様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９　（共通）

科学研究費助成事業　　研究成果報告書

令和　５ 年　 ６ 月　 ６ 日現在

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研究課題名（和文）Development of solid sorbents for the removal of elemental mercury from combustion flue gases

研究課題名（英文）Development of solid sorbents for the removal of elemental mercury from combustion flue gases

研究代表者

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交付決定額（研究期間全体）：（直接経費）　　3,100,000円

研究成果の概要（和文）：本研究の目的は，石炭ガス化燃料ガス及び石炭燃焼排ガスからの水銀除去用収着剤を開発し，除去メカニズムを解明することである。収着剤としてFe，Zn，Ce，Mn，Cuなどの金属の酸化物や硫化物を試みた。ガス化燃料ガスに関してCe-Fe及びCe-Znの二成分収着剤は，単一成分収着剤よりも水銀除去率が高く安定した。水銀は，酸化水銀と硫化水銀を形成することで収着剤に除去された。燃焼排ガスについては，FeO(OH)-Ca(OH)2とCuO- Ca(OH)2の除去率はそれぞれ79.6%と73.6%となった。以上から，金属酸化物および金属硫化物は，種々の水銀含有ガスからの水銀除去に対して有望な収着剤といえる。

研究成果の学術的意義や社会的意義
The present study will cancontributes to the reduction of carbon dioxide emissions by supporting the highly efficient power generation system for utilization of coal. If the mercury removal technology could be established in Japan it will contribute to the removal recovery of mercury in Japan.

研究成果の概要（英文）：The main purpose of this study was to develop mercury removal agent or adsorbents from coal gasification fuel gas and coal combustion flue gas with an emphasis on recovery of mercury through understanding of the removal and recovery mechanism. Various kinds metal compounds such oxides and sulfides of metals such as iron (Fe), zinc (Zn), cerium (Ce), manganese (Mn), copper (Cu), etc. were developed. Both the CeO2-Fe2O3 and CeO2-ZnO bi-component adsorbent were more efficient and stable than a mono component adsorbent for mercury removal. Mercury is adsorbed on the adsorbent by forming mercury oxides and mercury sulfide.For combustion flue gas,10%FeO(OH)-slaked lime and 10% CuO-slaked lime exhibited high mercury removal performance, with an average removal rate of was 79.6% and 73.6%, respectively. Metal oxides and metal sulfides are very promising sorbents for mercury removal from coal combustion flue gas, coal gasification gas as well as from municipal waste incineration flue gases.

研究分野：環境化学

キーワード：Mercury removal　Adsorbents　Coal combustion flue gas　Coal gasification gas　Incineration flue gas　Metal oxides　Metal sulfides

様　式　C－１９、F－１９－１、Z－１９（共通）

１．研究開始当初の背景

Mercury emissions from natural and anthropogenic sources enter the global mercury cycle and are distributed in the environment locally and globally through various processes. Atmospheric emissions of mercury can enter the environment through deposition onto soils and water and causes harm to the human and environment. "Minamata Convention on Mercury" was adopted in October 2013 with the aim of protecting human health and the environment from emissions. In order not to repeat health damage and environmental destruction by mercury Japan concluded in February 2016 that the Minamata Convention will enter into force on August 16, 2017 in Japan.

Coal-fired utilities are the single largest source of anthropogenic mercury emissions in the world. Because of its high volatility, almost all the mercury present in coal is transformed into gas phase during combustion or gasification of coal. Control of mercury emissions from coal-fired power plants is a difficult task, in part due to its high volatility and its much lower concentration (5–20 μg/m^3) in a large volume of flue gas. In addition, depending on the type of coal and combustion conditions, most of mercury in the flue gas can exist in the elemental form (Hg^0), which is more difficult to capture than its oxidized (Hg^{2+}) or particulate (Hg^p) forms.

Development and commercialization of efficient mercury removal technology has been demanded from such a viewpoint. Thus, with increasing interest in mercury pollution, various mercury capture methods have been proposed. We have been conducting research that focuses mainly on the removal of mercury and elucidation of mercury removal mechanism. In this study we propose to develop very active sorbents consisting of activated carbon, metal sulfides and metal oxides nano-composites for mercury removal from coal gasification fuel gas and coal combustion flue gas.

