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A Study of Zn–Ti-Based H₂S Removal Sorbents Promoted with Cobalt and Nickel Oxides

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To improve the sulfur-removing capacity of Zn–Ti sorbent, new Zn–Ti-based H₂S removal sorbents promoted with cobalt and nickel were prepared and tested in a packed bed reactor at middle-temperature conditions (H₂S absorption at 480 °C and regeneration at 580 °C). The new sorbents showed excellent sulfur-removing capacities without deactivation even after 15 cycles of absorption and regeneration, whereas the conventional Zn–Ti sorbent continuously deactivated. The nickel and cobalt that permeated the Zn₂TiO₄ worked not only as active sites during the sulfidation process, but also as a structural stabilizer to prevent a change of physical properties of the sorbents during multi-cycle reactions. Also, the cobalt additive increased the regeneration capacity of the Zn-based sorbents by supplying heat to initiate the regeneration reaction of zinc at lower temperatures while the nickel additive prevented SO₂ slippage that originated from the cobalt sulfate.

Introduction

The integrated gasification combined cycle (IGCC) is considered to be among the most efficient and environmentally acceptable technologies for power generation from coal.¹ To use this technology, the removal of pollutants from coal-derived fuel gas is needed. Among the pollutants, sulfur, which exists in the form of hydrogen sulfide (H₂S) under the highly reducing conditions of a gasifier, must be removed from the hot coal gas not only to protect equipment against corrosion 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 to develop regenerable sorbents in high- and middle-temperature ranges under the highly reducing conditions of a gasifier.^{2–22}

However, the roles of additives and structural stabilizers have not been clearly defined because of the lack of

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and their mechanisms. The main objective of this work was to investigate the sulfidation and regeneration of Zn-based sorbents and to propose sulfidation and regeneration cycles for this purpose. The reactivities of Zn-based sorbents with or without additives were studied in a fixed-bed reactor over multiple sulfidation and regeneration cycles at middle-temperature conditions. In addition, the changes in physical properties for the sorbents before and after the reaction, the identification of a new active site, and a mechanism were investigated with the aid of Hg porosimetry (Micrometrics, Poresizer 9320), X-ray diffraction (XRD; Philips, X'PERT), Fourier transform infrared (FT-IR; Mattson Instruments Inc., Galaxy 7020A), and scanning electron microscopy-energy-dispersive spectrometry (SEM-EDS; Hitachi, S-4200).

Experimental Section

Preparation of Sorbents. Zinc titanate (ZT) and modified zinc titanate (ZTC, ZTN, ZTCN) sorbents used in this study were prepared by a physical mixing method. Zinc oxide, titanium dioxide, nickel oxide, and cobalt oxide, of which particle size for each was about 200–300 mesh, were sufficiently mixed with an inorganic binder, bentonite, for 1–2 h. Next, a liquid binder, ethylene glycol (EG), was added to the mixture in order to make the slurry of mixed-metal oxide. An extruder in our lab was used to formulate pellets to an outer diameter of 1 mm from the slurry. These wet pellets were dried for 4 h to remove moisture from the material in the temperature range of 250–300 °C. The dried pellets were then ground to particle size in the range of 250–300 μm in diameter and calcined in a muffle furnace for 12 h in the temperature range of 900–1000 °C. The ramping rate of the temperature was maintained at 3 °C/min.

Apparatus and Procedure. Multiple cycles of sulfidation and regeneration were performed in a 1-cm diameter fixed-bed quartz reactor placed in an electric furnace. One gram of sorbents was packed in this reactor and the space velocity (SV) was maintained at 5000 h^{-1} to minimize a severe pressure drop and channeling phenomena. All of the volumetric flows of gases 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 during the sulfidation processes. The outlet 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. The effect of water vapor was fully explained in another paper²³ and omitted in this paper. When the H_2S concentration of the outlet gases reached 15 000 ppmv, the inlet stream of mixed gases containing 1.5 vol % hydrogen sulfide was stopped and an inert nitrogen gas was introduced to purge the system until it reached the

Table 1. Experimental Conditions for Zn-Based Sorbents

	sulfidation	regeneration
temperature (°C)	middle: 480	middle: 580
pressure (atm)	1	1
flow rate (ml/min)	50	50
gas composition (vol %)	H_2S 1.5 H_2 11.7 CO 9.6 CO_2 5.2 N_2 balance	O_2 3–5 N_2 balance

regeneration temperature. Finally, nitrogen gas mixed with 3 vol % of oxygen was introduced to regenerate the sulfided sorbents until the SO_2 concentration reached a value less than 200 ppmv.

