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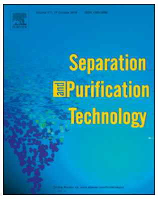

Adsorption/desorption behavior of carbonyl sulfide gas on Scheelite type MWO_4 adsorbent

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ABSTRACT

This study focused the metal oxide adsorbents to remove small amounts of carbonyl sulfide (OCS) during coal gasification, which was a preliminary step for Integrated Gasification Fuel Cell operation. This study attempted to improve the function of the adsorbent by introducing two kinds of metal species, alkaline earth metals (M = Ca, Mg, Sr, and Ba) and W, fabricated as a Scheelite-typed MWO_4 crystal. COS gases were broken down into CO and S segments on the surface of the adsorbents, and were then adsorbed onto the alkaline and W sides. The COS removals decreased in the order of $CaWO_4 > SrWO_4 > BaWO_4 > MgWO_4 > WO_3$. When the adsorbent had an ideal basicity, the CO and S adsorbed well on the surface of the adsorbent, resulting in easy breakage of the CO and S bonds. But, this study indicated that it was more influential to optimally align the adsorbate and adsorbent surface. For the Scheelite-type $CaWO_4$ adsorbent, the distance of the adsorbing active site, Ca—O—W, was similar in size to the COS adsorbate molecule, suggested a good alignment approaching the *C*-axis of the adsorbent. Moreover, an important result in this study determined by mass spectroscopy was that when COS adsorption was saturated on the MWO_4 surface, the adsorbed COS gases could desorb from the MWO_4 surface with CO_2, SO_2, CS, and CS_2 gases, which are more toxic than COS. This can be considered to other secondary environmental pollutants.

1. Introduction

Since gases such as carbon dioxide and nitrogen oxides cause environmental pollution, interest in integrated gasification fuel cell combined cycle (IGFC) technology, which has been recently shown to have a high removal efficiency with little emission of pollutant gas, is consistently growing worldwide [1]. IGFC is a technology produces syngas by gasification under high temperature/high pressure conditions and produces electricity by using this gas as fuel for the fuel cell [2]. During IGFC operation, the pollutants and impurities generated in the coal gasification process can be refined to ultra-high purity and then used as fuel. Therefore, it is as an eco-friendly power generation technology that reduces pollution because the final product discharged after the fuel cell power generation is water [3]. IGFC is 55% (net basis) more efficient compared with the latest supercritical boiler which achieved an efficiency of 41% and IGCC power generation efficiency of 46–48% [4,5]. Additionally, CO_2 emissions can be reduced by more than 25% compared to currently available coal-fired thermal power generation. However, since this method applies coal gas, which contains a large component H_2 and CO, to fuel cells, CO and sulfur poisoning must be prevented, and impurities must be removed [6,7].

Sulfur, which is a minor component of coal, is mainly converted to H_2S under the reducing atmosphere of gasification [8], and only approximately 3–10% of the sulfur content (COS formed naturally from the hydrolysis reaction: $H_2S + CO_2 \rightarrow COS + H_2O$) is carbonyl sulfide (COS) [9]. The H_2S and COS gases can be refined simultaneously or separately, but the refining methods are complicated. It is necessary to remove impurities to the ppb level because they poison the catalyst configured in the fuel cell and degrade the performance of the electrode [10]. H_2S is commonly treated by wet desulfurization technology, which is a technique to remove H_2S at low temperatures after hydrolysis. It is used for commercial refining processes in various fields such as gas purification of refinery/chemical plants flues and for the pretreatment of natural gas [11], and is also used in commercial gasification plants. Organic sulfur compounds such as COS can be converted to H_2S using a $CoMoS_4$ catalyst, and then treated with ZnO desulfurization for complete removal [12]. Alternatively, COS can be directly removed by adsorption on metal oxides. Initially, ZnO or SnO_2 were used as adsorbent to adsorb COS [13,14], after which Cu-loaded adsorbents were developed [15]. However, these adsorbents were

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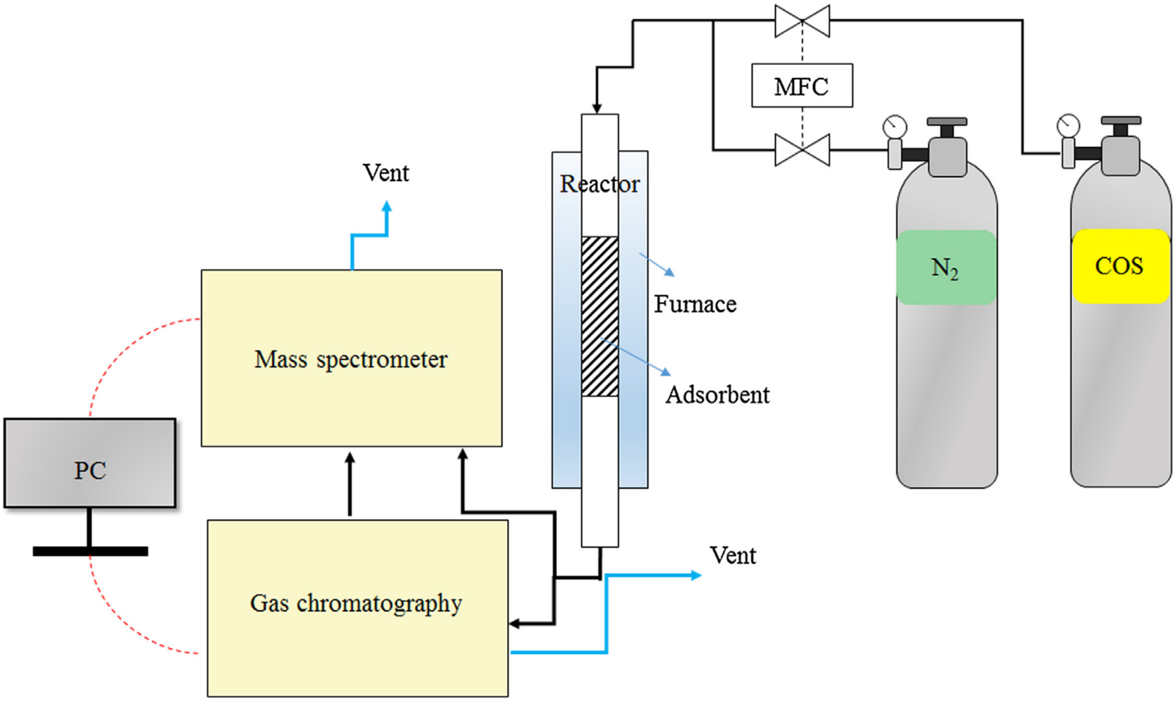