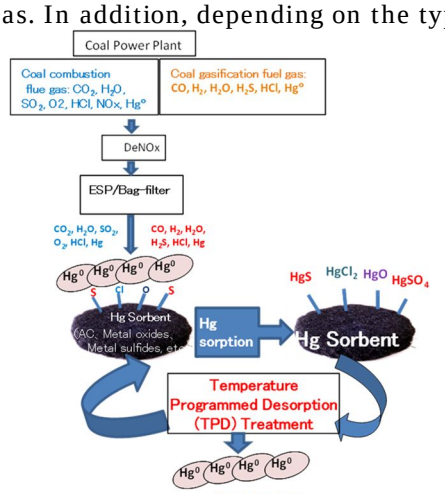


Fig. 1 Conceptual diagram of the project

２．研究の目的

The main target of this study is to develop mercury removal agent with an emphasis on recovery of mercury through understanding of the removal and recovery mechanism. Based on the results of this basic research, we aim to build a design guideline for the development of re-generable highly active sorbents. We have developed a thermal desorption method (Temperature Programmed Desorption, TPD method) commonly used for the catalytic studies as a method to identify the adsorbed mercury species and, it is a unique method which based on the thermal behavior of the adsorbed mercury species. Consideration of the mechanism of Hg adsorption will lead to new ideas for the development of the Hg removing agent. As described above, the present study can also contribute to the reduction of carbon dioxide emissions by supporting the highly efficient power generation system for utilization of coal.

３．研究の方法

1) Several potential sorbents will be prepared, and evaluation of mercury removal performance will be carried out. 2). If the predetermined activity is obtained, the sorbents will be evaluated for Hg recovery and regeneration. 3). The stability of the sorbents for repeated use after regeneration and the characterization of the sorbent will be carried out in parallel. 4). Our newly developed Temperature Programmed Decomposition and Desorption (TPDD) technique will be employed to identify the mercury species adsorbed on the sorbents, clarify the mechanism of mercury removal and regeneration of the sorbents.

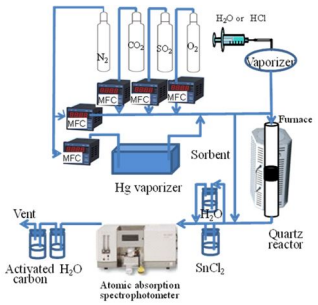


Fig. 2 Experimental setup for Hg capture experiment

(a)Preparation of sorbents:

Based on our previous study results, in these studies we planned to prepare metal compounds,

such as oxides and sulfides of Fe, Ce, Cu, Mn, Zn, etc. for mercury removal experiments

(b). Evaluation of mercury capture ability of the sorbents:

Evaluation of mercury removal performance sorbent was carried out in this study using a device that has been used so far in our laboratory. A fixed-bed flow type reactor as shown in Fig. 2 will be used under the conditions of simulated coal combustion flue gas and coal gasification fuel gas system. Reaction gas atmosphere is expected to use a simulated gas close to the actual system. Also, the reaction temperature range is considered to be practical temperatures in coal power plants such as 80-150 °C for coal combustion flue gas and 200-350 °C for coal gasification fuel gas.

(c). Regeneration of the sorbents and recovery of the adsorbed mercury:

Desorption and recovery of mercury after adsorption was carried out using the same apparatus as shown Fig. 2 by Temperature Programmed Decomposition and Desorption (TPDD) method. Effects of co-existing gases on the TPDD spectra was studied in order to understand the mechanism of Hg adsorption on the adsorbents.

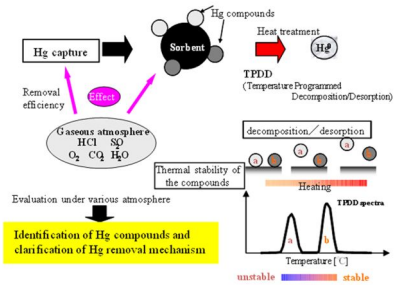


Fig. 3 Temperature Programmed Decomposition Desorption Method

４．研究成果

１）Ce-Zn 系酸化物による石炭ガス化ガス中の水銀除去 (Reference and Presentation [2])

Mercury Removal from Coal Gasification Gas by Ce-Zn Oxides

In this study, we focused on cerium oxide and zinc oxide, which are relatively cheap and stable. Cerium oxide has lattice oxygen and is reported to be effective in oxidizing mercury by redox reaction between Ce^{4+} and Ce^{3+}. A two-component mixed remover was prepared by combining these two kinds of metal oxides. The prepared remover was tested in a simulated coal gasification gas atmosphere, and its mercury removal performance and durability were evaluated.

