Simultaneous Removal of H₂S and NH₃ in Coal Gasification Processes

CONTRACT INFORMATION

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OBJECTIVES

The objective of this study is to develop advanced high-temperature coal gas desulfurization mixed-metal oxide sorbents with stable ammonia decomposition materials at 550–800° C (1022–1472° F). The specific objectives of the project are to:

- Develop a combined sorbent-catalyst materials shall be capable of removing hydrogen sulfide to less than 20 ppmv and ammonia by at least 90 percent.
- Carry out comparative fixed-bed studies of absorption and regeneration with various formulations of sorbent-catalyst systems and select most promising sorbent-catalyst type.

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Conduct long-term (at least 30 cycles) durability and chemical reactivity in the fixed-bed with the superior sorbent-catalyst.

BACKGROUND INFORMATION

Nitrogen (N\textsubscript{2}) occurs in coal in the form of tightly bound organic ring compounds, typically at levels of 1 to 2 wt\% on a dry-ash-free basis. During coal gasification, this fuel-bound nitrogen is released principally as ammonia and nitrogen, with smaller levels of HCN. The formation of NH\textsubscript{3} in a coal gasification processes is a function of the fuel gas composition and the gasifier operating conditions. During the use of coal gas to generate electricity in gas-fired turbines, fuel bound(N\textsubscript{2}) is converted to nitrogen oxides(NO\textsubscript{x}), which are difficult to remove and are highly undesirable as atmospheric pollutants. Recent results indicate that while the efficiency of molten carbonate fuel cell (MCFC) anodes is not effected by exposure to NH\textsubscript{3}, NO\textsubscript{x} is generated during combustion of the anode exhaust gas. Thus, NH\textsubscript{3} must be removed from the coal gas before it is used in IGCC or MCFC applications.

The product stream from a high temperature, oxygen-blown gasifier, such as Texaco, contains about 2000 ppmv of NH\textsubscript{3}, where higher concentrations (about 5000 ppmv) occur when the gasification is conducted at lower temperatures, such as in the Lurgi or GE air-blown gasifier. A range of 1500 to 3000 ppmv is considered for this study.

Removal of H\textsubscript{2}S using zinc-based sorbents, particularly zinc titanate, to < 20 ppmv levels has been well established (Lew et al., 1989; Jothimurugesan and Harrison, 1990; Woods et al., 1990; Gupta and Gangwal, 1993). Studies of NH\textsubscript{3} decomposition indicated that Ni, Ir, Co, Mo, Mn and Ru have high catalytic activities (Krishnan et al., 1988). If desulfurization sorbents such as zinc titanate could be used along with above metals to decompose ammonia present in hot coal gas, then the number of unit processes necessary to clean hot coal gas could be reduced by one.
The objective of this project is to develop successful combination of an NH₃ decomposition catalyst with the mixed-metal oxide sorbent so that the sorbent-catalyst activity remains stable for NH₃ decomposition in addition to H₂S removal under cyclic sulfidation-regeneration conditions in the temperature range of 550–800° C (1022–1472° F) and pressures up to 20 atm.

**PROJECT DESCRIPTION/RESULTS AND ACCOMPLISHMENTS**

The project consists of three major experimental tasks (Tasks 1–3) addressing the contract objectives described above.

Task 1: Sorbent – Catalyst Preparation and Characterization

Task 2: Experimental Testing

Task 3: Cyclic Testing

An one day trip was made by the principal investigator to Research Triangle Institute (RTI) on October 28, 1993, to plan the sorbent – catalyst preparation, and building the experimental apparatus for testing, with RTI consultant Dr. Santosh K. Gangwal.

The mixed metal–oxide sorbent will be prepared by the coprecipitation method in order to generate as high a surface area as possible. The sorbent will be prepared by coprecipitation using starting solutions of 1.0 M aqueous solutions of Zinc Nitrate (Zn(NO₃)₂) and Titanium Isopropoxide Ti[OCH(CH₃)₂]. These solutions will be mixed together in the proportions needed to obtain the desired compositions in the final sorbent. The precipitation will involve the direct addition of 28.3% Ammonium Hydroxide at a rate of approximately 5 cc/min. When the pH reaches 8.5 the precipitate will be filtered off, washed with deionized water for five times and then it will be dried overnight at 100° C(212° F). Finally it will be calcined in air at 871 ° C(1600° F) for 2 hours.

The catalyst will be added to zinc–titanium oxide by impregnation technique. After the
impregnation, the material will be dried at 110°C (230°F), followed by calcination in air at 800°C (1472°F) for 0.5 hours. Most of the chemicals and the instruments needed for the preparation of sorbent–catalyst have been received and the preparation of sorbent has been initiated.

A packed–bed microreactor set–up will be constructed as shown in Figure 1. A 316 stainless (1 cm i.d.) will be used as the reactor and will be suitable for operation up to about 900°C (1652°F) and 20 atm. Most of the parts required for the fabrication of the high pressure microreactor setup have been received (about 75% parts ordered) and construction of the unit has been initiated.

Problem encountered up to this has been in the timely receipt of the materials ordered for the sorbent–catalyst preparation as well as for the fabrication of the microreactor

FUTURE WORK

Various formulations of sorbent–catalyst will be prepared and then it will be characterized. Once the fabrication is completed, it will be tested for leaks before preliminary sorbent–catalyst evaluation begins.

REFERENCES


Figure 1. Schematic Diagram of Fixed-Bed Reactor System
END

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