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Advanced Hot-Gas Desulfurization Sorbents

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Advanced Hot-Gas Desulfurization Sorbents

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Introduction

Integrated gasification combined cycle (IGCC) power systems are being advanced worldwide for generating electricity from coal due to their superior environmental performance, economics, and efficiency in comparison to conventional coal-based power plants. Hot gas cleanup offers the potential for higher plant thermal efficiencies and lower cost. A key subsystem of hot-gas cleanup is hot-gas desulfurization using regenerable sorbents. Sorbents based on zinc oxide are currently the leading candidates and are being developed for moving- and fludized- bed reactor applications. Zinc oxide sorbents can effectively reduce the H_2S in coal gas to around 10 ppm levels and can be regenerated for multicycle operation. However, all current first-generation leading sorbents undergo significant loss of reactivity with cycling, as much as 50% or greater loss in only 25-50 cycles. Stability of the hot-gas desulfurization sorbent over 100s of cycles is essential for improved IGCC economics over conventional power plants.

This project aims to develop hot-gas cleanup sorbents for relatively lower temperature applications, 343 to 538°C with emphasis on the temperature range from 400 to 500°C. Recent economic evaluations have indicated that the thermal efficiency of IGCC systems increases rapidly with the temperature of hot-gas cleanup up to 350°C and then very slowly as the temperature is increased further. This suggests that the temperature severity of the hot-gas cleanup devices can be reduced without significant loss of thermal efficiency.

Objectives

The objective of this study is to develop attrition-resistant advanced hot-gas desulfurization sorbents which show stable and high sulfidation reactivity at 343°C (650°F) to 538°C(1000°F) and regenerability at lower temperatures than leading first generation sorbents.

Approach

A number of formulations were prepared and screened for testing in a fixed bed reactor at high temperatures and high pressures (HTHP) using simulated coal-derived fuel gases. One of the superior formulation was tested for long term durability and chemical reactivity. Also selected sorbents in attrition-resistant fluidizable form were tested in a HTHP fluid-bed reactor. To prevent sulfation, catalyst additives were investigated, which promote a lower regeneration temperature.

Project Description

Sorbent Preparation

A highly promising method was developed under this project in cooperation with a commercial sorbent manufacturer for preparing suitable sorbents. Various sorbents were prepared using this proprietary technique. Additives that promote a lower regeneration temperature were investigated. The role of the commercial manufacturer was to ensure scalability of the manufacturing process and to keep the cost competitive. The following analytical techniques were used to characterize the fresh, sulfided and regenerated sorbents: (1)X-ray Diffraction (XRD) for crystalline phase (2)the standard BET method for surface area measurement (3)Hg-porosimetry for determination of pore volume, bulk density, average pore diameter and pore size distribution determination; and (4)atomic absorption (AA) spectrometry for elemental composition analysis.

Experimental Setup

The sorbent materials prepared were tested in a laboratory scale, HTHP fixed bed reactor. Briefly, the experimental setup consisted of a gas delivery system, a fixed bed reactor, and a gas analysis system. In the gas delivery system, a simulated fuel gas of any desired composition could be generated using the bottled gases, a set of mass flow controllers, and high- pressure syringe pumps. Steam was added to the mixed dry gas by vaporizing liquid water and injecting it into the gas stream at a controlled rate by a high-pressure syringe pump. The reactor was constructed of stainless steel pipe. Inside the pipe there was a removable 316 stainless steel 1.0 cm I.D. tube with a porous alumina plate in the bottom that acted as a gas distributor. The inside of the pipe was Alon-processed to prevent corrosion of stainless steel by sulfurous gases in the presence of steam. The pressure inside the reactor was controlled by a back pressure regulator and measured by an electronic pressure sensor. The thermocouples were positioned to measure the temperatures of the preheated feed gas, the reactor bed, and the product gas. The tests were conducted with a simulated gas containing 10% H_2, 15% CO, 5 mol% CO_2, 1 mol% H_2S, 15 mol% H_2O, and balance N_2. The outlet H_2S and SO_2 concentrations were monitored using a HP5890 gas chromatograph.

