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The Effect of HCl and H_2O on the H_2S Removing Capacities of Zn-Ti-based Desulfurization Sorbents Promoted by Cobalt and Nickel Oxide

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Abstract−The sulfur removing capacities of various Zn-Ti-based sorbents were investigated in the presence of H_2O and HCl at high-(sulfidation, 650 °C; regeneration, 800 °C) and medium-(sulfidation, 480 °C; regeneration, 580 °C) temperature conditions. The H_2O effect of all sorbents was not observed at high-temperature conditions. At medium-temperature conditions, the reaction rate of ZT (Zn/Ti : 1.5) sorbent decreased with the level of H_2O concentration, while modified (ZTC, ZTN) sorbents were not affected by the water vapor. HCl vapor resulted in the deactivation of ZT sorbent with a cycle number at high-temperature due to the production of $ZnCl_2$ while the sulfur removing capacities of ZTC and ZTN sorbents were maintained during 4-5 cyclic tests. In the case of medium-temperature conditions, ZT sorbent was poisoned by HCl vapor while cobalt and nickel added to ZT sorbent played an important catalytic role to prevent from being poisoned by HCl due to providing heat, emitted when these additives quickly react with H_2S even at medium-temperature conditions, to the sorbents.

Key words: Desulfurization, Zn-Ti Based Sorbent, HCl and H_2O

INTRODUCTION

The integrated gasification combined cycle (IGCC) is considered to be among the most efficient and environmentally acceptable technologies for generating power from coal [Woudstra and Woudstra, 1995]. To use this technology, the removal of pollutants such as H_2S, NH_3 and HCl from coal-derived fuel gas is needed. Among the pollutants, sulfur, which exists in the form of hydrogen sulfide (H_2S) under the highly reducing conditions of a gasifier, must be removed from the hot coal gas not only to protect equipment against corrosiveness in the later stages of the process, but also to meet strict government regulations for sulfur emissions. To remove hydrogen sulfide from coal-derived gas, several metal oxide materials have been studied in order to develop regenerable sorbents in high- and medium-temperature ranges under the highly reducing conditions of a gasifier [Gupta et al., 2000; Gupta and O'Brien, 2000; Shemwell et al., 2000, 2001; Lee et al., 1997, 2001; Liu et al., 2000; Slimane and Abbsian, 2000, 2001; Jun et al., 2001, 2002; Siriwardane et al., 2000; Kang et al., 2000; Pineda et al., 2000; Sasaoka et al., 2000, 2001; Hatori et al., 2001; Jothimurugesan and Gangwal, 1998; Kirshnan et al., 1995; Yi et al., 2001; Song et al., 2000]. Nowadays, because of process equipment limitations and other variables such as fuel gas alkali content, the optimum temperature for fuel gas desulfurization within this process is estimated to be from 350-550 °C. The roles of additives and supporters, however, have not been clearly defined in this temperature range because of the lack of identification of new active sites and their mechanisms. In addition, there have been very few reports about the effect of H_2O and HCl in coal-derived fuel gas in medium temperature conditions. The major objectives of this work are to identify any deleterious changes in the ZT-based sorbents caused by H_2O and HCl in the fixed-bed reactor and in particular, the catalytic role of additives such as cobalt and nickel in the high- and medium-temperature conditions.

MATERIALS AND METHODS

1. Preparation of the Sorbent

The zinc titanate (ZT) and modified (ZTC, ZTN) sorbents used in this study were prepared by physical mixing. Zinc oxide, titanium dioxide and cobalt or nickel oxide, of which the particle size was about 200-300 mesh, were sufficiently mixed with an inorganic binder, bentonite, for 1-2 h. Next an organic binder, ethylene glycol (EG), was added to the mixture in order to make a slurry. An extruder was used to formulate pellets with an outer diameter of 1 mm from the slurry. These wet pellets were dried for 4 h in order to remove ethylene glycol from the material in the temperature range of 250-300 °C. The dried pellets were calcined in a muffle furnace for 12 h at 1,000 °C, and then ground to particle size in the range of 250-300 μm in diameter. The ramping rate of the temperature was maintained at 3 °C/min. The mole ratio of Zn to Ti and the amounts of additives added were fixed at 1.5 : 1 and 20 wt%, respectively.

