

PC7) 코발트를 이용한 중온 영역에서의 탈황반응에 관한 Middle-Temperature Desulfurization Using Cobalt Oxide

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1. Introduction

The developments on desulfurization have been focused on the application to the advanced power generation systems such as integrated gasification-combined cycle (IGCC) and the gasification-molten carbonate fuel cell (MCFC). The gas produced from the coal gasification contains H_2S and other hazardous sulfur compounds, which must be removed to avoid corrosion and environmental problems.

However, the recent economic evaluation on IGCC reported new result that operating at middle temperature of $343\sim 538^\circ C$ showed higher benefit, because the cost for operation and material would rise.⁽¹⁾ Therefore, the middle temperature desulfurization got to interest. At low temperature, the reactivity of sorbents is getting lower but the thermal stress and the volatility are also decreased. Ayala and coworkers screened with thermodynamic equilibrium between metal oxides and H_2S at the temperature range of $350\sim 550^\circ C$. CuO, Zn, Co, Mn, Mo, W, Fe, Ni, Sn and Cu showed thermodynamic feasibility for middle temperature desulfurization. Some of these metals have some drawbacks for practical use.^(2, 3)

Even though the cobalt oxide is one of the most thermodynamically feasible metals for sulfidation with H_2S , no attempt have been tried to apply the cobalt oxide as a major components for removing H_2S . Cobalt sulfide has been already widely used as desulfurization catalysts and many researches have been performed on its characteristics. This paper report on the various research results on the sulfidation of cobalt oxide with H_2S at low temperature range, $300\sim 500^\circ C$. In addition to its desulfurization efficiency, the kinetics of the reactions is studied by using various experiments. The results are interpreted by the mathematical mode.

2. Experimental

The weight change of the sample during sulfidation reaction was measured in a Chan System 113-X thermobalance analyzer (TGA), comprising a Chan 2000 microbalance, a Micricon temperature controller, and a data acquisition system. The TGA reactor system is shown in Figure 1. The gas-flow rate was varied to ensure the absence of diffusion limitation.

The inlet gas flows were controlled by Brooks Model 5850 mass flow controllers. The gas composition was 1mol% H_2S and 3 mol% of water vapor fed if necessary. Helium was used as a balance gas. Water vapor was added to the gas by bubbling Helium through the saturator, maintaining at $25^\circ C$. The saturated gas stream entered the apparatus side arm. A thin layer of solid particles was placed on a quartz pan suspended on a quartz hang-down wire. Isothermal sulfidation experiments were performed at temperatures between $300\sim 500^\circ C$. Each solid was pretreated in a dry oven at $90^\circ C$ for 1 h to remove any absorbed H_2O before it was reacted in the TGA

3. Results and Discussion

From the thermodynamical calculation, the cobalt oxide is chosen for the sorbents at temperature range, $300\sim 500^\circ C$. Bulk cobalt oxide and impregnated on porous supports, Al_2O_3 and TiO_2 , sorbents were prepared. The desulfurization activity of sorbents was tested with pack-bed microreactor and TGA. The bulk showed sufficient removal efficiency only at $500^\circ C$ but showed low utilization of sorbent. Due to the large surface area and small particle size, the supported sorbents showed high removal efficiency and degree of sulfidation over $400^\circ C$.

The kinetic parameters of sulfidation reaction were measured by TGA experiments. Except Co_3O_4/TiO_2 sorbent, similar activation energy (12 ± 2 kcal/mol) can be obtained from the initial reaction rate of bulk and supported on Al_2O_3 sorbent. Co_3O_4/TiO_2 showed very fast reaction rate and

appears independent on the reaction temperature in the range 300~500°C. The reaction mechanism of $\text{Co}_3\text{O}_4/\text{TiO}_2$ is concluded to be different from others. This is explained by generation of oxygen vacancy in TiO_2 structure during the reaction, which is reported very active in sulfidation reaction. From literature, the oxygen vacancies are generated from the synergistic effect between cobalt metal and TiO_2 support. No further effect of water on the sulfidation kinetics of cobalt oxide sorbent was observed over the reaction condition.

The mechanism of sulfidation was investigated by the Shrinking Core model.⁽⁴⁾ The model successfully predicted the experimental data at 300~500°C. The obtained effective diffusivity, D_e , and kinetic constant, k , reflect the correlation between diffusion and kinetic resistance. The effective diffusivity is observed to depend on temperature and crystalline structure of sorbents. At a reaction temperature, two supported sorbents have similar values. However, bulk oxide, which is produced by high temperature annealing, showed higher diffusion resistance. Thus, the global rate of sulfidation of bulk oxide is controlled by resistance of diffusion.

In conclusion, the sulfidation of cobalt oxide with H_2S is limited by the mobility of sulfur ion and by counter diffusion of oxygen ion through the product sulfide layer. The removal efficiency of sorbents can be improved by impregnation of cobalt on the structural supports, Al_2O_3 and TiO_2 .

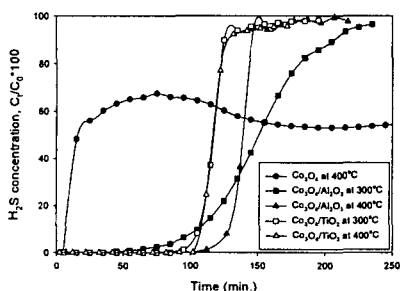


Fig. 1. H_2S breakthrough curves for cobalt sorbents. 3mol% H_2S with Helium balance, $\text{SV}=3000\text{h}^{-1}$.

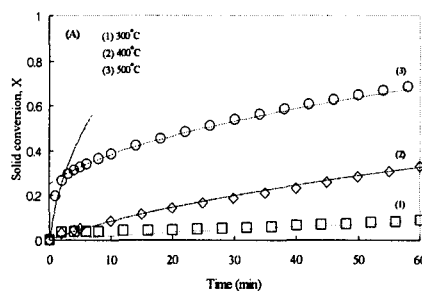


Fig. 2 Comparison of sulfidation profiles and calculated profiles of bulk Co_3O_4 at 300~500°C.

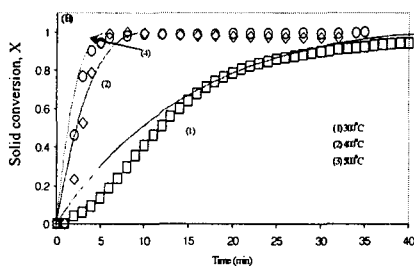


Fig. 3. Comparison of sulfidation profiles and calculated profiles of $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$ at 300~500°C.

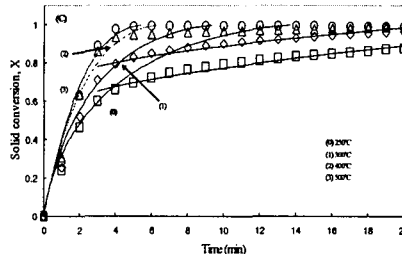


Fig. 4. Comparison of sulfidation profiles and calculated profiles of $\text{Co}_3\text{O}_4/\text{TiO}_2$ at 300~500°C.

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