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A Study on Selective Oxidation of Hydrogen Sulfide over Zeolite-NaX and -KX Catalysts

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Abstract−Selective oxidation of hydrogen sulfide (H_2S) was studied on zeolite-NaX and zeolite-KX. Elemental sulfur yield over zeolite-NaX was achieved about 90% at 225 °C for the first 4 hours, but it gradually decreased to 55% at 40 hours after the reaction started. However, yield of elemental sulfur on zeolite-KX was obtained within the range of 86% at 250 °C after 40 hours. The deactivation of the zeolite-NaX and -KX catalysts was caused by the coverage of a sulfur compound, produced by the selective oxidation of H_2S over the catalysts. The coverage of a sulfur compound over the zeolite-NaX and -KX was confirmed by the TPD (temperature-programmed desorption) tests utilizing thermogravimetric analysis and FT-IR analysis. Even though high temperature was required to prevent the deactivation of zeolite-NaX, the temperature cannot be raised to 250 °C or above due to the SO_2 production and the decrease of thermodynamic equilibrium constant. Zeolite-KX was superior to the zeolite-NaX for both its selectivity to elemental sulfur and its resistance to deactivation in the selective oxidation of H_2S.

Key words: Elemental Sulfur, Selective Oxidation of Hydrogen Sulfide, Zeolite-NaX, Zeolite-KX, Deactivation

INTRODUCTION

New technologies for coal utilization have been developed in the advanced countries. The integrated gasification combined cycle (IGCC) is considered as one of the most environmentally sustainable technologies for power generation from coal. Main components in an IGCC power plant are gasification unit, gas cleanup system and power generation facilities [Hamamatsu, 1993]. Hydrogen sulfide (H_2S) in hot coal gas can cause air pollution and corrosion either on gas turbines or on fuel cells. Therefore, it is necessary to reduce the sulfur content of the gasified fuel gas to several hundred ppmv for gas turbines [Ryu et al., 2004; Pi et al., 2003; Lee et al., 1997].

The selective catalytic oxidation of H_2S, which is commercially used in MODOP (Mobil Direct Oxidation Process) [Eur. Patent 78,690, 1982; Eur. Patent 422,992, 1990] and Super Claus process [Goar et al., 1994; Van Nisselrooya et al., 1993], is selected for the treatment of tail gas [Cho et al., 2002; Chun et al., 1998; Keller et al., 2002; Kim et al., 2004; Laperdrix et al., 2000; Shin et al., 2001].

These processes are based on the following chemical reactions [Terorde et al., 1993].

$$H_2S + \frac{1}{2}O_2 \rightarrow \frac{1}{n}S_n + H_2O \tag{1}$$

$$H_2S + \frac{3}{2}O_2 \rightarrow SO_2 + H_2O \tag{2}$$

$$\frac{1}{n}S_n + O_2 \rightarrow SO_2 \tag{3}$$

$$2H_2S + SO_2 \Leftrightarrow \frac{3}{n}S_n + 2H_2O \tag{4}$$

Eq. (1) is the main reaction, Eqs. (2) and (3) are further oxidation and Eq. (4) is the Claus reaction as a side reaction.

In order to apply the selective oxidation of H_2S for the gas clean-up in the IGCC system, the selective oxidation of H_2S as a basic experiment was performed at a dry condition, where water vapor did not exist in feeding gases, using a stoichiometric amount of oxygen.

In our previous work [Pi et al., 2003] on the selective oxidation of H_2S over zeolite-HX, -LiX, -NaX and -KX, it was reported that the reactivity of the various zeolite-X catalysts depended on their acidity.

This study will provide basic information for gas clean-up in an IGCC system via detailed experiments for long-term reaction behavior, cause of deactivation and production of SO_2 over zeolite-NaX and -KX catalysts.