A typical run consists of loading the sorbent and heating the reactor to a desired temperature of 300-500^oC with continuous flow of nitrogen. Once the desired temperature was attained, the flow of fuel gas to the reactor was started and the concentration of H_2S was measured continuously in the effluent gas. When the H_2S concentration in the effluent gas reached 500 ppmv, indicating breakthrough, the sulfidation was stopped and the system was prepared for regeneration. The regeneration of sulfided material was carried out at the desired temperature ranging between 400-550°C with 2 to 4 % oxygen in nitrogen. In all the runs, space velocity used was in the range of 2000-3000 $h^{-1.}$ The regeneration of the sulfided material was carried out until the SO_2 concentration in the reactor effluent chopped below 50 ppm. These sulfidation-regeneration cycles were repeated as many times as desired. Typically each material was tested for 5-10 cycles to obtain meaningful data on material durability. At the end of a 5-10 cycle run, the material was removed from the reactor and all physical and chemical characterizations, as listed above, were carried out on the reacted material to determine changes due to reaction.

Results

A series of sorbents (designated by the MCRH series) have been prepared in attrition resistant form (Table 1). Table 1 shows that the attrition resistance of the sorbents prepared with our proprietary method is extremely high compared to first generation sorbents and it satisfies the target of Table 2, set by Kellogg for their transport reactor at the Sierra-Pacific Clean Coal Technology IGCC demonstration plant

Table 1. Attrition Test of MCRH Sorbents

Sorbent	**3-hole attrition loss (wt %)**	
	5 hour	***20 hour***
MCRH-51	0.00	0.62
MCRH-52	0.25	0.25
MCRH-53	0.28	0.56
MCRH-54	0.36	0.36
MCRH-55	0.56	1.41
MCRH-56	0.00	1.06
ZT-4	40.00	89.00
Z-SorbIII	16.00	32.40

Table 2: Sorbent Selection Criteria for Sierra-Pacific

Sulfidation	**Properties**
1 to 2 s contact time	80 μm aps
<10 ppmv H_2S leakage	>50 lb/ft^3 bulk density
482 to 538°C operation	
Regeneration	**Attrition**
<538°C light-off	<2.5 x 10^{-5} lb/lb circulated (TRTU)
no O_2 breakthrough	3-hole air-jet attrition <5 %
neat air oxidation	in 5 hours

Figure 1 shows the breakthrough profiles for a recently prepared zinc-based sorbent MCRH-61 (with attrition resistance equivalent to MCRH-56). This sorbent was modified to regenerate at temperatures as low as 475ºC. It was tested for 50 cycles of sulfidation in the laboratory-scale reactor at 482ºC. Regeneration between cycles was conducted with 2 volume percent O_2 in N_2 at 550ºC. The gas hourly space velocity for the 50-cycle test was about 2500 h^{-1} both in sulfidation and in regeneration. Sulfidation tests were carried out with a sulfidation gas containing (vol%): H_2=10%, CO=15%, CO_2=5%, H_2S=0.4%, H_2O=15% and bal N_2. MCRH-61 sorbent showed excellent sulfidation behavior. The pre-breakthrough H_2S level was less than 100 ppm and the breakthrough conversion was 100%. There was no deactivation in 50 cycles in this fixed bed study.

