

Removal of Elemental Mercury from Dry Methane Gas with Manganese Oxides

Junya Takenami, Md. Azhar Uddin, Eiji Sasaoka, Yasushi Shioya, and Tsuneyoshi Takase

Abstract—In this study, we sought to investigate the mercury removal efficiency of manganese oxides from natural gas. The fundamental studies on mercury removal with manganese oxides sorbents were carried out in a laboratory scale fixed bed reactor at 30 °C with a mixture of methane (20%) and nitrogen gas laden with 4.8 ppb of elemental mercury. Manganese oxides with varying surface area and crystalline phase were prepared by conventional precipitation method in this study. The effects of surface area, crystallinity and other metal oxides on mercury removal efficiency were investigated. Effect of Ag impregnation on mercury removal efficiency was also investigated. Ag supported on metal oxide such titania and zirconia as reference materials were also used in this study for comparison. The characteristics of mercury removal reaction with manganese oxide was investigated using a temperature programmed desorption (TPD) technique.

Manganese oxides showed very high Hg removal activity (about 73-93% Hg removal) for first time use. Surface area of the manganese oxide samples decreased after heat-treatment and resulted in complete loss of Hg removal ability for repeated use after Hg desorption in the case of amorphous MnO₂, and 75% loss of the initial Hg removal activity for the crystalline MnO₂. Mercury desorption efficiency of crystalline MnO₂ was very low (37%) for first time use and high (98%) after second time use. Residual potassium content in MnO₂ may have some effect on the thermal stability of the adsorbed Hg species. Desorption of Hg from manganese oxides occurs at much higher temperatures (with a peak at 400 °C) than Ag/TiO₂ or Ag/ZrO₂. Mercury may be captured on manganese oxides in the form of mercury manganese oxide.

Keywords—Mercury removal, Metal and metal oxide sorbents, Methane, Natural gas.

I. INTRODUCTION

THE main components of most natural gases (NG) are methane and other lighter hydrocarbons. Elemental and compounded mercury is present in many natural gas regions of the world. Complete removal is needed to avoid catastrophic failures in cryogenic equipment or chemical processes catalyst poisoning. Additionally, hydrocarbon products which are mercury free sometimes command an enhanced product value. The mercury contents in the NG from various parts of the world

vary greatly from 0.04 ppb to several hundred ppb [1].

A small amount of mercury in process gases can destroy aluminum heat exchangers used at LNG and olefin plants. Therefore, it is necessary to remove mercury from the natural gas to protect the process equipments, particularly aluminum heat exchangers. Numerous methods for Hg removal from NG have been suggested [2]. It is known that Au and Ag are active in reacting with Hg in gas phase through amalgamation at 30 °C. However the cost consideration of Au and Ag may make it difficult for practical application. A process has been reported to remove the residual mercury in gas with 4A mol. sieves (4A sieves) modified with a small quantity of silver. It has also been reported that sulfur impregnated activated carbon performed better than other noncarbon materials as Hg removing sorbent [3]. Sulfide containing alumina is also reported to be effective for removal of elemental mercury. In the cases of sulfur containing sorbents, Hg is captured as HgS. It should be mentioned here that silver and sulfur containing sorbents are only capable of absorbing elemental mercury and in order to remove compounded mercury, e.g. organomercury species, a primary or pre-processing stage is required.

Manganese oxides are used as catalysts or catalyst supports for many oxidation reaction due to their ability of oxygen mobility. Mn occurs in natural systems in three different oxidation states: +2, +3, and +4, giving rise to a range of multivalent phases. Mn oxides in soils and sediments readily participate in a wide variety of oxidation-reduction and cation-exchange reactions. They exhibit large surface areas and can be very chemically active. Birnessite directly oxidizes Se(IV) to Se(VI) via a surface mechanism [4], Cr(III) to Cr(VI) [5], and As(III) to As(V) [6]. Certain Mn oxide minerals easily oxidize arsenate (III), the more toxic form of inorganic As, to arsenate(V), which can more effectively be removed from drinking water by existing water treatment procedures [7]. It can be expected that mercury can be captured on the manganese oxide sorbents.