Results and Discussion

Comparison of Sulfur-Removing Capacity. The amounts of sulfur absorbed were calculated from H_2S breakthrough curves, and those for conventional ZT sorbents are shown in Figure 1a. When sulfidation and regeneration together are considered as a one-cycle process, the horizontal axis indicates the number of cycles repeated. The vertical axis indicates the percent of sulfur absorbed per 1 g of sorbent until the H_2S concentration in the outlet gas of the reactor reaches 200 ppmv. The sulfur absorption capacities during the initial 2–3 cycles were about 10% at the sulfidation temperature, while the sorbent was deactivated during multiple sulfidation and regeneration cycles. The sulfur-removing capacities of the various ZTC sorbents with different loadings of cobalt oxide are shown in Figure 1b. The initial sulfur absorption capacities of all the sorbents were about 15% at the sulfidation temperature regardless of the amount of cobalt loadings. Their deactivations during multiple sulfidation and regeneration cycles were improved as the amount of cobalt additives increases. In the case of ZTC-25, the sulfur absorption capacity was maintained even after 15 cycles. Figure 1c shows the sulfur-removing capacities of ZTN sorbents prepared by adding nickel to the conventional ZT sorbents. The ZTN-10 and -20 sorbents showed about 15% sulfur-removing capacity and no deactivation even after multiple cycles of sulfidation and regeneration at middle temperature. However, in the case of the ZTN-5, its deactivation was observed during repeated sulfidation and regeneration as shown in Figure 1c. The sulfur-removing capacities for ZTCN sorbents prepared by physical mixing of the ZT sorbent with cobalt and nickel additives are shown in Figure 1d. All the ZTCN sorbents with different loadings of cobalt and nickel additives showed excellent sulfur-removing capacities and were not deactivated during multiple sulfidation and regeneration cycles regardless of their relative ratios of cobalt and nickel loadings.

Identification of the Structure of the Sorbents by XRD. The XRD pattern for ZT sorbents before and after the reaction (sulfidation or regeneration) is shown in Figure 2-1a. The phase of ZT sorbents before the reaction was assigned to the Zn_2TiO_4 having a general spinel structure without an unreacted single oxide such as zinc oxide or titanium dioxide. After the sulfidation process, the peaks of TiO_2 separated from the spinel structure and metal sulfides were observed, while the peaks of Zn_2TiO_4 disappeared in the XRD pattern. The

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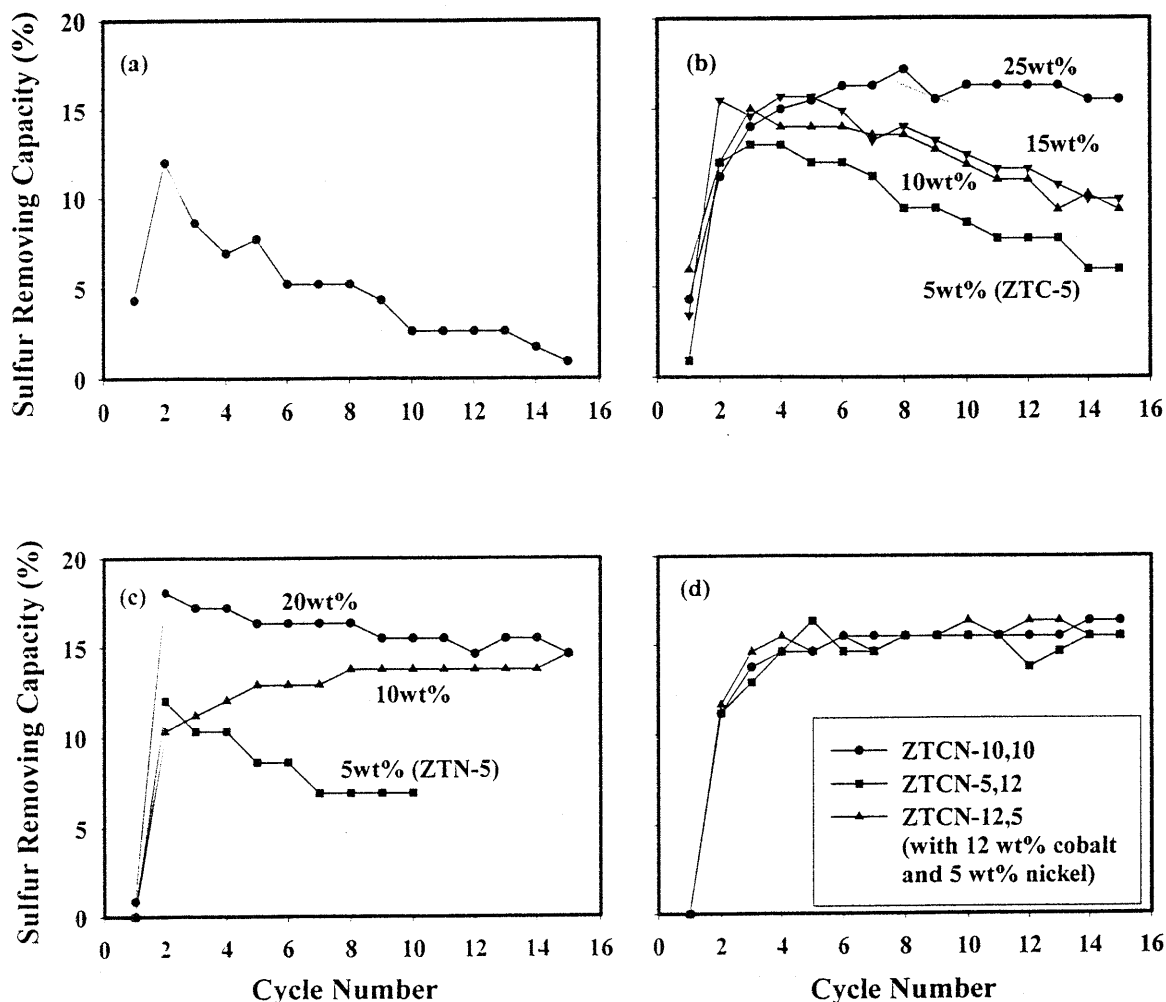