EXPERIMENTAL

1. Reaction Test

Zeolite-HX, -NaX and -KX were selected as the target catalysts for this study. Zeolite-HX was prepared from zeolite-NaX by a conventional ion-exchange technique [Chang et al., 2000; Huang et al., 1995]. A 5 wt% NH4Cl aqueous solution was used and its salt solution was taken in the aliquot of 15 ml per gram of zeolite-NaX. High degree of ion-exchange was achieved after five times of exchange treatment at 80 °C. The ion-exchanged solid was washed thoroughly with distilled water to remove chloride after filtration. The solid was then dried at 120 °C for 12 hours in an air oven before being decomposed to zeolite-HX by calcination at 350 °C, and then zeolite-KX was prepared from zeolite-HX, by using a 5 wt% KOH aqueous solution. Its salt solution was taken in the aliquot of 15 ml per gram of zeolite-HX, and high degree of ion-exchange was also achieved by five times of exchange treatment at 80 °C. The ion-exchanged solid was treated by the same procedure as for the zeoltie-HX to remove chloride. The solid was then dried at 120 °C in an air oven for 12 hours before calcination of zeolite-KX at 350 °C.

Catalytic activity for the selective oxidation of hydrogen sulfide

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was performed in a fixed-bed quartz reactor with 0.5 inch I.D. All catalysts were dried at 200 °C for 2 hours by passing nitrogen gas before the reaction started. The selective oxidation of hydrogen sulfide was conducted at a pressure of 101 kPa and in the temperature range of 175-300 °C on 0.3 gram catalyst. The feeding gases flowing through the reactor consisted of hydrogen sulfide and oxygen balanced with nitrogen at a gas hourly space velocity (GHSV) of 20,000 h^{-1}. Gas flow rates were controlled by mass flow controllers (Brooks, 5850 TR), and gas compositions were analyzed by an on-line gas chromatograph (Donam, DS 6200).

The conversion of H_2S, the selectivity to elemental sulfur and the yield are defined as follows [Pi et al., 2004; Shin et al., 2001; Park et al., 2002] respectively:

$$\text{Conversion of } H_2S\ (\%)=([H_2S]_{in}[H_2S]_{out})/[H_2S]_{in}\times 100$$

$$\text{Selectivity to sulfur } (\%)=([H_2S]_{in}[H_2S]_{out}[SO_2]_{out})/([H_2S]_{in}[H_2S]_{out})\times 100$$

$$\text{Yield } (\%)=((\text{the conversion of } H_2S)\times(\text{the selectivity of sulfur}))/100$$

The conversion of H_2S was typically monitored for 5 hours on-stream at each reaction temperature.

After each reaction test, the catalyst sample was cooled down to room temperature under nitrogen flow and was subjected to a temperature-programmed desorption (TPD) experiment. The TPD test was carried out under helium flow (20 ml/min) with temperatures ramping from 25 to 500 °C.

In the TPD experiment, the deposition of the sulfurous species over zeolite-NaX and -KX was examined by thermogravimetric analysis (Thermo-Cahn, D-200) and infrared spectroscopy (Bio-Rad, FTS-3000MX).

2. H_2S TPD Test

The zeolite-NaX and -KX catalysts were dried at 300 °C for 2 hours by passing nitrogen gas. The catalysts were saturated with 2 vol% H_2S balanced with nitrogen at 100 °C for the H_2S TPD test. The weakly adsorbed H_2S was then removed by 100 ml/min N_2 flow at 100 °C until the desorbed H_2S was not detected by a thermal conductivity detector (TCD). After adsorption of H_2S, the TPD test of the H_2S was carried out in a heating rate of 3 °C/min at the temperature range 100-300 °C with N_2 gas (100 ml/min). The relative adsorption intensity of H_2S over zeolite-NaX and -KX catalysts was compared with the peak temperatures of the desorbed H_2S from zeolite-NaX and -KX, and the relative amount of adsorption sites was compared with the amount of desorbed H_2S from the both catalysts.

RESULTS AND DISCUSSION

1. Reaction over the Zeolite-NaX Catalyst

In order to investigate the selective oxidation of H_2S over zeolite-NaX at various reaction temperature, the reactivity of the selective oxidation was studied at 25 °C intervals from 175 to 300 °C for 4 hours at 20,000 h^{-1} GHSV and a 0.5 O_2/H_2S molar ratio. Fig. 1 and Fig. 2 show the conversion of H_2S and the selectivity to elemental sulfur, respectively. The conversion of H_2S over zeolite-NaX at 200 °C was 90%, which was higher than that at other reaction temperatures, while the selectivity to elemental sulfur below 225 °C was 100%.