2. Apparatus and Procedure

Multiple cycles of sulfidation/regeneration were performed in a fixed-bed quartz reactor with a diameter of 1 cm placed in an electric furnace. One gram of sorbent was packed into the reactor, and the space velocity (SV) was maintained at 5,000 h^{-1} to minimize severe pressure drops and channeling phenomena. All of the volumetric flows of gas were measured at standard temperature and pressure (STP) conditions. The temperature of the inlet and outlet lines of the reactor was maintained above 120 °C to prevent condensation of water vapor produced in the sulfidation processes. The out-

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Table 1. Experimental conditions for Zn-Ti-based sorbents

	Sulfidation		Regeneration	
Temperature (°C)	480-650		580-800	
Pressure (atm)	1		1	
Flow rate (ml/min)	50		50	
Gas composition (vol%)	H_2S	1.5	O_2	3-5
	H_2	11.7	N_2	balance
	CO	9.6		
	CO_2	5.2		
	HCl	0.2		
	H_2O	5-20		
	N_2	balance		

let gases from the reactor were automatically analyzed every 8 min by a thermal conductivity detector (TCD) equipped with an auto-sampler (Valco). The column used in the analysis was a 1/8-in. Teflon tube packed with Porapak T. The conditions of sulfidation and regeneration and the composition of mixed gases are shown in Table 1. When the H_2S concentration of the outlet gases reached 15,000 ppm, the concentration of H_2S at the inlet stream of mixed gases, an inert nitrogen gas without H_2S was introduced to purge the system until it reached the regeneration temperature. Finally, nitrogen gas mixed with 3 vol% of oxygen was introduced to regenerate the sulfurized sorbents until the SO_2 concentration reached 200 ppm.

RESULTS AND DISCUSSION

1. H_2S Performance in the Presence of H_2O

Fig. 1 shows the sulfur removing capacities of various Zn-Ti-based sorbents under gas compositions with 10 vol% H_2O at high-temperature conditions. The X-axis indicates the cyclic number considering sulfidation/regeneration reaction as 1 cycle, and the Y-axis indicates the amount of the sulfur absorbed per 1 g sorbent until H_2S concentration emitted from the reactor reached 200 ppm. The sulfur removing capacities of all the sorbents showed about 16-24 g S/g sorbent at the initial cyclic number. These sulfur removing capacities were almost completely consistent with the theoretical values of the sorbents, indicating that the slope of the H_2S breakthrough curves suddenly increased at the H_2S breakthrough point and most of the metal oxides besides TiO_2, found as a non-active component for H_2S removal in a previous paper [Jun et al., 2001, 2002], participated in H_2S absorption before reaching the breakthrough point. From the results of an experiment, in which the capacities were tested in the gas composition without H_2O vapor, it was observed that the sulfur removing capacities of the Zn-Ti-based sorbents were not affected by water vapor at high-temperature conditions. Deactivation of sulfur removing capacity for the ZT sorbent with the cyclic number, unlike ZTC and ZTN, can be explained by the change of physical properties of the ZT sorbent as reported in a previous paper [Kang et al., 2002]. Fig. 2 shows the sulfur removing capacities of various Zn-Ti-based sorbent under gas compositions with/without 10 vol% H_2O at medium-temperature conditions. Most of the sorbents showed lower sulfur removing capacities compared with the results at high-temperature conditions. The sulfur removing capacities of ZT sorbent in the absence of H_2O decreased with the cyclic number, while those of the ZTC and ZTN sorbent maintained initial values even at over 10 cycles. In the case of gas composition with 10 vol% H_2O, the sulfur removing capacities of the ZTC and ZTN sorbent did not depend on water vapor while the ZT sorbent showed the sulfur removing capacity less than 5 g S/g sorbent at every cycle. To explain the deactivation of the ZT sorbent in the presence of H_2O, the H_2S breakthrough curves of the ZT sorbent were