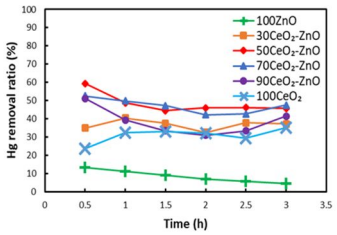


Fig.4 Mercury removal rate on ZnO, CeO_2 and CeO-ZnO mixed oxides

Figure 4 shows the time course of mercury removal rate for 3 hours with each remover. It was found that the combined adsorbent improved the mercury removal performance more than the remover consisting of CeO_2 and ZnO alone. In addition, the higher the CeO_2 content of the compositeadsorbent, the higher the mercury removal performance tended to be. The average mercury removal rate was highest with the 50 %CeO_2-ZnO. Therefore, we decided to conduct a detailed study focusing on 50 %CeO_2-ZnO. Fig. 5 shows the results of the TPDD experiment for the adsorbent used in the mercury removal experiment. Mercury desorption peaks appeared around 300 °C for all adsorbents. Since it has been confirmed from previous studies that this peak is derived from HgO, it is presumed that the adsorbents prepared in this study immobilizes mercury in the form of HgO. Furthermore, since CeO_2 has an oxygen storage capacity, it is thought that HgO was produced by the reaction between the active oxygen of CeO_2 and mercury.

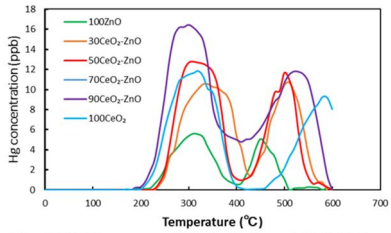


Fig. 5 TPDD spectra of ZnO, CeO_2 and CeO-ZnO mixed oxides

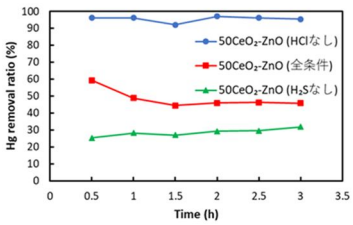


Fig. 6 Effect of HCl and SO_2 on the Hg removal rate of ZnO, CeO_2 and CeO-ZnO mixed oxide

Since sulfur species are believed to contribute significantly to the mercury removal reaction, the effect of H_2S as a source of sulfur was investigated. In addition, as previous studies have shown that chlorine also affects mercury oxidation, the effect of HCl as a source of chlorine was also investigated (Fig. 6). Mercury removal rate decreased significantly when the experiment was conducted in the absence of H_2S. This indicates that H_2S is required for mercury removal. However, when the experiment was performed in the absence of HCl, the mercury removal rate increased significantly. This is probably because HCl consumes the active oxygen of CeO_2, which is important for mercury removal.

２）Development of sorbents for the removal of elemental mercury from coal gasification gas

(Reference and Presentation [1] and [4])

The aim of this study is development of sorbents suitable for the removal of elemental mercury from coal gasification gas. Fe_2O_3 and CeO_2 were chosen as sorbents because they are inexpensive and stable in the mercury removal reaction. The effects of combination of Fe_2O_3 and CeO_2 at various ratio were investigated.

The simulated coal gasification gas was used for the mercury removal experiment. It was found that the inclusion of Fe_2O_3 in CeO_2 improves the mercury removal performance and also improves the durability in repeated use. After the mercury removal experiment, TPDD experiment was performed to examine the adsorption state of mercury by the sorbents from the desorbed mercury peak (Fig. 7). Since the peaks derived from HgS appeared in all the sorbents, it was suggested that the mercury was captured in the form of HgS. When the experiment was performed in the absence of H_2S and in the absence of HCl, the mercury removal rate decreased. Both H_2S and HCl are believed to contribute to the mercury removal reaction (Fig. 8).