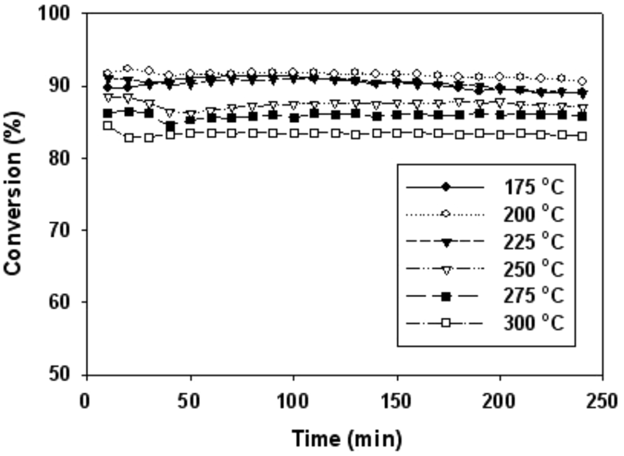

Fig. 1. Time-variant conversion of H_2S for zeolite-NaX catalyst in the temperature range of 175 to 300 °C.

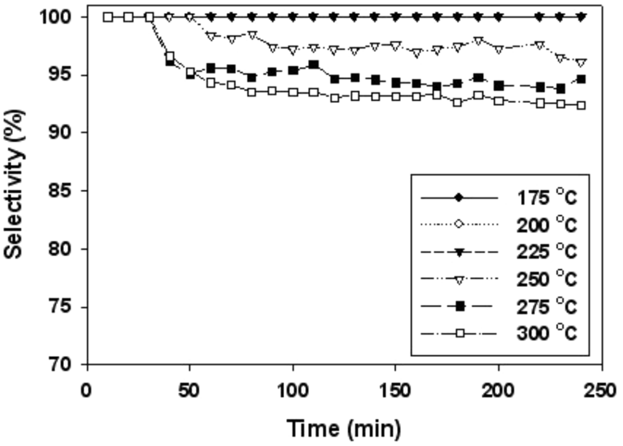

Fig. 2. Time-variant selectivity to elemental sulfur for zeolite-NaX catalyst in the temperature range of 175 to 300 °C.

The highest value of conversion was achieved at 200 °C. This indicates that the reaction at temperatures below 200 °C was controlled kinetically and the reaction at temperatures above 200 °C was controlled by thermodynamic equilibrium. It is consistent with the report of Shin et al. [2001], in which the value of thermodynamic equilibrium constant decreased as reaction temperature increased.

Fig. 2 presents that the selectivity to elemental sulfur decreased with increasing reaction temperatures. The oxidation of elemental sulfur loaded on zeolite-NaX was conducted over zeolite-NaX in order to investigate the cause of the selectivity decrease with increasing temperatures. As reported in the previous study [Pi et al., 2003], the amount of SO_2 produced from the oxidation of elemental sulfur was proportional to the reaction temperatures. There is a direct correlation between the oxidation of elemental sulfur and the decrease of selectivity. In other words, the decrease of selectivity with increasing reaction temperature was caused by the secondary oxidation of elemental sulfur formed in the selective oxidation of H_2S. Since the activation energy of elemental sulfur oxidation is much higher than that of H_2S selective oxidation [Shin et al., 2001], a nearly 100% selectivity to elemental sulfur over zeolite-NaX could be obtained only at temperatures below 225 °C.

2. Reaction over the Zeolite-HX and -KX Catalysts

Reactivity for the selective oxidation of H_2S over zeolite-HX and

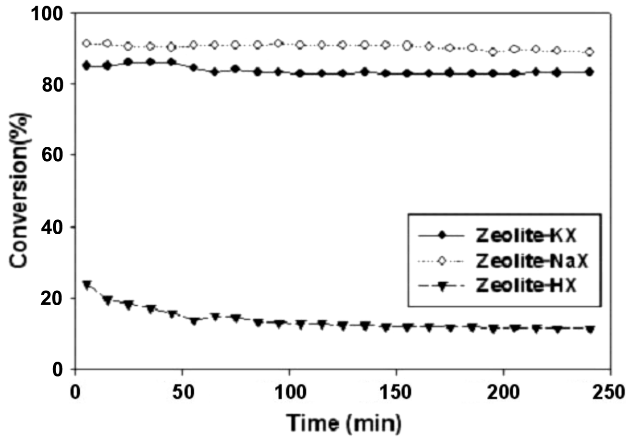

Fig. 3. Time-variant conversion of H_2S for zeolite-HX, -NaX and KX catalysts at 200 °C.

