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Catalytic Reduction of SO_2 with CO over Supported Iron Catalysts

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Iron oxides supported on several types of carriers (γ-Al_2O_3, HZSM-5, SiO_2, and MgO) were investigated for the catalytic reduction of SO_2 by CO. The catalytic tests show that the activity of the catalysts followed the order Fe_2O_3/γ-Al_2O_3 > Fe_2O_3/HZSM-5 ≫ Fe_2O_3/SiO_2 > Fe_2O_3/MgO. The X-ray diffraction analysis characterization of the presulfided catalysts revealed that FeS_2 formation was greatly dependent on the acidic nature of the supports, with an evident FeS_2 phase detected on both γ-Al_2O_3 and HZSM-5, in contrast with Fe_7S_8 formed on SiO_2 and MgO. Presulfidation with a reacting gas mixture above 500 °C was necessary for obtaining a high activity because of the formation of active-phase FeS_2 during this process. The catalytic activity correlated well with the sulfidation degree of Fe_2O_3, which is mainly dependent on the acidic nature of the support and the choice of the presulfidation conditions. When the Fe content was at 20 wt %, under the optimal feed compositions (CO/SO_2 = 2:1), the Fe_2O_3/γ-Al_2O_3 catalyst exhibited the best catalytic performance, with 99.31% SO_2 conversion and a 99.17% sulfur yield obtained at 380 °C.

1. Introduction

Sulfur dioxide emitted into the atmosphere as a byproduct of combustion processes, such as coal-fired power plants, is one of the major components of acid rain and other forms of atmospheric pollution.[1] Commercial flue gas desulfurization processes are mostly of the throw-away type in which alkaline materials react with SO_2 to form alkaline metal sulfate that is often stockpiled. Because of the large amount of sulfur dioxide being produced, the disposal of these solid wastes will lead to another environmental problem. To minimize the waste disposal problem associated with the existing technologies, several regenerable sulfur dioxide scrubbing systems have been developed.[2] In these regeneration processes, sulfur dioxide from flue gas is first absorbed in an alkaline solution or adsorbed on a solid substrate and is subsequently desorbed to produce a stream of high-concentration sulfur dioxide. The recovery of elemental sulfur from this stream in a single-stage catalytic converter would be the best choice for it is easy to treat, handle, and transport and there are no secondary pollution issues.[3,4]

Direct reduction of sulfur dioxide by carbon monoxide is a promising approach for the recovery of elemental sulfur because CO is converted to CO_2 and simultaneously removed from the flue gas stream.[5,6] The overall reactions involved in this process are as follows:

$$SO_2 + 2CO = 2CO_2 + {}^1/_xS_x$$

$$CO + {}^1/_xS_x = COS$$

$$2COS + SO_2 = 2CO_2 + 3{}^1/_xS_x$$

where x = 2−8 or higher. A part of S_x can further react with CO to form carbonyl sulfide, COS. This, in turn, may again reduce SO_2 to elemental sulfur. However, COS is a more toxic compound than SO_2, and its production should be minimized in a sulfur recovery process.

So far, the catalytic reduction of SO_2 to elemental sulfur with CO as reducing agent has been extensively studied using various types of catalysts including perovskite,[7−10] mixed oxides,[11−15] and alumina-supported transition metals.[16−21] Both perovskite and mixed oxides required a high reaction temperature (above 500 °C) to obtain complete conversion of SO_2, although they possessed the advantage of high selectivity to sulfur formation (COS formation was largely limited).[9,11] To lower the light-off temperature, Chen and Weng[14] employed nanosized CeO_2 as a support and found that Cr_2O_3/nano-CeO_2 exhibited the highest activity with full SO_2 conversion at 320 °C. However, compared with other widely used commercial supports, such as alumina and silica, the high cost of nano-CeO_2 limits its application to some extent.

On the other hand, alumina-supported transition metals were the earliest-studied catalysts for SO_2 reduction with CO. However, in the early development of the alumina-supported catalyst, a substantial amount of COS, which is much more harmful than SO_2, was formed as a byproduct during the SO_2 reduction by CO.[16−18,21] This is probably because the alumina support used in their work was α-Al_2O_3 and the preparation method was simple mechanical mixing. Instead, using γ-Al_2O_3 as the support, Lee and Han found that about a 97% conversion of sulfur dioxide and selectivity to elemental sulfur were achieved at temperatures above 400 °C over LaNi/γ-Al_2O_3.[20] Recently, Zhuang et al. found that $CoMo/Al_2O_3$, which had been used primarily for hydrodesulfurization reactions, exhibited very high activity and selectivity for the reduction of sulfur dioxide by CO,[19] with a complete conversion of SO_2 at 300 °C. This is one of the most active catalysts reported so far for SO_2 reduction with CO, showing the great potential of alumina-supported transition metals as catalysts for this reaction.

