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Comparative Study of the Reactions of Metal Oxides
with H_2S and SO_2

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Technical Progress Report
for the Period April-June 1991

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EXECUTIVE SUMMARY

This quarterly report presents technical progress made during the second calendar quarter of 1991 on a comparative investigation of the reactions of porous metal oxides with sulfur dioxide and hydrogen sulfide. The report is divided into two parts. In the first part, a statement of the work proposed to be carried out under this project is given and the various tasks associated with the project are identified and outlined. In the second part, the work carried out during the above mentioned period is described.

The primary objective of this project is the investigation of the effects of pore structure on the capacity of porous metal oxides for removal of gaseous pollutants from flue gases of power plants (SO_2) and hot coal gas (primarily H_2S). Specifically, we intend to appropriately exploit the differences of the sulfidation and sulfation reactions (for instance, different molar volumes of solid products) to elucidate the dependence of the sorptive capacity of a porous sorbent on its physical microstructure. The following tasks have been identified in the proposed project:

1. Literature survey and identification of solids to be used in experimental studies.
2. Experimental study of the reaction of the chosen solids with SO_2 and/or H_2S .
3. Experimental study of the evolution of the structure of the solids during reaction with SO_2 and/or H_2S using pore structure analysis and effective diffusivity measurements.
4. Model testing and validation using the obtained experimental data.

During the second quarter of the 1991 calendar year, work was primarily done on Tasks 2 and 4. A brief description of the work done is given below.

More experiments were carried out on the reaction of calcium oxide sorbents, produced through limestone calcination, with H_2S . We worked on the analysis of the experimental reactivity evolution data and their comparison with sulfation data of the same sorbents using a detailed mathematical model (generalized random pore model (Yu and Sotirchos, 1987)) for gas-solid reactions occurring in pore network structures. Finally, we developed a new mathematical model for gas-solid reactions occurring in porous media with structure represented by a population of spherical dense grains, each having a hard core and a soft permeable shell. The development of the model was based on the scaled-particle approximation for the structural properties, porosity and surface area, of structures of partially permeable spheres and the randomly overlapping grain model that was developed in the past by my research group. A detailed parametric sensitivity analysis of the partially overlapping grain model was carried out, and its flexibility was demonstrated by applying it to a set of experimental data for the $\text{ZnO-H}_2\text{S}$ reaction. The results showed that the extent of grain overlapping has a strong influence on the variation of the reactivity of a solid of given porosity and internal surface area, which depends in a complex fashion on the intraparticle and product layer diffusional limitations.

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STATEMENT OF WORK

1. PROJECT OBJECTIVES

The primary objective of this project is the investigation of the effects of pore structure on the capacity of porous metal oxides for removal of gaseous pollutants from flue gases of power plants (SO_2) and hot coal gas (primarily H_2S). Porous calcines obtained from natural precursors (limestones and dolomites) and sorbents based on oxides of zinc, iron, and/or copper will be used as model systems in our experimental studies, which will include reactivity evolution studies and pore structure characterization using a variety of methods. Our work will focus on oxides that can react (sufficiently fast) both with SO_2 and H_2S . We intend to appropriately exploit the differences of the sulfidation and sulfation reactions (for instance, different molar volumes of solid products) to elucidate the dependence of the sorptive capacity of a porous sorbent on its physical microstructure.

2. INTRODUCTION

The reactions of metal oxides with sulfur-containing compounds, such as SO_2 and H_2S , find extensive use in controlling emissions of gaseous pollutants from coal utilization systems. Limestone and dolomite, for instance, are used in the control of emissions of sulfur dioxide from coal-fired power plants. In the high temperature environment of a combustor, the limestone or dolomite particles undergo calcination, and the calcined product (CaO or MgO) reacts with the sulfur dioxide produced during coal combustion forming, mainly, calcium or magnesium sulfate. Calcium oxide and other metal oxide sorbents (iron oxide, zinc oxide, zinc ferrite, zinc titanate, etc.), on the other hand, are used to remove sulfur-containing compounds (predominantly H_2S) from hot coal gas.