Figure 1. Sulfur-removing capacity (g sulfur/g sorbent $\times 100$) of various sorbents at middle temperature: (a) ZT, (b) ZTC, (c) ZTN, (d) ZTCN.

sulfide peaks of the ZT sorbent at 28° and 47.5° were reported to be assigned to ZnS in the literature [JCPDS No. 39-1363]. The XRD pattern after the regeneration process showed that most sulfides were converted into the initial phases of Zn_2TiO_4 without sulfate formation, although a little unreacted single oxide such as zinc oxide was observed. The XRD pattern of ZTC-25 sorbent is shown in Figure 2-1b. The XRD pattern of the fresh ZTC-25 sorbent showed perfect spinel structures such as Zn_2TiO_4 , Co_2TiO_4 , and $ZnCoTiO_4$. Unfortunately, it was impossible to distinguish the difference among them by XRD analysis. After a sulfidation process, other sulfide peaks defined as Co_9S_8 were observed at 30° and 52° [JCPDS No. 19-0363]. These results indicate that the cobalt additives will contribute to an increase in the desulfurization capacity and work as another active site. The ZTC-25 after the regeneration process showed another peak defined as Co_3O_4 along with the spinel structure. These results indicate that sulfides of ZnS and Co_9S_8 were not completely restored to their initial phases having spinel structures because the regeneration temperature was not high enough. Figure 2-2a shows the XRD patterns of ZTN-20 sorbents before and after the reaction. The ZTN-20 before the reaction had a perfect spinel structure, and its phase was expected to yield Zn_2TiO_4 , Ni_2TiO_4 , and $ZnNiTiO_4$. After a sulfidation process, the XRD results of the ZTN-20 sorbent showed only a ZnS peak without any other sulfide peaks

resulting from the nickel additives. This indicates that nickel additives were nonactive at this sulfidation temperature or that nickel sulfides produced in the sulfidation process were amorphous. Because the total absorption capacity of ZTN-20 is more than 20% and the theoretical value is 16.8% when only zinc is considered as an active site of this sorbent, a nickel additive with an amorphous structure is believed to contribute to an increase in the desulfurization capacity and work as another active site. The ZTN-20 sorbent after regeneration showed three single oxides separated from spinel structures: ZnO , TiO_2 , and NiO . The XRD patterns of ZTCN-10,10 before and after the reaction are shown in Figure 2-2b. The XRD pattern of this sorbent before the reaction showed a perfect spinel structure like Zn_2TiO_4 , although some TiO_2 having a rutile phase was observed. After the sulfidation process, only a ZnS peak was observed without any other sulfide peaks resulting from the nickel or cobalt additives. Also, unlike sorbents mentioned previously, the TiO_2 separated from the spinel structure had two kinds of phases (anatase and rutile), even though it was impossible to measure the relative amount of the two phases by XRD analysis. The ZTCN-10,10 sorbent after the regeneration process showed a new peak defined as a NiO phase along with a spinel structure.

Comparison of Total Sulfur-Removing Capacity and Pore Size Distribution. The sulfur-removing