A careful comparison of the catalytic activities of alumina-supported transition metals in the literature reveals that the textural properties of alumina have an important effect on the catalytic performance of the metals supported on it. Prompted

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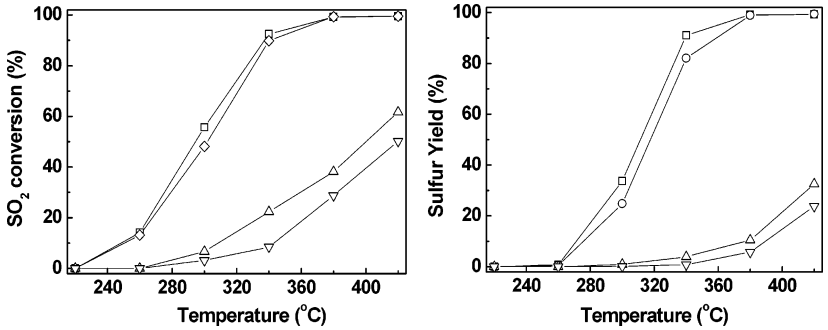

Figure 1. Effect of support nature on SO_2 conversion and sulfur yield. (□) Fe_2O_3/γ-Al_2O_3, (◇) Fe_2O_3/HZSM-5, (△) Fe_2O_3/ SiO_2, and (▽) Fe_2O_3/MgO. Feed compositions: 5000 ppm SO_2 and 10 000 ppm CO, SV= 18 000 mL/g h.

by this, we believe that Fe/Al_2O_3, which was initially investigated by Khalafalla et al.[16,17,21] for the catalytic reduction of SO_2 by CO, may be undervalued, because the low surface area of α-Al_2O_3 would make the active phase poorly dispersed. In this paper, we used γ-Al_2O_3, ZSM-5, silica, and MgO to support Fe_2O_3 and found that the Fe_2O_3/γ-Al_2O_3 catalyst exhibited the highest catalytic activity, with 99.31% SO_2 conversion at around 380 °C. More importantly, the formation of COS was largely limited, and the COS concentration was less than 60 ppm above 380 °C.

2. Experimental Section

2.1. Catalyst Preparation. γ-Al_2O_3 (homemade, surface area 238 m^2/g, pore volume 0.35 cm^3/g), HZSM-5 (SiO_2/Al_2O_3 = 25, surface area 365 m^2/g, supplied by NanKai University, China), SiO_2 (surface area 400 m^2/g, Qingdao Ocean Chemical Company, China), and MgO (surface area 35 m^2/g, AR grade, Shenyang Agent Company, China) were used as catalyst supports. The supports were impregnated with an appropriate aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O$. Then, the samples were dried at 120 °C for 12 h and calcined at 500 °C for 5 h. In the tests for the influence of Fe content, the loading of Fe that was calculated on an Fe_2O_3 basis was varied between 2.5 and 40 wt %, while Fe loading was fixed at 20 wt % for other tests. All of the catalysts were pelletized, crushed, and sieved to 40−60 mesh for use in activity tests.

2.2. Activity Measurement. The catalytic reaction between SO_2 and CO was carried out in a fixed-bed flow reactor system at atmospheric pressure. A total of 0.2 g of the catalyst was placed in a quartz reactor (6 mm i.d.). After being purged in a He flow (36 mL/min) at 500 °C for 2 h, the catalyst was in situ presulfided with a reaction gas mixture containing 10 000 ppm CO and 5000 ppm SO_2 in He at a flow rate of 60 mL/min at 500 °C for 2 h. In some cases, a different presulfidation temperature (400, 500, or 600 °C) was employed in order to compare the effects of presulfidation methods. After presulfidation, the catalyst was cooled to 220 °C for activity tests. The feed gas typically consisted of 10 000 ppm CO and 5000 ppm SO_2 except for testing the effect of feed concentration. The effluent gas was passed through an ice-water trap, where elemental sulfur was condensed. Concentrations of SO_2 and COS in the effluent gas were separated by a Gaspro capillary column and detected by a flame photometric detector, while CO and CO_2 were separated by a Porapack Q column and detected by a thermal conductivity detector (TCD).

