# The Study on the Selective Oxidation of H₂S over the Mixture Zeolite NaX-WO₃ Catalysts

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**Abstract**−At temperatures lower than 250 °C the deactivation of zeolite NaX catalyst occurred in the presence of water vapor. The gradual accumulation of water vapor on the surface of catalyst could cause deactivation of catalyst. The zeolite NaX-WO₃ catalysts were prepared to study a method preventing deactivation of catalysts from the adsorption of water vapor. The zeolite NaX-WO₃ (9 : 1) with a low content of WO₃ showed the highest conversion of H₂S. It is believed that the addition of WO₃ caused either a decrease of the strong adsorption of water vapor on the zeolite NaX or an increase of the reducibility of WO₃ by some interactions between zeolite NaX and WO₃.

Key words: Elemental Sulfur, Hydrogen Sulfide, Selective Oxidation, WO₃, Zeolite NaX

## INTRODUCTION

Clean coal technologies have been developed to reduce air pollutants emitted from the coal-derived power plants. The integrated coal gasification combined cycle (IGCC) is considered as one of the most environmentally sustainable technologies for power generation. The IGCC system consists of coal gasifier, gas cleanup unit and power generation facilities. During the coal gasification process, the sulfur contained in coal is converted into hydrogen sulfide ($H_2S$). Since hydrogen sulfide is very corrosive material, its high concentration in hot coal gas can cause not only air pollution but also serious damage to gas turbines and fuel cells in advanced power plants. It is well known that the concentration of $H_2S$ in the cleaned coal gas should be maintained below 20 ppmv in order to prevent the gas turbine from corroding [Hamamatsu, 1993]. Furthermore, the concentration of $H_2S$ must be reduced below 1 ppmv either for solid oxide fuel cells (SOFC) [Chan et al., 2003] or for molten carbonate fuel cells (MCFC) [De Simon et al., 2003] in a integrated gasification fuel cell (IGFC) power plant [Jansen et al., 1994]. The hot gas desulfurization process is an essential process for removing $H_2S$ from coal-derived fuel gas [Jang et al., 2003; Lee et al., 1997, 2001; Wi et al., 2002; Yi et al., 2001]. However, the current sorbents for the HGD system have some difficulties reducing the $H_2S$ content of the coal gas less than 20 ppmv. Therefore, additional desulfurization is required for the treatment of the tail gas emitted from a fluidized-bed. In order to reduce the $H_2S$ concentration less than 1 ppmv, the selective oxidation of $H_2S$ [Chun et al., 1998; Keller et al., 2001, 2002; Laperdrix et al., 2000; Shin et al., 2001], which is used in MODOP (Mobil Direct Oxidation Process) [Chopin et al., 1990; Kettner et al., 1982] and Super Claus process [Goar et al., 1994; Van Nisselrooya et al., 1993], was selected for the treatment of tail gas. These processes are based on the following chemical

reactions [Terorde et al., 1993].

$$H_2S + \frac{1}{2}O_2 \rightarrow \frac{1}{n}S_n + H_2O \quad \text{(1)}$$

$$H_2S + \frac{3}{2}O_2 \rightarrow SO_2 + H_2O \quad \text{(2)}$$

$$\frac{1}{n}S_n + O_2 \rightarrow SO_2 \quad \text{(3)}$$

$$2H_2S + SO_2 \Leftrightarrow \frac{3}{n}S_n + 2H_2O \quad \text{(4)}$$

It is well known that catalysts such as $V_2O_5$, $Fe_2O_3$, and $WO_3$ supported on the $TiO_2$, $SiO_2$ and $Al_2O_3$ are used in the selective oxidation of $H_2S$ [Cho et al., 2002; Chun et al., 1997]. The reactions of these catalysts occur via the redox mechanism. Catalysts containing weak acidic sites showed high activity in the selective oxidation of $H_2S$. The zeolite X was selected due to an easy modification of its acidity. In previous work, the selective oxidation of $H_2S$ was investigated over zeolite X with various acidity [Pi et al., 2003]. Zeolite NaX showed the highest activity among the various zeolite X. In the presence of $H_2O$ the activities of the zeolite NaX and the zeolite NaX-WO₃ catalysts were compared in this study. The characteristics of catalysts were analyzed by X-ray diffraction analysis (XRD), temperature programmed desorption (TPD) and temperature programmed reduction (TPR).

