

Selective Oxidation of Hydrogen Sulfide to Elemental Sulfur with Fe/MgO Catalysts in a Slurry Reactor

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Received May 11, 2004

The Fe/MgO catalysts with different Fe loadings (1, 4, 6, 15 and 30 wt% Fe) were prepared by a wet impregnation with iron nitrate as precursor. All of the catalysts were characterized by BET surface analyzer, X-ray diffraction (XRD), temperature-programmed reduction (TPR), and X-ray photoelectron spectroscopy (XPS). The maximum removal capacity of H₂S was obtained with 15 wt% Fe/MgO catalyst which had the highest BET surface area among the measured catalysts. XRD of Fe/MgO catalysts showed that well dispersed Fe particles could be present on Fe/MgO with Fe loadings below 15 wt%. The crystallites of bulk α -Fe₂O₃ became evident on 30 wt% Fe/MgO, which were confirmed by XRD. TPR profiles showed that the reducibility of Fe/MgO was strongly related to the loaded amounts of Fe on MgO support. Therefore, the highest removal efficiency of H₂S in wet oxidation could be ascribed to a good dispersion and high reducibility of Fe/MgO catalyst. XPS studies indicated that the H₂S oxidation with Fe/MgO could proceed via the redox mechanism (Fe³⁺ \leftrightarrow Fe²⁺).

Key Words : Fe/MgO catalyst, Wet oxidation, H₂S, Redox mechanism

Introduction

The Claus process has been most commonly employed to remove H₂S from natural gas facilities or refinery plants. Claus plants generally convert 94-98% of sulfur compounds in the feed gas into elemental sulfur.^{1,2} As the restrictions on sulfur emissions are annually strengthening worldwide, a number of tail gas clean-up processes have been developed to reduce sulfur emission to permissible levels.³ The development of the new processes to deal with the Claus tail gas is based on the direct oxidation of remaining traces of H₂S by oxygen or H₂S absorption/recycling technologies.⁴

Up to now, two main catalytic processes dealing with the selective oxidation of H₂S by oxygen into elemental sulfur have been developed. The high temperature Superclaus process, working above the sulfur dewpoint (>180 °C) with an overall sulfur removal efficiency of 99.5%, is based on Fe catalysts supported on alumina or silica.⁵⁻⁷ Doxosulfreen process, operated on Cu catalysts/modified alumina below the sulfur dewpoint in a discontinuous mode of reaction/regeneration, reaches the efficiencies of 99.9%.⁸⁻¹⁰ Nonetheless, the reaction temperature is too high to prevent the SO₂ and the metal sulfide formation.

The wet oxidation processes have been attempted to minimize SO₂ formation in H₂S oxidation. These have some advantages over other processes in terms of simplicity and performance. The developed processes are using either a V⁵⁺/V⁴⁺ couple (Stretford and Unisulf) or a Fe³⁺/Fe²⁺ couple (Lo-Cat, Sulferox, and Bio-SR) with chemicals for stabilizing the vanadium or iron.¹¹⁻¹⁸

Carbon has been used as catalyst in H₂S wet oxidation at room temperature.¹⁹⁻²¹ In these systems, H₂S could be

catalytically converted into elemental sulfur without SO₂ formation. H₂S removal capacity of carbon was 0.66 g sulfur/g carbon, which was governed by the features of carbon surface such as surface area, porosity, and surface chemistry. The carbon-based systems need the chemicals for controlling the pH of an aqueous solution and should be improved in the removal efficiency of H₂S. Recently, Fe/MgO catalytic system, prepared by the incipient wetness impregnation method, has been attempted to improve the carbon removal capacity in H₂S wet oxidation at the room temperature, showing that 6 wt% Fe/MgO showed 1.0 g sulfur/gcatalyst in air and 2.6 g sulfur/gcatalyst in O₂.²² The isolated Fe ion was proposed to be active site for the reaction.²³ In this study, the impregnation method of the support suspension with salts solution has been tried to disperse Fe ions well on MgO support for enhancing H₂S removal capacity.

Experimental Section

The catalysts were prepared by impregnation of MgO suspension with Fe nitrate. A 0.5 M Fe(NO₃)₃·9H₂O (Merck, p.a.) solution was added to an MgO (Aldrich 22036-1) suspension in distilled water. This suspension was prepared by adding *ca.* 500 mL per 25 g of solid. The concentration of Fe(NO₃)₃ in solution was controlled to obtain the desired Fe content on MgO. The suspension remained under stirring for 4 h at room temperature in a rotary evaporator and then water was evaporated at 40 °C in a vacuum of 30 mbar. The obtained solid was kept in an oven at 110 °C overnight. Finally, it was calcined in air flow at 450 °C for 5 h.

