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Carbon behavior in the cyclic operation of dry desulfurization process for oxy-fuel integrated gasification combined cycle power generation

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ABSTRACT

The dry sulfur-removal process is essential to provide suitable syngas treatment for the oxy-fuel integrated gasification combined cycle power generation plant. It is required that the dry sulfur-removal process to be durable to the carbon deposition due to syngas containing high concentration of carbon monoxide in addition to achieve sufficient performance for sulfur removal. Zinc ferrite sorbent is the most promising candidate for the dry sulfur-removal process. The sorbent was improved to enhance durability to the carbon deposition by modifying preparation. The improved sorbent was prepared from sulfates as the raw materials of zinc ferrite, while the former sorbent was using nitrates as the raw materials. The improved sorbent as well as the former sorbent were evaluated on the performance and carbon deposition tendency in oxy-fuel syngas condition in a fixed bed reactor at elevated pressure and temperature. The results expressed that the improved sorbent has higher desulfurization performance and durability to carbon deposition in the condition expected for cyclic operation of the sulfur-removal process in comparison with the former sorbent. The improved sorbent possessed the superior desulfurization performance as well as the capability for inhibit carbon deposition in the oxy-fuel syngas conditions. The results confirmed the enhanced feasibility of the dry sulfur-removal process by utilizing the improved sorbent.

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1. Introduction

Sequestration of carbon dioxide is one of the attempts for reducing greenhouse effect arising from anthropologic energy utilization. Various attempts to capture carbon dioxide efficiently in coal gasification combined cycle power generation were obstructed by the thermal efficiency penalty due to the huge energy consumption of conventional carbon capture processes [1]. The major factor of the energy consumption of the pre-combustion type capturing process arose from the steam injection to the fuel stream to enhance water gas shift reaction and to the CO₂ stripping process of the saturated solvent [2]. The exothermic nature of the water gas shift reaction also diminishes the calorific value of the coal gas that is fueled to the gas turbine [2]. The concept of oxy-fuel integrated gasification combined cycle (IGCC) power generation might be put to practical use more likely in the near future, because most of the component processes in the system based on modification of existing technology. It is pointed that the technical development needed for the oxy-fuel IGCC is less critical than the other concepts, while the hot gas cleaning process

and semi closed CO₂ gas turbine requires further development [3]. The dry gas desulfurization is key technology of the hot gas cleaning, which will bring significant advantage in thermal efficiency of electric power production in IGCC power generation [4]. The technology was studied lengthily along with the development of conventional IGCC. The principle used in the dry sulfur removal is sulfidation reactions of metal oxides, which can be selected from the thermodynamic estimation of the sulfidation properties of the metal oxides according to the specific operating condition and sulfur tolerance limit. Initially the single oxide was sought by thermodynamic calculation of sulfidation reactions of the candidate oxides [5]. Among various metal oxides, zinc oxide was selected from the favorable equilibrium of the sulfidation reaction [6]. Although zinc oxide can remove sulfur compounds at moderate temperature of 350 °C, oxidative regeneration of zinc sulfide will cause sintering of the sorbent due to the required temperature of over 800 °C for sulfate decomposition [7]. Then the research was shifted to the mixed oxides, such as zinc ferrite [8], zinc titanates [9], in order to reconcile the performance of sulfur removal and regenerability at the moderate temperature. Recent review of mid- to high-temperature sulfur sorbents containing zinc, copper, iron, calcium, manganese, and ceria summarized the distinctive feature of the regenerable sorbents to assess their sulfur removal