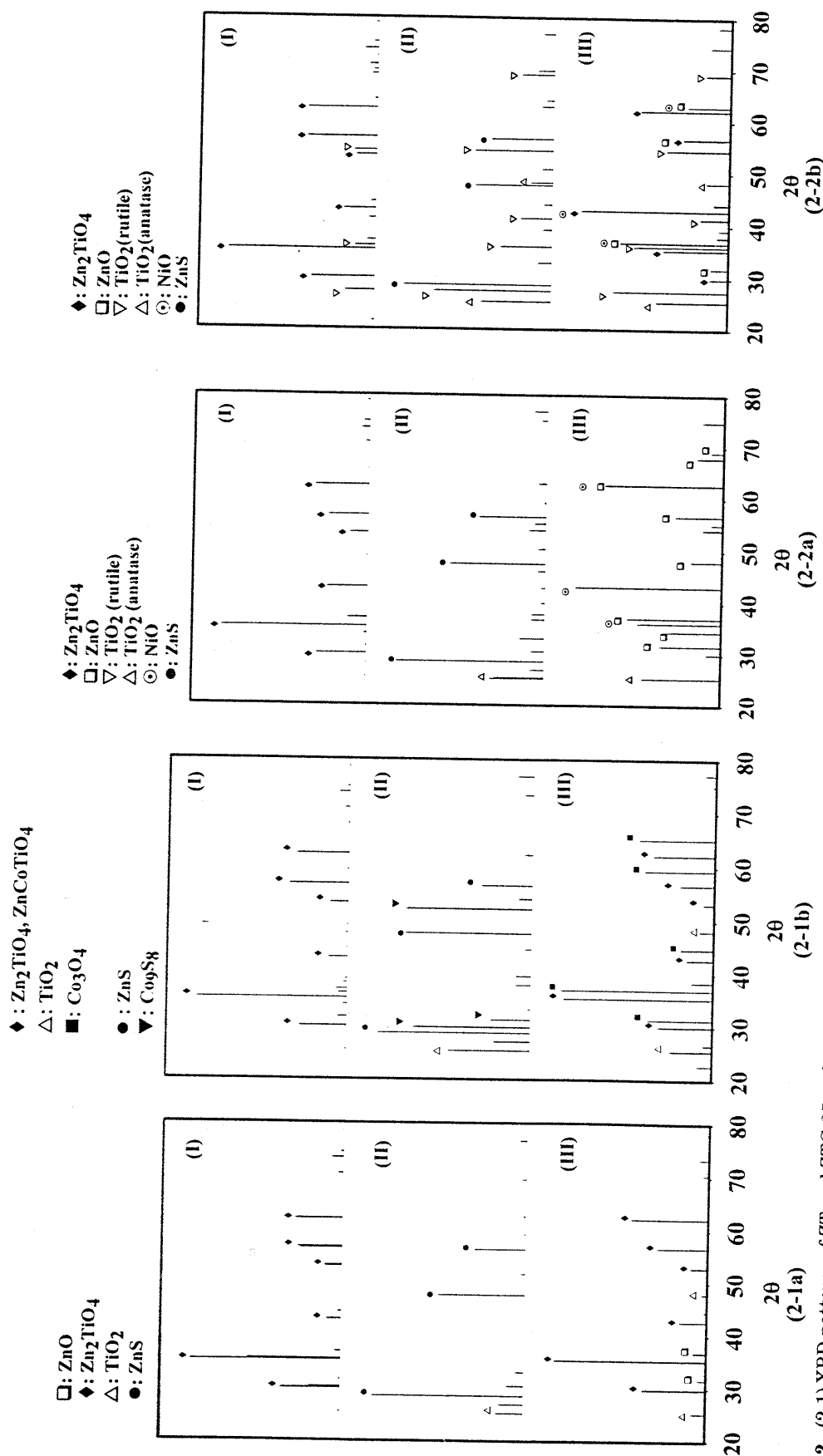


Figure 2. (2-1) XRD patterns of ZT and ZTC-25 sorbents before and after reactions at middle temperature: (a) ZT, (b) ZTC-25, (I) fresh, (II) sulfurized, (III) regenerated. (2-2) XRD patterns of ZTN-20 and ZTCN-10,10 sorbents before and after reactions at middle temperature: (a) ZTN-20, (b) ZTCN-10,10, (I) fresh, (II) sulfurized, (III) regenerated.