The percent conversion (X) of SO_2 and the selectivity (S) and percent yield (Y_s) of elemental sulfur are defined as follows:

$$X = \frac{[SO_2]_{in} - [SO_2]_{out}}{[SO_2]_{in}} \times 100\%$$

$$S = \frac{[SO_2]_{in} - [SO_2]_{out} - [COS]_{out}}{[SO_2]_{in} - [SO_2]_{out}} \times 100\%$$

$$Y_s = XS$$

where $[SO_2]_{in}$ is the inlet concentration of SO_2 and $[SO_2]_{out}$ and $[COS]_{out}$ are the outlet concentrations of SO_2 and COS, respectively.

2.3. NH_3 Temperature-Programmed Desorption (NH_3-TPD) and CO_2-TPD Measurements. NH_3-TPD of the three acidic supports (HZSM-5, γ-Al_2O_3, and SiO_2) and CO_2-TPD of the MgO support were measured with the Micromeritics AutoChem II 2920 Automated Catalyst Characterization System. A total of 150 mg of the sample was placed in a quartz reactor. Before each experiment, the sample was treated in a He flow at 600 °C for 30 min at a flow rate of 30 mL/min in order to remove water and other contaminants. Then, the reactor was cooled to 100 °C for NH_3 adsorption or 50 °C for CO_2 adsorption. After the saturation of adsorption of NH_3 (or CO_2) was reached at that temperature, the reactor was heated from 100 °C (or 50 °C for CO_2) to 600 °C at a rate of 10 °C/min, and the NH_3-TPD (or CO_2-TPD) spectra were recorded with a TCD as a detector.

2.4. CO Temperature-Programmed Reduction (CO-TPR) Measurement. CO-TPR of the Fe_2O_3/γ-Al_2O_3 was performed using the same system as that described for $NH_3(CO_2)$-TPD. A total of 150 mg of the sample was placed in a quartz reactor. Before each experiment, the sample was treated in a He flow at 100 °C for 30 min at a flow rate of 30 mL/min in order to remove physically adsorbed water. Then, the reactor was cooled to room temperature and heated to 700 °C at a rate of 10 °C/min. The CO-TPR spectra were recorded with a mass spectrometer as a detector.

2.5. X-ray Diffraction Analysis (XRD) Measurements. XRD patterns were obtained with a Rigaku (D/MAX-βB) diffractometer equipped with an online computer. Ni-filtered Cu Kα radiation was used.

3. Results and Discussion

3.1. The Effect of Support Natures. In this study, we chose four types of material as the catalyst supports, including γ-Al_2O_3, HZSM-5, SiO_2, and MgO. These four supports are widely used in the chemical industry and with different acid−base natures. The SO_2 conversion and sulfur yield on these four different supported Fe_2O_3 catalysts are illustrated in Figure 1. Both the

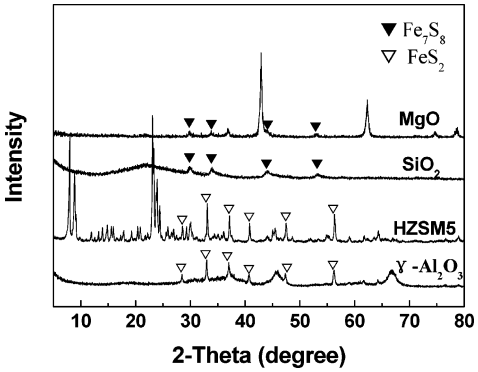

Figure 2. X-ray diffraction patterns of four different supported Fe_2O_3 catalysts after sulfidation at 500 °C for 2h.

SO_2 conversion and the sulfur yield follow the order Fe_2O_3/γ-Al_2O_3 > Fe_2O_3/HZSM-5 ≫ Fe_2O_3/SiO_2 > Fe_2O_3/MgO. Especially, when γ-Al_2O_3 and HZSM-5 were used as the support, the catalysts were very active and selective. A total of 99.31% SO_2 conversion and 99.17% sulfur yield were obtained over Fe_2O_3/γ-Al_2O_3 at a reaction temperature of 380 °C. Meanwhile, the COS concentration in the effluent gas was lower than 60 ppm. In contrast, the SO_2 conversion and sulfur yield were lower than 40% over SiO_2- and MgO-supported catalysts at 380 °C.