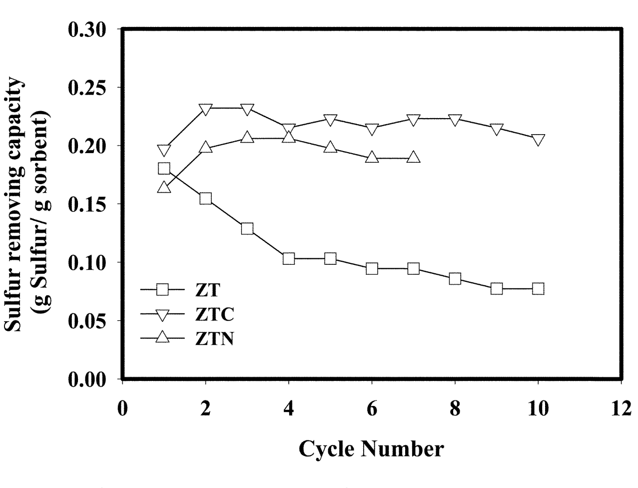

Fig. 1. Sulfur removing capacities of various Zn-Ti-based sorbents under gas compositions with 10 vol% H_2O at 650 °C.

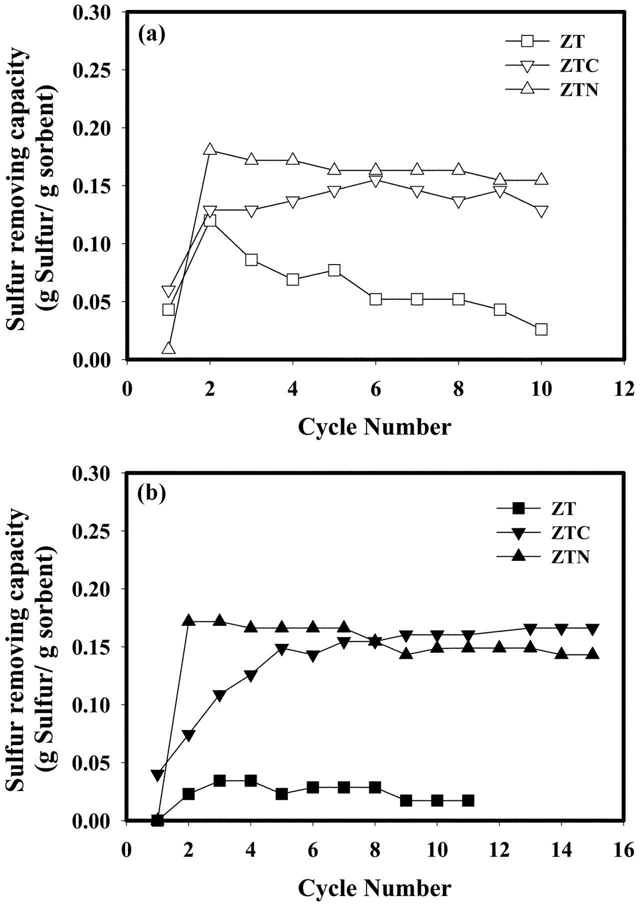

Fig. 2. Sulfur removing capacities of various Zn-Ti-based sorbents under gas compositions with/without 10 vol% H_2O at 480 °C; (a) in the absence of H_2O, (b) in the presence of H_2O.

