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H_2S removal and regeneration properties of Zn–Al-based sorbents promoted with various promoters

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Abstract

In order to improve the poor regeneration properties of the $ZnO–Al_2O_3$ (ZA)sorbent with a high sulfur removing capacity and fast H_2S absorption rate, 5–10 wt.% of various additives such as iron (Fe_2O_3), cobalt (Co_3O_4), nickel (NiO) and cerium oxide (CeO_2) were added to the ZA sorbent. These sorbents were prepared by the co-precipitation method and their sulfur removing capacities and regeneration properties were measured in a fixed-bed reactor during multiple cycles at middle-temperature ranges between 480 and 580 °C. The sulfur removing capacities of these sorbents measured 0.17–0.20 g S/g sorbent, which corresponded to 80% of the theoretical value and the values were maintained to within 10 cycles. The poor regeneration property of the ZA sorbent, which needed a long time (600 min), was also improved by addition of these promoters. These sorbents were regenerated completely within 300 min. The additives such as Fe, Co and Ni formed their aluminates, which did not change into sulfide form during sulfidation. The additives/aluminates played an important role in transforming S in ZnS into SO_2. Cerium dioxide showed a similar role with such aluminates in the oxidation of sulfur. The catalytic roles of the promoters and the changes in the physical properties of sorbents, during multiple cyclic tests, are discussed.

Keywords: H_2S removal; Regeneration; Zn–Al-based sorbent

1. Introduction

The integrated gasification combined cycles (IGCC) is considered to be one of the most efficient and environmentally acceptable technologies for power generation from coal. In order to utilize this technology, the removal of pollutants such as hydrogen sulfide from coal-derived gas is necessary. To remove hydrogen sulfide from coal-derived gas, several metal oxides have been studied to develop regenerable sorbents in various temperature ranges under highly reducing conditions [1–5]. Due to equipment limitations and other variables such as alkali contents, however, the optimum temperature for the fuel gas desulfurizaion process was estimated to be between 350 and 550 °C. The affinities of many metal oxides for reduced sulfur species have improved as the temperature decreased. This makes many solids potentially suitable for hot gas clean up applications within the middle-temperature range. Zn-based sorbents have been studied to develop regenerable sorbents for the middle-temperature range (sulfidation 480 °C, regeneration 580 °C). Zn-based sorbents, which are regarded as the best among leading sorbents at high temperatures, brought about the reduction of chemical reactivity and a very low initial sulfur removing capacity, as well as some problems regarding the regeneration of spent zinc titanate sorbents [6–10,18]. Therefore, copper-based sorbents have received considerable attention, allowing gas desulfurization to be reduced to sub-ppm levels. Under the strong reducing power of coal gas, however, they are reduced to metallic copper whose sulfidation thermodynamics are not so favorable [11–16]. Agent deal of effort has been directed toward given to achieving a stable copper within an oxidation state of 2+ or 1+, through the formation of mixed oxides with Fe, Al, Mn, Ti, or Cr.

On the other hand, suitable transition metal additives have been tested to improve the sulfidation and regeneration

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properties of the Zn–Ti based sorbents, even at middle-temperatures [6–18]. In order maintain the sulfur removing capacity and excellent regeneration property in multiple cycles, however, a loading of more than 20 wt.% of such promoters is needed in the case of conventional preparation method like physical mixing, which increased the cost of the sorbent. Zn–Al-based (ZA) sorbents showed better sulfur removing capacity and absorption rate than the Zn–Ti-based (ZT) sorbents without deactivation, even after multiple cycles. These sorbents however, also brought about a low initial sulfur removing capacity and these were some problem regarding the regeneration of the spent Zn–Al (ZA) sorbent [17–19]. The objectives of this work were to investigate the reactivity of the Zn–Al-based sorbents with/without various promoters (5 wt.%) such as Fe, Ce, Co and Ni, which were prepared by the co-precipitation method, and to improve regeneration properties by adding these additives to the Zn–Al-based sorbents within middle-temperature environments.