## EXPERIMENTAL

### 1. Reaction Test

The zeolite NaX-WO₃ catalyst was prepared by a mechanical mixing method using a zeolite NaX powder (3 µm, Aldrich) and a WO₃ powder (3 µm, Junsei). The weight ratios of the zeolite NaX to the WO₃ were varied from 1 to 20. The test for the catalyst performance was carried out in a fixed-bed Pyrex® reactor with an 1/2 inch inside diameter under atmospheric pressure. The amount of catalyst charged into the reactor was 0.3 g. Reactant was composed of 2 vol% of hydrogen sulfide ($H_2S$), 1 vol% of oxygen ($O_2$) and

10 vol% of water vapor with nitrogen ($N_2$) balance. The flow rate of gas was set to 100 cm³/min and was controlled by mass flow controllers (Brooks MFC 5850E). The water was injected by using a syringe pump and a vaporizer was located in front of the reactor. A sulfur condenser was attached to the effluent side of the reactor. A line filter was installed to trap residual sulfur mist, which had not been captured by the condenser. The $H_2S$ and $SO_2$ were analyzed by an on-line gas chromatographer equipped with a chromosil 310 column and a thermal conductivity detector. Gas hourly space velocity (GHSV), $O_2/H_2S$ mole ratio and reaction temperature range were 20,000 $h^{-1}$, 0.5 and 200-300 °C, respectively. The conversion of $H_2S$, selectivity and yield of sulfur was computed by the following equations:

$$\text{Conversion of } H_2S (\%) = \frac{[H_2S]_{inlet} - [H_2S]_{outlet}}{[H_2S]_{inlet}} \times 100$$

$$\text{Selectivity of sulfur } (\%) = \frac{[H_2S]_{inlet} - [H_2S]_{outlet} - [SO_2]_{outlet}}{[H_2S]_{inlet} - [H_2S]_{outlet}} \times 100$$

$$\text{Yield of sulfur } (\%)$$
$$= \frac{\text{Conversion of } H_2S(\%) \times \text{Selectivity of sulfur } (\%)}{100}$$

## 2. Characterization of Catalysts

### 2-1. XRD Analysis

The phase analysis of catalyst was carried out by using an X-ray analyzer (RIGAKU, D/MAX-2500). Ni-filtered Cu K$\alpha$ radiation was used with an X-ray gun operated at 40 kV and 100 mA. The diffraction patterns were analyzed in the range of $2\theta$=5-70° with a scan rate 10°/min.

### 2-2. Temperature Programmed Desorption (TPD) Test

The TPD test of the $H_2O$ over zeolite NaX catalyst was carried out by mass spectroscopy. The zeolite NaX was dried at 300 °C for 2 hours and then saturated with $H_2O$ for 2 hours at room temperature. The weakly adsorbed $H_2O$ was removed by introducing $N_2$ (100 cm³/min) at 150 °C for 5 hours. The TPD test was carried out in a heating rate of 1.5 °C/min over the temperature range 150-400 °C.

A TPD test of the $H_2S$ over zeolite NaX catalyst was also performed with/without water vapor in $N_2$ gas. For a TPD test without water vapor, the zeolite NaX catalyst was dried at 300 °C for 2 hours and then 2 vol% of $H_2S$ gas balanced with $N_2$ was introduced at 100 °C. For a TPD test with water vapor, $H_2S$ and water vapor were introduced to the reactor simultaneously. After adsorption of $H_2S$, the TPD test of the $H_2S$ was carried out in a heating rate of 3 °C/min over the temperature range 100-300 °C with $N_2$ gas (100 cm³/min).

### 2-3. Temperature Programmed Reduction (TPR) Test

The prepared catalysts were packed in the Pyrex® reactor with 6 mm diameter and dried at 300 °C for 2 hours with He gas (50 cm³/min) to eliminate the water vapor. The reduction test was carried out in a heating rate of 2 °C/min over the temperature range 300-700 °C. Flow rates of CO and He were maintained in 25 cm³/min and 25 cm³/min, respectively. In order to compare the reducibility of $WO_3$ catalyst with that of zeolite NaX-$WO_3$ composite catalyst, 0.5 g of $WO_3$ powder and the mixture of $WO_3$ (0.5 g)-zeolite NaX (0.5 g) were used. For the evaluation of the reducibility the amount of the consumed CO was analyzed with a gas chromatography and the color changes of $WO_3$ were monitored with an image analyzer.
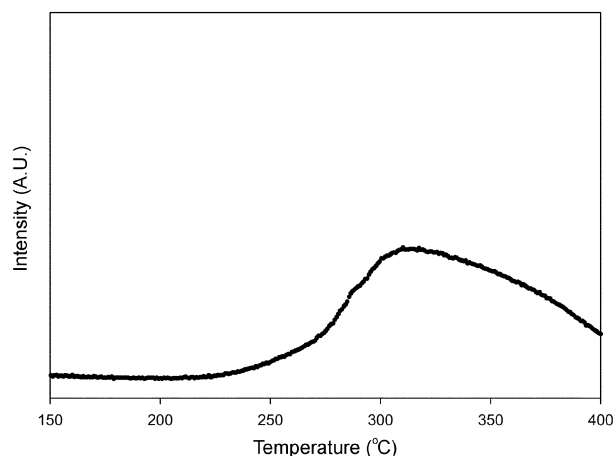
## RESULTS AND DISCUSSION



