacity of the sorbents was also measured by allowing the bed outlet odorant concentrations to rise to their inlet values. At the end of each test, the feed concentrations were measured one more time to ensure that no drift occurred in the inlet mixed gas sulfur concentration throughout the test.

3. Test Results

3.1 Comparison of Performance with Other Sorbents

In the sorbent development effort, TDA collaborated with Siemens Westinghouse Power Corporation (SWPC, Pittsburgh, PA). In 2000, SWPC initiated a test program to identify a strategic supplier for a natural gas desulfurization process and carried out extensive engineering scale tests to evaluate potential natural gas desulfurization sorbents. In their study, they evaluated a number of commercial and specially prepared physical adsorbents and high temperature chemical sorbents for removing sulfur odorants. The results of their screening study were presented elsewhere (Ref 3).

As part of the new sorbent development effort, several low temperature adsorbents were received from SWPC for testing to compare their performance to the new material. Some of these sorbents, identified here as Siemens samples 4 and 5, were Ce- and Cu-exchanged zeolite-Y, respectively. Sample 4 was prepared to be similar to those reported by University of Michigan (Ref 5) as effective for desulfurizing diesel fuel and by Pennsylvania State University (Ref 6) for desulfurizing jet fuel. Sample 5 was similar to the sorbents reported by Pacific Northwest National Laboratory (Ref 4) and Pennsylvania State University (Ref 6). For quick comparison, accelerated tests were carried out at high gas hourly space velocities, 60,000/h (corresponding to very short gas-solid contact times). The performance of each sorbent was evaluated at an identical baseline condition; the sulfur-laden natural gas stream was contaminated with 12.3 ppmv DMS, 8.9 ppmv TBM, and 8.9 ppmv THT. These higher than pipeline gas sulfur concentrations and short contact times allowed observation of the breakthrough profiles of these odorants in relatively short times.

Figure 4 shows the DMS breakthrough profiles for various sorbent samples. Special emphasis is given to DMS because in all prior work DMS was found to be the most difficult sulfur compound to be removed from the natural gas (Ref 3). Among the samples provided by SWPC, the DMS breakthrough occurred first with the Norit carbon sample at 30 min. The DMS breakthrough for an unpromoted zeolite-X occurred at 72 min, indicating that the zeolite-X has a DMS absorption approximately 2.5 times higher than that of Norit activated C. The specially prepared samples provided by SWPC showed better

Table 2 Pre-breakthrough capacities calculated for the samples shown in Fig. 4

Sample	Pre-breakthrough capacity, %
TDA's SulfaTrap sorbent	3.12
Siemens sample 5	1.96
Siemens sample 4	0.85
Grace X zeolite	0.36
Norit RGM3 activated carbon	0.13

performance than commercial sorbents, but one of TDA's preparations showed the best performance of all sorbents. DMS breakthrough occurred at 720 min, corresponding to a sulfur adsorption capacity of 3.1 wt.%. Table 2 lists adsorption capacities for all samples shown in Fig. 4. The pre-breakthrough sulfur adsorption capacity is defined as the mass of total sulfur adsorbed per unit mass of sorbent when the breakthrough of the first sulfur compound was observed.

The breakthrough profiles of all sulfur species are presented in Fig. 5. In agreement with the prior literature, DMS breakthrough occurred first at 720 min, followed by the breakthrough of TBM at 1080 min. THT breakthrough was never observed during 1400 min of testing. These results suggest that the affinity of the sorbent is weakest for the DMS and strongest for the THT. The saturation capacity of the sorbent was calculated as 3.9 wt.%. (The saturation capacity is defined as the total sulfur loading of the sorbent measured when the DMS concentration at the exit of the bed was equal to its inlet value.)

The comparison tests were performed using dry simulated natural gas. Pipeline natural gas may contain up to 150 ppmv water vapor. It is anticipated that the competition by water vapor for adsorption sites will reduce the sulfur capacity of activated carbon, zeolite-X, and to some extent zeolite-Y in real-world pipeline natural gas applications.

