Removal of Dilute HCl in Exhaust Gases by Oxide Sorbents

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Various metal oxides which were supported on γ -Al₂O₃ were investigated as HCl sorbents. Sorption capacities of gaseous HCl and sorptive and desorptive characteristics for HCl were determined from the measurement of HCl removal on these sorbents at 200°C. Mn₂O₃, La₂O₃ and alkaline earth oxides supported on Al₂O₃ sorbents demonstrated high sorption capacities and regenerated on heating the samples under oxidation conditions at 700°C. In particular, Mn₂O₃ supported on Al₂O₃ showed the highest capacity in our investigation. The X-ray diffraction patterns of Mn₂O₃/Al₂O₃ showed that MnCl₂•2H₂O phase existed after sorption and this phase disappeared after desorption treatment. These results indicate that Mn₂O₃ was reduced by gaseous HCl and formed chloride MnCl₂•2H₂O which was oxidized by oxygen at oxidation conditions. This investigation has indicated the possibility of Mn₂O₃/Al₂O₃ as a new material for sorption of HCl in exhaust gases. Key Words: HCl, Oxide, Sorbents

1. INTRODUCTION

Deadly poisonous dioxin detected in emissions of waste incinerators have been deeply interested as a serious problem. Gaseous HCl serves as a source of dioxin which is generated on combustion of polyvinyl chloride and salts in the presence of the waste⁽¹⁾. Removal of HCl from emission gas is effective to suppress the evolution of dioxin.

Lime dry powder sorbents are used to remove gaseous HCl from incinerators. Spent sorbent materials from such acid gas scrubbing applications contain soluble chlorides. Chlorine-containing spent sorbent materials are usually landfilled. However, these salts are water soluble and could leach into the groundwater. Such disposal alters the soil pH. Furthermore, disposal costs for such materials have increased significantly. The economics of the acidic gas emission control are highly dependent on the amount of fresh sorbent required, since the cost of sorbent replacement material is quite significant⁽²⁾. Thus, from an economic as well as an environmental viewpoint, it is desirable to regenerate the spent sorbent materials recovered from the acid gas cleanup processes so that they can be reused.

In this study, we investigated the materials which have high capacity of HCl and regenerative on heating, and tried to clarify the mechanism.

2. EXPERIMENTAL

2.1 Sample Preparation

Various oxides supported on Al₂O₃ were prepared by impregnation method. Calculated amounts of nitrates or carbonates were dissolved in water. Then, γ -Al₂O₃ powder was immersed in the solution. The solution was evaporated to dryness. The obtained powder was then heated at 750°C for 6h, and as sieved to 10-20 mesh.

2.2 HCl removal experiment and sample characterization.

Sorption and desorption experiments of HCl were carried out in a flow system. The reaction gas which consisted of HCl and O₂ was diluted in Ar. One gram of the solid sample was fixed in a quartz tube reactor. The sorption and desorption characteristics of HCl were tested over a temperature range from 200 to 700°C. Total gas flow rate was 60ml/min, which corresponded to 1.0 g s cm⁻³.

The concentration of HCl was continuously monitored by an infrared spectrometer (JASCO, IR810) with a gas analysis chamber by observing a band intensity at a fixed wave number (2821cm⁻¹). The gaseous composition of the inlet and outlet mixture was also analyzed by mass spectroscopy. Phases in the samples were identified with an X-ray diffractometer (Rigaku, RINT-1400). The BET surface area of the samples was determined with Micromeritics Gemini 2375.

3. RESULTS AND DISCUSSION

3.1 Removal of HCl by Various Oxide Sorbents

HCl removal of γ -Al₂O₃, which was used for a carrier was tested, as shown Figure 1. For the first time, 0.934% HCl was supplied to the sample at 200°C. The outlet concentration of HCl was almost zero at the beginning of supplying the HCl gases. Then, the removal of HCl gradually decreased with time, and approached zero. After the sorption, HCl sorbed was released on heating at 700°C in the oxidizing atmosphere. The second sorption was carried out at 200°C again. This cycle was carried out three times. The total amount of sorbed HCl was estimated by integrating the removal curve.