**Fig. 1. The amount of desorbed H₂O over the zeolite NaX catalyst.**

## 1. The Activity and Characterization of the Zeolite NaX Catalyst

In the previous work it was reported that the zeolite NaX catalyst was effective for the selective oxidation of $H_2S$ in the absence of water vapor [Pi et al., 2003]. In this case, the yield to the elemental sulfur was 90% at 200 °C. To investigate the effect of water vapor on the activity of zeolite NaX, TPD test of water vapor was carried out using mass spectroscopy. Fig. 1 shows that the intensity of the desorbed $H_2O$ increased as temperature increased. The desorption of water vapor over zeolite NaX was started at around 225 °C. It is indicated that the activity of catalysts could be affected by the addition of water vapor due to its strong adsorption on the zeolite NaX. Figs. 2 and 3 show the conversion of $H_2S$ and the selectivity of zeolite NaX catalyst versus time at different temperatures in presence of water vapor, respectively. The selective oxidation of $H_2S$ was performed for 4 hours in the temperature range of 200-300 °C for every 25 °C intervals. The composition ratio of gas was $O_2/H_2S/H_2O/N_2$ (1/2/10/87) and the gas hourly space velocity was fixed to 20,000 $h^{-1}$. While the $H_2S$ conversion of the zeolite NaX catalyst increased, the selectivity to sulfur decreased as temperature increased.
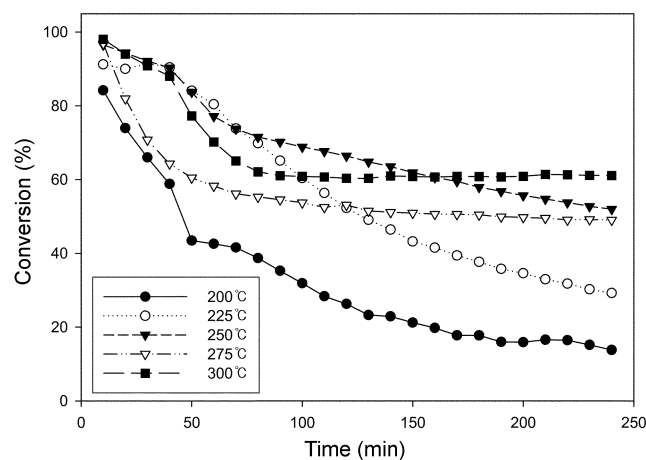


**Fig. 2. The conversion over zeolite NaX catalyst with reaction temperature change (2 vol% H₂S, 1 vol% O₂, 10 vol% H₂O, 87 vol% N₂, GHSV=20,000 h⁻¹).**

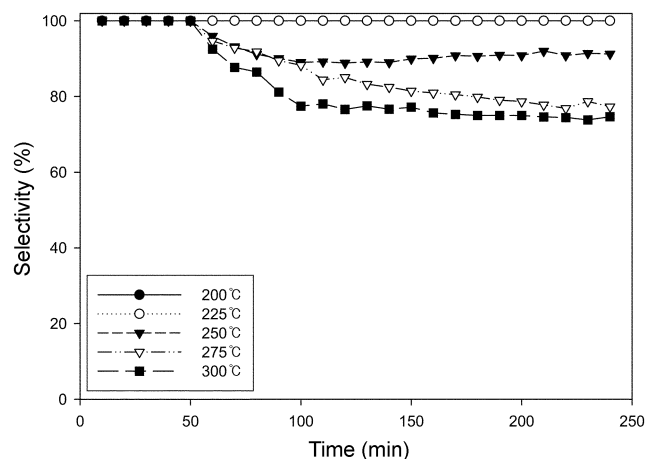**Fig. 3. The selectivity over zeolite NaX catalyst with reaction temperature change (2 vol% H₂S, 1 vol% O₂, 10 vol% H₂O, 87 vol% N₂, GHSV=20,000 h⁻¹).**