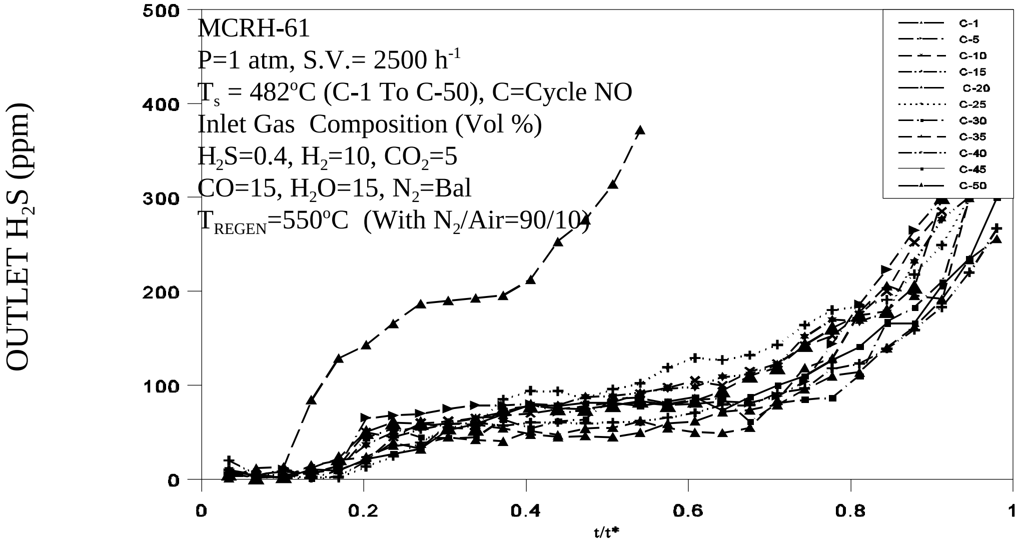

Figure 1. H_2S Breakthrough Curves in Successive Sulfidation Cycles of MCRH-61

Based on fixed-bed microreactor screening of numerous sorbents, the above attrition-resistant fluidizable sorbent designated MCRH-61 was selected for high temperature, high pressure (HTHP) testing. A 10 cycle test was conducted at RTI using their HTHP 2.0-inch fluidized-bed reactor system at conditions simulating the Sierra-Pacific conditions. The sulfidation is carried out using Kellogg gasifier gas with 0.4 % H_2S at 18.8 atm pressure, 480-510ºC, and 15 slpm through the sorbent bed. The regeneration was conducted with pure air with an initial temperature of 480-510ºC. The H_2S breakthrough results shown in Figure 2 indicate essentially complete removal of H_2S until a sharp breakthrough in all 10 cycles. The sorbent lost some capacity after the first cycle presumably due to pure air regeneration that increased the bed temperature to around 700°C. After the first cycle, the capacity stabilized even with temperature excursions to 675-700°C and no attrition of the sorbent occurred in the 10 cycle test. Due to pure air regeneration, some sulfate formation did occur as seen from the SO_2 curves for cycles 2-10 during sulfidation. The sorbent demonstrated high reactivity over the 10 cycle test and its attrition resistance was comparable to equilibrium fluidized cracking catalyst (FCC). However, sulfate formation was observed during neat regeneration at elevated pressures. Overall the test was a success with potential for an optimized MCRH-61 to be a candidate for Sierra-Pacific.

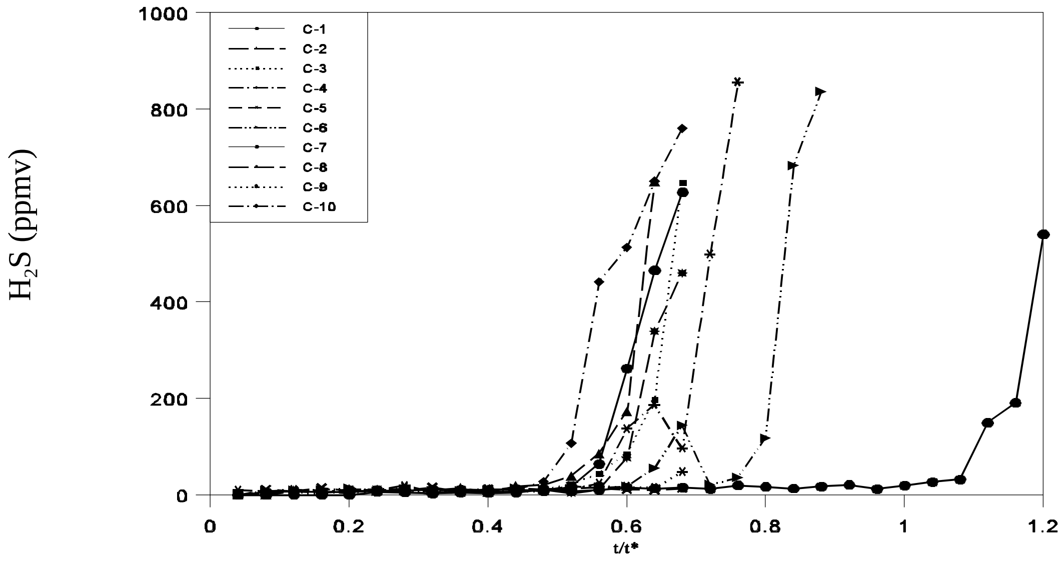

Figure 2. Breakthrough Behavior of MCRH-61

Modifications were made to the MCRH-61 formulation to eliminate the sulfate formation observed during bench-scale tests at RTI. Microreactor screening tests indicated that the formulation designated MCRH-67 showed little or no evidence of sulfate formation. A 2 cycle HTHP test at RTI also showed no sulfation problem with this modified sorbent.

Application

Preparation of the MCRH-67 sorbent is now being scaled up to 100 lb by United Catalysts Inc for potential testing in M.W. Kellogg’s transport reactor test unit. RTI is planning to conduct this test under a separate contract with DOE.

Future Activities

The grant expires on August 29, 1997. A final report is being prepared.

Contract Information

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