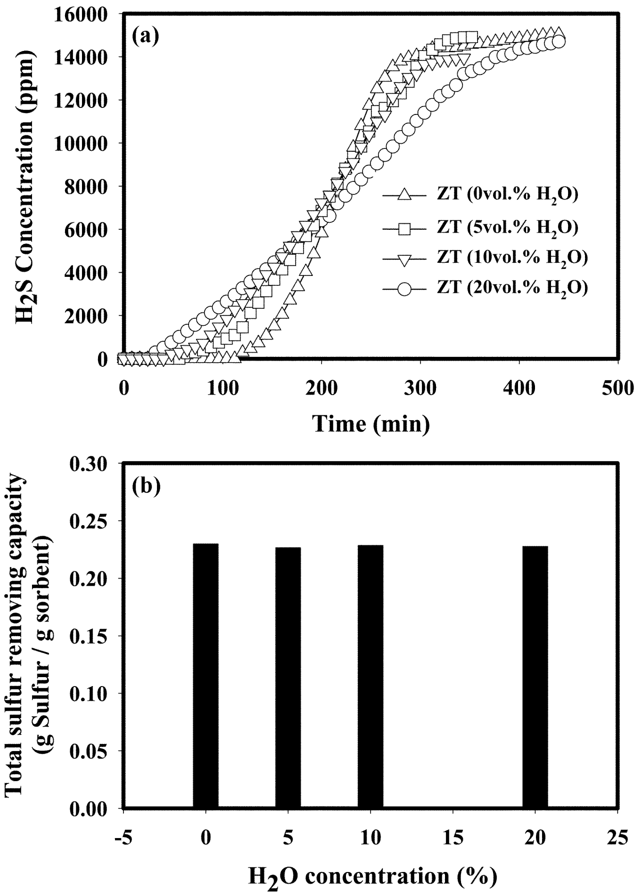

Fig. 3. Breakthrough curves (a) and total sulfur removing capacities, (b) of ZT sorbent with H_2O concentration at 480 °C.

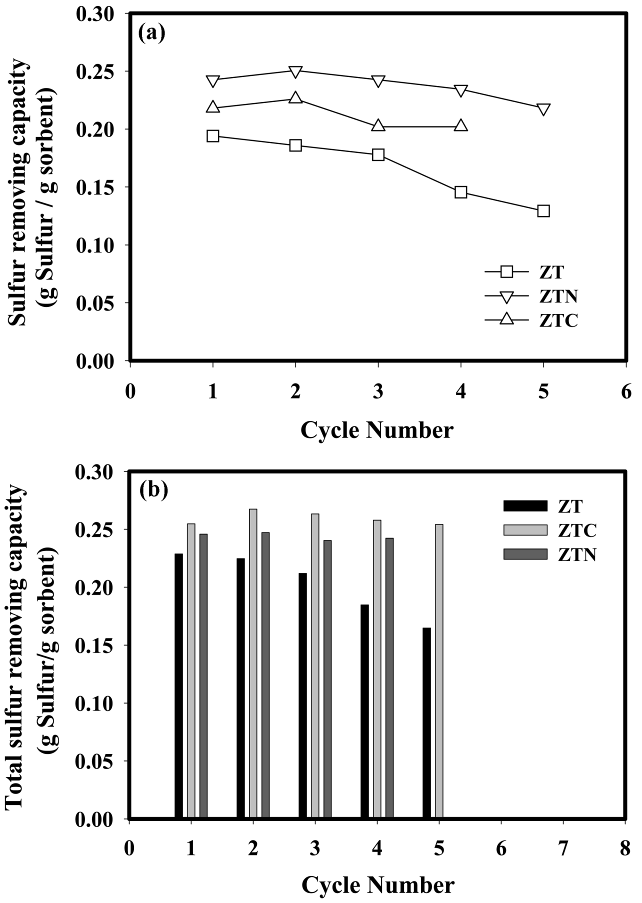

Fig. 4. Sulfur removing capacities (a) and total sulfur removing capacities, (b) of various Zn-Ti-based sorbents under gas composition with 5 vol% H_2O and 0.2 vol% HCl at 650 °C.