In this study, we sought to investigate the mercury removal efficiency of manganese oxides from natural gas. The fundamental studies on mercury removal with manganese oxides sorbents were carried out in a laboratory scale fixed bed reactor at 30 °C with a mixture of methane (20%) and nitrogen gas laden with 4.8 ppb of elemental mercury. Manganese oxides with varying surface area and crystalline phase were prepared by conventional precipitation method in this study. The effects of surface area, crystalline phase and other metal on

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mercury removal efficiency were investigated. Effect of Ag impregnation on mercury removal efficiency of manganese oxide was investigated. For comparison, Hg removal was also performed with Ag supported on titania and zirconia sorbents. The characteristics of mercury removal reaction with manganese oxide was investigated using a temperature programmed desorption (TPD) technique.

II. MATERIALS AND METHODS

A. Preparation of Metal Oxide Sorbents

In this study the manganese oxide and the mixed metal oxides were prepared by conventional precipitation and co-precipitation methods using their corresponding metal sulfate salts as metal sources and potassium permanganate as precipitating agents. After decantation and filtration the samples were dried at 120 °C, 8 h and calcined at 250 °C. 2 wt% Ag was supported on the metal oxides by impregnation method followed by liquid phase reduction with sodium formate. Titania and zirconia were commercial catalyst supports obtained from SUD-CHEMIE CATALYSTS JAPAN, INC.

B. Hg Removal Experiments

The Hg removal experiment with metal oxide sorbents was carried out in a flow-type packed bed reactor under atmospheric pressure at 30 °C. The detail of the apparatus for Hg⁰ removal has been described elsewhere [8]. The apparatus consisted of an Hg⁰ vaporizer, a feed system, a quartz glass reactor, a furnace with temperature controller and a cold vapor Hg⁰ analyzer. About 0.0625 cm³ of the sorbent sample (particle diameter: 1 mm.) was packed into a quartz tube reactor. The reaction is commenced when a mixture of Hg⁰ (4.8 ppb), CH₄ (20%), and N₂ (balance gas) was fed into the reactor at 500 cm³·STP·min⁻¹ (SV: 48.0×10⁴ h⁻¹). Measurements of the inlet and outlet concentrations of mercury were carried out using an atomic absorption spectrophotometer (NIPPON Jarrell Ash AA-855). The inlet concentration of Hg (Hg_{in}) was measured by passing the Hg-laden gas mixture through the reactor by-pass to the mercury analyzer before and after the adsorption experiments. During mercury contact period, the reactor exit concentration of mercury (Hg_{out}) was continuously monitored. The instantaneous removal of Hg⁰ at any time was obtained by

$$\text{Percent of Hg removal} = \frac{(\text{Hg}_{\text{in}} - \text{Hg}_{\text{out}})}{\text{Hg}_{\text{in}}} \times 100 \quad (1)$$

Amount of Hg adsorption was determined by integrating and evaluating the area under the removal curve over the entire time of adsorption.

After Hg⁰ removal experiment, the desorption of mercury was carried out with a temperature programmed desorption technique by heating the sample at atmospheric pressure in a packed bed quartz tube reactor at a constant heating rate. In the temperature programmed decomposition (TPD) experiments, about 0.0625 cm³ of the mercury-adsorbed metal oxide sample was packed in a quartz tube reactor and N₂ was flowed in the reactor at a rate of 250 cm³·STP·min⁻¹. Then the sample was heated from room temperature to 500 °C at a heating rate of 10 °C per min and the reactor effluent was monitored for Hg continuously with an atomic absorption spectrophotometer.

The TPD spectra were constructed by plotting the amount of Hg desorption against the temperature and the amount of Hg desorption was determined by integrating and evaluating the area under the TPD spectra over the entire time of desorption.

C. Characterization of the Metal Oxides Sorbents

The metal oxides sorbents were characterized by N₂ adsorption BET method for specific surface area using a N₂ adsorption Analyzer (Gemini 2375, SHIMADZU). The crystalline phase of the sorbents was characterized with X-ray diffraction Spectrophotometer (XRD-6100, SHIMADZU).