Activity measurements were carried out using a stirred

batch tank reactor (cylindrical type with 10 cm (dia.) \times 60 cm (height)) with a two-blade turbine impeller 8 cm in diameter. The stirring speed was maintained at 300 rpm. The catalyst samples (3.0 g, if not specified) were dispersed in the reactor charged with the distilled water (1.5 L, if not specified) and the reactant gases were supplied through a perforated rubber plate at the bottom of the reactor. H₂S concentrations from the reactor were measured with on-line GC with FPD detector which can detect up to 0.1 ppm H₂S. Porapak Q column (1/8" O.D \times 2 m) was used for separating the product gases.

The specific surface areas of the catalysts were obtained in an ASAP 2000 instrument by a BET method from the nitrogen adsorption isotherms at 77 K, taking a value of 0.164 nm² for the cross-section of nitrogen. The XRD patterns were collected with Rint 2000 (Rigaku, Co.) using Cu K α radiation ($\lambda = 0.1542$ nm). Temperature-programmed reduction experiments were carried out in a micro-reactor system with a TCD detector. The samples of 50 mg were first treated in argon at room temperature for 1 h. After that, the samples were reduced in a stream of 5% H₂/Ar (30 mL/min) at a ramping rate of 20/min from 100 °C to 1000 °C. XPS spectra were obtained using a Kratos XSAM 800pci X-ray photoelectron spectrometer with Al K α monochromatic X-ray (1487 eV) radiation. The charging effect of XPS spectra was carefully corrected with adventitious carbon at 284.6 eV as a reference.

Results and Discussion

Figure 1 shows the H₂S removal capacities of Fe/MgO catalysts with different Fe loadings. In experiments, feed gases (H₂S: 5 mL/min, O₂: 100 mL/min) are introduced into the stirred slurry reactor with 1.5 L of distilled water and 3 g of catalyst. The H₂S removal capacity was obtained by calculating the total amount of H₂S removed up to 50% of the H₂S removal efficiency. No sulfur oxides are detected in the exit gas streams, indicating that total oxidation of H₂S to

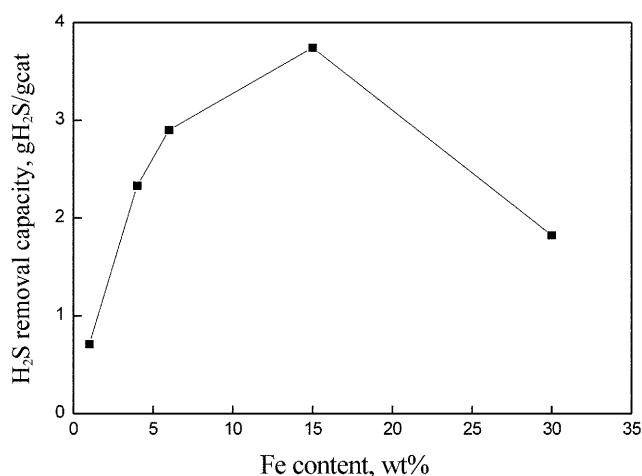


Figure 1. H₂S removal capacities of Fe/MgO catalysts with different Fe loadings in H₂S wet catalytic oxidation. H₂S flow rate: 5 mL/min, O₂ flow rate: 100 mL/min.

SO₂ can be prevented in the wet catalytic oxidation. The removal capacity in H₂S oxidation increases up to 15 wt% Fe, and then decreases with further increase in Fe loading. The removal capacity of H₂S for 15 wt% Fe/MgO was 3.74 gSulfur/gcatalyst, while that for 1 wt% Fe/MgO was 0.71 gSulfur/gcatalyst. It is interesting to note that the H₂S removal capacity was maximized at 15 wt% Fe/MgO on the catalysts prepared by the impregnation method of the support suspension with salts solution, while reaching a maximum value (2.6 gSulfur/gcatalyst) at 6 wt% Fe/MgO among the catalysts prepared by the incipient wetness impregnation method.²² During the preparation, the acidic Fe solution dissolves basic MgO support partly to increase the pH of the solution. The co-precipitation of the dissolved Fe salt and the dissolved MgO occurs at the condition above the pH of 6.0. Therefore, Fe can be dispersed on MgO better by the impregnation of the support suspension with salts solution than by the incipient wetness impregnation.