Khallafalla[16,17] et al. proposed the following carbonyl sulfide intermediate mechanism when they investigated SO_2 reduction with CO over Fe/Al_2O_3:

$$FeS_2 + CO = COS + FeS$$

$$COS + 0.5SO_2 \text{ (on alumina)} = CO_2 + 0.75S_2$$

$$FeS + 0.5S_2 = FeS_2$$

According to this mechanism, FeS_2 was the active phase for the catalytic reduction of SO_2. To examine the effect of support nature on FeS_2 formation, we conducted an XRD detection on the four catalysts after sulfidation, as shown in Figure 2. On the sulfided Fe_2O_3/γ-Al_2O_3 and Fe_2O_3/HZSM-5 catalysts, the diffraction peaks corresponding to FeS_2 (2θ = 28.5°, 33.0°, 37.1°, 40.8°, 47.4°, and 56.3°) were clearly observed, indicating that an FeS_2 crystalline phase was formed during sulfidation. In contrast, the XRD patterns of sulfided Fe_2O_3/SiO_2 and Fe_2O_3/MgO show four peaks at 2θ of around 30.0, 34.0, 44.0, and 53.3°, characteristic of pyrrhotite (specifically, Fe_7S_8), indicating that the sulfidation of Fe_2O_3/SiO_2 and Fe_2O_3/MgO was not sufficient. Because iron disulfide is a relatively unstable sulfide and can be more easily reduced by CO to form the intermediate COS,[20] FeS_2 is generally thought of as an active phase for SO_2 reduction with CO. Therefore, we can conclude from the above XRD characterizations that variation of the support will lead to a great difference in the degree of sulfidation and thereby affects the catalytic activity for SO_2 reduction with CO.

The four supports employed in this work differ mainly in their acid−base properties. To give quantitative evidence, we conducted NH_3-TPD experiments on the γ-Al_2O_3, HZSM-5, and SiO_2 supports and CO_2-TPD experiments on the MgO support to determine their acid−base properties. The TPD curves are shown in Figure 3. These results are consistent with those reported in the literature.[22−25] In the TPD profiles, the number of the acidic/basic sites is reflected in the peak area, and the strength of the acidic/basic sites is reflected by the maximum desorption temperature. For HZSM-5, two peaks can be

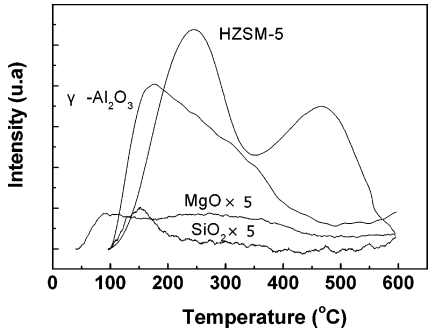

Figure 3. NH_3-TPD spectra of γ-Al_2O_3, HZSM-5, and SiO_2 and CO_2-TPD spectrum of MgO.

Table 1. Comparison of SO_2 Conversions over the Four Supports and the Four Catalysts[a]

supports	SO_2 conversion	catalysts	SO_2 conversion
γ-Al_2O_3	76.43	Fe_2O_3/γ-Al_2O_3	64.33
HZSM-5	74.36	Fe_2O_3/HZSM-5	62.38
SiO_2	18.63	Fe_2O_3/SiO_2	12.47
MgO	10.11	Fe_2O_3/MgO	8.58

[a] Feed compositions: 5000 ppm SO_2 and 10 000 ppm COS, SV = 18 000 mL/g h. Reaction temperature: 300°C.