TPDD spectra of CeO_2, Fe-Ce mixed oxide supported on slaked lime revealed that desorption peaks corresponded to HgS and HgO decomposition and, for Fe_2O_3-slaked lime, the TPDD peak corresponding to HgS decomposition was observed. Figure 9 shows the stability of the adsorbents used in this study. It was found that CeO_2-Fe_2O_3 bi-component adsorbent is more stable than a mono component sorbent.

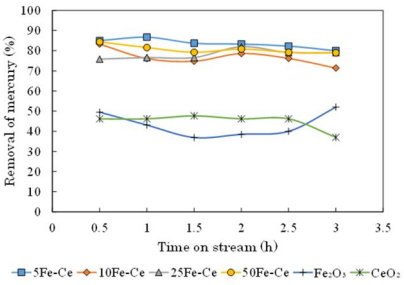


Fig. 7 Mercury removal rate on Fe_2O_3, CeO_2 and Fe_2O_3 - CeO_2 mixed oxide

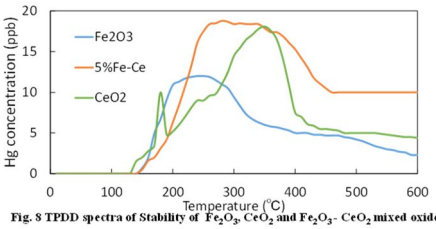
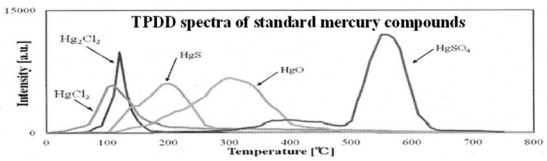


Fig. 8 TPDD spectra of Stability of Fe_2O_3, CeO_2 and Fe_2O_3 - CeO_2 mixed oxide after Hg removal



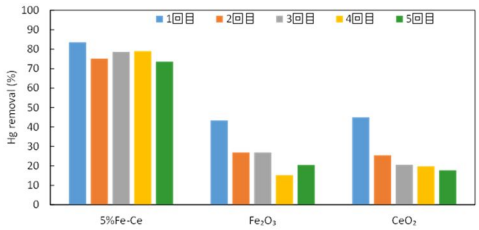


Fig. 9 1 Stability of Fe_2O_3, CeO_2 and Fe_2O_3 - CeO_2 mixed oxide for Hg removal

3）金属化合物と消石灰を組み合わせた除去剤を用いた廃棄物焼却排ガス中の金属水銀の除去

(Reference and Presentation [5])

Removal of metallic mercury from waste incineration flue gas using a remover that combines metallic compounds and slaked lime

The main purpose of this study was to extend this research to the removal of elemental mercury removal from municipal waste incineration flue gases using metal oxides (FeO(OH), MnO_2, RuO_2 and CuO) and metal sulfides (FeS, FeS_2, ZnS) supported on slaked lime.

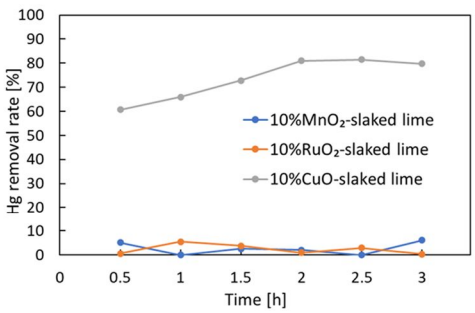


Fig. 10 Mercury removal rate on ZnO-, CeO_2-, and CuO-slaked lime composite

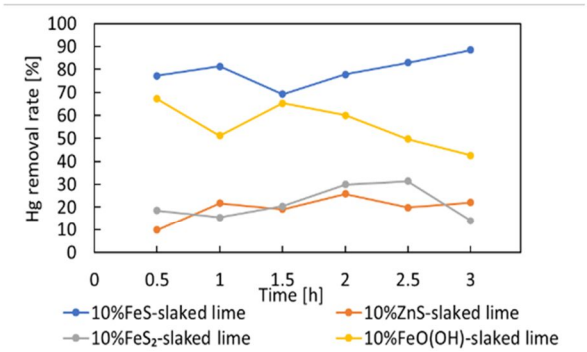


Fig. 11 Mercury removal rate on FeS-, FeS_2, Zns, FeO(OH)-slaked lime composite

Figure 10 and 11 show the mercury removal rate on the 10 wt%MnO_2-, RuO_2, CuO, FeS, FeS_2, ZnS, FeO(OH)-slaked lime sorbents. 10%FeO(OH)-slaked lime and 10% CuO-slaked lime exhibited high mercury removal performance, with an average removal rate of was 79.6%