In order to investigate changes in surface areas caused by different Fe loadings, the BET surface areas of Fe/MgO catalysts were measured. Table 1 shows the physical properties of Fe/MgO samples. As the loading of Fe increases from 1 to 15 wt%, the BET surface area increases from 23.2 to 86.8 m²/g, and then decreases to 44.9 m²/g with further increase in Fe loading. The observed results in surface area with increase in Fe loading is similar to that

Table 1. Physical characterization of Fe/MgO Samples

Sample	Fe content (wt%)	S _{BET} (m ² /g)	Pore volume (cm ³ /g)	Average pore diameter (Å)
1 Fe/MgO	1	23.2	0.16	225
4 Fe/MgO	4	27.3	0.09	142
6 Fe/MgO	6	44.4	0.18	167
15 Fe/MgO	15	86.8	0.25	118
30 Fe/MgO	30	44.9	0.15	135

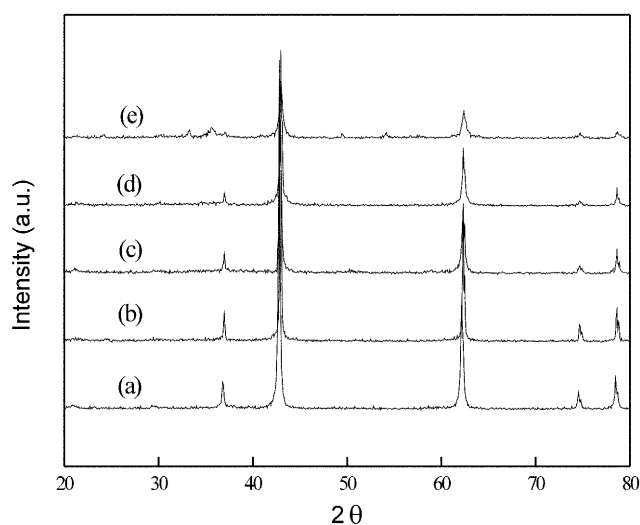


Figure 2. X-ray diffraction patterns of (a) 1 wt% Fe/MgO, (b) 4 wt% Fe/MgO, (c) 6 wt% Fe/MgO, (d) 15 wt% Fe/MgO and (e) 30 wt% Fe/MgO: (■) MgO; (○) α -Fe₂O₃.

reported previously for the Fe/MgO catalysts prepared by a impregnation method.²⁴ The increase in the surface area with an increase in Fe content can be due to MgO dissolution and the co-precipitation of the dissolved MgO and Fe on the undissolved MgO support. The decrease in the surface area with high Fe content can be due to the coagulation among the co-precipitates and the crystallization. The XRD data shows the crystalline Fe₂O₃. It is found that H₂S removal capacities of Fe/MgO catalysts are proportional to their BET surface areas.

Figure 2 shows XRD patterns for the Fe/MgO catalysts after calcination at 460 °C. The sharp diffraction peaks at $2\theta = 36.9, 42.9, 62.3, 74.6,$ and 78.6 are ascribed to MgO support (JCPDS 4-829). Fe/MgO catalysts with below 15 wt% Fe show the peaks attributable to MgO and no evidence for Fe₂O₃. In the case of the sample containing 30 wt% Fe, newly appeared peaks are attributed to crystallized α -Fe₂O₃ (JCPDS 24-0072).

Therefore, it can be deduced that the decrease of H₂S removal capacity results from the formation of the crystalline α -Fe₂O₃ and decreases in surface area of Fe/MgO.

Figure 3 shows temperature-programmed reduction (TPR) profiles. For the sample with 1 wt% Fe, the peak at *ca.* 560 °C is observed, corresponding to the reduction of Fe³⁺ species in Fe/MgO catalyst.²⁵ With increasing Fe loading up to 15 wt%, the peak slightly shifts from 560 to 580 °C. The further Fe loading, 30 wt% Fe/MgO, shows the peak at 600 °C with a shoulder peak at 670 °C, indicating that new phases can be formed. The peak at 560-580 °C can be assigned to the reduction of Fe³⁺ in well dispersed small domains of Fe₂O₃ which are not observed in XRD patterns. The TPR peak at 670 °C can be assigned to the reduction of Fe³⁺ in crystalline α -Fe₂O₃.