3.2 Side Reactions

One of the critical features of a successful sorbent is that it be inert to potential side reactions. The sorbent should not alter the properties of the natural gas. Chemisorption of high molecular weight hydrocarbons is highly undesirable. Such reactions have potential to reduce sulfur uptake of the sorbent by competitive adsorption and blocking of active sulfur adsorption surface sites. These reactions could also make sorbent disposal difficult due to development of pyrophoricity. Unselective sorbents, such as activated carbons, become flammable due to adsorption of higher hydrocarbons at the end of their life and need to be disposed as hazardous materials, creating disposal handling safety and cost issues.

In this study, the concentration profiles of the natural gas components, including the ethane, propane, and all the C4s, C5s, and hexane, were continuously monitored throughout the tests. The flat concentration profiles for these hydrocarbons, even for the hexane, show that their adsorption by the sorbent is minimal and the SulfaTrap sorbent selectively removes sulfur (Fig. 6).

To further test the catalytic inertness of the SulfaTrap sorbent, potential side reactions of the organic sulfur species were also investigated. It is also highly undesirable that the organic sulfur species recombine into higher molecular weight compounds or change their forms by decomposition reactions. To ensure that no long-chain sulfur species are forming due to catalytic effects induced by the sorbent, the GC column was operated for several hours at its maximum temperature to drive off any high molecular weight sulfur species that may be retained in the column. Analysis showed no sulfur species were retained in the column. This indicates that the sorbent is not catalyzing any side reactions to cause the formation of high molecular weight sulfur compounds. Figure 7 shows a collection of several chromatograms through the duration of a typical test. The peaks in the initial chromatograms during the inlet feed analysis are the same as the peaks when breakthrough occurs. Over the course of the test, no other sulfur compounds were detected.

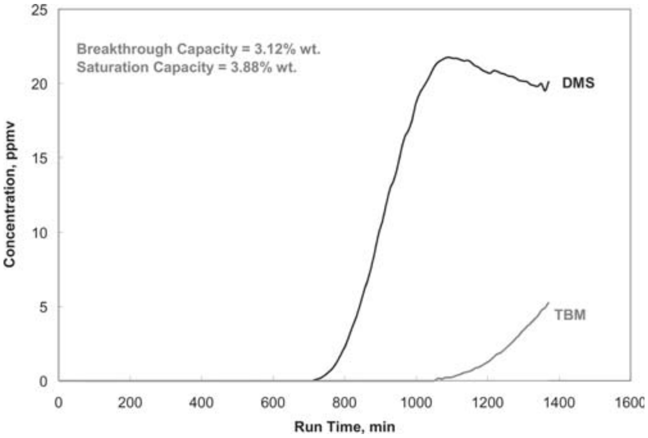

Fig. 5 Breakthrough profiles of sulfur components from TDA's SulfaTrap sorbent; natural gas with 12.3 ppmv DMS, 8.9 ppmv TBM, and 8.9 ppmv THT at 60,000 h^{-1}

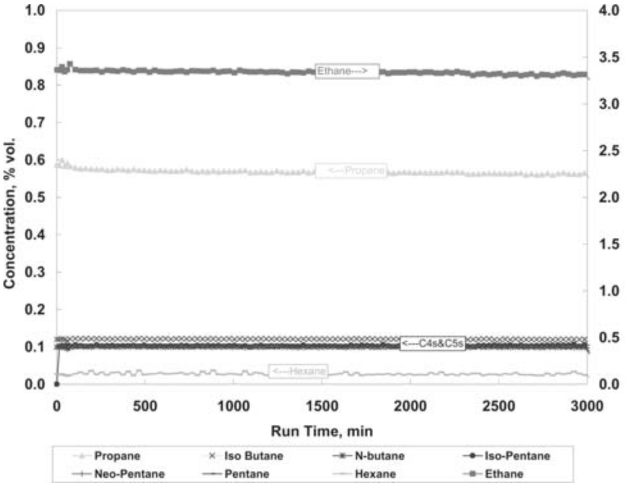

Fig. 6 Concentration profiles of the natural gas species over the course of a typical test

3.3 Sorbent Regeneration

The regeneration potential of the SulfaTrap sorbent was also investigated. The ability to reuse the sorbent has great potential for cost reduction and to reduce the landfill disposal requirements. To test regenerability, a mild temperature swing was applied to drive adsorbed sulfur species from the sorbent.

