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HOT COAL-GAS DESULFURIZATION WITH MANGANESE-BASED SORBENTS

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Abstract

Manganese (Mn) based hot-gas-desulfurization sorbents are under investigation for use in Integrated Gasification Combined Cycle (IGCC) advanced electric-power-generation systems. The objective of this project is to develop a regenerable Mn-based pellet formulation that can achieve low sulfur partial pressures, has a high capacity for sulfur and sufficient strength for potential use in fluidized beds, and can be regenerated for many cycles.

Fifteen different formulations of manganese sesquioxide, each with either titania or alumina, were prepared and characterized at the University of Minnesota. Each formulation was indurated under conditions sufficient to achieve 1 lb/pellet/mm of diameter crush strength. Sulfidation screening was performed in a thermogravimetric analyzer (TGA) at 500 to 900 °C.

A sorbent containing MnCO_3 and TiO_2 , which showed superior crush strength and reactivity, was selected for multi-cycle fixed-bed testing at the Morgantown Energy Technology Center (METC). Four cycles of sulfidation showed that the sorbent had excellent efficiency and capacity for sulfur removal. Good regenerability was achieved with air-steam at 871 °C.

Introduction

IGCC is one of the most promising proposed processes for advanced electric power generation to replace conventional coal combustion. This emerging technology will not only improve the thermal efficiency, but will also reduce or eliminate the environmentally adverse effects normally associated with coal combustion.

Zinc ferrite and zinc titanate have received much attention over the past several years because, from a theoretical point of view, they have desirable properties; e.g., high sulfur capacity and the ability to remove H_2S from coal-derived fuel gas to levels of a few ppmv.

However, Zn-based sorbents show volatility problems under high-temperature highly reducing gas environments.

A number of studies led to the consideration of Mn-based sorbents. Westmoreland et al. [1], screened the high-temperature desulfurization potential of 28 solids, primarily metal oxides, based upon thermochemical considerations alone. This earlier work, which was subsequently followed by kinetic studies [2], predicted Mn oxide stability and a high degree of desulfurization to temperatures in excess of 1,000 °C. In addition, Mn showed desulfurization potential in the range of 600 to 700 °C, where traditional metal oxides known to be reactive with H_2S proved unsatisfactory. Turkdogan and Olsson [3] examined the feasibility of using Mn oxide pellets to desulfurize hot reducing gases. They found that a mixture of Mn ore and alumina, formed into pellets in a 3:1 weight ratio, readily accepted sulfur from hot (800 °C) H_2 - H_2S gas mixtures and that the pellets could be regenerated. During their investigation of zinc ferrite, Jha and Hepworth [4] reported favorable results on the substitution of MnO for some of the ZnO as a means of enhancing the durability and reactivity of the zinc ferrite. Ben Slimane et al. [5] addressed the physical and chemical behavior of several manganese and alumina sorbent formulations, established the thermodynamic feasibility of H_2S removal from hot simulated coal gases, and presented an analysis of the sulfidation kinetics based on thermogravimetric experimental results.

The objective here is to develop a regenerable pellet formulation that can achieve low sulfur partial pressures and has a high capacity for sulfur removal from a hot fuel gas. The pellet must also be durable for potential use in fluidized beds and regenerable for many cycles.

Methods

Fig. 1 shows the equilibrium concentrations of H_2S in the presence of Mn oxide mixed with various substrates, as calculated using an energy minimization program, Outokumpu HSC Chemistry for Windows. Although alumina has been frequently used to enhance the reactivity of Mn oxide by previous researchers [3,6], it is apparent from this figure that certain high ratios of Mn oxide to titania may potentially exhibit greater efficiency for H_2S removal.

Fifteen formulations were prepared that varied as follows: (1) Mn source was either $MnCO_3$ or MnO_2 -ore, (2) molar ratio of Mn to substrate, (3) weight percent of bentonite (0, 2, or 5%), and (4) types of porosity promoters added; i.e., activated carbon, dextrin, or MoO_3 . Feed powders were hand mixed and pelletized in a balling wheel, forming "green" pellets. Green pellets were air dried for one day, then dried to a constant weight at 100 °C. Dry pellets were calcined for four hours at 350 °C. Immediately after calcination, pellets were placed in a high-temperature furnace (preheated to 500 °C), where the temperature was ramped up for two hours until final induration temperature was achieved. Induration temperatures ranged from 1,100 to 1,300 °C, and some sorbents were indurated for 2 h, more than once, to achieve the desired crush strength. The indurated pellet size was formulated in the range of 1 to 4mm.

Several methods of physical and chemical characterization were used. A limited number of fresh (unreacted) formulations were subjected to mercury porosimetry for pore structure characterization. Also, inductively coupled plasma analysis (ICP) of the Mn content of unreacted sorbent was conducted. Sorbent with requisite crush strength of 1 lb/pellet/mm

of diameter was reduced and sulfided in a TGA with a Cahn 1000 electrobalance to determine reactivity. The test conditions for the 1 atm TGA reduction/sulfidation with 200 to 800 mg of sorbent were (a) reduction: 1 L/min of H_2 , same temperature (T) as sulfidation, 30 min duration for $T > 550^\circ C$ or 60 min duration for $T < 550^\circ C$; and (b) sulfidation: 1 L/min of 3.0 mol% H_2S /balance H_2 , 500 to 900 $^\circ C$, 120 min duration.