2. Materials and methods

2.1. Preparation of the sorbents

The ZA and ZT sorbents were prepared by the conventional physical mixing method [16]. The zinc-loading amount of the ZA and ZT sorbent were 34.7 and 48.0 wt.%, respectively. The ZA-cp sorbents used in this study were prepared by the co-precipitation method and its zinc loading amount was 45.4 wt.%. Metal salts such as zinc, aluminum, iron, cobalt, nickel, and ceria nitrates were dissolved in water. Precipitation was carried out by adding a raw salt solution to the NaOH (1.5 mol solution), under vigorous mixing at room temperature. The product of the precipitation was aged for 12 h, and then washed and separated by filtration. An extruder was used to form pellets from the slurry with an outer diameter of 1 mm. The dried pellets were calcined in a muffle furnace for 4 h at 700–800 °C, and then ground to particle size raging between 250 and 300 μm in diameter. The ramping rate of the temperature was maintained at 3 °C/min. An X-ray diffraction (XRD) study was performed with a Philips XPERT instrument, using the Cu Kα radiation source at the Korea Basic Science Institute.

2.2. 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 5000 h^{-1} to minimize severe pressure drops and channeling phenomena. Volumetric flow rate of the gas was measured under 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 in 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. The teflon tube was 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 gas reached 10,000–15,000 ppm, the concentration of H_2S at the inlet stream of mixed gas, 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% oxygen was introduced to regenerate the sulfurized sorbents until the SO_2 concentration reached 200 ppm.

Table 1
Experimental conditions

	Sulfidation	Regeneration
Temperature (°C)	480	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; N_2: balance

3. Results and discussion

3.1. Sulfidation and regeneration properties of ZA-cp promoted with various promoters

The best way to evaluate the absorption capacity of sorbents is to determine the so-called breakthrough curves for H_2S absorption. In a typical fixed-bed experiment, the H_2S concentration of the outlet gas from the reactor is negligible until the entire bed is saturated with sulfur. In this study, the breakthrough time is defined as the time necessary to detect 200 ppm of H_2S concentration in the outlet gas. Fig. 1 shows the breakthrough curves of the ZT, ZA and ZA-cp sorbents in the first cycle. The ZA and ZT sorbents were prepared by a conventional physical mixing method. The breakthrough times of these sorbents were 40 and 80 min, respectively, then, the concentration of H_2S in the outlet stream slowly increased to 15,000 ppm. In the case of the ZA-cp sorbent, the breakthrough time was 160 min and the H_2S concentration of outlet gas rose rapidly up to the H_2S concentration level.

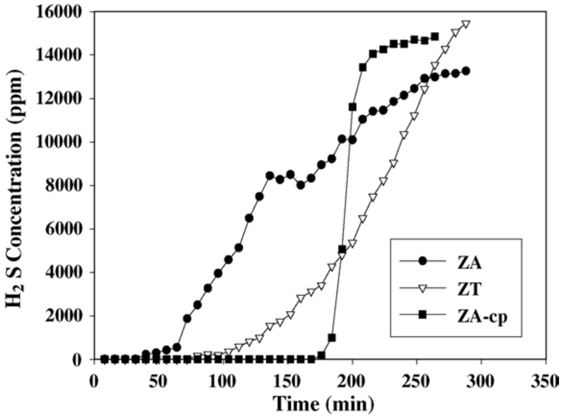


Fig. 1. Breakthrough curves of various sorbents.

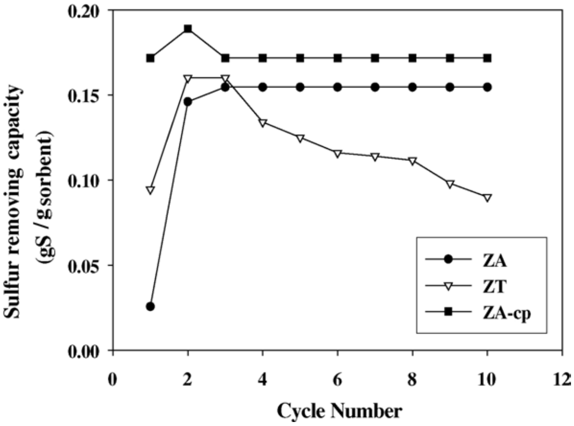


Fig. 2. Sulfur removing capacities of various orbents.