The amounts of sorbed HCl for various sorbents are summarized Table I. Various metal oxides supported on γ -Al₂O₃ were investigated for HCl sorbents. Supported alkaline oxide sorbents exhibited high sorption capacities. For example, 20wt%Na₂O/Al₂O₃ absorbed 2.76 × 10⁻³ mol-HCl / g-sorbent, which corresponded to 0.43 mol-HCl / mol-Na. But these sorbents did not exhibit reversible sorption-desorption properties. The XRD pattern indicated that an Na₂AlO₄ phase disappeared and an NaCl phase was formed after the



Figure 1. Time course of HCl removal for Al₂O₃. T=200°C, W/F=1.0 g s cm⁻³.

Absorption condition : 0.934%HCl/Ar.

Desorption condition : $20\%O_2/N_2$, heated from $200^{\circ}C$ to $700^{\circ}C$ at $200^{\circ}C/hr$.

Sample : γ -Al₂O₃, calcined at 750°C in H₂ atmosphere

supprted on	γ -AI ₂ O ₃				
Supported oxides	Amount of HCl removal ($/ \times 10^{-3}$ mol g-sorb ⁻¹)				
	lst	2nd	3rd		
Na2O	2.76	0.44	0.33		
K2O	1.10	0.65	0.26		
MgO	0.88	0.66	0.66		
CaO	2.42	1.64	1.43		
SrO	2.86	1.21	1.05		
BaO	1.39	0.82	0.97		
Y2O3	1.19	0.80	0.80		
ZrO2	0.66	0.52	0.53		
Cr2O3	0.46	0.79	0.71		
La2O3	1.14	0.75	0.78		

Table I Amount of HCl removal for various oxides

La2O3	1.14	0.75	0.78			
Mn2O3	2.26	1.96	1.93			
Fe2O3	0.43	0.35	0.36			
CoO	1.51	0.65	0.54			
ZnO	1.18	0.69	0.66			
SnO ₂	1.00	0.59	0.36			
La2O3	1.14	0.75	0.78			
CeO ₂	0.72	0.42	0.43			
Al2O3	0.79	0.45	0.48			
Reaction temperature, 200°C, W/F=1.0 g s cm ⁻³ .						

Reaction temperature, 200 C. w/F=1.0 g s cm⁻³. Absorption condition : 0.934%HCl/Ar. Desor_ption condition : 20%O₂/N₂, heated from 200°C to 700°C at 200°C/hr.

sorption. This chlorides were stable even on heating at 700°C, so these sorbents could not be regenerated. Alkaline earth oxides supported on Al₂O₃ sorbents demonstrated high sorption capacities and regenerated on heating the samples at 700°C. In particular, CaO supported on Al₂O₃ showed high capacity in our investigation. We could not confirm the state of Ca atom from its XRD pattern (Figure 2). The XRD pattern was unchanged after sorption. This indicated that sorbed HCl may exist on the surface of the sorbent as an amorphous phase. Mn₂O₃/Al₂O₃ sorbents showed the highest capacities and high reversibility (Figure 3). This



Figure 2. XRD patterns of CaO/Al₂O₃ sorbents. a) Fresh, b) After HCl sorption at 200°C. All peaks are attributed to γ -Al₂O₃.



Figure 3. Time course of HCl removal for Mn_2O_3/Al_2O_3 . T=200°C, W/F=1.0 g s cm⁻³.

Absorption condition : 0.934%HCl/Ar.

Desorption condition : $20\%O_2/N_2$, heated from $200^{\circ}C$ to $700^{\circ}C$ at $200^{\circ}C/hr$.

Sample : 20wt%Mn₂O₃/Al₂O₃, calcined at 750°C in air.

mechanism was described below. Although same other supported oxides sorbents showed reversibility, their capacities were not enough to use as sorbent materials. For almost all sorbents, the amount of HCl removal decreased by ca. 10-20% in the second cycle with reference to the first cycle. The BET surface area decreased by ca.10% after the experiment for all samples. This may indicate that absorption sites of HCl decrease by aging.