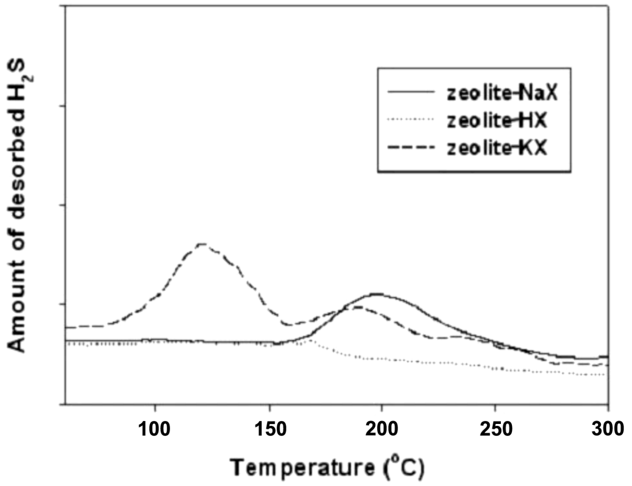

Fig. 4. The desorbed amount of H_2S in temperature-programmed desorption test for zeolite-HX, -NaX and -KX catalysts.

-KX, produced from zeolite-NaX using an ion-exchange method, was also investigated; the conversion of H_2S for the selective oxidation for zeolite-HX, -NaX and -KX at 200 °C is shown in Fig. 3. The conversions of H_2S over zeolite-HX, -NaX and -KX catalysts after 4 hours were 13%, 90%, and 83%, respectively.

In order to examine in detail, the H_2S TPD tests were conducted for zeolite-HX, -NaX and -KX over the temperature range 100-300 °C. Fig. 4 shows the amount of desorbed H_2S from zeolite-HX, -NaX and -KX in terms of temperatures. As shown in Fig. 4, a significant amount of H_2S was desorbed from zeolite-NaX and -KX, while there was no adsorption site over zeolite-HX at temperatures higher than 100 °C. Zeolite-KX catalyst has two adsorption sites. One is a less strong adsorption site, in which the adsorbed H_2S can be desorbed over the temperature range 100-150 °C, and the other is a strong adsorption site, in which the adsorbed H_2S can be desorbed over the temperature range 160-250 °C. On the other hand, zeolite-NaX catalyst has only the strong adsorption site. Since zeolite-NaX and -KX have adsorption sites for H_2S, those catalysts show an excellent reactivity. However, zeolite-HX, in which there are no adsorption sites, achieves only 20% conversion of H_2S.

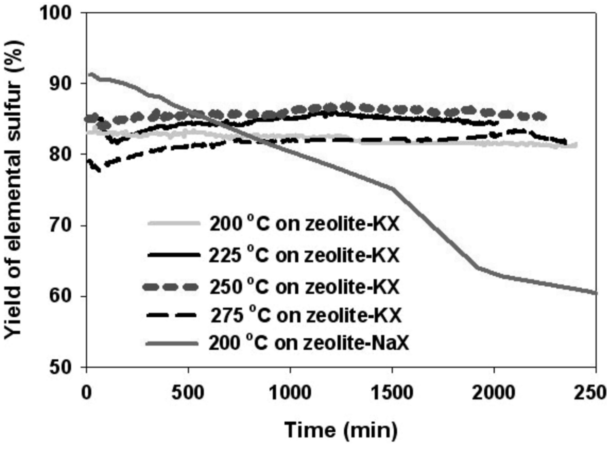

Fig. 5. Time-variant conversion of H_2S for zeolite-NaX and -KX catalysts.

It is concluded that the number of adsorption sites and adsorption intensity were the most important factors for the reactivity of selective oxidation of H_2S over zeolite-HX, -NaX and -KX.

3. Long-Term Reactivity and Deactivation of Zeolite-NaX and -KX

A 40 hour long-term test over zeolite-NaX and -KX catalysts was performed to investigate their reactivity and deactivation. The results are shown in Fig. 5. Even though the initial conversion of H_2S at 200 °C for zeolite-NaX was higher than that for zeolite-KX, its conversion decreased continuously along with the lapse of time. The value of H_2S conversion for zeolite-NaX varied from 90% at initial stage to 54% at 40 hours after the reaction started. On the other hand, slow deactivation of zeolite-KX was observed during the test over the temperature range 200-275 °C. The deactivation rate of zeolite-KX decreased with increase of reaction temperature. However, the production of SO_2 was not observed during the test over the temperature range 200-275 °C. The yield of elemental sulfur over zeolite-KX at 250 °C was 86%, the best reactivity at those reaction temperatures.