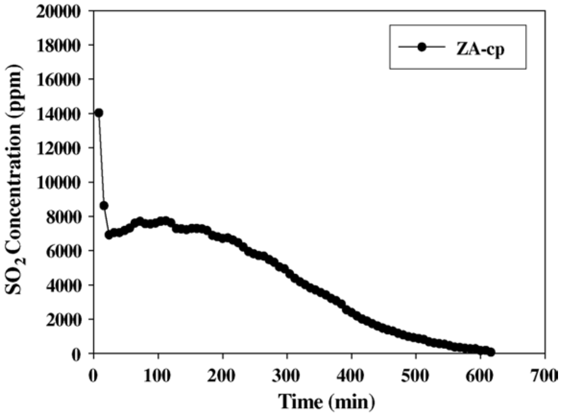


Fig. 3. SO_2 breakthrough curves of ZA-cp sorbent.

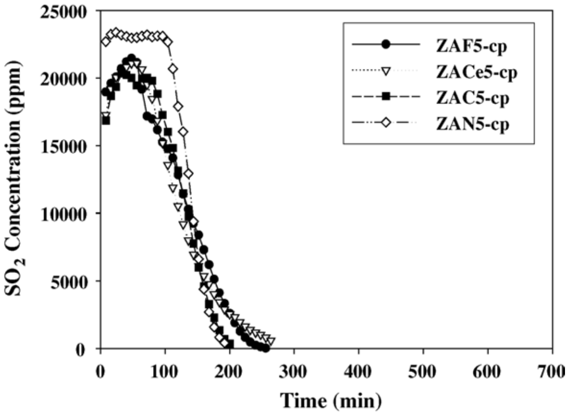


Fig. 4. SO_2 breakthrough curves of Zn–Al-based sorbents promoted with Fe, Ce, Co and Ni.

The absorption rate (the absorption amount per time from the breakthrough point to the saturation point) was calculated and the rate of the ZA-cp sorbent was much faster than those of the ZA and ZT sorbents in the first cycle. The amounts of sulfur absorbed were calculated from the amount absorbed up to the H_2S breakthrough point, and those for the ZT, ZA and ZA-cp sorbents are shown in Fig. 2. When both sulfidation and regeneration are considered to be a one-cycle process, the horizontal axis indicates the number of cycles repeated and the vertical axis indicates the gram of sulfur absorbed per gram of sorbent, until the H_2S concentration in the outlet gas of the reactor reached 200 ppmv. The sulfur absorbed into the ZA-cp sorbent was 0.17 g S/g sorbent in the first cycle. This amount was maintained during the multiple sulfidation/regeneration cycles. In the case of the ZA and ZT sorbents, the sulfur removing capacities in the initial cycle were 0.04 g S/g sorbent and 0.08 g S/g sorbent, respectively. The capacity of the ZA sobent increased to 0.15 g S/g sorbent and the value was maintained from the second cycle. On the other hand, the ZT sorbent was deactivated from 0.16 to 0.09 S/g sorbent during multiple cycles.