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performance and suitability for cleaning of syngas derived from coal or biomass [10]. Oxidative regeneration of the sorbent is extremely important in treating vast amount of syngas in IGCC power plant, because the repetitive utilization of the sorbent is essential to establish the feasible and economical desulfurization process [7]. Zinc titanates require high temperature for proper operation of both sulfidation and regeneration. Although the various modification of zinc titanate sorbents with additives were particularly investigated to reduce regeneration temperature [10], temperature reduction of 100 °C was achieved in the best case [11]. Regeneration of the modified zinc titanate sorbents in a fixed bed reactor showed that the complete regeneration requires 550–600 °C, at which the cumulative percent regeneration of the sorbent exceeded 90% [11]. Zinc ferrite was the other promising candidate for the desulfurization sorbent providing both high sulfur removal ability and sufficient oxidative regeneration capability for multiple cycle operation. Side reactions that are anticipated during coal gas application were investigated in earlier work under contract with US Department of Energy. One of the work illustrated that the fearful byproducts are wüstite (FeO), metallic iron or metallic zinc, which were produced by over reduction of zinc ferrite, iron carbide or carbon deposit, which were produced by CO in coal gas [12]. Those byproducts are significantly produced when the zinc ferrite sorbent are used at their target temperature, i.e. around 600 °C. Review on zinc based sorbent elucidated that the zinc ferrite sorbent has disadvantage of the over reduction of iron and vaporization of zinc at higher temperature above 600 °C [13]. Because of the disadvantage, the trends of research on zinc based sorbent shifted toward the series of zinc titanate and modified zinc titanate sorbents. There is another approach to solve the issue of the side reaction on the zinc ferrite sorbents [14]. The zinc ferrite–silica composite powder was prepared by delicate precipitation method to accelerate the reaction kinetics of the oxide, which will reduce the operation temperature of the sulfur removal process. The earlier investigation revealed that the zinc ferrite–silica composite powder, which was prepared by homogeneous precipitation and was supported on titanium oxide, has superior sulfur removal ability in simulated coal gas condition to attain sub ppm concentration for both H₂S and COS at 450 °C during multiple cycle operation [14]. The sorbent has sufficient regeneration characteristics at the same temperature for multiple cycle use of repetitive desulfurization [14]. Detailed study of the sulfidation mechanism of the composite powder using in situ XRD and Mössbauer spectroscopy revealed that the iron in the powder remained as zinc bearing magnetite during reductive environment of simulated syngas at 450 °C [15]. This evidence confirms that the zinc ferrite does not suffer from the over reduction producing wüstite or metallic iron at the moderate temperature. The durability of the desulfurization sorbent containing the zinc ferrite–silica composite powder during multiple cycle desulfurization operation was estimated [16]. The estimation showed that the sulfur removal performance of the sorbent achieves sub ppm level of sulfur compounds at pre-breakthrough if the sulfur capacity of zinc portion is maintained [16]. The zinc ferrite sorbent was evaluated with the syngas simulating air-blown type coal gasification. Thus, the crucial issue for applying zinc ferrite to the dry sulfur removal is to avoid deteriorative carbon deposition on the sorbent, when it is applied to the condition of oxygen–carbon dioxide blown syngas condition which is expected in the oxy-fuel IGCC system. Although the carbon deposition issue is still investigated on the catalyst for CO₂ reforming of methane [17], CO methanation [18], and steam reforming of methane [19] in recent works, the issue seems to be less investigated in the fields of syngas purification since the zinc ferrite sorbent was abandoned. It is empirically understood that the (reverse) Boudouard reaction shown in Eq. (1) is major reaction path for carbon deposition. As syngas contains hydrogen and steam

together with carbon monoxide and carbon dioxide, the water gas shift (WGS) reaction, which is shown in Eq. (2), always affects on the partial pressures of CO and CO₂. Chemical equilibrium of the WGS reaction should be taken into consideration when the progress of Boudouard reaction is discussed.



Iron is plausibly determinative element for acceleration of carbon deposition on the sorbent containing zinc ferrite. The reaction path of carbon deposition over iron was investigated for hematite, Fe₂O₃, in pure carbon monoxide, which concluded that the Boudouard reaction is slow at the temperature over 800 °C [20]. The Boudouard reaction tends to accelerate at lower temperature and over reduction of zinc ferrite might be affected by the presence of WGS reaction. Thus, we have to experimentally confirm the tendency of the carbon deposition reaction on the actual desulfurization sorbent at the specific condition of concern.

When the syngas produced at gasifier is cool down to the lower temperature, preventing carbon deposition is not possible from the viewpoint of chemical equilibrium. Thus, it is obvious that kinetic prevention of carbon deposition from syngas is essential to operate the plant properly. In the former work of authors [21] revealed that the proper exhaust circulation to the dry sulfur removal process could prevent significant carbon deposition in the zinc ferrite desulfurization sorbent under the oxy-fuel IGCC condition. Despite of the retardation of carbon deposition, the former desulfurization sorbent, which was prepared by batch process according to a procedure described earlier [14], exhibited slight amount of deposited carbon during reduction and sulfidation procedures that are the operation steps of desulfurization process under syngas environment. The maximum amount totaling 0.8 wt% of deposited carbon was observed during the start-up reduction without exhaust circulation that is the most severe condition expected in the actual operation of the process. Although the deposited carbon can be released as carbon dioxide during subsequent regeneration steps in the frame of ordinary operation [22], the amount of deposited carbon corresponds to the loss of calorific value of the syngas. Thus, inhibiting carbon deposition in the dry desulfurization process is essentially important for the efficient operation of the process in the oxy-fuel IGCC power generation. If improvement of the desulfurization sorbent reduces the amount of deposited carbon intrinsically, the durability and reliability of the dry sulfur removal process will be significantly enhanced. Except the fear of carbon deposition, the zinc ferrite sorbent has superior benefits of coexistence of sulfur removal performance attaining sub ppm level for both H₂S and COS and operability at the moderate temperature of 450 °C during sulfur removal and regeneration for multiple cycle operation. This work makes a challenge to improve the resistance to the carbon deposition of the zinc ferrite sorbent by modifying raw materials to prepare the sorbent. The sulfur-removal performance and the carbon-deposit behavior of the improved sorbent were investigated to clarify the effect of the sorbent improvement.

2. Oxy-fuel IGCC and dry sulfur removal process

2.1. Inhibiting carbon deposition for oxy-fuel IGCC power generation

The system configuration of the oxy-fuel IGCC power generation plant that includes dry gas cleaning processes for halides and sulfur compounds is expressed in Fig. 1. Net thermal efficiency of the plant is evaluated by a static system analysis providing the results as the efficiency in lower heating value (LHV) base of 44.0% and the higher heating value (HHV) base of 41.9% at 99%

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