In case of zeolite-NaX, there was a limit to increase the temperature to prevent the deactivation due to decrease of the thermodynamic equilibrium constant and the selectivity to sulfur by production of SO_2. However, for zeolite-KX, the reaction temperature can be increased to prevent the deactivation up to 275 °C.

It is concluded that zeolite-KX having a less strong adsorption site of H_2S showed superior reactivity to zeolite-NaX in a 40 hour long-term test.

4. Cause of Deactivation

4-1. TGA Analysis

A TGA analysis with a Cahn-balance (Thermocahn, D-200) was carried out to investigate the cause of deactivation over zeolite-NaX and -KX. The results of TGA for fresh zeolite-NaX, fresh zeolite-KX, zeolite-NaX after 5 hours reaction and zeolite-KX after 40 hours reaction at 200 °C are shown in Figs. 6-9. Weight losses of fresh zeolite-NaX in Fig. 6 and zeolite-KX in Fig. 8 were caused by the desorption of water, which was adsorbed in the storage.

Figs. 6 and 7 show the weight loss and the weight loss rate in TPD tests of the fresh zeolite-NaX and zeolite-NaX sample after 5 hours reaction at 200 °C. From Fig. 6, it is confirmed that the ad-

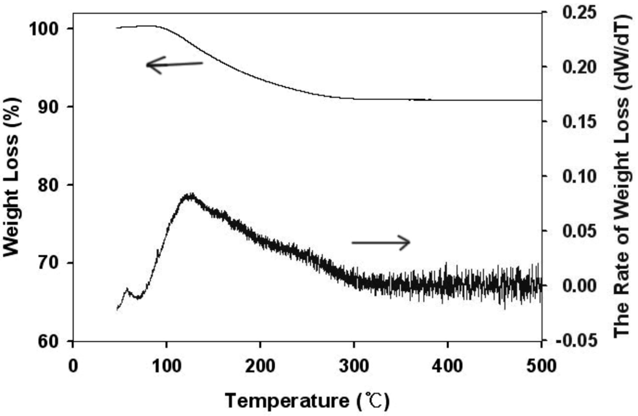

Fig. 6. Weight loss and weight loss rate of a fresh zeolite-NaX by TPD under helium (He) flow.

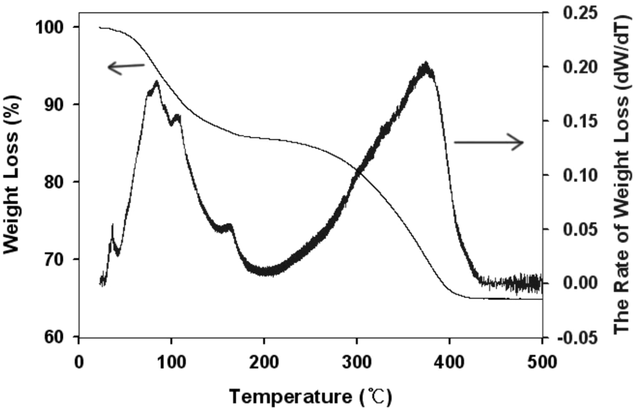

Fig. 7. Weight loss and weight loss rate of zeolite-NaX sample after 5 hours reaction at 200 °C by TPD under helium (He) flow.

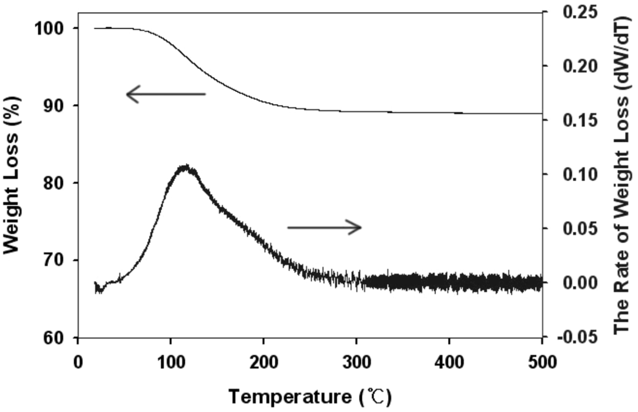

Fig. 8. Weight loss and weight loss rate of a fresh zeolite-KX by TPD under helium (He) flow.

sorbed H_2O over zeolite-NaX can be completely desorbed about 300 °C. In Fig. 7, there is a significant peak of weight loss rate at 380 °C. The fraction of weight loss was 0.2 above 200 °C. The weight loss rate below 200 °C could be ignored because the selective oxidation of H_2S was conducted over the temperature range 200-300 °C.