distinguished: one at 245 °C can be attributed to the weak acid sites, and the other at about 470 °C belongs to the strong acid sites. The NH_3-TPD spectrum of γ-Al_2O_3 contains a very broad signal from 100 to 500 °C, which can be ascribed to the NH_3 desorbed from the acid sites with low and medium to high strength, while for SiO_2, a very weak ammonia desorption peak was found at 150 °C. Clearly, from the NH_3-TPD, we can see that both the acid strengths and the acid numbers of the three supports follow the order HZSM-5 > γ-Al_2O_3 ≫ SiO_2. On the other hand, the MgO support does not adsorb NH_3 at all, but it can adsorb a small amount of CO_2, which is indicated by a very weak and broad CO_2 desorption peak at temperatures ranging from 50 to 450 °C, showing the weakly basic nature of MgO. Thus, the acidity of the four supports follows the order HZSM-5 > γ-Al_2O_3 ≫ SiO_2 > MgO. This order coincides very well with the degree of sulfidation. Therefore, we can conclude that acidic support will facilitate the formation of FeS_2. On the other hand, we also found that acidic support can speed up the reaction between COS and SO_2, as shown in Table 1. It was suggested that, in the case of acidic support, the carbonyl sulfide chemisorbed cationically on the Lewis acid sites and the sulfur dioxide chemisorbed anionically on the Brönsted sites, allowing the adsorbed species to react according to a Langmuir−Hinshelwood mechanism.[17] Acid sites will facilitate them to adsorb and react with each other. Therefore, in our catalyst systems, acid supports had dual functions: one is to facilitate the formation of active-phase FeS_2; the other is to speed up the reaction between COS and SO_2. Finally, we should mention that the minor discrepancy between the activity level and the acidity of Fe_2O_3/HZSM-5 may be due to the diffusion limits of the micropores of the HZSM-5 support.

3.2. The Effect of Sulfidation Methods. From the above XRD results, we know that Fe_2O_3 is transformed to active species FeS_2 in the process of presulfidation. Therefore, sulfidation is the key step to activating the catalyst for SO_2 reduction with CO. In this work, we investigated in detail the effect of the sulfidation temperature on the catalytic behavior of Fe_2O_3/γ-Al_2O_3, and the results are shown in Figure 4. We can see that the catalysts presulfided above 500 °C have a similar activity, whereas the catalysts presulfided at 400 °C show a lower activity. In addition, presulfidation under a temperature-

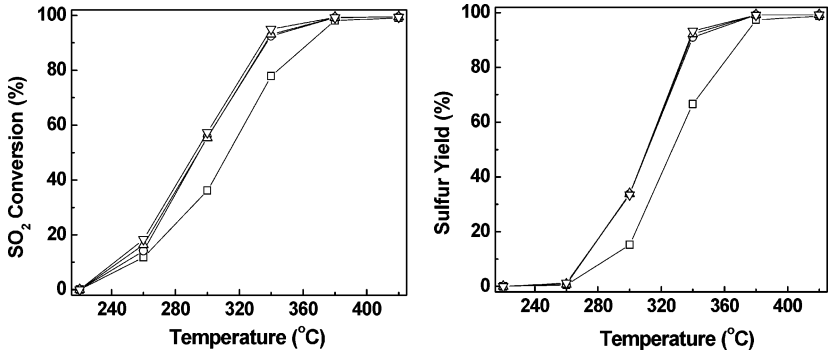

Figure 4. SO_2 conversion and sulfur yield over Fe_2O_3/γ-Al_2O_3 presulfided at (□) 400 °C, (◇) 500 °C, and (△) 600 °C and (▽) by temperature-programmed mode. Feed compositions: 5000 ppm SO_2 and 10 000 ppm CO, SV = 18 000 mL/g h.

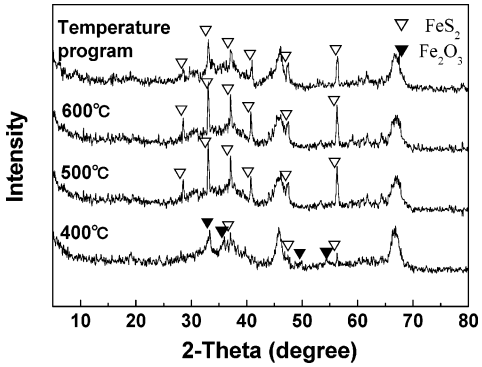

Figure 5. X-ray diffraction patterns of Fe_2O_3/γ-Al_2O_3 under different sulfidation conditions.