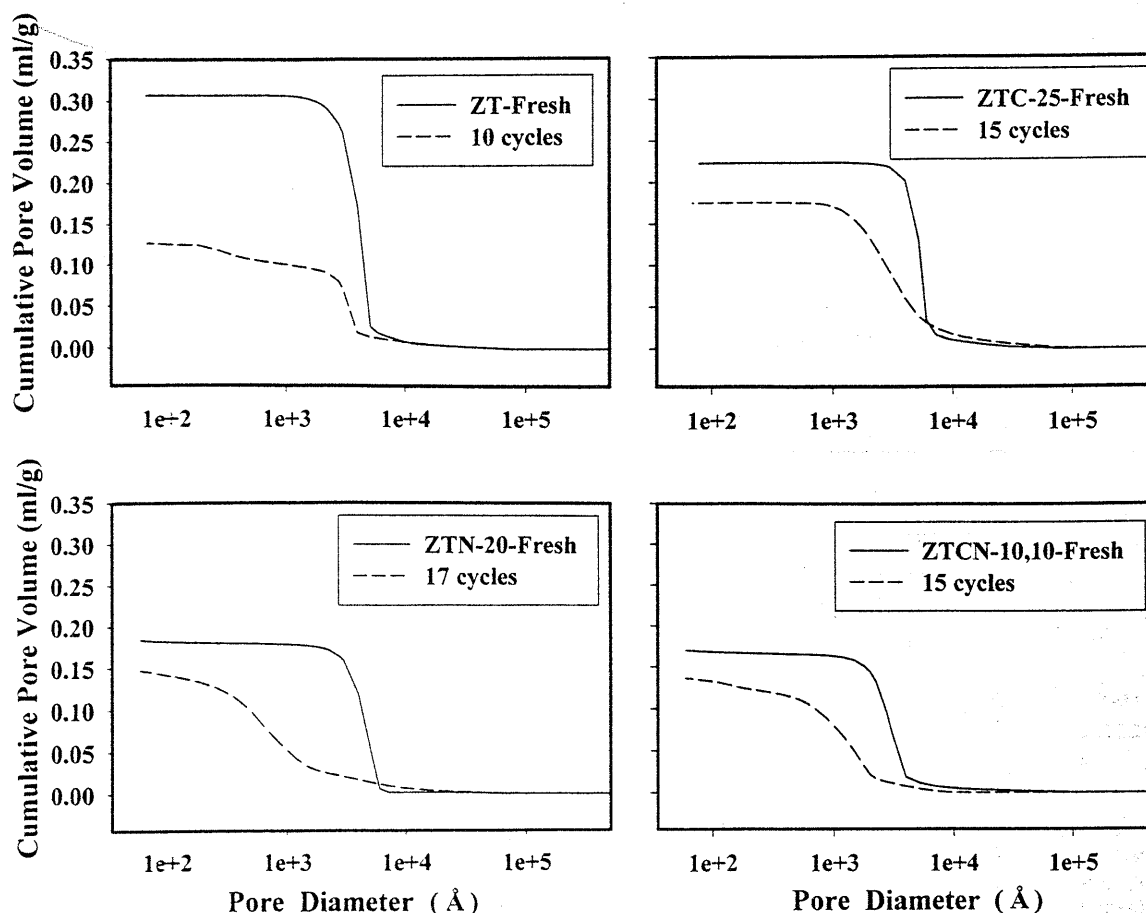


Figure 3. Cumulative pore volume as a function of pore diameter for various sorbents after selected cycles at middle temperature.

capacity in this paper means the amount of sulfur absorbed per 1 g of sorbent until the H₂S concentration in the outlet gas of the reactor reaches 200 ppmv in H₂S breakthrough curves. However, if the sulfur-removing capacity is determined by the amount of sulfur absorbed until the H₂S concentration in the outlet gas of the reactor reaches the concentration in the inlet gas (15 000 ppmv), the value always approaches the theoretical value of each sorbent and does not change during multiple sulfidation and regeneration cycles as if there was no deactivation. These results mean that the deactivation of sorbent is not due to a change in chemical properties such as the formation of metal sulfate and the vaporization of active sites, but instead due to the amount of active sites used until breakthrough time. In the comparison of total sulfur capacity with the amount of sulfur absorbed at breakthrough point, in the case of ZT, it was found that the 42% of total active zinc sites participated in the H₂S absorption reaction at initial cycles whereas only 15% zinc was used after 15 cycles. In the case of the sorbents such as ZTC-25, ZTN-20, and ZTCN-10,10, however, the active sites used until breakthrough time did not change much and reached over 62.5% of total active sites even at 15 cycles. This means that the slope of the breakthrough curve of the ZT sorbent gradually decreases during multiple cycles, indicating that much more time is needed to saturate the deactivated ZT sorbent with sulfur. No variation in slope was found for the ZTC-25, ZTN-20, and ZTCN-10,10 sorbents. So far, the variation in pore size was checked to estimate the kinetic parameter which affects the absorption rate. The

pore size distribution of the ZT, ZTC-25, ZTN-20, and ZTCN-10,10 sorbents was measured before and after the reaction using a mercury porosimeter. Figure 3 shows the plots of cumulative pore volumes as functions of pore diameter. It was found that the pore volume of ZT sorbent after regeneration was reduced by over 50% when compared to fresh sorbent, while those of the ZTC-25, ZTN-20, and ZTCN-10,10 sorbents was reduced by only 20% in comparison with their fresh sorbents. Even though further study is necessary, it is thought that the broadening of the slope in the breakthrough curve during repeated cycles is directly related to the physical properties of the sorbents and that additives such as cobalt and nickel promoters used in ZT-based sorbents play important roles as supporters, thus preventing a change in the physical properties of sorbents.

Regeneration Properties

SO₂ Breakthrough Curves. In addition to sulfur-removing capacity, regeneration characteristics are among the most important factors to be considered. Nitrogen gas mixed with 3 vol % of oxygen was introduced to regenerate the sulfided sorbents until SO₂ concentration reached a value less than 200 ppmv. The SO₂ breakthrough curves and the amount of O₂ used during regeneration at middle temperatures are plotted in Figure 4. From the stoichiometric coefficient of the regeneration reaction equation for Zn-based sorbents, we see that 2 moles of SO₂ are produced when 3 moles of oxygen are consumed during regeneration. In the case of the ZT, ZTN-20 sorbent, it was observed that the

