Reaction of H_2S with Sorbents of Waste Seashell

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Abstract

The waste seashells were used for the removal of hydrogen sulfide from a hot gas stream. The sulphidation of waste seashells with H_2S was studied in a thermogravimetric analyzer at temperature between 600 and 800℃. The desulfurization performance of the waste seashell sorbents was experimentally tested in a fixed bed reactor system. Sulfidation experiments performed under reaction conditions similar to those at the exit of a coal gasifier showed that preparation procedure and technique, the type and the amount of seashell, and the size of the seashell affect the H_2S removal capacity of the sorbents. The pore structure of fresh and sulfided seashell sorbents was analyzed using mercury porosimetry, nitrogen adsorption, and scanning electron microscopy.

Introduction

The reactions of hydrogen sulfide with various metal oxides have been investigated extensively in connection with the desulfurization of coal gas to be used in advanced power generation cycles. Although hydrogen sulfide removal can be carried out at ambient temperatures by established liquid absorption processes, desulfurizations by reaction with metal oxides at high temperatures can improve considerably the economics of power generation. Thermodynamic calculations have shown that the oxides of the metals Ca, Fe, Co, Cu and Zn can be used as sulphur sorbents to be applied for high-temperature coal gas desulphurization. On basis of these metals, many sorbents have been developed. One can roughly discriminate between synthetic sorbents, which are relatively expensive but have a long lifetime, and natural sorbents which are cheap but possibly are less stable. Sorbents that belong to the category of natural sorbents are iron ore, limestone and seashells, either in raw or calcined form.

The objective of this study is the evaluation of the desulfurization performance of seashell sorbents in a fixed bed reactor. Seashell sorbents were tested under reaction conditions that are typical for hot coal gas streams. Experiments were carried out to study the parameters that affect the H_2S removal ability of a seashell sorbents. In addition to the sulfidation experiments, the pore structure of reacted and sulfided sorbents was analyzed.

Materials and Method

Four samples of seashells were the solid reactants of this study. A Norelco intermittent diffractometer employing Ni-filtered Cu radiation was used for qualitative chemical analysis of the components present in a sample. X-ray powder diffraction patterns were obtained in a 2Θ range of 25-40°, which enabled detection of various phases. Seashell sorbents were examined by an ETEC Corporation electron microscope operating at 20kV with resolution of 70Å. A Perkin Elmer thermogravmetric analyzer(TGA7) interfaced through an analog-to-digital converter to a computer served to measure the sample weight continuously. The quartz housing and flow path of the TGA were modified so that the system could accommodate corrosive gases such as H_2S. A gas flow of 30ml/min was used for both the protective N_2 backflow and the feed. A N_2 gas was used for reduction runs, a 3% H_2S in N_2 mixture was used for sulfidation runs. Typically, a 45mg sample of particles, 10/100mesh, was employed.

The rector consist of a quartz tube of 1/8inch i.d. and 8inch length loaded to a bed height of 4inch with a sorbent granules(10/100 mesh). The reactor tube was mounted vertically inside an electric furnace, and the bed temperature was monitored by a K-type thermocouple moving inside a quartz thermowell concentric to the reactor tube. In a typical sulfidation run, shell sorbent was exposed to feed gas containing 99% N_2 and 1% H_2S, at a constant temperature of 600 - 800℃. Feed gas rate of a 200㎤/min(STP) were typically used.

Results and Discussion

The desulfurization performance of seashell depends on the nature and physicochemical propreties of the sorbents and the composition of the reactive gas.

Limestone and waste shell were mostly consisted of $CaCO_3$ and rest of components were similar. Final calcinations temperature were completed at 780℃, 850℃ for oyster, natural limestone respectively. Another waste shell were calcinated at 810-830℃.

XRD analysis to identy major components before and after calcination and product CaS, showed that maximum intensity peak of precalcinated samples mostly consist of $CaCO_3$ were occurred 2Θ was 31°. In the case of the samples after calcinations, $CaCO_3$ was converted into CaO, so this was observed at 37°. After sulfurization maximum intensity peak of CaS was observed at 32°

According to SEM/BET analysis were investigated pore distribution and surface area of particles. Additive pores were formed after calcinations. Also, small grains were formed after sulfurization. BET surface area of limestone, oyster, clam before calcinations were 0.2363, 2.4465, 1.69㎡/g, and after calcinations were 1.1543, 2.1209, 2.17 ㎡/g, respectively.

TGA results showed that activation energy of desulfurization sorbents were about 167-207kJ/mole. Short nacked shell and oyster had lower activation energy. This means that energy requirement was low in the calcinations. And, $CaCO_3$ was converted into CaO. Reaction velocity and order of hard-shelled mussel was the highest.

According to TGA results, temperature had influenced on H_2S removal efficiency. As desulfurization temperature increased, desulfurization efficiency increased. Aiso, maximum desulfurization efficiency was observed at 800℃. Desulfurization was related to calcinations temperature. Considering temperature ranges of exhausted gas from hot gas gasification equipment were 400-800℃. Thus, desulfurization efficiency would be increased desulfurization temperature situation at highly.

Experiments by TGA showed that particle size of sorbents had influenced on desulfurization capacity. Maximum desulfurization capacity was observed at 0.631mm for oyster and clam. Rest of sorbents showed similar capacity within 0.171-0.335mm particle size range. So, particle size would be considered.

Fixed bed desulfurization experiments, to obtain basic data for scale-up was indicated. Oyster was the best among the various sorbents, like the results of TGA. Expecially, H_2S removal efficiency of uncalcined oyster was the highest. When use oyster as desulfurization sorbents, calcinations process was not needed. Thus, desulfurization efficiency would be expected.

Fixed bed reactor experiments were indicated particle size of sorbents. These had influenced on desulfurization capacity. As smaller particle size was found better desulfurization capacity. Large capacity difference was found between 0.631mm and 0.335mm. But, differences between 0.335mm and 0.241mm was relatively small. As bed temperature increased, H_2S removal capacity increased. Therefore, both particle size and bed temperature should be considered to remove H_2S by sorbents.

Conclusion

Measurements of the reaction of H_2S with waste seashells show that particles smaller than 0.631mm can can achieve high conversion to CaS. According to TGA and fixed bed reactor results, temperature had influenced on H_2S removal efficiency. As desulfurization temperature increased, desulfurization efficiency increased. Also, maximum desulfurization efficiency was observed at 800℃. Desulfurization was related to calcinations temperature. Considering temperature ranges of exhausted gas from hot gas gasification equipment were 400-800℃. Thus, desulfurization efficiency would be increased desulfurization temperature situation at highly. When would be used waste sesshells as IGCC(integrated gasification combined cycle) sorbent.

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