A temperature-programmed desorption (TPD) experiment was performed where the sorbent was exposed to a sulfur-laden

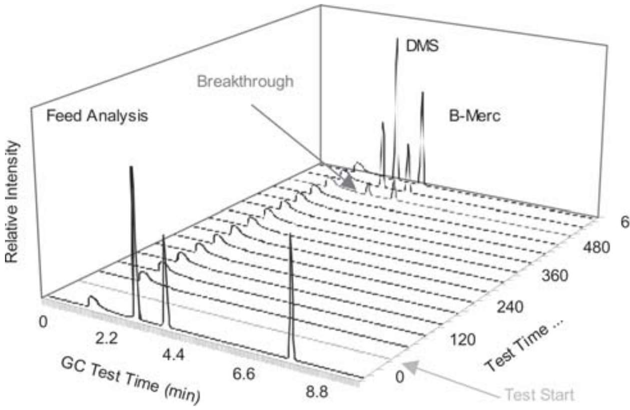

Fig. 7 GC profiles over the course of a typical test

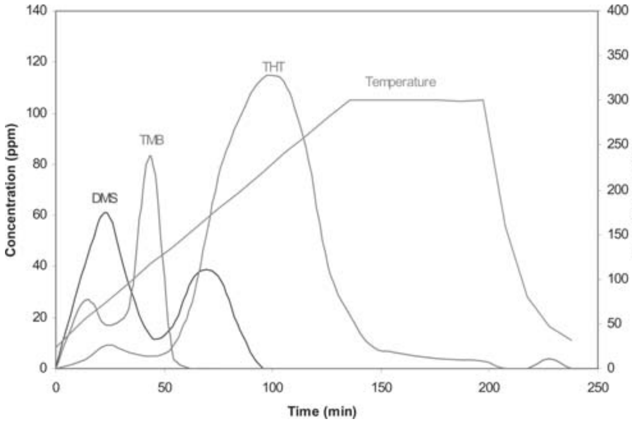

Fig. 8 Temperature-programmed desorption profile for the TDA SulfaTrap sorbent

natural gas stream, containing DMS, TBM, and THT odorants until saturation. Following sorbent saturation, the lines of the test system and the reactor were purged with nitrogen to remove any remaining sulfur components from the dead volume of the system to establish a baseline. The bed temperature was slowly increased at a rate of 2 °C/min to 300 °C to drive off the adsorbed sulfur species from the sorbent (Fig. 8). As the temperature approached 100 °C, first the release of DMS was observed. This was followed by TBM desorption at 150 °C and THT desorption at 250 °C. For each sulfur species, the authors observed a bimodal desorption profile. This was due to the presence of two different types of active materials that are responsible for the adsorption of these species. DMS desorption occurred at lower temperatures than other components, indicating that the interaction between the DMS and the sorbent is weakest and that only a small increase in temperature is needed to drive the DMS off the surface. The sorbent has the highest affinity for THT, and as a result, higher temperatures are required to drive off the THT.

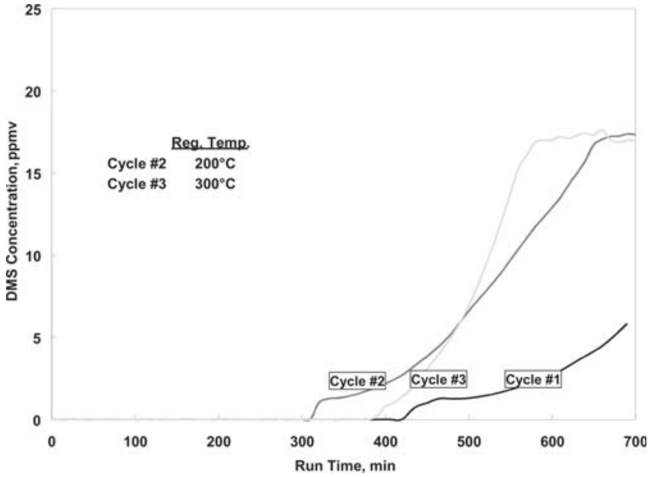

Fig. 9 DMS breakthrough profiles in the first three cycles with regenerations in between: $T = 20$ °C, $p = 17$ psia, DMS Inlet = 17 ppmv, TBM Inlet = 7 ppmv, THT Inlet = 5 ppmv, GHSV = 60,000 h^{-1}