investigated with the H_2O concentration and shown in Fig. 3(a). It was shown that the slope of the breakthrough curve gradually decreased with the H_2O concentration. In addition, the total sulfur removing capacities of the ZT sorbent, the amount of sulfur absorbed until the output concentration reached the input value of the reactor, were calculated from these breakthrough curves and are shown in Fig. 3(b). The total sulfur removing capacities of the ZT sorbent showed 24 g S/g sorbent regardless of the H_2O concentrations. Considering that the theoretical value of the ZT sorbent was about 24 g S/g sorbent, these results indicate that water vapor resulted in the reduction of the reaction rate between zinc oxide, major active sites for H_2S absorption, and H_2S at medium-temperature conditions.

2. H_2S Performance in the Presence of HCl

To identify the HCl effect of the Zn-Ti-based desulfurization sorbents, their sulfur removing capacities were investigated in the presence of 5 vol% H_2O and 0.2 vol% HCl at high- and medium-temperature conditions. An aqueous solution with 20% HCl was used, and the concentration of H_2O and HCl was controlled by their relative vapor pressures. Fig. 4(a) shows the sulfur removing capacities of various sorbents with the cyclic number under gas composition with HCl and H_2O at high-temperature conditions. The sulfur removing capacity of all the sorbents was slightly increased compared with the results obtained at gas composition without H_2O and HCl. Fig. 4(b) shows the total sulfur removing capacities of various sorbents with the same experimental condition. The total sulfur removing capacities of the ZT sorbent gradually decreased with the cyclic number, while those of the ZTC and ZTN sorbent did not change. The deactivation of the ZT sorbent, as other researchers mentioned [Gupta and O'Brien, 2000], can be explained by the vaporization of $ZnCl_2$ formed by the side reaction between ZnO and HCl and reported as a liquid phase in the range of 283 °C to 732 °C. In the case of ZTC and ZTN sorbents, it was thought that the cobalt and nickel chloride formed by the side reaction with HCl were not a liquid phase at our experimental conditions and that they were transformed to their sulfides through reaction with H_2S without vaporization. In addition, it is clear the cobalt and nickel intercalated within the lattices of spinel structure such as Zn_2TiO_4 played an important role in preventing the deactivation of Zn-based sorbent. Fig. 5(a) shows the sulfur removing capacities of various sorbents with the cyclic number under gas composition with HCl and H_2O at medium-temperature conditions. The sulfur removing capacity of the ZT sorbent showed about 5 g S/g sorbent at the initial period and this value was maintained until four cycles. In addition, as shown in Fig. 5(b), its total sulfur removing capacity was about 6 g S/g sorbent, regardless of the cyclic number. From these results, it was thought that HCl could adsorb on the zinc oxide, active site, and prevent zinc oxide from reacting with H_2S at medium-temperature conditions. The existence of chloride within the spent ZT sorbent was confirmed by using ion chromatography after sulfidation.