The reaction of metal oxides with SO_2 and H_2S are typical examples of noncatalytic gas solid reactions with solid product formation and pore closure behavior. Such gas-solid reactions with solid product are encountered in a number of chemical process industries with applications ranging from ceramic material manufacture to gas scrubbing for pollution control. The calcination and sulfation reactions of limestone and dolomite have been the subject of extensive experimental investigation, but unambiguous experimental evidence that leads to a clear understanding of the effects of pore size distribution of calcined stones on their capacity for SO_2 removal is still lacking. Most investigators tend to focus on the global kinetics of the sulfation or sulfidation reactions while paying little attention to the pore structure of the calcined solid. As a result, the identification of sorbents exhibiting optimal reactivities and capacities for pollutant removal still remains an essentially haphazard, hit-or-miss operation. A review of the experimental evidence of the literature reveals an anomalous dependence of the reactivity and SO_2 uptake of calcined limestones on the initial values of average properties of their pore structure, such as porosity and surface area, indicating strong effects of the pore size distribution on the overall reactivity of the calcined solids (Borgwardt and Harvey, 1972; Wen and Ishida, 1973; Hartman and Coughlin, 1974, 1976; Ulerich et al., 1977; Vogel et al., 1977; Hasler et al., 1984; Simons and Garman, 1986; Yu, 1987; Gullett and Bruce, 1987).

Analogous observations apply to the reaction of metal oxides (calcium oxide, zinc oxide, zinc ferrite, zinc titanate, etc.) with H_2S . A good deal of experimental effort has been put in the area of hot gas desulfurization into the investigation the reactivity and capacity of various metal/metal oxide

sorbents for sulfur compound removal from coal gas (e.g., see studies by Gibson and Harrison (1980), Tamhankar et al., (1981 and 1985), Ranade and Harrison (1981), Jalan (1983), Anderson et al. (1984), Sick and Schwerdtfeger (1987), and Sa et al. (1989)). However, limited work has been done on the characterization of these sorbents in terms of their pore size distribution and resistance for intraparticle diffusion. Simplistic models of structure evolution are usually employed for data treatment and interpretation, while few studies have looked into the variation of the properties of the pore structure, such as the internal surface area (Caillet and Harrison, 1982; Sa et al., 1989), with the progress of the reaction.

A systematic investigation of the dependence of the transient behavior of large limestone particles reacting with SO_2 in the presence of oxygen on pore structure and particle size related factors has been carried out by my research group (Zarkanitis and Sotirchos, 1989; Yu, 1987). Our results have shown strong dependence of the transient behavior of reacting particles of calcined limestone and, consequently, of their sorptive capacity for SO_2 removal on their initial pore size distribution, but this dependence seems to follow an anomalous pattern when the sulfation capacities of calcines obtained from different precursors (stones) are compared. Specifically, calcines of similar composition and pore structure properties have been found to exhibit considerably different capacities for removal of SO_2 from flue gases. Comparison of the experimental data with the predictions of a generalized pore model for gas-solid reactions with solid product (Yu and Sotirchos, 1987) showed that these differences could be due to the formation of inaccessible pore space in the course of the reaction, which takes place when the small feeder pores of finite clusters of large pores or large cavities, in aperture-cavity pore structures, are filled with solid product.

Similar conclusions have been reached by analyzing reactivity data for zinc oxide sulfidation obtained in our laboratory (Efthimiadis and Sotirchos, 1989). However, an important difference exists between the reaction of metal oxides with H_2S and their reaction with SO_2 . The sulfide produced during reaction with H_2S occupies less space than the solid product produced during sulfation (sulfate (mainly) or sulfite), and as a result, complete pore closure in the case of sulfidation can happen only for low initial porosities. In the case of CaO , for instance, the initial porosity should be lower than 38% for pore closure to occur during sulfidation, while during sulfation pore closure is possible even for initial porosities as high as 65%. Thus, porous CaO with 50% initial porosity can reach complete conversion during sulfidation but only about 50% conversion during sulfation. These differences suggest that a comparative study of the reactions of porous metal oxides with SO_2 and H_2S can lead to a better assessment of the effects of pore structure on sorptive capacity than studies of the effects of the parameters of a single reaction only. Nevertheless, our survey of the literature on sulfation and sulfidation reactions has not uncovered any comparative study of the two processes.

Based on the above observations, a research program has been proposed for the comparative investigation of the reactions of metal oxides with SO_2 and H_2S . Particular emphasis will be placed on the connectivity of the pore space of the solids and the formation of inaccessible pore space in the course of the sulfation or sulfidation process. In order to be able to assess the effects of the formation of inaccessible pore space, a detailed characterization of the pore structure of fresh and partially reacted samples will be carried out using gas adsorption, mercury porosimetry, and photomicrographic methods. A detailed investigation of the effects of the various parameters on the sorptive capacity of the solids will be carried out (e.g., concentration of SO_2 or H_2S , composition of reactant mixture, particle size, and reaction temperature).