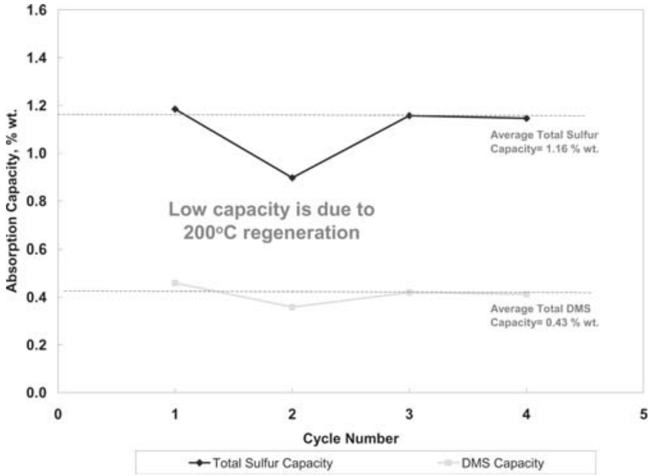

Fig. 10 Cyclic adsorption capacity of the sorbent: $T = 20$ °C, $p = 17$ psia, DMS Inlet = 17.0 ppmv, TMB Inlet = 7.0 ppmv, THT Inlet = 5 ppmv, GHSV = 120,000 h^{-1}

3.4 Cyclic Tests

After the TPD tests, the cyclic sulfur adsorption capacity of the sorbent was measured for four cycles. Each cycle started with a feed analysis, followed by sulfur adsorption, and then a nitrogen purge. Once a stable baseline was established, the sorbent bed was heated for the regeneration. After regeneration was complete (no further sulfur release was observed), the sorbent was cooled down in nitrogen to room temperature. The next cycle was then started.

Figure 9 shows the DMS breakthrough curves for the first three cycles of this test. The sorbent maintained a stable total sulfur capacity and the DMS capacity through this four-cycle test (Fig. 10). A slightly lower adsorption capacity was observed only after the second regeneration cycle because the regeneration cycle temperature was carried out at 200 °C. When regeneration was carried out at 300 °C for the subsequent cycles, a stable sulfur adsorption capacity was maintained. Apparently, for full sorbent regeneration, the higher temperature (300 °C) is needed.

3.5 Next Steps

This paper presents the early results of a more comprehensive desulfurization adsorbent development program. Testing is currently underway to demonstrate the efficacy of the TDA's

Table 3 Comparison of TDA's SulfaTrap sorbent with a state-of-the-art activated carbon sorbent to protect a 5 kW_e solid oxide fuel cell system for one year

	SulfaTrap sorbent	Activated carbon
Operating temperature	Ambient	Ambient
Bed volume	4 L	~300-360 L
Hydrocarbon adsorption	Minimal	Substantial
End-of-life indication?	Yes	No
Easy regenerability?	Yes	No
Flammability	No	Yes
Disposability	Easy, small volume	Difficult due to flammability, toxicity

SulfaTrap sorbent under engineering test conditions. This testing includes lower space velocity of the fuel flow, larger adsorbent bed size, and water vapor in the natural gas. The test program will also demonstrate a large number of regeneration cycles (>50) and assess performance degradation, if any.

4. Conclusions

A low-cost, high-capacity, regenerable sorbent was developed for removing sulfur-bearing odorants from natural gas at ambient temperature. The sorbent does not interact with hydrocarbons or alter the composition of the natural gas. It does not alter the sulfur compounds that it removes by physical adsorption. It contains no toxic ingredients, and it is not pyrophoric. Therefore, it does not require any special handling for disposal, if its regenerability is not exploited. Table 3 summarizes a comparison of the new material with state-of-the-art activated carbon sorbent for sulfur removal.

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