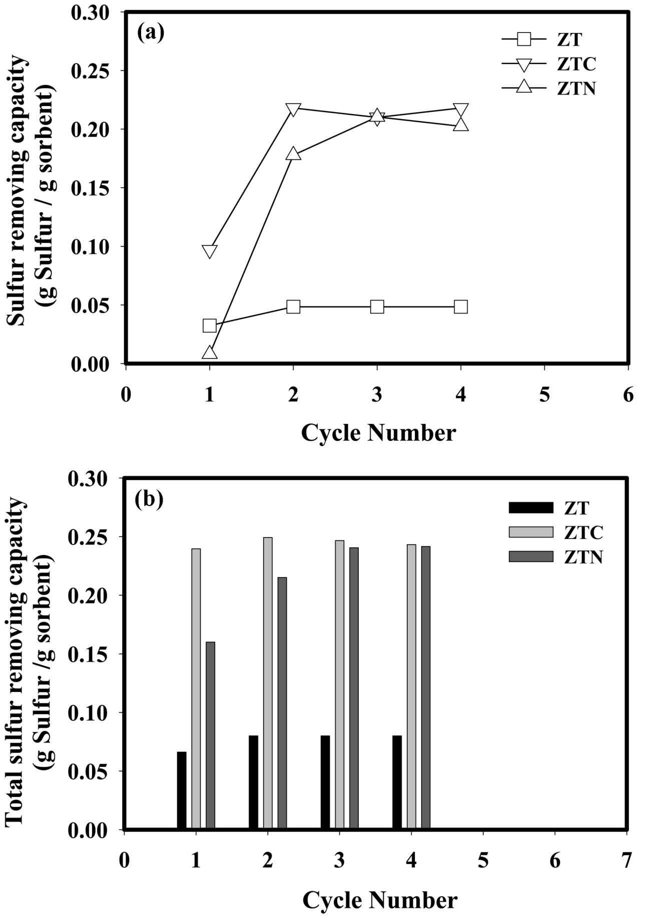

Fig. 5. **Sulfur removing capacities (a) and total sulfur removing capacities, (b) of various Zn-Ti-based sorbents under gas composition with 5 vol% H_2O and 0.2 vol% HCl at 480 °C.**

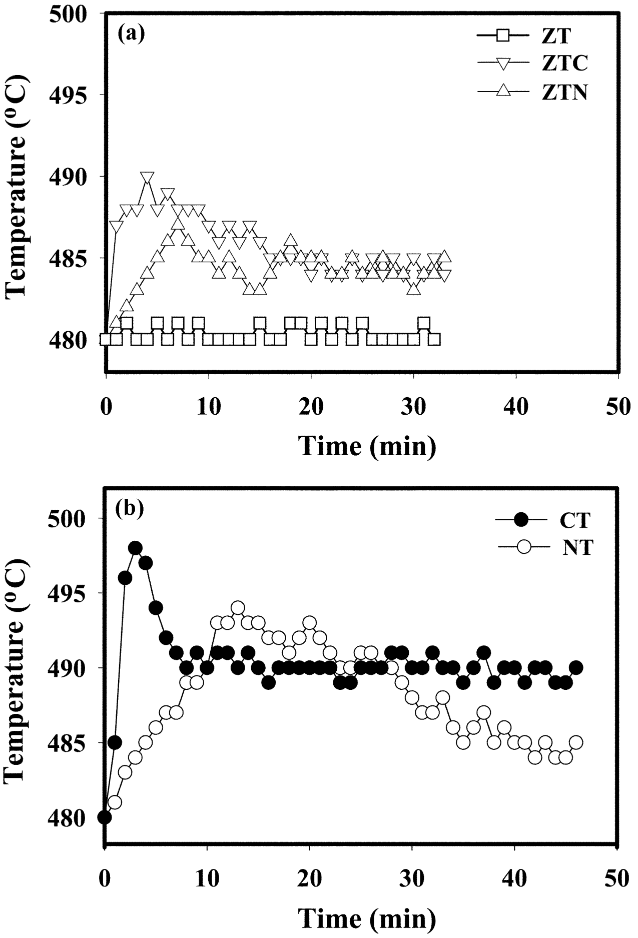

Fig. 6. **The change of reactor temperature during sulfidation at 480 °C; (a) various Zn-Ti-based sorbents, (b) CT, NT sorbents without zinc.**

The sulfur removing capacities of the ZTC and ZTN sorbent were maintained nearly 20 g S/g sorbent without deactivation after two cycles and these values were 6 g S/g sorbent higher than those obtained at gas composition without HCl and H_2O. Considering that the total sulfur removing capacities, as shown in Fig. 5(b), were not changed (about 23-24 g S/g sorbent) by addition of HCl and H_2O. These results indicate that the slope of the breakthrough curve increased at gas composition with HCl, which can be explained by the increase of the reaction rate between the ZTC, ZTN sorbents and H_2S. Also, as mentioned in the previous section, the sulfur removing capacities of the ZTC and ZTN sorbent did not depend on the amount of H_2O even at medium-temperature conditions; the increase of the reaction rate can be related with the presence of HCl and can be explained from the following section.