To evaluate the regeneration properties, the amount of sulfur desorbed (SO_2 emission) was measured as a function of time. The sulfurized sorbent, during the sulfidation process, reacted with oxygen and recovered to the oxide phase, along with the emission of SO_2. The SO_2 emission of the ZA-cp sorbent during regeneration is shown in Fig. 3. It was observed that the concentration of SO_2 was about 8000 ppm until approximately the 200 min level and then the concentration gradually decreased. In order to improve this regeneration property of ZA–cp, 5 wt.% of various additives such as iron (ZAF5-cp), cobalt (ZAC5-cp), nickel (ZAN5-cp) and cerium oxide (ZACe5-cp) were loaded into the ZA sorbent by the co-precipitation method. Fig. 4 showed the SO_2 breakthrough curves of the Zn–Al-based sorbent promoted with various additives. All sorbents tested were regenerated within approximately 80–120 min. In previous experiments [6–10], 20 wt.% of the transition metal additives had been promoted to the Zn-based sorbent by the physical mixing method, within a middle temperature range, in order to improve regeneration properties. In this work, however, it was found that the regeneration property of the sorbent promoted with only 5 wt.% of additive by the co-precipitation method was analogous to that of the sorbent promoted with 20 wt.% of additive by the physical mixing method.

Fig. 5 showed the sulfur removing capacities of the Zn–Al-based sorbents promoted with various additives during multiple cycles. The sulfur removing capacities of all sorbents were 0.17–0.20 g S/g sorbent, which corresponded to the theoretical

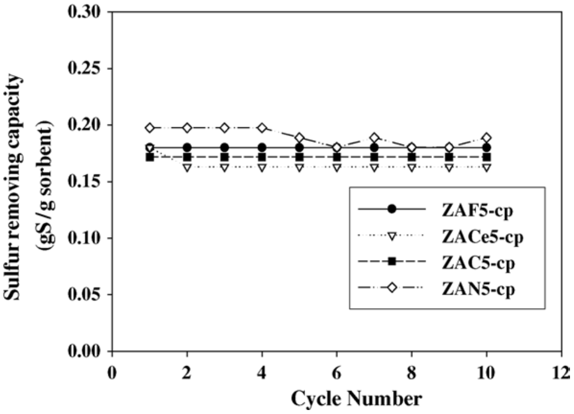
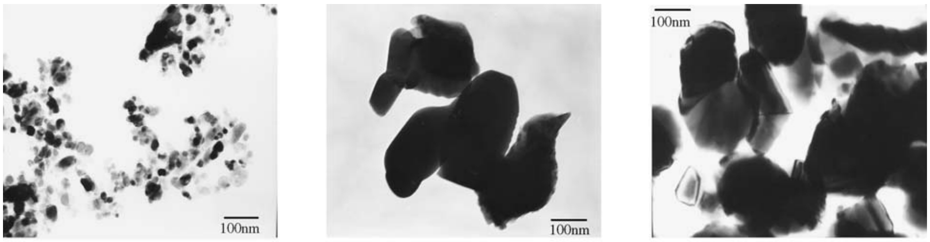
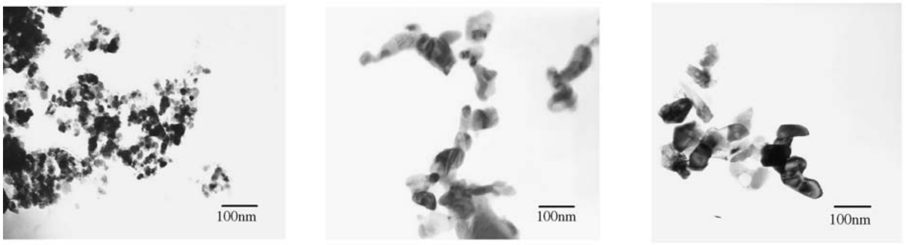


Fig. 5. Sulfur removing capacities of Zn–Al-based sorbents promoted with Fe, Ce, Co and Ni.



(a) (b) (c)
Fresh



(a) (b) (c)
regenerated after 10 cycles

Fig. 6. TEM images of fresh and regenerated (a) ZA-cp, (b) ZA, (c) ZT sorbents after 10 cycle.

value of 77.9%. Also, the values were maintained without deactivation even at the 10 cycle period.