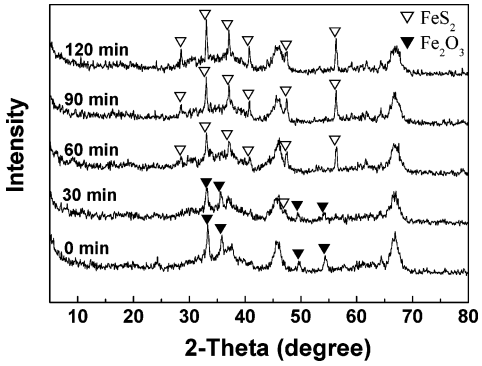

Figure 6. X-ray diffraction patterns of Fe_2O_3/γ-Al_2O_3 under different sulfidation times.

programmed mode (the temperature was first increased from 300 to 500 °C over 200 min, then kept at 500 °C for 30 min) seems to have no effect on the catalytic performance, as long as the sulfidation temperature was above 500 °C.

The XRD patterns of Fe_2O_3/γ-Al_2O_3 after sulfidation at different temperatures are depicted in Figure 5. FeS_2 was the only Fe species when sulfidation occurred above 500 °C, while both Fe_2O_3 (2θ = 33.2°, 49.5°, and 54.1°) and FeS_2 were observed when sulfidation occurred at 400 °C. Clearly, 400 °C is not high enough to completely presulfide Fe_2O_3 to FeS_2. Full sulfidation was obtained at temperatures above 500 °C, and temperature-programmed sulfidation does not improve the activity of the catalyst.

To further investigate how the phase transformation from Fe_2O_3 to FeS_2 occurred during the sulfidation process, Fe_2O_3/γ-Al_2O_3 was subjected to an X-ray diffraction analysis after a certain period of sulfidation at 500 °C, and the corresponding XRD peaks are depicted in Figure 6. It can be seen that Fe_2O_3 was the only Fe phase on the catalyst before sulfidation. After sulfidation for 30 min, the XRD peak intensity of Fe_2O_3 decreased and FeS_2 (2θ = 47.4°) appeared. When sulfidation proceeded for 60 min, no Fe_2O_3 phase was detected. With the sulfidation time further prolonged, the intensity of FeS_2 became even stronger. This result indicates that the phase transformation from Fe_2O_3 to FeS_2 will not be complete until sulfidation has occurred at 500 °C for 2 h.

To reveal the sulfidation mechanism of Fe_2O_3/γ-Al_2O_3 with a reacting gas mixture, we detected the changes in the effluent gas concentration with time when the catalyst was pretreated by SO_2, CO, or a mixture of the two gases,. Figure 7 presents the results. When only 5000 ppm SO_2 passed over the catalyst (Figure 7a), the effluent concentration of SO_2 first decreased to zero at 10 min and then increased quickly to its initial value. The decline of SO_2 concentration at the initial 10 min was probably due to SO_2 adsorption on Fe_2O_3/γ-Al_2O_3. When only 10 000 ppm CO passed over the catalyst (Figure 7b), the effluent CO gas concentration change was very similar to the case of SO_2; meanwhile, the formation of CO_2 was observed in line with the CO consumption, indicating that CO was oxidized by Fe_2O_3 to form CO_2 in the initial stage. In contrast, when 5000 ppm SO_2 and 10 000 ppm CO simultaneously passed over the catalyst, the SO_2 concentration first decreased to zero at 10 min and then increased quickly to a maximum of 2580 ppm (about half of the initial concentration) at 30 min. After that, the SO_2 concentration decreased gradually to zero. The CO concentration decreased more sharply during the initial 10 min, then leveled at a low value as the sulfidation progressed. In contrast, the CO_2 concentration increased quickly at the initial stage and then leveled at a high value. To confirm that the CO consumption was due to the reduction of Fe_2O_3, a TPR of Fe_2O_3/γ-Al_2O_3 with CO as the reductant was conducted, and the results are shown in Figure 8. Three reduction peaks were observed. The two peaks positioned at 327 and 370 °C can be attributed to the reduction of Fe_2O_3 to Fe_3O_4 and of Fe_3O_4 to FeO, respectively, and the third peak positioned at 620 °C is due to the reduction of FeO to Fe.[26,27] However, XRD detection of the CO-reduced samples at 500 and 700 °C reveals the formation of Fe_3O_4 at 500 °C and Fe at 700 °C (Figure 9). We did not detect the existence of FeO or Fe at 500 °C probably because they were low in amount below the XRD detection limits or because they were reoxidized by air when subjected to XRD examination. On the basis of the above experimental results, though a detailed sulfidation mechanism is not clear with CO and SO_2, it is speculated as follows. In the initial stage, most of the CO was consumed by Fe_2O_3 and reduced Fe_2O_3 to Fe_3O_4, FeO, and Fe, while another smaller amount of CO was able to reduce SO_2 to sulfur; sulfur then reacted with the reduced Fe species to form FeS_2. Once FeS_2 was produced, the catalytic reaction between SO_2 and CO on FeS_2 was very fast.