III. RESULTS AND DISCUSSION

A. Mercury Removal with Ag supported on Titania and Zirconia

It has been reported that Ag supported on zeolite, metal oxides and activated carbons are active in elemental mercury removal and the elemental mercury is captured on the sorbents in the form of silver amalgam. In order to verify these phenomena, we carried out the mercury removal experiments with TiO₂, ZrO₂ and Ag supported on TiO₂ and ZrO₂ at 30 °C using a gas mixture containing 4.8 ppb of Hg, 20% CH₄ and N₂ balance. Fig. 1 shows the percent of Hg removal after 2 h time-on-stream for each sorbent sample. It is evident from this figure that the support TiO₂ and ZrO₂ has no Hg removal capacity and the Hg removal efficiency of the sorbents increased drastically to 80% for Ag/TiO₂ and 65% for Ag/ZrO₂. Therefore, it can be concluded that Ag is active in capturing Hg from methane at room temperature.

The desorption characteristic of the Hg were studied by measuring the TPD spectra of the Ag-adsorbed sorbents by heating the sample from room temperature to 500 °C at a heating rate of 10 °C per min in N₂. The TPD spectra or TPD profile was constructed by plotting the concentration of Hg in the desorption stream against the temperature. Fig 2 shows a typical TPD profile of Ag/TiO₂ and Ag/ZrO₂. In this plot, the Hg concentration was shown as the absorbance intensity of the atomic absorption spectrophotometer for elemental mercury. The TPD profile of Ag/TiO₂ showed that mercury desorption occurs in the temperature range of 100 °C to 400 °C with a peak at 180 °C. This peak may be corresponded to desorption of Hg from silver amalgam. In the case of Ag/ZrO₂, Hg desorption was observed in the temperature range of 100 °C to 450 °C with two distinct peaks: one at around 180 °C and another at around 370 °C. At this stage we can suggest that the second peak may be related to Hg captured on support ZrO₂.

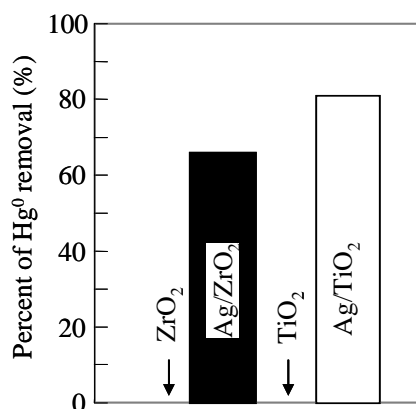


Fig. 1 Mercury removal efficiency of TiO₂, ZrO₂, and Ag supported on TiO₂ and ZrO₂ at 2 h time-on-stream

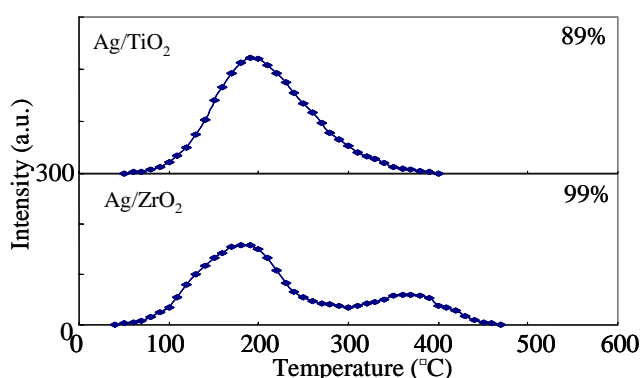


Fig. 2 TPD profile of Hg desorption from Hg adsorbed Ag supported on TiO₂ and ZrO₂

B. Mercury Removal with Manganese Oxide and Ag Supported on Manganese Oxide Sorbents

Mercury removal experiments were carried out with manganese oxides having with different surface area, crystallinity and residual potassium content: Mn-08, amorphous MnO₂ (K-content: 7%, surface area: 395 m²·g⁻¹); Mn-12 (surface area: 61 m²·g⁻¹); Mn-13, tunnel type crystalline MnO₂ (K-content: 3%, surface area: 229 m²·g⁻¹). Ag was supported on Mn-08 and Mn-13 to prepare Ag/Mn-08 and Ag/Mn-13 samples in order to study the effect of Ag on Hg removal activity of manganese oxides. Fig. 3 shows the mercury removal activity of manganese oxides and Ag supported manganese oxide sorbents. All manganese oxide sorbents showed high Hg removal efficiency. Among the manganese oxides, Mn-13 with tunnel structure and 3% K showed the highest Hg removal activity (93%) followed by Mn-12 (80%) and Mn-08 (73%). Additions of Ag to the manganese oxides have no significant effect on the Hg removal of the sorbents. Therefore, it can be suggested that Hg is captured on MnO₂ by forming some kind of surface oxides and there are no direct correlations between surface area and Hg removal and, residual potassium content and Hg removal activity of the manganese oxides sorbent. However, it seems likely that the crystalline MnO₂ has higher Hg removal activity