Fig. 1 showed that the conversion of $H_2S$ as a function of time decreased more rapidly at 200 °C than at 225 °C. The deactivation at lower temperature was closely connected with the adsorption of water vapor on the zeolite NaX. It could be explained by the extent of desorption of water vapor at different temperatures. Since water vapor was rarely desorbed from the catalysts at 200 °C as shown in Fig. 1, the larger amount of water vapor was adsorbed on the surface of catalysts at 200 °C rather than 225 °C. The gradual accumulation of water vapor on the surface of catalyst could cause deactivation of catalyst as it prevents $H_2S$ from access to reaction sites. However, the deactivation of catalyst did not occur at the same condition in the absence of water vapor in the previous work. At temperatures higher than 250 °C, reactivity of catalysts became steady from 70 minutes after reaction was initiated. The reason for the steady conversion of $H_2S$ might be that adsorption rate and desorption rate reached equilibrium after 70 minutes. While the selectivity to sulfur at temperatures lower than 250 °C was 100%, the selectivity at temperatures higher than 250 °C tended to be decreased as the reaction temperature increased because of the oxidation of product sulfur. It is considered that the equilibrium values decreased as the
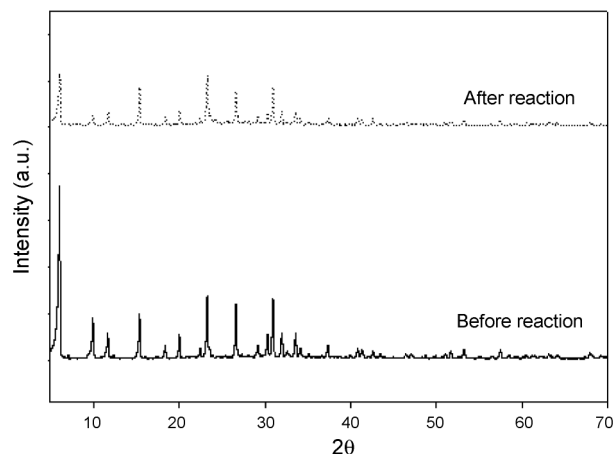


**Fig. 5. The amount of desorbed H₂S over the zeolite NaX catalyst (with and without feeding 10 vol% H₂O).**

reaction temperature increased. XRD and TPD tests were performed to investigate the effect of water vapor. Fig. 4 showed the XRD patterns of zeolite NaX before and after reaction. Even though the intensity of peaks was slightly decreased after the reaction, the major peaks of XRD were not varied noticeably. It is difficult to determine the correlation between the deactivation and the structural change of the catalysts from the experimental results. Fig. 5 shows the result of $H_2S$ TPD test with/without water vapor. The amount of $H_2S$ desorbed in the presence of water vapor was much less than that of $H_2S$ desorbed in the absence of water vapor. The implication is that the increase in the amount of water vapor adsorbed may cause the deactivation of catalysts because water vapor and $H_2S$ were competing with each other to be adsorbed on the same sites.

## 2. The Activity Test of Metal Oxide Catalysts

Fig. 6 shows the conversion of $H_2S$ and the selectivity of various metal oxides in the presence of water vapor at 275 °C. The $H_2S$ conversions of $MnO_2$ and $WO_3$ were about 58% and 56%, respectively. $MoO_3$ and $WO_3$ catalysts showed high selectivity to the ele-
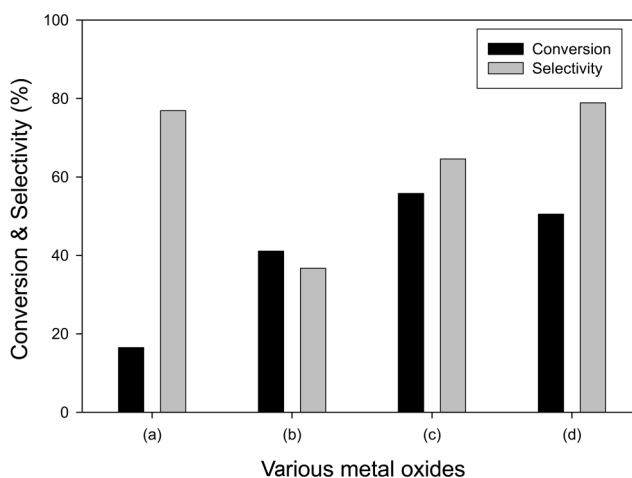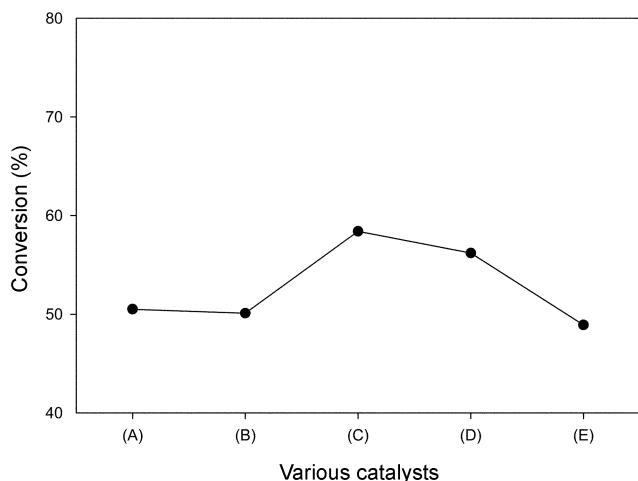