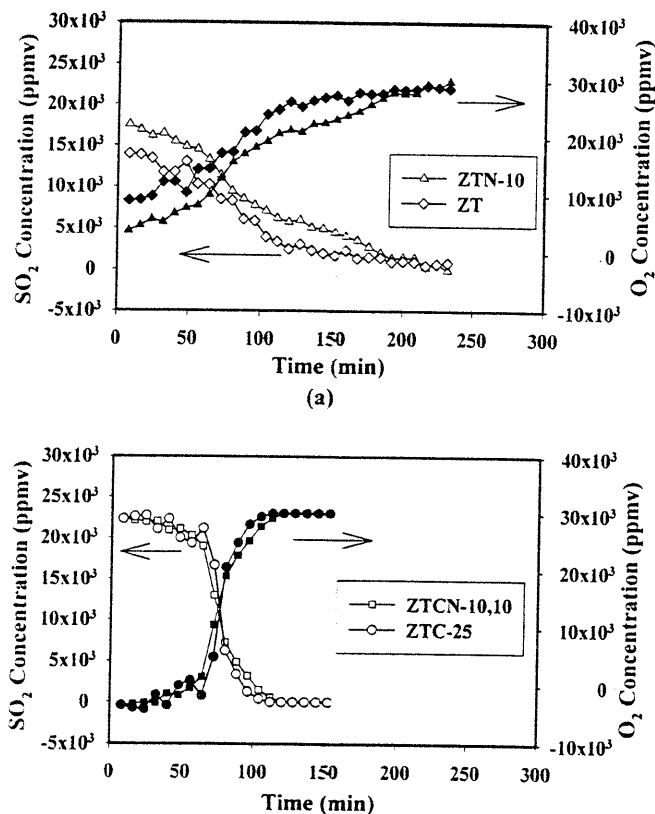


Figure 4. SO₂ breakthrough curves and amounts of oxygen used for various sorbents during regeneration at middle temperature: (a) ZT, ZTN-20, (b) ZTC-25, ZTCN-10,10. Filled symbols: O₂ concentration; open symbols: SO₂ concentration.

concentration of SO₂ had a maximum value at approximately 30 min and then the outlet concentration of SO₂ gradually decreased. On the other hand, the concentration of SO₂ and the amount of O₂ used for ZTC-25 and ZTCN-10,10 during regeneration sharply changed to steady values at about 70 min as shown in Figure 4b. Most of the sulfur absorbed during sulfidation was desorbed during regeneration for a short time. It is thought that SO₂ and O₂ were not simultaneously emitted from the reactor and that a cobalt additive played an important role in the regeneration of metal sulfide.

Temperature-Programmed Desorption (TPD).

To identify the effect of promoters on the regeneration ability of sorbents, TPD tests were performed after sulfidation. The tests were carried out by measuring the concentration of SO₂ desorbed by the introduction of nitrogen gas containing 3 vol % of oxygen when the ramping rate of the temperature was 1 °C/min. The TPD experimental results are shown in Figure 5. In the case of the ZT sorbent, the SO₂ was not desorbed during the initial period while most of the sulfur was desorbed in the temperature range 600–630 °C. The TPD result for the ZTN-20 sorbent is similar to that of the ZT sorbent. However, the desorption temperature shifted to a lower temperature (530–580 °C). On the other hand, the TPD results for the ZTC-25 and ZTCN-10,10 sorbents show that most of the sulfur absorbed during sulfidation was desorbed from the initial experimental temperature of 500 °C. The only difference between the two sorbents is a very weak peak around 750 °C in the case of ZTC-25 sorbent. To explain these results, TPD tests for single metal oxides were performed and are shown in Figure

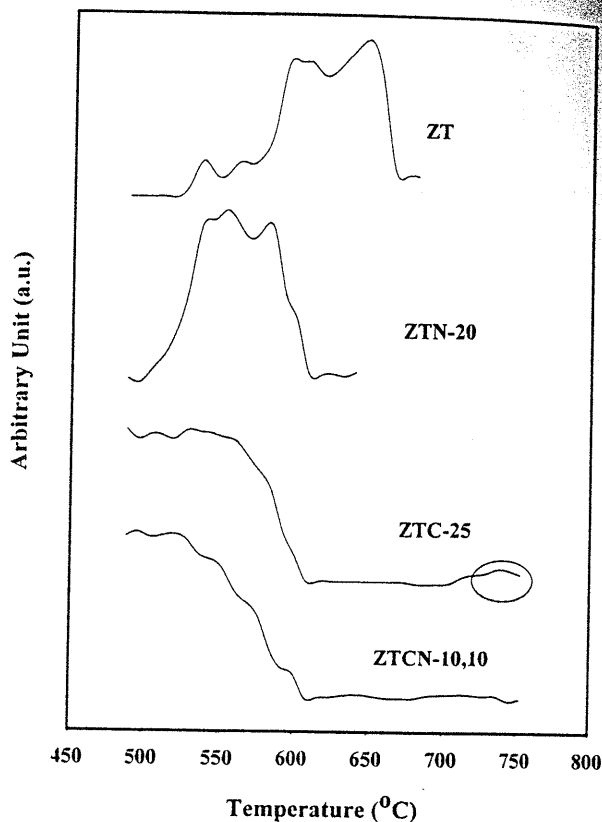


Figure 5. SO₂ TPD results of various sorbents.