than the amorphous MnO₂, although the amorphous MnO₂ have higher surface area.

The TPD profiles of Mn-13 and Ag/Mn-13 are shown in Fig. 4. As we mentioned earlier that both Mn-13 and Ag/Mn-13 showed high Hg removal activities. However the TPD profiles of these samples are different from each other: Mn-13 showed a Hg desorption peak at around 400 °C which is quite different from Ag/TiO₂ or Ag/ZrO₂ (Fig. 2). In contrast, Ag containing MnO₂ (Ag/Mn-13) showed Hg desorption peaks at lower temperatures in the range of 180 °C to 370 °C. Furthermore, the Hg desorption efficiency of Mn-13 was very low (37%) compared to 74% for Ag/Mn-13 as shown in Fig.3. Therefore, although the mercury removal levels of these two samples are the same but the Hg capture mechanism seems to be different because different types of Hg species on the sorbent surface might be formed on these sorbents. Although the results are not shown here, it was observed that the TPD profiles and the Hg desorption peak temperatures of Mn-08 (with low K content) and Ag loaded Mn-08 were very similar. Therefore the content of residual potassium in the MnO₂ may have some effect on the TPD profile. We need to more detailed studies in order to clarify the above results.

Table I shows the surface area of the manganese oxide sorbents (Mn-08, Mn-12 and Mn-13) before and after use in Hg removal experiments followed by Hg desorption (TPD) experiments. It is clear that surface area of all manganese oxide samples decreased, particularly the surface area of amorphous MnO₂ (Mn-08) decreased drastically. Therefore, it is evident that the pore structure of all MnO₂ samples might be collapsed during heating in TPD experiments.

C. Stability and Mercury Removal Activity of Manganese Oxides after the Heat Treatment in TPD Experiments

In these experiments, the stability and activity of the different MnO₂ oxides for repeated use after TPD experiments were evaluated. Fig. 5 shows the Hg removal activity of Mn-08 for repeated use after Hg desorption (TPD) experiment. It is strikingly evident that the amorphous manganese oxide Mn-08 has lost its Hg capturing ability completely after heat treatment up to 500 °C during TPD experiments. So, the active structure of Mn-08 for Hg removal might be damaged totally by heat-treatment. In the case crystalline MnO₂ (Mn-13), Hg removal efficiency decreased from 80% to about 60% after TPD experiments (second time use) as shown in Fig. 6. It is note worthy that the Hg desorption efficiency of Mn-13 in first time use was about 37%, while it was 98% after second time use. It seems likely that more stable phase of MnO₂ was formed after heat-treatment in the case of Mn-13 which is both active and stable for Hg capture. However, more detail investigation is required to clarify these results.

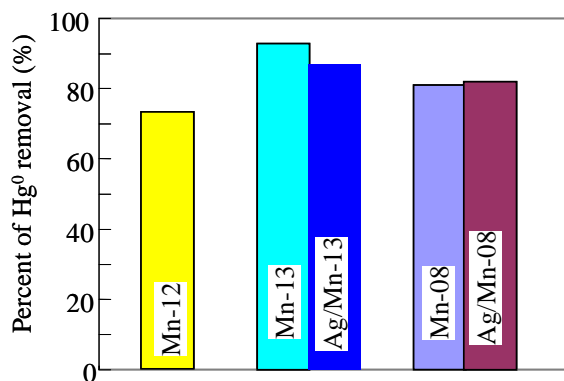


Fig. 3 Comparison of Hg removal efficiency of MnO₂ and Ag supported on MnO₂ at 2 h time-on-stream