**Fig. 4. XRD patterns of zeolite NaX catalysts before and after the reaction.**



**Fig. 6. The conversion and selectivity over various metal oxide catalysts at 275 °C (a) MoO₃ (b) Fe₂O₃ (c) MnO₂ (d) WO₃ (2 vol% H₂S, 1 vol% O₂, 10 vol% H₂O, 87 vol% N₂, GHSV= 20,000 h⁻¹).**

**Fig. 7. Effect of weight ratio of zeolite NaX and WO₃.**
(A) WO₃ (B) zeolite NaX-WO₃ (5 : 5) (C) zeolite NaX-WO₃ (9 : 1) (D) zeolite NaX-WO₃ (9.5 : 0.5) (E) zeolite NaX



**Fig. 8. The conversion over mixed zeolite NaX-WO₃ catalysts with reaction temperature change (2 vol% H₂S, 1 vol% O₂, 10 vol% H₂O, 87 vol% N₂, GHSV=20,000 h⁻¹).**



**Fig. 9. The selectivity over mixed zeolite NaX-WO₃ catalysts with reaction temperature change (2 vol% H₂S, 1 vol% O₂, 10 vol% H₂O, 87 vol% N₂, GHSV=20,000 h⁻¹).**

mental sulfur. Although MoO₃ catalyst showed high selectivity, it had low yield due to a very low conversion of H₂S. WO₃ catalyst had the highest yield (39.9 %) among the various metal oxides.
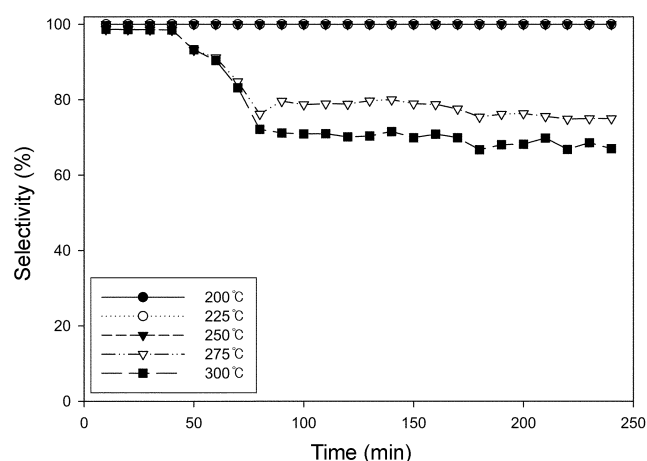
**3. The Activity Test of the Mixed Zeolite NaX-WO₃ Catalysts**

In the presence of water vapor, the activity of the zeolite NaX catalysts was low due to the strong adsorption of water vapor on the surface of catalyst. From the experimental results, WO₃ showed the highest yield among the metal oxides. Therefore, the zeolite NaX-WO₃ catalysts were prepared by the mechanical mixing of zeolite NaX and WO₃ to study a method preventing deactivation of catalysts from the adsorption of water vapor contained in a feed gas. Weight ratios of zeolite NaX to WO₃ were varied from 5.0 : 5.0 to 9.5 : 0.5 in order to investigate the effect of loading ratio of the mixed catalysts. Fig. 7 shows the conversion of H₂S for different catalysts at 4 hours after reaction started. At 275 °C the conversion of H₂S over a pure zeolite NaX catalyst was 48.9%, while the conversion of H₂S over the zeolite NaX-WO₃ with weight ratio of 5 : 5 was slightly higher than that of zeolite NaX only. The zeolite NaX-WO₃ (9 : 1) with a low content of WO₃ showed the highest conversion of H₂S. It was concluded that the optimum weight ratio of the zeolite NaX-WO₃ catalysts was 9 : 1 because the conversion of H₂S decreased at the weight ratio of the zeolite NaX-WO₃ higher than 9 : 1. This may be due to not only the interaction of the zeolite NaX and WO₃ but also the decrease of adsorption site on the zeolite NaX by adding the WO₃.