One of the most promising sorbents, C6-2-1100, containing $MnCO_3$ and TiO_2 , was tested for 3.5 cycles of sulfidation/regeneration in a 2.21-cm diameter fixed-bed reactor. Details of this apparatus are given elsewhere [7]. Previous screening experiments on another Mn-based sorbent, C4-2, prepared by Hepworth and Slimane [8] with $MnCO_3$ and alundum, suggested that the sorbent performed better with respect to capacity and efficiency of sulfur removal with simulated Shell gas than with KRW gas. Sorbent efficiency was better at 538 $^\circ C$ than at 871 $^\circ C$. Therefore, the conditions for the 3.5-cycle experiment included the following: (a) sulfidation: 538 $^\circ C$, 205 kPa, 2,000 h^{-1} , Shell gas containing molar percentages 3.0 H_2S , 2.0 CO_2 , 64.1 CO , 4.4 N_2 , 27.3 H_2 , and 2.0 H_2O ; and (b) regeneration: 871 $^\circ C$, 205 kPa, 600 h^{-1} , molar percentages 50 air/50 steam. Outlet H_2S and SO_2 concentrations were measured with a VG Prima 600 mass spectrometer.

Results

All fifteen sorbents were sufficiently indurated so as to pass the crush strength criterion of 1 lb/pellet/mm diameter. Each formulation was tested in a TGA for at least one induration condition. The total intrusion volumes were in the range of 0.16 to 0.29 cc/g, with average pore diameters of 2-11 micrometers, and porosities of 39 to 55 percent. Theoretical sulfur capacities, based on ICP analysis of Mn content, were within the range of 21 to 34 g sulfur/100 g fresh sorbent.

Three main groups of formulations were tested: (A) $MnCO_3$ supported with TiO_2 — with or without bentonite; (B) MnO_2 ore supported with alundum — with and without bentonite, and (C) $MnCO_3$ supported with Al_2O_3 — with or without porosity enhancers. These will hereafter be referred to as group A, B, and C sorbents.

Fig. 2 shows the relative reactivity during the TGA tests for representative formulations of groups A, B, and C (C6-2-1100, A2-2-1175, and C5-5-1150, respectively). The formulation representing group A had the highest conversion. This suggests that sorbents containing $MnCO_3$ and TiO_2 should be selected for further study.

The temperature dependence of reactivity during the TGA tests of group A sorbent C6-2-1100 is shown in Fig. 3. Higher temperatures resulted in greater sorbent conversion. Note that the rates of the $MnCO_3$ - TiO_2 formulations decreased rapidly between 12 to 20 percent conversion. This kinetic deceleration may be because of plugging of the pellet pores with sulfur, creating inaccessible pore volume or a large increase in diffusional resistance from MnO to MnS .

Fig. 4 shows the H_2S breakthrough curves for the 3.5-cycle fixed-bed test with simulated Shell gas at 538 $^\circ C$. The prebreakthrough H_2S level was usually below 10 ppmv for all four sulfidations. The calculated sorbent loading during the fourth sulfidation was 27 g S/100 g fresh sorbent, whereas the theoretical sulfur loading was 32 g sulfur/100 g fresh sorbent; therefore, the sorbent utilization was 84 percent. Sorbent capacity appeared to have increased between the first and second sulfidations, then stabilized to some extent (however,

there was a slight drop in breakthrough time between the third and fourth sulfidations; more cycles are needed to determine whether this is because of random error or the beginning of a loss of capacity). This suggests that the air-steam mixture at 871 °C was sufficient to attain reasonably good regenerability during these cycles. Further evidence of good regenerability was shown by the low SO₂ levels, i.e. < 50 ppmv, which were released at the beginning of the second and subsequent sulfidations.

Conclusions

- Pellet strength was primarily determined by induration temperature. All formulations met the required crush strength. The sensitivity of this parameter requires further optimization.
- Preliminary work appears to indicate TiO₂ is a better substrate than Al₂O₃, probably because the Mn/TiO₂ bond is chemically weaker than the Mn/Al₂O₃ bond. This means the Mn, which is tied up in forming a spinel, has a higher activity in the TiO₂ form than the Al₂O₃ form and is more effective in reacting with sulfur.
- Current pellet formulations are somewhat limited by intra-particle transport resistances. Pore structure design and characterization are to be the direction of additional research through higher substrate fractions and with no bentonite addition.
- Fixed-bed tests with the sorbent containing MnCO₃ and TiO₂ showed that good regenerability could be achieved with a air-steam mixture at 871 °C, and that stable, excellent performance with respect to capacity and efficiency of H₂S removal could be achieved.

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Figure 1. Equilibrium composition of H₂S with Mn-based sorbents containing various substrates in a simplified Shell type fuel gas at 1 atm.

Figure 2. Comparison of the reactivity of Mn-based sorbents of groups A, B, and C

Figure 3. Effect of sulfidation temperature on reactivity for C6-2-1100

Figure 4. Hydrogen sulfide breakthrough curves for four sulfidations of C6-2-1100, containing MnCO_3 and TiO_2 , at 538 °C