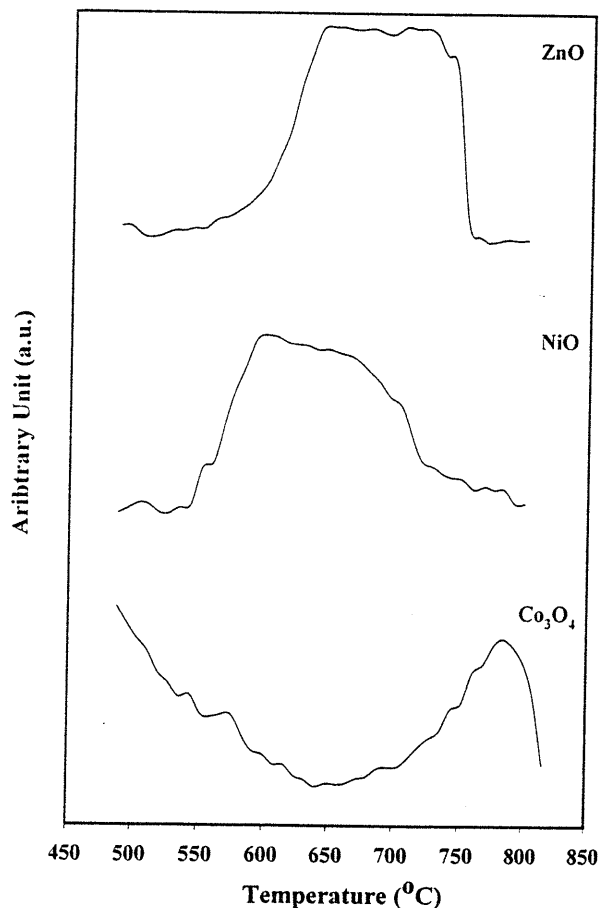


Figure 6. SO₂ TPD results of various metal oxides.

6. In the case of the zinc and nickel sulfide, the peak of SO₂ was observed at a temperature higher than 550 °C, while two peaks at 480 °C and 780 °C were observed

for the cobalt sulfides. It was already illustrated in our previous study that a peak observed at low temperatures was due to Co₉S₈ which was formed during sulfidation.²² Meanwhile, the other peak observed at a high temperature is due to CoSO₄, which was formed during the regeneration of Co₉S₈ in the oxygen stream. Comparing the TPD peaks of single metal oxides with those of the ZTC-25 and ZTCN-10,10 sorbents as shown in Figure 5, the excellent regeneration ability of the sorbents promoted with cobalt additives could be explained by the catalytic role of a cobalt additive in the oxidation or by the heat effects released from the exothermic reaction of cobalt sulfide with oxygen which can supply the necessary heat to initiate the reaction of zinc and nickel sulfide. However, the ZTC-25 sorbent showed a small peak of SO₂ due to the CoSO₄ around 750 °C in addition to the peak that resulted from the ZnS or Co₉S₈. These results imply that a sulfate might be formed in the ZTC-25 sorbent during regeneration at the middle temperature. Because the CoSO₄ is known to be a very stable sulfate, it cannot be removed by treatment at a low regeneration temperature (580 °C) and can cause SO₂ slippage in the subsequent reductive sulfidation process. SO₂ slippage means a sulfur leakage during H₂S absorption or sulfidation, which is against our goal for desulfurization at the middle temperature. Despite sulfate formation during regeneration at the middle temperature, the deactivation of ZTC-25 sorbent during multiple cycles was not observed (Figure 1). This can be explained by the fact that metal sulfate produced during regeneration was decomposed to metal and gave rise to SO₂ slippage under reductive sulfidation conditions. To explain sulfate formation on each active site such as zinc, cobalt, and nickel, the FT-IR experiments for various sorbents after regeneration at the middle temperature were carried out as shown in Figure 7. In the case of the ZT and ZTN-20, only a small trace peak at 1100 cm⁻¹ designated to sulfate was observed after regeneration, while a new peak at 680 cm⁻¹ assigned to Co₃O₄ and at 1100 cm⁻¹ designated to sulfate were clearly observed in FT-IR spectra in the case of the ZTC-25 sorbents after regeneration in the middle temperature ranges. The two peaks disappeared as cobalt loading was decreased from 25 wt % to 10 wt %. It is concluded that the added cobalt additives will separate from the spinel structure and that the sulfate peak was due to the cobalt additives. The surface composition of sorbents before and after the reaction was examined by SEM-EDS analysis. The results for the various sorbents before and after the reaction are tabulated in Table 2. The amounts of sulfur remaining in the ZT, ZTN-20, and ZTCN-10,10 sorbents after regeneration at 580 °C were less than 0.6 wt % as shown in Table 2, while the ZTC-25 sorbent contained nearly 5 wt % of sulfur. As mentioned previously, these results are explained by the formation of a metal sulfate such as CoSO₄ during regeneration.