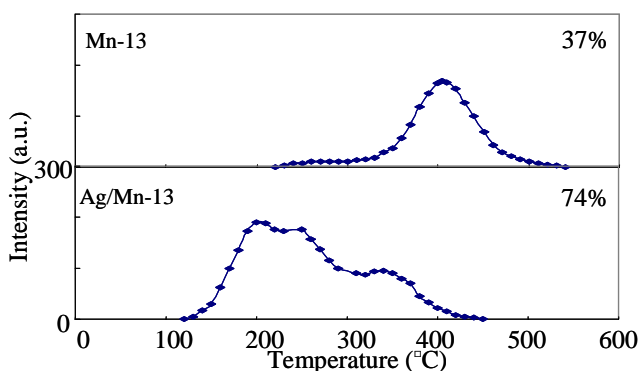


Fig. 4 TPD profile of Hg desorption from Hg adsorbed Mn-13 and Ag/Mn-13

In order to investigate the reason for loss of Hg removal activity of Mn-08 after heat-treatment during TPD experiment, the sample was heated in air after Hg removal experiment, because it was thought that the amorphous MnO₂ (Mn-08) might have lost its active surface or structural oxygen during TPD in N₂ at high temperature. Sample Mn-08 was heated in a muffle furnace at 450 °C for 5 min in air, cooled down to 30 °C and then used in Hg removal experiments. The results of Hg removal experiments are shown in Fig. 8. The Hg removal activity of the Mn-08 in second time use (after air heating) revived slightly compared to zero activity for second time use after TPD in N₂ (Fig. 2). Although the Hg removal activity was not recovered fully, but it seems that treatment of Mn-08 with air has some effect on Hg removal. In the same way, Mn-13 was also heat-treated in air after first time use and then Hg removal was performed with the sample for second time. Figure 9 compares the results. If we compare the results of Fig. 6 with Fig. 9, we can see that the heat-treatment of the Mn-13 sample in air after Hg removal has no effect on Hg removal activity of the sample for second time use.

Finally, it is interesting that manganese oxides Mn-08 and Mn-13 possess very high initial Hg removal activity, but Mn-08 lost its Hg removal activity completely after heat treatment, where as Mn-13 retained 75 % of its initial activity even after heat-treatment. We need detailed characterization of the

samples and more investigation to clarify these results.

TABLE I
THE BET SURFACE AREA OF THE MANGANESE OXIDE SORBENTS

Sample	BET surface area (m ² /g)	
	before	after
Mn-08	395	59
Mn-12	61	51
Mn-13	229	129

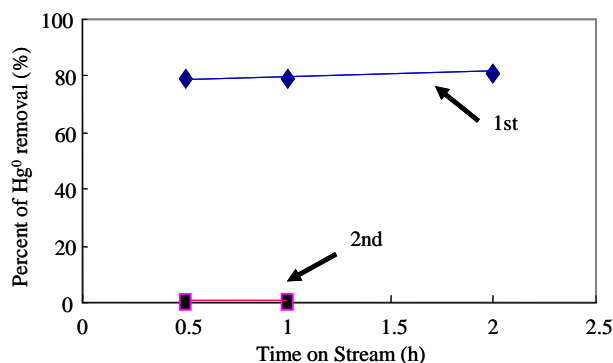


Fig. 5 Hg removal activity of Mn-08 for repeated use after Hg desorption (TPD) experiments

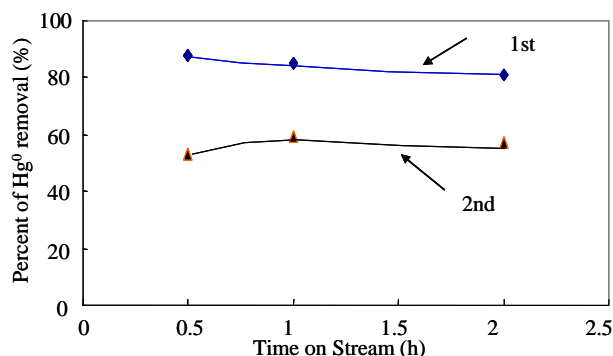


Fig. 6 Hg removal activity of Mn-13 for repeated use after Hg desorption (TPD) experiments