and 73.6%, respectively. Thus, metal oxides and metal sulfides are very promising sorbents for mercury removal from coal combustion flue gas, coal gasification fuel gas as well as from municipal waste incineration flue gases

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[1] Kento FUJIYAMA , Md. Azhar UDDIN , Yoshiei KATO; “Development of sorbents for the removal of elemental mercury from coal gasification gas”; Proceedings of The 18th Asian Pacific Confederation of Chemical Engineering Congress (APCChE 2019); September 23-27, 2019, Sapporo, Japan.

[2] **山田隆成、**Uddin Md. Azhar, **加藤嘉英** [Ce-Zn **系酸化物による石炭ガス化ガス中の水銀除去]、第** 22 **回化学工学会学生発表会 (岡山大会)** 2020 **年** 3 **月** 7 **日(土)岡山大学津島キャンパス**.

[3] **藤山健人**, UDDIN Md Azhar, **加藤嘉英：「消石灰と金属硫化物複合体による廃棄物焼却排ガス中の金属水銀の除去」化学工学会第** 51 **回秋季大会** , W117 (2020)

[4] Md. Azhar Uddin, Kento Fujiyama, Yoshiei Kato; “DEVELOPMENT OF ADSORBENTS FOR THE REMOVAL OF ELEMNTAL MURCURYFROM COAL GASIFICATION GAS"; Proceeding of the Thirty-Eighth Annual Virtual International Pittsburgh Coal Conference; September 20- 23, 2021.

[5] **是石 悠斗**,Uddin Md Azhar, **福田 伸子**, **坂本 裕一「金属化合物と消石灰を組み合わせた除去剤を用いた廃棄物焼却排ガス中の金属水銀の除去」学工学会 第** 53 **回秋季大会** SY-82 (2022)

５．主な発表論文等

〔雑誌論文〕　計0件

〔学会発表〕　計5件（うち招待講演　0件／うち国際学会　2件）

１．発表者名 Azhar Uddin, Kento Fujiyama, Yoshiei Kato
２．発表標題 DEVELOPMENT OF ADSORBENTS FOR THE REMOVAL OF ELEMNTAL MURCURY FROM COAL GASIFICATION GAS
３．学会等名 Thirty-Eighth Annual Virtual International Pittsburgh Coal Conference（国際学会）
４．発表年 2021年

１．発表者名 藤山健人, UDDIN Md Azhar, 加藤嘉英
２．発表標題 消石灰と金属硫化物複合体による廃棄物焼却排ガス中の金属水銀の除去
３．学会等名 化学工学会第51回秋季大会 , W117 (2020
４．発表年 2020年

１．発表者名 山田隆成、Uddin Md. Azhar、加藤嘉英
２．発表標題 Ce-Zn系酸化物による石炭ガス化ガス中の水銀除去
３．学会等名 第22回化学工学会学生発表会（岡山大会）
４．発表年 2020年

１．発表者名 Kento FUJIYAMA , Md. Azhar UDDIN , Yoshiei KATO
２．発表標題 Development of sorbents for the removal of elemental mercury from coal gasification gas
３．学会等名 The 18th Asian Pacific Confederation of Chemical Engineering Congress（国際学会）
４．発表年 2019年

１．発表者名 山田隆成、Uddin Md. Azhar、加藤嘉英
２．発表標題 Ce-Zn系酸化物による石炭ガス化ガス中の水銀除去
３．学会等名 第22回化学工学会学生発表会(岡山大会)
４．発表年 2020年

〔図書〕　計0件

〔産業財産権〕

〔その他〕

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６．研究組織

	氏名 （ローマ字氏名） （研究者番号）	所属研究機関・部局・職 （機関番号）	備考

７．科研費を使用して開催した国際研究集会

〔国際研究集会〕　計0件

８．本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関