3.2. *Initial sulfur removing capacities of the various sorbents*

The theoretical sulfur absorption values for the ZT, ZA and ZA-cp sorbents were 0.235, 0.17 and 0.22 g S/g sorbent, respectively, when only the metal zinc was considered to be and active site and the ratio of metal zinc to sulfur was 1:1. Only 34% and 23% of the total active zinc sites of the ZT and ZA sorbent, respectively, participated in the H_2S absorption reaction at the initial cycle. On the other hand, the ZA-cp sorbent used 77% of the total active sites, as shown in Fig. 2. Therefore, the sorbent prepared by the co-precipitation method showed excellent initial sulfur removing capacity compared with the sorbent prepared by the physical mixing method.

To explain these differences, surface area, and pore volume and particle size of the various sorbents were measured. Table 2 shows the surface area and average particle size for the fresh state of the ZT, ZA and ZT-cp sorbents. In the case of the ZT and ZA sorbents, their surface areas were 7.2 and 3.0 m^2/g, respectively, while that of the ZA-cp sorbent was 25.7 m^2/g.

Table 2
Physical properties of various sorbents with preparation method

		Surface area (m^2/g)	Average particle size (nm)
ZT	Fresh	7.2	350–450
	Regenerated (10 cycle)	19.2	80–100
ZA	Fresh	3.0	400–500
	Regenerated (10 cycle)	10.9	70–80
ZA-cp	Fresh	25.7	20–30
	Regenerated (10 cycle)	21.5	20–30

Fig. 6 shows the TEM images of various fresh sorbents. As shown in Fig. 6, the particle sizes of the ZT and ZA sorbents were 350 and 400 nm, respectively, while that of the ZA-cp sorbent was 10–20 nm. Fig. 7 shows the incremental pore volume of the ZT, ZA and ZA-cp sorbents, as a function of pore size. The pore volumes of the ZT and ZA sorbents were about 0.06 and 0.01 mL/g, respectively, while that of the ZA-cp sorbent was about 0.11 mL/g, with the pore size distribution ranged from between 10 and 200 nm. This large surface area and pore volume of the ZA-cp was mainly due to the nano-particle characteristics. The wide surface area and large pore size (50–200 nm) caused the easy absorption of sulfur and assisted the movement of gases such as H_2S, CO, CO_2, H_2 and N_2. Therefore, it was considered that the higher initial sulfur removing capacity of the ZA-cp sorbent, as shown in Fig. 2, was due to the improvement of physical properties such as pore volume, surface area and particle size by the co-precipitation method. In this work, all Zn–Al-based sorbents promoted with

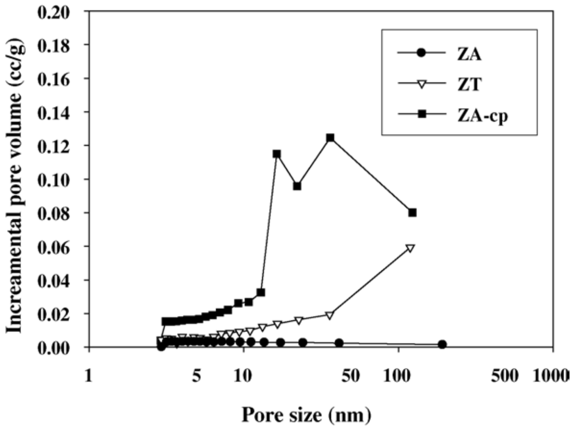


Fig. 7. The incremental pore volume of various sorbents.