The selective oxidation of H₂S at the optimum weight ratio (9 : 1) of the zeolite NaX-WO₃ was performed at different reaction temperatures between 200 °C and 300 °C. Figs. 8 and 9 show the conversion of H₂S and the selectivity in the temperature range from 200 to 300 °C. Below 250 °C the conversion of H₂S rapidly decreased with time on stream. However, SO₂ was not produced below 250 °C. This is similar to literature results [Shin et al., 2001]. Shin et al. reported that the oxidation rate of sulfur to SO₂ was quite slow compared with that of H₂S to sulfur since the activation energy for the sulfur oxidation (125±10 kJ/mol) is much higher than that for the H₂S oxidation (~10 kJ/mol). Above 275 °C the conversion of H₂S gradually decreased during the initial 80 min, but after 80 min it
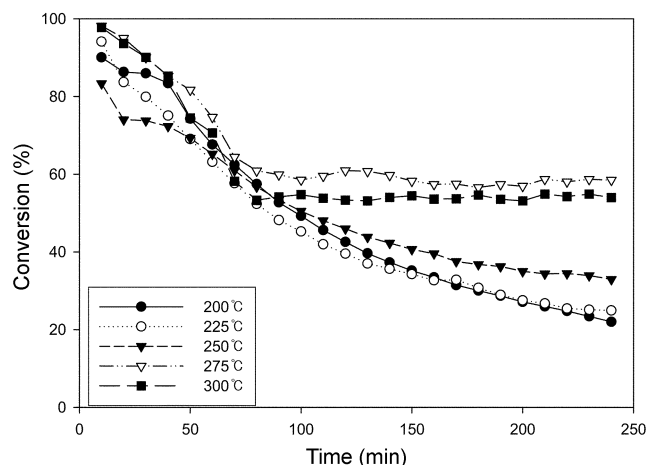
was maintained almost constant. The selectivity to sulfur showed almost the same tendency of variation with reaction temperatures.

**4. Characterization of the Zeolite NaX-WO₃ Catalysts**

XRD analysis, TPR tests and electron microscope images were conducted to investigate the interaction within the mixed zeolite NaX-WO₃ catalysts. Fig. 10 shows the XRD patterns of the fresh catalysts and the used catalysts. The change of crystal structure was not observed even after the reaction. This indicates that the activity of mixed zeolite NaX-WO₃ catalysts was not linked to the change of crystal structure. In order to investigate the effect of zeolite NaX on the reduction of WO₃ catalyst, the TPR test with CO over the WO₃ and the zeolite NaX-WO₃. Electron microscope images were carried out in this study. Fig. 11 shows the results of the TPR test of WO₃ and zeolite NaX-WO₃. The reducibility of sample could be evaluated from the amount of the consumed CO. The amount of the consumed CO over the zeolite NaX-WO₃ was much more than that of the WO₃. This implies that the reduction of WO₃ was affected by zeolite NaX. Electron microscope image is shown in
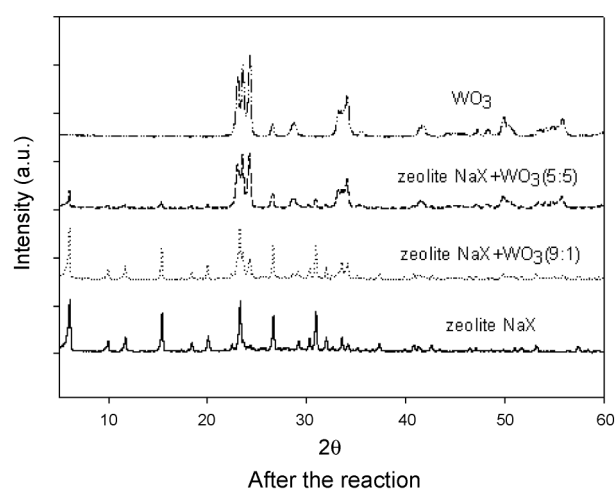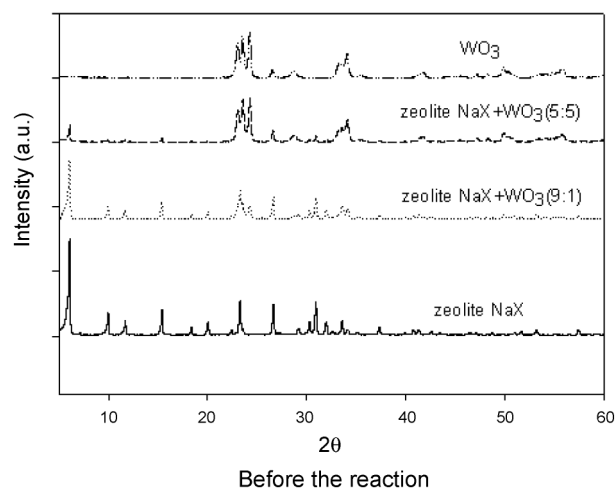
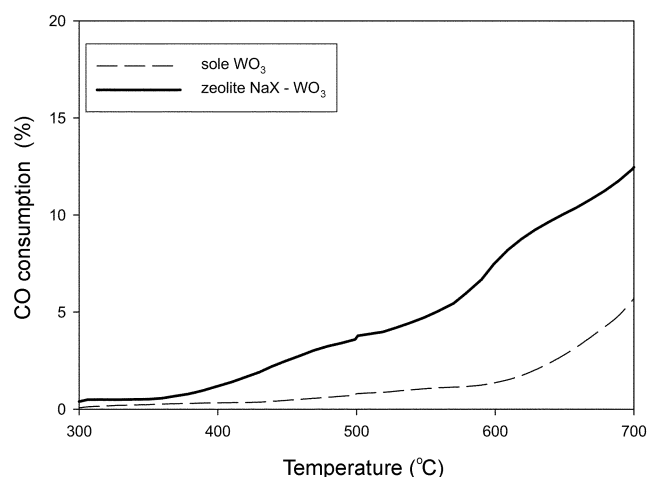Fig. 10. XRD patterns of various catalysts before and after the reaction.



