Kinetics of Sulfidation Reactions Between H₂S and Bulk Oxide Sorbents

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Abstract. This paper considers the sulfidation kinetics of bulk single oxides as well as mixed metal oxides that have promising overall properties for application to regenerative hot gas desulfurization. The hot fuel gas typically contains a large excess of reductant gases (H₂, CO), hence the kinetics of the potential parallel reduction reaction of the oxide sorbent are also considered. Effects of water vapor, typically present in various amounts in coal-gas streams, on the sulfidation/reduction kinetics are addressed as well. In addition to gas composition, the impact of sorbent physical properties and composition on the sulfidation reaction kinetics is examined in this paper. Two major classes of bulk oxide sorbents, namely: ZnO- and CuO-based materials, are used to illustrate the important issues in sulfidation of bulk oxides.

1 Introduction

Over the past two decades significant effort has been devoted to the development of regenerable hot-gas desulfurization sorbents. Regenerable sorbents would allow the desulfurization of coal-derived fuel gas streams at high temperatures, in the range of 550-750°C, in emerging advanced coal-fired power generation such as the integrated gasification combined-cycle (IGCC) power plants. Hot gas desulfurization offers energy efficiency gains over low-temperature liquid scrubbers of H₂S and avoids costly wastewater treatment. The projected cost of hot gas cleanup is approximately half that of commercially-available cold gas desulfurization; hence, the high interest in developing the new process. However, the development of a low-cost, highly efficient, rapidly reacting, regenerable sorbent, which also provides high sulfur capacity and durability still eludes the art. All sorbents studied to date lack one or more of the above features. As a consequence, they have limited range of application, e.g. to narrow gas composition-temperature domains, and may require frequent cycling and/or make-up rates that incur high operating costs.

Bulk metal oxides have been studied more extensively than supported oxides as potential hot gas desulfurization sorbents. This is due to lower manufacturing costs and higher sulfur capacity (defined as g sulfur per 100 g of total sorbent) of bulk oxides than for the corresponding supported oxides. The theoretical sorbent capacity, however, can only be realized if the sulfidation rate is not limited by poor intrinsic kinetics and/or slow gas diffusion through the sorbent pores or slow diffusion through the solid sulfide product layers. Thus, the sorbent utilization depends critically on the sulfidation kinetics and...
physical properties (pore structure, grain size) of the sorbent and the change of physical properties in cyclic operation.

Justifiably, initial sorbent screening studies focused on the thermodynamic equilibria of sulfidation, which determine the H$_2$S removal efficiency. From a large number of elements, Westmoreland and Harrison in 1976 arrived at eleven metals and their oxides as feasible H$_2$S sorbents on the basis of favorable thermodynamics of sulfidation (1). Another criterion applied to regenerable sorbents is the thermal stability of the corresponding sulfate that may be formed during regeneration. Sorbents forming thermally stable sulfates are not practical for regenerative desulfurization.

Kinetic investigations of reduction/sulfidation coupled with studies of associated solid structural changes have been undertaken sporadically over the years. This was due primarily to lack of understanding of their importance in the overall sorbent performance, but also due to premature process development efforts using promising, but insufficiently studied sorbent compositions.

Early kinetic studies of sulfidation of metal oxides include the half-calcined dolomite system (2), the oxides: MnO, ZnO, CaO and V$_2$O$_3$ (3), and iron oxides (4-8). The intrinsic kinetics of sulfidation of Fe$_2$O$_3$ are rather slow (in the absence of H$_2$ or CO) while those of metallic iron are faster (8). The sulfidation of iron has slower kinetics than ZnO, CaO or MnO, even though the opposite has often been quoted in the literature on the basis of an early report (9), which used inconsistent data to calculate the kinetic constant of Fe$_2$O$_3$ sulfidation. However, as reported later by Tamhankar et al. (8) who studied iron oxide dispersed in a silica matrix in a simulated coal gas mixture, Fe$_2$O$_3$ is quickly reduced to spongy iron, which then reacts with H$_2$S to form iron sulfide.

Reduction during sulfidation is an important issue for all reducible oxide sorbents. At the high temperature of coal gas desulfurization, the reduced metal oxide or the metal itself may be the stable phase predicted by thermodynamics, and in addition the kinetics of reduction may be faster than the sulfidation kinetics. For example, depending on the molar ratio of (H$_2$ + CO)/(H$_2$O + CO$_2$) and the temperature of the coal gas, iron may exist in Fe$_2$O$_3$, Fe$_3$O$_4$, FeO or Fe form, while copper oxide will be reduced to Cu metal in typical fuel gas compositions. Even non-reducible oxides, such as ZnO, can be prone to reduction effects, in this case magnified by the immediate vaporization of any elemental zinc that might be formed. Thus, in general, the reduction reaction should be considered along with the sulfidation of the sorbent:

$$\text{MO}_x + \text{H}_2\text{S} + \text{H}_2(\text{CO}) \rightarrow \text{MS}_y + \text{H}_2\text{O} + (\text{CO}_2); \quad y \leq x$$

More importantly, reduction kinetics should be studied separately from the sulfidation kinetics to obtain reliable kinetic parameters for each reaction.

In this paper, we present an overview of kinetic studies of reduction/sulfidation of single and mixed oxide sorbents that have appeared in the recent literature, and then consider two main classes of regenerable sorbents, ZnO-based and CuO-based materials, from a kinetics viewpoint as examined by our group to illustrate the importance of sulfidation kinetics and structural changes on the overall sorbent performance.

2 Overview of Bulk Sorbent Sulfidation Kinetics

Because of its low cost and its earlier use for desulfurization of town gas, iron oxide was the first material to be examined as a regenerable sorbent for coal gas desulfurization. The