On the other hand, Figs. 8 and 9 show the weight loss and the weight loss rate in the TPD tests of the fresh zeolite-KX and zeolite-KX sample after 40 hours reaction at 200 °C. From Fig. 8, it is confirmed that the adsorbed H_2O over zeolite-KX can be completely desorbed at about 250 °C, which is lower temperature than that of zeolite-NaX. In Fig. 9 there are two peaks (at 220 and 340 °C) of weight loss rate above 200 °C, and the fraction of weight loss is 0.12 above 200 °C. This indicates that the deactivation of zeolite-NaX and -KX is caused by the adsorption of some materials. Not only is the adsorption intensity of adsorbed materials over zeolite-KX less strong than that of zeolite-NaX, but also the amount of adsorbed materials over zeolite-KX is less than that on zeolite-NaX.

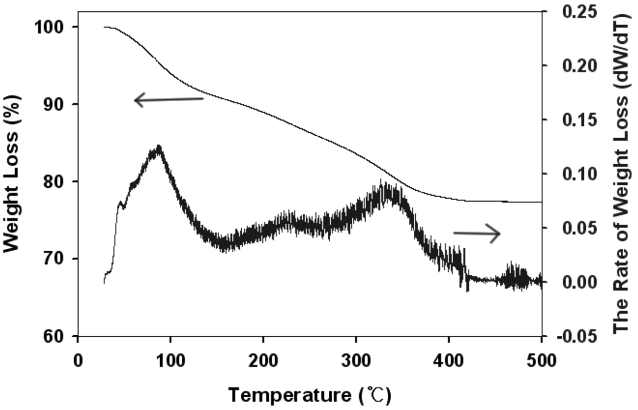

Fig. 9. Weight loss and weight loss rate of zeolite-KX sample after 40 hours reaction at 200 °C by TPD under helium (He) flow.

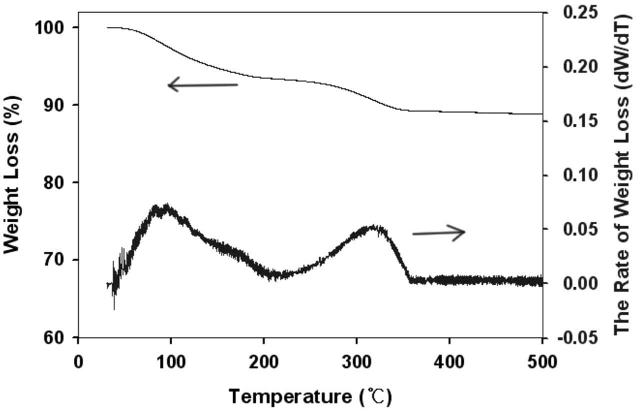

Fig. 10. Weight loss and weight loss rate of zeolite-KX sample after 40 hours reaction at 250 °C by TPD under helium (He) flow.

Fig. 10 shows the weight loss and weight loss rate in a TPD test of zeolite-KX sample after 40 hours reaction at 250 °C. There is only one peak (at 340 °C) of weight loss rate above 200 °C, and the fraction of weight loss is just 0.05 above 200 °C. As shown in Fig. 5, the production of SO_2 and the deactivation of catalyst was not observed. The yield of sulfur was 86% after 40 hours at 250 °C. It means that the deactivation of zeolite-KX can be prevented by increasing reaction temperature.