The following tasks have been identified in the proposed project:

1. Literature survey and identification of solids to be used in experimental studies.
2. Experimental study of the reaction of the chosen solids with SO_2 and/or H_2S .
3. Experimental study of the evolution of the structure of the solids during reaction with SO_2 and/or H_2S using pore structure analysis and effective diffusivity measurements.
4. Model testing and validation using the obtained experimental data.

These tasks are outlined in the following section.

3. OUTLINE OF PROJECT TASKS

Task 1. Literature survey and identification of solids to be used in experimental studies

Calcines from natural precursors (limestones and dolomites) and commercially available desulfurization sorbents (e.g, zinc oxide) of qualitatively (or quantitatively) different pore size distributions will be used in our experiments. Our initial experiments will be carried out using solids whose reaction with SO_2 (calcines) or H_2S (zinc oxide-based) has been studied in detail in past studies by our group. Literature survey and consultation with scientists from PETC and METC will help us identify other sorbents to be used in the experiments.

Task 2. Experimental study of the reaction of the chosen solids with SO_2 and/or H_2S

Reactivity Experiments will be carried out for a wide range of particle size -- in order to isolate the effects of the formation of inaccessible pore space from those of other factors -- and in a rather wide concentration and temperature range. Reactivity vs. time or conversion vs. time studies will be conducted using thermogravimetry and fixed-bed and fluidized-bed reactors.

Task 3. Experimental study of the evolution of the structure of the solids during reaction with SO_2 and/or H_2S using pore structure analysis and effective diffusivity measurements

The pore structure of partially reacted samples collected at selected time instants or conversion levels will be analyzed by gas adsorption, using a Quantachrome Autosorb 1 system, and by mercury porosimetry, using a Micromeritics Autopore 9220 II unit. The structure of the porous solids will also be analyzed by photomicrographic methods, such as optical and scanning electron microscopy. Adsorption isotherms may also be determined using flow-type and thermogravimetric apparatuses available in our laboratory. For better characterization of the pore structure of the solid samples we will also carry out intraparticle diffusivity measurements by the peak-broadening (chromatographic) method, using a system developed for this purpose in our laboratory. The fluidized-bed reactor will be used to prepare the relatively large amounts of partially reacted solid that are needed for diffusivity measurements by the peak-broadening method.

Task 4. Model testing and validation using the obtained experimental data

A class of detailed models for transport, reaction, and structure evolution

in chemically reacting porous media, developed by our research group, will be used for the analysis of the obtained reactivity and structure evolution data. Conversely, the experimental data from the fixed-bed and fluidized-bed reactors will be used to test and validate design models for these types of desulfurization reactors. analyze the experimental data obtained from our reactivity studies.

4. SCHEDULE AND MILESTONES

A tentative schedule for execution of the project tasks is shown in Fig. 1, and a list of project milestones for each task follows.

Fig. 1. Schedule of Project Tasks.

Task 1. Milestones

1.1. Literature survey of previous work and selection of first batch of sorbents to be used in experimental studies completed, 1/91.

1.2. Final decision on other sorbents to be used in experiments made, 8/92.

Task 2. Milestones

2.1. Reactivity evolution studies for the first batch of sorbents completed, 4/92.

2.1. Reactivity evolution studies for the second batch of sorbents completed, 3/93.

Task 3. Milestones

3.1. Pore structure characterization of the first batch of sorbents completed, 4/92.

3.2. Pore structure characterization of the second batch of sorbents completed, 3/93.

3.3. Diffusivity measurements for the first batch of sorbents completed, 6/92.

3.4. Diffusivity measurements for the second batch of sorbents completed, 5/93.

Task 4. Milestones

4.1. Testing of single particle models completed, 3/93.

4.2. Validation of reactor models completed, 8/93.

TECHNICAL PROGRESS IN THE PERIOD 4/91-6/91 BY TASK

Tasks 2 and 4

Our experimental results on the reaction of calcined limestones with H_2S will be presented in our next quarterly report. A manuscript describing our partially overlapping grain model (Task 4) is attached as an appendix to this report.

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