3. The Heat Effect of Sorbent

To investigate the role of cobalt and nickel added to the ZT sorbent, the temperature change of the reactor in which sorbents were packed was measured during sulfidation in gas composition without H_2O at medium-temperature conditions. As shown in Fig. 6(a), the temperature change of the ZT sorbent was not observed, while the temperature of the reactor in which the ZTC and ZTN sorbent was packed increased 7-10 °C at the initial period and this gradually decreased with the reaction time until sulfidation temperature. In addition, the CT and NT sorbents were prepared by mixing additives such as cobalt and nickel oxides with TiO_2, respectively. The amount of additives added to the TiO_2 was the same as that of ZnO added to the TiO_2. As shown in Fig. 6(b), the reactor temperature individually increased 18 °C for CT and 13 °C for NT in the initial period and gradually decreased with the reaction time. The reason why the reactor temperature of the ZT sorbent did not change during sulfidation was thought to be that the reaction rate between the zinc oxide and H_2S was too slow in order to measure the temperature change in our experimental conditions. In the case of the ZTC and ZTN sorbent, however, their temperature change during sulfidation can explain that the reaction rates between the additives and H_2S are so fast even at medium-temperature conditions. This heat effect, as reported in previous papers [Jun et al., 2001, 2002], was also observed in ZTC sorbent during regeneration. The temperature of ZTC sorbent increased (about 10 °C) during regeneration by using 3% oxygen. It was found that this heat emitted when cobalt sulfides were regenerated to their oxides improved the regeneration of zinc sulfides even at low temperature due to the catalytic role of cobalt additive. If the additives, cobalt and nickel, quickly react with H_2S during sulfidation even at medium-temperature conditions and this reaction can emit absorption heat, this heat can prevent the reaction rate between ZnO and H_2S from reducing under gas composition with H_2O and prevents HCl from poisoning the active site such as ZnO at medium-temperature conditions. In addition, this heat can improve the reaction rate between ZnO and HCl as well as between ZnO and H_2S at medium-temperature condition. If ZnO within the ZTC and ZTN sorbent reacts with HCl and transforms to $ZnCl_2$, it is the liquid phase in the temperature range of 283 °C to 732 °C and it is more accessible for reactions with H_2S than the solid phase ZnO [Gupta and O'Brien, 2000]. This mechanism, therefore, explains the enhancement in the sulfur removing capacity of the sorbent in the presence of HCl, as shown in Fig. 4(a) and Fig. 5(a).

CONCLUSIONS

The sulfur removing capacities of various Zn-Ti-based sorbents were investigated in the presence of H_2O and HCl at high- and medium-temperature conditions. The H_2O effect of all the sorbents was not observed at high-temperature conditions. At medium-temperature conditions, the reaction rate of the ZT sorbent decreased with H_2O concentration, while the ZTC and ZTN sorbent were not affected by the water vapor. The presence of HCl resulted in the deactivation of the ZT sorbent with the cycle number at high-temperature conditions due to the production of $ZnCl_2$ while the sulfur removing capacity of the ZTC and ZTN sorbent was maintained during 4-5 cyclic tests. In the case of medium-temperature conditions, the ZT sorbent showed very low sulfur removing capacity while that of ZTC and ZTN increased 6% compared with the results obtained at gas composition without HCl. From these results, it was concluded that cobalt and nickel added to the ZT sorbent played an important catalytic role in preventing the reaction rate of the Zn-Ti-based sorbent from reducing in the presence of H_2O and preventing HCl from poisoning the active site for H_2S removal in the presence of HCl due to providing heat, emitted when these additives quickly reacted with H_2S even at medium-temperature conditions, to the sorbents.

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