4-2. FT-IR Analysis

In section 4.1 there was the TGA analysis, the FT-IR analyses of fresh zeolite-NaX, fresh zeolite-KX, zeolite-NaX sample after

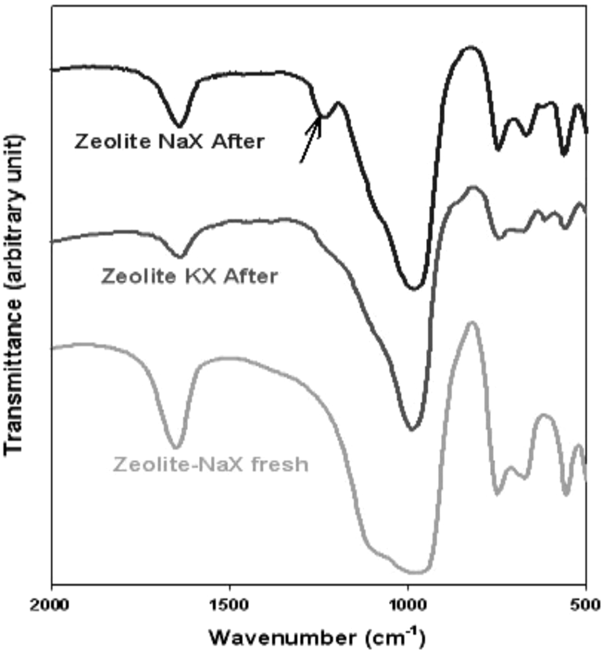

Fig. 11. FT-IR spectra of fresh zeolite-NaX, zeolite-NaX sample after 5 hours reaction and zeolite-KX sample after 40 hours reaction.

5 hours reaction, and zeolite-KX sample after 40 hours reaction at 200 °C to investigate the adsorbed material on catalysts after reaction. Because the fresh zeolite-NaX and KX represented a similar absorption band in FT-IR measurements, Fig. 11 shows FT-IR spectra of fresh zeolite-NaX, zeolite-NaX after 5 hours reaction and zeolite-KX after 40 hours reaction at 200 °C. The zeolite-NaX after 5 hours reaction and zeolite-KX after 40 hours reaction at 200 °C exhibited an obvious absorption band associated with the sulfur-compound bond vibration at 1,240 cm^{-1} [Nyquist and Kagel, 1994], and the zeolite-KX after 40 hours reaction at 200 °C exhibited an indiscernible absorption band at 1,240 cm^{-1}. These results obtained in the FT-IR spectra indicated that the adsorbed material on the catalyst was a sulfur compound formed during reaction. Therefore, it was confirmed that a strong adsorption of sulfur compound would cause the deactivation of the catalysts.

4-3. Discussion

It is confirmed that the deactivation of zeolite-NaX and -KX was caused by the adsorption of sulfur compound formed during reaction through the TGA analysis with a Cahn-balance and the FT-IR analysis. The adsorption intensity of the adsorbed sulfur compound over zeolite-NaX was much stronger than that over zeolite-KX due to the adsorption intensity and distribution of H_2S on the zeolite-NaX and -KX catalysts. Even though a slow deactivation of zeolite-KX catalyst was observed during 40 hours reaction at 200 °C, it could be solved by raising the reaction temperature to 250 °C.

It is concluded that the strong adsorption site of H_2S on zeolite-NaX could cause the high catalytic activity, catalytic deactivation, and production of SO_2.

CONCLUSION

The selective oxidation of hydrogen sulfide was performed over zeolite-NaX and zeolite-KX catalysts over the temperature range between 200 and 300 °C. The catalytic behavior and causes of their deactivation could be summarized as follows.

1. For the reaction over the zeolite-NaX catalyst, the conversion of H_2S over zeolite-NaX and the selectivity to elemental sulfur at 200 °C was 90% and 100%, respectively.
2. Even though the initial conversion of H_2S at 200 °C for zeolite-NaX was higher than that of zeolite-KX, its conversion decreased continuously along with the lapse of time. On the other hand, deactivation of zeolite-KX was not significantly observed during the test over the temperature range 200-275 °C.
3. TGA analysis and FT-IR spectra measurement confirmed that a strong adsorption of sulfur compound would cause the deactivation of the zeolite-NaX and -KX catalysts.
4. Strong adsorption site of H_2S on zeolite-NaX could cause both the high catalytic activity and the catalytic deactivation.
5. The deactivation of zeolite-KX could be prevented by the increase of reaction temperature, and the conversion of H_2S and the selectivity to elemental sulfur in the selective oxidation of H_2S over zeolite-KX at 250 °C were, respectively, 86% and 100%.

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