Fig. 11. The accumulated CO consumption ratio of the reaction with sole $WO_3$ and zeolite $NaX-WO_3$.

Fig. 12 in order to confirm the reduced degree of $WO_3$ catalyst. Since the color of tungsten oxides could be varied by their oxidation states, the reducibility of sample was evaluated by its color. $WO_3$, $WO_{2.8}$ and $WO_2$ display their colors in yellow, blue and brown, respec-
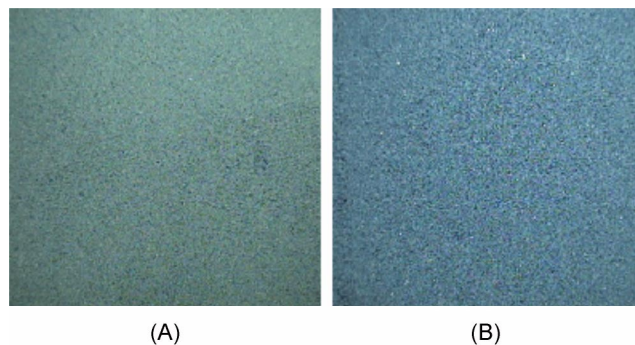
Fig. 12. Photograph image after reduction at 450 °C for 4 hours. (A) Only $WO_3$ (B) zeolite $NaX-WO_3$

tively. As shown in Fig. 12, (A) is the sample image after reduction of $WO_3$ and (B) is the sample image after reduction of the zeolite $NaX-WO_3$ by CO gas for 4 hours. Comparing the colors of two samples, (A) showed relatively yellow color, but on the other hand (B) showed a relatively blue one. From the above results, it is believed that the reducibility of $WO_3$ could be improved by the interaction between zeolite NaX and $WO_3$. In general the selective oxidation of $H_2S$ proceeds via redox mechanism. Oxygen in $WO_3$ was consumed by an $H_2S$ oxidation, while oxygen in the supplied gas phase reactants was provided to the reduced site in $WO_3$. It is expected that the activity of the mixed zeolite $NaX-WO_3$ would be higher than $WO_3$ because the addition of zeolite NaX enhanced the reduction of $WO_3$.

## CONCLUSIONS

The activity of the zeolite NaX was low because the water vapor was strongly adsorbed on the zeolite NaX. The adsorbed water vapor started to desorb at about 225 °C. Therefore, the activity of catalyst rapidly decreased by the adsorption of water vapor at 200 °C. The $WO_3$ among the metal oxides was selected to reduce the effect of water vapor. The optimum weight ratio of the zeolite $NaX-WO_3$ catalysts was 9 : 1 since the zeolite $NaX-WO_3$ (9 : 1) with a low content of $WO_3$ showed the highest conversion of $H_2S$. It is believed that the addition of $WO_3$ caused either the decrease of the strong adsorption of water vapor or the increase of the reducibility of $WO_3$ by the some interactions between zeolite NaX and $WO_3$. In this study it is confirmed that the zeolite $NaX-WO_3$ catalyst had high enough performance to improve reactivity for the selective oxidation of $H_2S$.

## ACKNOWLEDGMENT

## REFERENCES

Chan, S. H., Ho, H. K. and Tian, Y., "Multi-level Modeling of SOFC Gas Turbine Hybrid System," *Int. J. Hydrogen Energy*, **28**, 889 (2003).
Chopin, T., Hebrard, J. L. and Quemere, E., "Process for the Reduction

of the Sulfur Content in a Gaseous Stream," Eur. Patent, 422,999 (1990).

Cho, Y. G., Hwang, B. H., Park, D. W., Woo, H. C. and Chung, J. S., "Phase Cooperation of V$_2$O$_5$ and Bi$_2$O$_3$ in the Selective Oxidation of H$_2$S Containing Ammonia and Water," *Korean J. Chem. Eng.*, **19**, 611 (2002).

Chun, S. W., Jang, J. Y., Park, D. W., Woo, H. C. and Chung, J. S., "Selective Oxidation of H$_2$S to Elemental Sulfur over TiO$_2$/SiO$_2$ Catalysts," *Appl. Catal. B*, **16**, 235 (1998).

Chun, S. W., Jang, J. Y., Park, D. W., Woo, H. C. and Chung, J. S., "Selective Oxidation of H$_2$S in the Presence of Ammonia and Water using Co$_3$O$_4$/SiO$_2$ Catalyst," *Korean J. Chem. Eng.*, **14**, 216 (1997).