Fig. 1. Experimental apparatus of the fixed-bed reactor for COS adsorption test.

moisture sensitive due to the presence of Cu, which causes rapid adsorbent deterioration. In addition, FeO and MnO have been studied as adsorbent supports [16,17]. Moreover, W-based materials with good sulfur binding properties have been developed, but their adsorption temperature remained stubbornly high despite attempts at lowering it [18]. Recently, adsorbents loaded with small amounts of lanthanide metals have been developed. Among them, CeO_2, La_2O_3, and Sm_2O_3-loaded adsorbents showed good performances [19–21], and Fe and Mn mixed oxides were used as promoters [22].

In general, COS adsorption can be described by the following equation $2MO(s) + COS(g) \rightarrow MS(s) + MCO_3(s)$ [23,14]. Here, we attempted to accelerate the decomposition rate of COS by adding small metal ions to the CO segment and large metal ions to the S segment following the hard soft acid base (HSAB) rule of Pearson [24]. Thus, this study had two main goals. First, as the main active species in the prepared adsorbent, we used W and alkaline earth metals, which can combine with S and CO segments, respectively, in COS. The same amount of alkaline earth metals, Mg, Ca, Ba, and Sr, were added to observe the adsorption extent of COS as a function of the basicity. Secondly, the metals were crystallized approaching them as close as possible: alkaline earth metals and W, were mixed and formed Scheelite typed MWO_4 crystals. Then, we used the fabricated adsorbents to induce the following reaction, $COS(g) + MWO_4(s) \rightarrow MCO_3(s)$ (or exactly $OCMO_2$) + $WSO_2(s)$ (or exactly SWO_2), to minimize the direct poisoning of the metal catalyst by carbon and sulfur impurities. This prevents the binding of the CMC and the SMS for maximizing the adsorption capacity over long periods of operation. Finally, we attempted to find the most suitable alkaline earth metal for COS removal, to discuss the adsorption and desorption mechanisms, and to understand the correlation of adsorption/desorption with surface properties through XRD, SEM, EDS/element mapping, BET, XPS, FT-IR, and Mass spectrometry.

2. Experimental

2.1. Preparations and characterizations of WO_3 and MWO_4 adsorbents

WO_3 was synthesized as a base material in first step and adjacent to the MWO_4 materials which were composed of W and either Mg, Ca, Sr, or Ba, and were prepared by a conventional sol-gel method. In first step, sodium tungstate ($Na_2WO_4 \cdot 2H_2O$, 99.99%, Junsei Co. Japan) was dissolved in distilled water and which was adjusted to pH 9 with an ammonia solution with stirring for 2 h. A precipitate was obtained and washed with deionized (DI) water until its pH reached a value of 7. The washed powder was dried at 70 °C for 24 h in a dry oven, and calcined at 600 °C for 4 h to form the crystals. Conversely, in the MWO_4 synthesis step, the hydroxide precursors of each alkaline earth metal ($M(OH)_2$, M = Mg, Ca, Sr, and Ba, 99.9%, Junsei Co. Japan) were dissolved in beakers with DI water and the pH was adjusted to 5 with nitric acid (A solution). Sodium tungstate was dissolved in DI water and adjusted pH 9 with an ammonia solution (B solution). The A and B solutions were slowly mixed and stirred for 2 h. Four kinds of precipitates formed, were washed with DI water until reaching pH 7, and dried at 70 °C for 24 h in a dry oven. Finally, the powders were calcined at 600 °C for 4 h to induce crystallization. Thus, in this study, the obtained adsorbents were WO_3, $MgWO_4$, $CaWO_4$, $SrWO_4$, and $BaWO_4$.

The synthesized adsorbents were identified through powder X-ray diffraction (XRD, model MPD, PANalytical, Netherland), scanning electron microscopy (SEM, S-4100, Hitachi, Japan), energy dispersive X-ray spectroscopy (EDX, EX-250, Horiba, Japan), and adsorption-desorption isotherms of N_2 (Belsorp II, Japan). The COS adsorption/desorption behavior was evaluated using Fourier transform infrared (FT-IR) spectroscopy (Nicolet iS10 spectrometer, Thermo Fisher Scientific Inc., USA), Mass spectrometry (BELMASS, BEL Japan, Inc., Japan), and X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermoscientific, UK).

2.2. COS removal tests using the WO_3 and MWO_4 adsorbents

The COS removal tests for the adsorbents are conducted using a fixed-bed reactor as shown in Fig. 1. The powdered adsorbent (1.0 g) was placed in a Pyrex column with an internal diameter of 10 mm of the reactor and heated to 400 °C under an N_2 atmosphere at a heating rate of 5 °C/min. After the temperature was completely stabilized at 400 °C for 1 h, a feed gas of 100 ppm COS balanced with N_2 gas was introduced from the top of the reactor which controlled by mass flow meters