As shown Figure 3, the dispersion of Fe component increases up to a Fe loading of 15 wt%. The steady increase in H₂S removal capacity seen in Figure 1 up to a Fe loading of 15 wt% suggests that well dispersed Fe are active phases

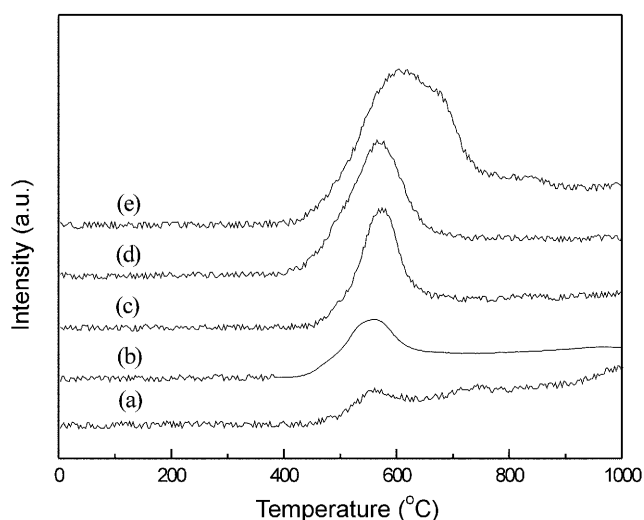


Figure 3. TPR profiles of (a) 1 wt% Fe/MgO, (b) 4 wt% Fe/MgO, (c) 6 wt% Fe/MgO, (d) 15 wt% Fe/MgO and (e) 30 wt% Fe/MgO.

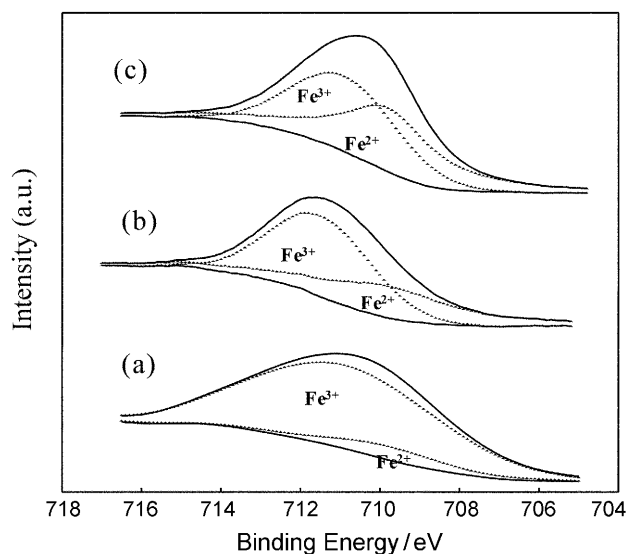
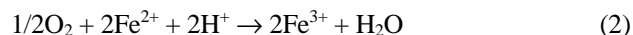
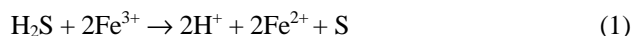


Figure 4. XPS spectra of (a) Fe/MgO after 4 h reaction, (b) Fe/MgO after 12 h reaction, and (c) Fe/MgO after 30 h reaction.

for H₂S oxidation. A considerable decrease in the H₂S removal capacity occurs with increase in the loading from 15 to 30 wt% Fe. XRD show that the characteristic peaks of crystalline Fe₂O₃ appear with an increase in the Fe loading from 15 to 30 wt%. Therefore, it can be suggested that the reducibility of Fe³⁺ in Fe/MgO can be related to the H₂S removal capacity of Fe/MgO catalysts.

The XPS spectra were obtained for the observation of changes in the catalyst surface after reactions. Figure 4 shows the XPS spectra of the 15 wt% Fe/MgO catalysts after 4, 12, and 30 h reaction. XPS peaks of Fe 2p_{3/2} for Fe³⁺, Fe²⁺, and Fe are located at 711.0, 709.9 and 706.7 eV, respectively.^{26,27} Iron component in a fresh Fe/MgO catalyst is in the state of Fe³⁺. Fe valence state in Fe/MgO catalyst changes from Fe³⁺ to Fe²⁺ during the reaction. Such results indicate that H₂S can reduce Fe³⁺ to Fe²⁺ at room temperature.

It has been reported that liquid redox processes use the reduction/oxidation cycle, as the followings.^{28,29}



The Fe³⁺ is reduced to Fe²⁺ by H₂S, where the Fe²⁺ is regenerated back to Fe³⁺ via a re-oxidation reactions involving oxygen on the heterogeneous catalyst as shown in Fe/MgO.³⁰ The reduction degree of the Fe/MgO catalyst during the reaction can be governed by the relative magnitudes of the reduction rate by H₂S with the oxidation rate by oxygen.