Table 3
XRD patterns of various sorbents by co-precipitation

Sorbents	Fresh	Sulfidation	Regeneration
ZA-cp	ZnO, $ZnAl_2O_4$(few)	ZnS, $ZnAl_2O_4$ (few)	ZnO, $ZnAl_2O_4$ (few)
ZAN5-cp	ZnO, $ZnAl_2O_4$ (few)	ZnS, $ZnAl_2O_4$ (few)	ZnO, $ZnAl_2O_4$ (few)
ZAF5-cp	ZnO, $ZnAl_2O_4$ (few)	ZnS, $ZnAl_2O_4$ (few)	ZnO, $ZnAl_2O_4$ (few)
ZACe5-cp	ZnO, $ZnAl_2O_4$ (few),CeO_2	ZnS, $ZnAl_2O_4$ (few), CeO_2	ZnO, $ZnAl_2O_4$ (few) CeO_2
ZAC5-cp	ZnO, $ZnAl_2O_4$ (few)	ZnS, $ZnAl_2O_4$ (few)	ZnO, $ZnAl_2O_4$ (few)

additives were prepared by the co-precipitation method. They showed similar initial capacity with that of the ZA-cp sorbent, as shown in Fig. 5.

In addition, as shown in Table 2 and Fig. 6, the surface area and particle size of ZA-cp sorebnt were maintained even after 10 cycle. Therefore, the steady high sulfur removing capacity of the sorbents could be explained by the stable physical properties maintained during multiple cycles. The great changes in the structure of the ZT and ZA sorbents, prepared by the physical mixing method during multiple cycles, have already been reported in previous papers [16].

3.3. The role of additives verified by XRD and TPR

Table 3 shows the XRD results of various sorbents prepared by the co-precipitation method before/after H_2S absorption at 480 °C and regeneration at 580 °C. The XRD patterns of the ZA-cp, ZAN5-cp, ZAF5-cp, ZACe5-cp and ZAC5-cp sorbents, before H_2S absorption, showed a separated ZnO main peak and a few alloy structure-like $ZnAl_2O_4$ phases. In the case of the ZAC5-cp, ZAN5-cp and ZAF5-cp sorbents, the iron oxide, cobalt oxide, and nickel oxide phases were not observed. In the case of the ZACe5-cp sorbent, the cerium oxide phase was observed. After H_2S absorption, all of the separated ZnO was transformed to ZnS. It was found that the $ZnAl_2O_4$ phases remained and they did not participate in H_2S absorption, as already reported in a previous paper [16]. The XRD patterns, after the regeneration process, illustrated that most sulfides converted into the initial phases of ZnO without sulfate formation. In addition, it must be mentioned that the transition metal sulfides or oxides originated additives were not found in either sorbent after sulfidation and regeneration.

To identify the role of promoter for the regeneration ability of sorbents, TPR tests were performed after sulfidation. The tests were carried out by measuring the concentration of SO_2 desorbed by the introduction of nitrogen gas, containing 3 vol.% of oxygen, when the ramping rate of the temperature was 1 °C/min. The TPR experimental results are shown Fig. 8. In the case of the ZA-cp sorbent, most sulfur was desorbed above 650 °C. In the case of the ZAN5-cp, ZAF5-cp, ZACe5-cp and ZAC5-cp sorbents, most sulfur was desorbed within the temperature range of 580 and 600 °C. It was clear that the Zn–Al-based sobents promoted with various additives, were more easily regenerated at lower temperature than that of the ZA-cp sorbent. This phenomenon could not be explained by the

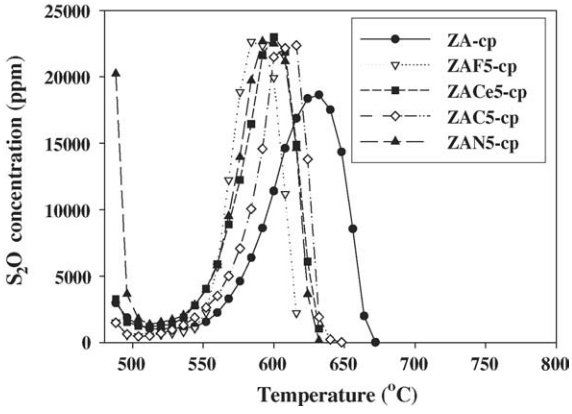


Fig. 8. TPR (temperature programmed regeneration) of ZA-cp and Zn–Al-based sorbents promoted with Fe, Ce, Co and Ni.