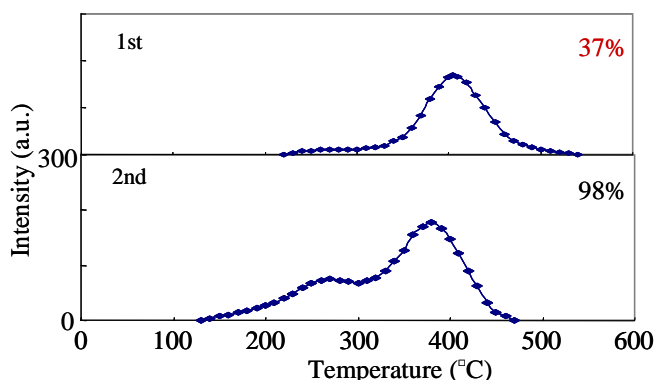


Fig. 7 TPD profiles of Mn-13 after repeated use for Hg removal

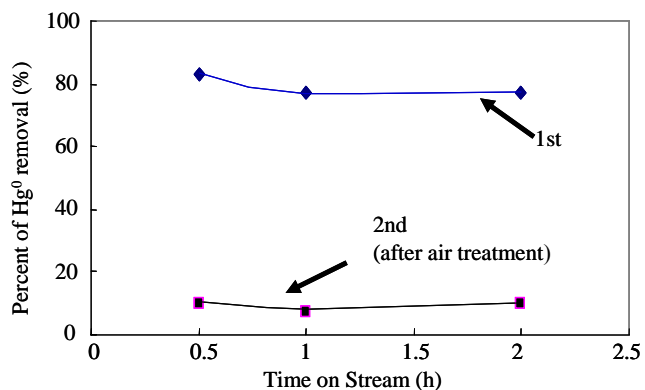


Fig. 8 Hg removal activity of Mn-08 for repeated use after Hg desorption (TPD) and heat-treatment in air

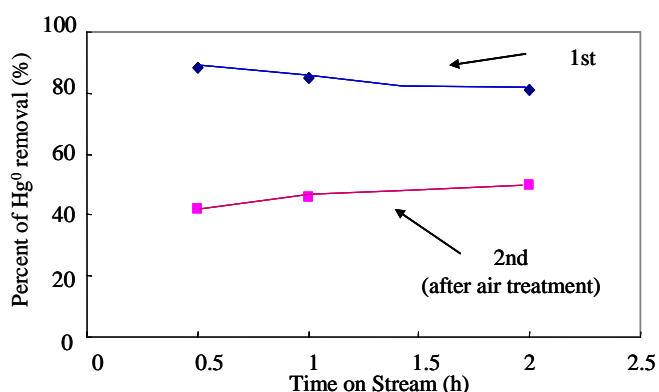


Fig. 9 Hg removal activity of Mn-13 for repeated use after Hg desorption (TPD) and heat-treatment in air

IV. CONCLUSION

In this study, the Hg removal activity of manganese oxide having different surface area, crystallinity and residual potassium content from natural was investigated at 30 °C. Silver supported on metal oxide such titania and zirconia as reference materials were also used in this study for comparison. Mercury desorption efficiency of the Hg-adsorbed samples were investigated by Temperature Programmed Desorption (TPD) method. It was confirmed from Hg removal activity of Ag/TiO₂ and Ag/ZrO₂ that mercury was captured with silver probably forming silver amalgam and desorption of Hg from Hg captured with Ag occurs at 100-400 °C with a peak at 180 °C. Manganese oxides showed very high Hg removal activity (about 73-93% Hg removal) for first time use. Surface area of the manganese oxide samples decreased after heat-treatment and resulted in complete loss of Hg removal ability for repeated use after Hg desorption in the case of amorphous MnO₂, and 75% loss of the initial Hg removal activity for the crystalline MnO₂. Mercury desorption efficiency of crystalline MnO₂ was very low (37%) for first time and high after second time use. Residual potassium content in MnO₂ may have some effect on the thermal stability of the adsorbed Hg species. Desorption of Hg from manganese oxides occurs at much higher temperatures

(with a peak at 400 °C) than Ag/TiO₂ or Ag/ZrO₂. Mercury may be captured on manganese oxides in the form of mercury manganese oxide.

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