Cobalt additive added to conventional Zn-Ti-based sorbents works as an active site during sulfidation and as an oxidation catalyst during regeneration. It also plays an important role as a structural stabilizer which prevents physical changes in the sorbents that result from their expansion and contraction during repeated cycles.²² However, using a cobalt additive alone pro-

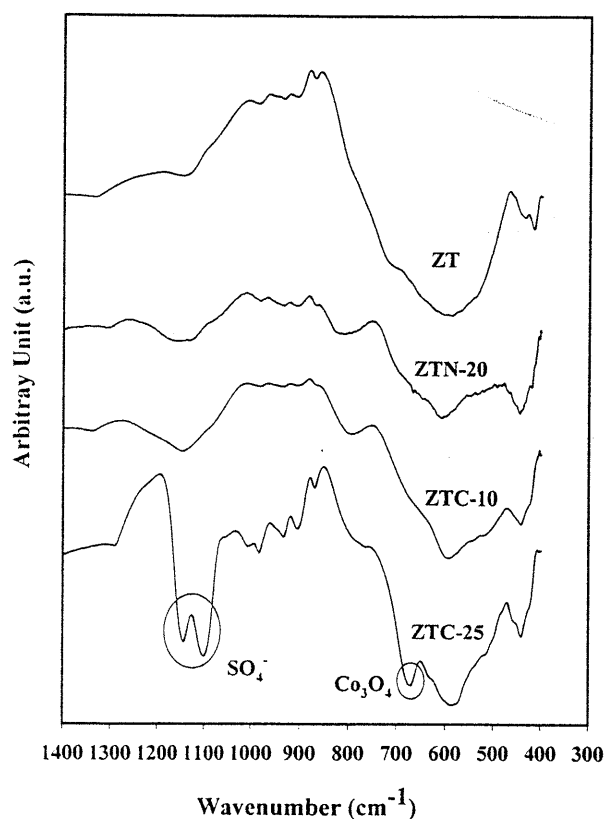


Figure 7. FT-IR spectra of various results after reactions at middle temperature.

Table 2. EDS Analysis for ZT-Based Sorbent before and after Reactions at Middle Temperature

sorbent		EDS atomic (%)					
		Zn	Ti	Co	Ni	S	Zn/Ti
ZT	fresh	44.29	21.94				2.02
	5 cycle	31.30	17.30			0.56	1.81
	15 cycle	39.72	19.25			0.53	2.06
ZTC-25	fresh	24.80	14.91	23.71			1.66
	5 cycle	17.12	10.78	16.60		3.82	1.59
	15 cycle	14.92	10.20	17.64		4.99	1.64
ZTN-10	fresh	26.35	15.09		7.79		1.75
	15 cycle	22.68	12.31		8.68	0.64	1.84
ZTCN-10,10	fresh	12.24	18.28	5.13	5.08		0.67
	10 cycle	10.91	15.30	5.59	7.73	0.87	0.71

duced a sulfate like CoSO₄, which in turn gave rise to SO₂ slippage during the subsequent sulfidation process when over 10 wt % of the Zn-Ti-based sorbent was added as shown in Table 2 and Figure 7. To overcome this problem, nickel was added in addition to the cobalt additive. Even though the reason is not clear yet, nickel added to the ZTC sorbent prevents the formation of sulfate and SO₂ slippage in the sulfidation process without much change in the sulfur-removing capacity and deactivation behavior.

Conclusions

To improve the sulfur-removing capacity of Zn-Ti sorbent, new Zn-Ti-based H₂S removal sorbents promoted with cobalt and nickel additives were prepared and tested in a packed-bed at middle temperature conditions (H₂S absorption at 480 °C and regeneration at 580 °C). They showed excellent sulfur-removing capacities which were maintained without deactivation even after 15 cycles of absorption and regeneration,

whereas that of the conventional Zn-Ti sorbent was continuously deactivated to a value less than 5% after 15 cycles. The nickel and cobalt that permeated the Zn_2TiO_4 worked not only as an active site during the sulfidation process, but also as a structural stabilizer to prevent a change in the physical properties of sorbents during the multi-cycle reaction. In particular, cobalt increased the regeneration capacity of the Zn-based sorbents because the exothermic reaction of its sulfides desorbed below 500 °C can supply the necessary heat to initiate the reaction of zinc and nickel sulfides. However, the ZTC-25 sorbent with 25 wt % cobalt gave rise to SO_2 slippage during the subsequent sulfidation process involving reductive gases because of metal sulfates such as CoSO_4 . By adding nickel in

addition to the cobalt, the slippage of SO_2 was prevented without much change to the excellent properties of ZTC sorbents. As a result, it is believed that the ZTCN-10,-10 sorbent in which 10 wt % cobalt and 10 wt % nickel were simultaneously added to the conventional ZT sorbent is the best sorbent during multiple sulfidation and regeneration cycles at the middle temperature.

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