De Simon, G., Parodi, F., Fermeglia, M. and Taccani, R., "Simulation of Process for Electrical Energy Production Based on Molten Carbonate Fuel Cells," *J. Power Sources*, **115**, 210 (2003).

Goar, E. N., MacDougall, R. S. and Lagas, J. A., "New Catalysts Improves Sulfur Recovery at Canadian Plant," *Oil & Gas J.*, **28**, 45 (1994).

Hamamatsu, T., "Future View of Fossil Fuel Power Generation of Coal IGCC," *J. Gas. Turb. Soc. Jpn.*, **18**, 3 (1993).

Jang, H. T., Kim, S. B. and Doh, D. S., "The Removal of Hydrogen Sulfide with Manganic Sorbent in a High-Temperature Fluidized-Bed Reactor," *Korean J. Chem. Eng.*, **20**, 116 (2003).

Jansen, D., van der Laag, P. C., Oudhuis, A. B. J. and Ribberink, J. S., "Prospects for Advanced Coal-fuelled Fuel Cell Power Plants," *J. Power Sources*, **49**, 151 (1994).

Keller, N., Pham-Huu, C. and Ledoux, M. J., "Continuous Process for Selective Oxidation of H$_2$S over SiC-Supported Iron Catalysts into Elemental Sulfur above its Dewpoint," *Appl. Catal. A*, **217**, 205 (2001).

Keller, N., Pham-Huu, C., Estournes, C. and Ledoux, M. J., "Low Temperature Use of SiC-Supported NiS$_2$-Based Catalysts for Selective H$_2$S Oxidation: Role of SiC Surface Heterogeneity and Nature of the Active Phase," *Appl. Catal. A*, **234**, 191 (2002).

Kettner, R., Luebcke, T. and Libermann, N., "Catalysts for Treating Exhaust Gases and Process for Treating These Exhaust Gases," Eur. Patent 78,690 (1982).

Laperdrix, E., Costentin, G., Nguyen, N., Studer, F. and Lavalley, J. C., "Study of H$_2$S Selective Oxidation on New Model Catalysts: Influence of Composition," *Catal. Today*, **61**, 149 (2000).

Laperdrix, E., Costentin, G., Saur, O., Lavalley, J. C., Nedez, C., Savin-Poncet, S. and Nougayrede, J., "Selective Oxidation of H$_2$S over CuO/Al$_2$O$_3$: Identification and Role of the Sufurated Species Formed on the Catalyst During the Reaction," *J. Catal.*, **189**, 63 (2000).

Lee, H. S., Kang, M. P., Song, Y. S., Lee, T. J. and Rhee, Y. W., "Desulfurization Characteristics of CuO-Fe$_2$O$_3$ Sorbents," *Korean J. Chem. Eng.*, **18**, 635 (2001).

Lee, T. J., Kwon, W. T., Chang, W. C. and Kim, J. C., "A Study on Regeneration of Zinc Titanate Sorbents for H$_2$S Removal," *Korean J. Chem. Eng.*, **14**, 513 (1997).

Pi, J.-H., Lee, J.-D., Park, N.-K., Ryu, S.-O. and Lee, T.-J., "The Effect of Modified Zeolite X Catalysts on the Selective Oxidation of H$_2$S," *J. Korean Ind.. Eng. Chem.*, **14**, 813 (2003).

Shin, M. Y., Nam, C. M., Park, D. W. and Chung, J. S., "Selective Oxidation of H$_2$S to Elemental Sulfur over VOx/SiO$_2$ and V$_2$O$_5$ Catalysts," *Appl. Catal. A*, **211**, 213 (2001).

Terorde, R. J. A. M., van den Brink, P. J., Visser, L. M., van Dillen, A. J. and Geus, J. W., "Selective Oxidation of Hydrogen Sulfide to Elemental Sulfur Using Iron Oxide Catalysts on Various Supports," *Catal. Today*, **17**, 217 (1993).

Van Nisselrooya, P. F. M. T. and Lagasb, J. A., "Superclaus Reduces SO$_2$, Emission by the use of a New Selective Oxidation Catalyst," *Catal. Today*, **16**, 263 (1993).

Wi, Y. H., Park, S. J., Rhu, C. K. and Lee, J. B. "Shaping Technology of Coal Gas Sorbents by Using a Spray Dryer," *Korean J. Chem. Eng.*, **19**(5), 756 (2002).

Yi, C. K., Jo, S. H., Lee, B. H., Lee, S. Y., Son, J. E. and Jin, G. T., "Simultaneous Experiments of Sulfidation and Regeneration in Two Pressurized Fluidized-bed Reactors for Hot Gas Desulfurization of IGCC," *Korean J. Chem. Eng.*, **18**, 1005 (2001).