Conclusions

The Fe/MgO catalysts with different (1, 4, 6, 15 and 30 wt%) Fe loadings were prepared by an impregnation of MgO suspension with aqueous iron nitrate solution. The H₂S

removal capacity was maximized with 15 wt% Fe/MgO. The structural analysis suggests that well dispersed Fe can be active phase and crystalline α -Fe₂O₃ should be avoided for H₂S oxidation. TPR study suggests that the reducibility of Fe³⁺ can be closely related to the H₂S removal capacity of Fe/MgO.

The XPS study shows that the H₂S oxidation with Fe/MgO can be explained by the redox mechanism and the formation of Fe²⁺ gradually increases with reaction time.

References

1. Estep, J. W.; McBride, G. T.; West J. R. *Advances in Petroleum Chemistry and Refining* **1962**, 6, 315.
2. Goar, B. G. *Oil Gas J.* **1975**, 25, 96.
3. Anon, *Sulfur* **1995**, 20, 236.
4. Keller, N.; Huu, C. P.; Ledoux, M. J. *Appl. Catal.* **2001**, 217, 205.
5. Lagas, J. A.; Borboom, J.; Berben, P. H.; Geus, J. W. *Eur. Patent Applic.* 0242006 (1988).
6. Berben, P. H.; Geus, J. W. *US Patent* 4818740 (1989).
7. Berben, P. H.; Geus, J. W. *Eur. Patent Applic.* 0242920 (1987).
8. Bandel, G.; Willing, W. In *The Doxosulfreen Claus Tail Gas Processing-Meeting Enhanced Sulfur Emission Standard*; Sulphur: 1987; p 96.
9. Savin, S.; Legendre, O.; Nougayrede, J. B.; Nedez, C. *Sulfur* **2000**, 296, 523.
10. Savin, S.; Nougayrede, J. B.; Willing, W.; Bandel, G. *Int. J. Hydrocarbon Eng.* **1998**, 4, 54.
11. Vrieland, G. E.; Murchison, C. B. *Appl. Catal.* **1996**, 134, 101.
12. Lefers, J. B.; Koestsier, W. T.; Swaaij, W. P. M. V. *Chem. Eng. J.* **1978**, 15, 111.
13. Quinlan, M. P.; Leppin, D. In *AIChE Spring National Meeting*; New Orleans, 1993; p 155.
14. Johnson, J. E.; Tzap, S. J.; Kelley, R. E.; Laczko, L. P. *Oil Gas J.* **1993**, 22, 20.
15. Cadus, L. E.; Abello, M. C.; Gomez, M. F.; Rivarla, J. B. *Ind. Eng. Chem. Res.* **1996**, 35, 14.
16. Meunier, F. C.; Yasmeen, A.; Ross, J. R. H. *Catal. Today* **1997**, 37, 33.
17. Lee, K. H.; Yoon, Y. S.; Ueda, W.; Moro-Oka, Y. *Catal. Lett.* **1997**, 46, 267.
18. Shimada, J.; Sato, T.; Yoshimura, Y.; Hiraishi, J.; Nishijima, A. *J. Catal.* **1988**, 110, 275.
19. Dalai, A. K.; Tollefson, E. L. *Can. J. Chem. Eng.* **1998**, 75, 902.
20. Mikhalovsky, S. V.; Zaitsev, Y. P. *Carbon* **1997**, 35, 1367.
21. Adib, F.; Bagreev, A.; Badosz, T. *J. Environ. Sci. Technol.* **2000**, 34, 686.
22. Jung, K. D.; Joo, O. S.; Cho, S. H.; Han, S. H. *Appl. Catal.* **2001**, 240, 213.
23. Jung, K. D.; Joo, O. S.; Kim, C. S. *Catal. Letters* **2002**, 84, 53.
24. Spretz, R.; Marchetti, S. G.; Ulla, M. A.; Lombardo, E. A. *J. Catal.* **2000**, 194, 167.
25. Shen, J.; Guang, B.; Tu, M.; Chen, Y. *Catal. Today* **1996**, 30, 77.
26. Graat, P. C. J.; Somers, M. A. *J. Appl. Surf. Sci.* **1996**, 100, 36.
27. Bukhtiyarova, G. A.; Bukhtiyarov, V. I.; Sakaeva, N. S.; Kaichev, V. V.; Zolotovskii, B. P. *J. Mol. Catal.* **2000**, 158, 251.
28. Hardison, L. C. In *AIChE Spring National Meeting*; New Orleans, 1993; p 124.
29. Newman, D. W.; Lynn, S. *Am. Inst. Chem. Eng. J.* **1984**, 30, 62.
30. Shin, M. Y.; Nam, C. M.; Park, D. W.; Chung, J. S. *Appl. Catal.* **2001**, 211, 213.