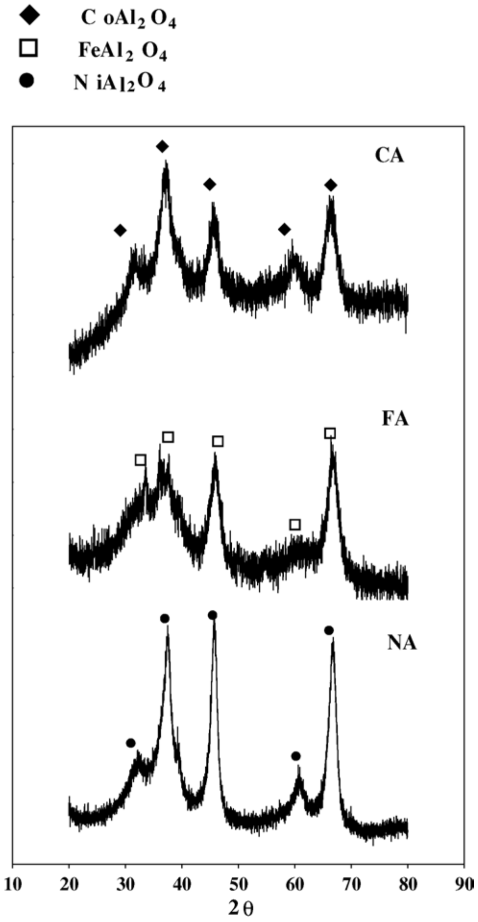


Fig. 9. XRD patterns of CA, FA and NA sorbents.

physical properties because of the similar properties of the ZA-cp sorbent, with the others that were promoted with various additives. In the previous XRD patterns before/after sulfidation and regeneration, the oxide and sulfide phases of nickel, iron and cobalt were not observed.

To explain the relation between the additives and alumina, pure additive transition metals supported on alumina (NA; Ni 5 wt.% + Al_2O_3, FA; Fe 5wt.% + Al_2O_3, and CA; Co 5 wt.% + Al_2O_3) were prepared by the co-precipitation method proposed in this work. Their XRD patterns are in Fig. 9. In the separate XRD experiment, the $NiAl_2O_4$, $FeAl_2O_4$, and $CoAl_2O_4$, phases were observed from the NA, FA and CA samples, respectively. These phases did not react with the H_2S gas as well as the $ZnAl_2O_4$ phase. Also, CeO_2 did not react with the H_2S gas. It was found that metal aluminates and CeO_2 did not affect the sulfur absorption rate and the absorption amount of sulfur of the sorbents during sulfidation process. Considering the promotion effect of CeO_2 which was well known as an oxidation catalyst and also the previous reports, concerning the catalytic oxidation of SO_2, CO and NH_3 with these transition metal aluminates [20–22], it could be suggested that the additives play an important catalytic role in transforming S in zinc sulfide into SO_2.

4. Conclusions

The Zn–Al-based sorbents, which were promoted with various promoters like Fe, Ni, Co, and Ce, were prepared by the co-precipitation method and tested in a packed bed under middle-temperature conditions (H_2S absorption at 480 °C and regeneration at 580 °C). They showed excellent sulfur removal capacity and regeneration properties, which were maintained without deactivation even after 10 cycles of sulfidation and regeneration, as compared with the conventional ZT and ZA sorbents prepared by the physical mixing method. These results could be explained by a high surface area and a large pore volume, which originated from the characteristics of the nano-size particles. The particle size of the ZA-cp sorbent was 20 nm, while those of the ZT and ZA sorbents were 350 and 400 nm, respectively. The physical properties of this nano-size sorbent were maintained during multiple cycles. In addition, the promoted sorbent could be regenerated at lower temperature (580 °C) than that of ZA-cp sorbent (650 °C). These improvements of the regeneration properties of the Zn–Al-based sorbents, promoted with various additives, were explained by the catalytic role of the transition metal aluminates, which were formed during calcinations in the oxidation reaction of sulfide.

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