3.2 Sorption characteristics of Mn₂O₃/Al₂O₃

In our investigation, the Mn₂O₃/Al₂O₃ sorbent showed the highest sorption capacity. The XRD patterns of Mn₂O₃/Al₂O₃ at various conditions are shown



Figure 4. XRD patterns of Mn₂O₃/Al₂O₃ sorbents. a) Fresh, b) After HCl sorption at 200°C, c) After HCl desorption in oxidation atmosphere.



Figure 5. Time course of HCl removal for Mn2O3/Al₂O3 at O₂ coexistance. T=200°C, W/F=1.0 g s cm⁻³. Absorption condition : 0.841%HCl+10%O2/Ar. Desorption condition : 20%O2/N2, heated from 200°C to 700°C at 200°C/hr. Sample : 20wt%Mn2O3/Al₂O3, calcined at 750°C.

in Figure 4. After gaseous HCl sorption, Mn species was reduced and converted into MnCl₂•2H₂O phase. This indicates that the reaction (1) probably occurred during sorption.

$$Mn_2O_3 + 4HCl \rightarrow MnCl_2 + 2H_2O + 1/2O_2 \quad (1)$$

However, after the thermal desorption, this phase disappeared and Mn species formed Mn2O3 again. This indicated Mn was oxidized by gaseous O2.

The absorption behavior was examined in the presence of O₂, since these gases are always contained in the exhaust gases. The coexisting O₂ affected absorption curves in Figure 5 were at high removal region, but the total absorption capacity of the Mn₂O₃/Al₂O₃ sorbents were hardly affected, or slightly increased even in the presence of 10% O₂.

We investigated the effect of loading amount

Table II Amount of HCl removal and BET surface area at various loading amount of Mn₂O₃

Loading amount	Amount of HCl removal /×10 ⁻³ mol g ⁻¹			BET surface
of Mn2O3 / wt%	1 st	2nd	3rd	area / m ² g ⁻¹
10	2.41	1.87	1.63	135.2
20	2.14	1.52	1.34	121.3
30	1.87	1.52	1.22	93.8
40	1.47	1.36	1.14	75.8
50	1.40	1.10	1.01	64.8

Reaction temperature, 200°C. W/F=0.5 g s cm⁻³.

of Mn₂O₃ in the sorbents. The amount of HCl removal at the condition of W/F=0.5 g s cm⁻³ and BET surface area at several loading amounts of Mn₂O₃ are summarized in Table 2. This results indicates that an increase in loading amount of Mn₂O₃ is not effective in increasing capacity of sorbents. For example, sample with 10wt%Mn₂O₃ sorbed 1.63×10^{-3} mol-HCl / g-sorbent in the 3rd run, which corresponded to 1.16 mol-HCl / mol-Mn. But the sample with 50wt% Mn₂O₃ sorbed 1.01 mol-HCl / mol-Mn, which correspond to only 0.14 mol-HCl / mol-Mn. Mn species do not efficiently take part in sorption for the latter sample. But the decrease in the BET surface area is one of the reasons.

4. CONCLUSION

We tested various oxide supported on γ -Al2O3 as new HCl sorbents. The Mn2O3/Al2O3 sorbent demonstrated the highest sorption capacity and could be regenerated on heating under oxidation conditions at 700°C. The X-ray diffraction patterns of Mn2O3/ Al2O3 showed that the MnCl2•2H2O phase existed after sorption and this phase disappeared after desorption treatment. These results indicate that Mn2O3 was reduced by gaseous HCl and formed chloride MnCl2•2H2O was oxidized on heating in oxidation conditions. The Mn2O3/A12O3 sorbents could be regenerated by this redox cycle. The total absorption capacity of the Mn2O3/Al2O3 sorbents was hardly affected by the coexisting O2. An increase in loading amount of Mn2O3 was not always effective in increasing capacity of sorbent. This may indicate that BET surface area affects the amount of HCl removal. The present investigation has indicated the possibility of Mn2O3/Al2O3 sorbent as a new material for sorption of HCl in the exhaust gases.

5. REFERENCES

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