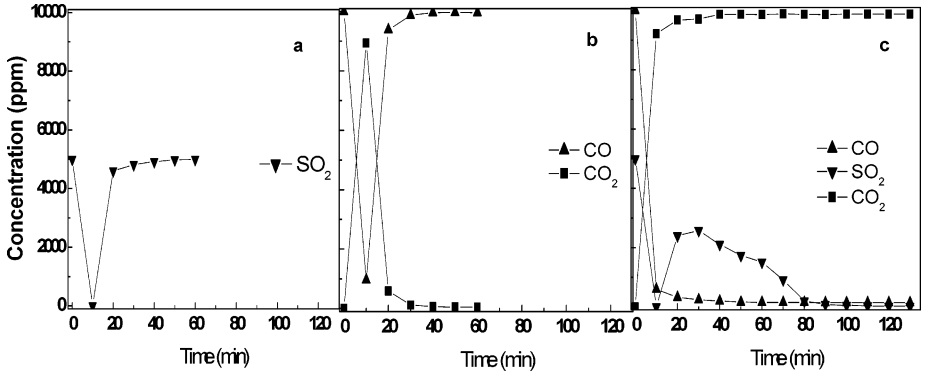

Figure 7. Changes in effluent gas concentration with reaction time under different feed compositions at 500 °C over Fe_2O_3/γ-Al_2O_3. Feed gas compositions: (a) 5000 ppm SO_2, (b) 10 000 ppm CO, and (c) 5000 ppm SO_2 and 10 000 ppm CO.

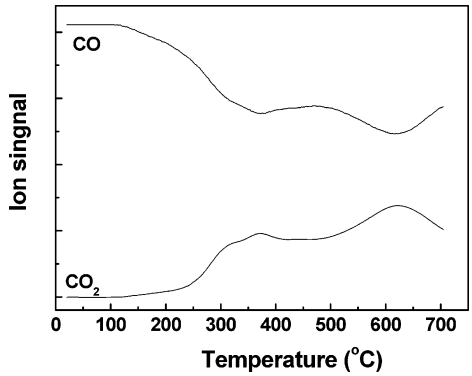

Figure 8. CO-TPR profile of Fe_2O_3/γ-Al_2O_3.

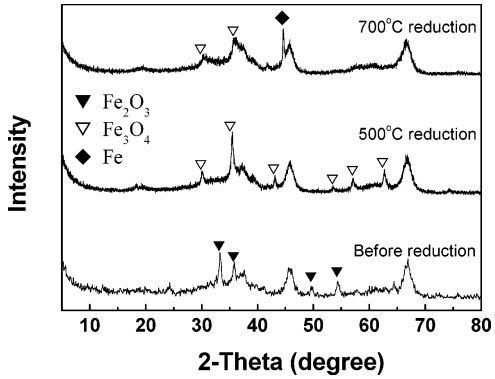

Figure 9. X-ray diffraction patterns of Fe_2O_3/γ-Al_2O_3 before reduction, after 500 °C reduction, and after 700 °C reduction.

3.3. The Effect of Fe Content. From the above results, it can be found that Fe_2O_3/γ-Al_2O_3 and Fe_2O_3/HZSM-5 exhibited similar activities and selectivities. However, from the perspective of industrial application, Fe_2O_3/γ-Al_2O_3 is more promising than Fe_2O_3/HZSM-5 because of the higher hydrothermal stability and mechanical strength of γ-Al_2O_3. Therefore, further study on the optimization of parameters was focused on for Fe_2O_3/γ-Al_2O_3. First of all, the effect of Fe content in Fe_2O_3/γ-Al_2O_3 on catalytic performance was investigated, and the results are shown in Figure 10. We noted that there was no reaction between SO_2 and CO occurring with γ-Al_2O_3 as a catalyst in the temperature range investigated. In fact, substantial SO_2 conversion over γ-Al_2O_3 was not observed until 600 °C. This is in agreement with that reported by Lee and Han.[20] However, with an increase of Fe content from 0 to 20%, both the SO_2 conversion and the sulfur yield increased and reached their maxima at an Fe content of 20%. Then, with a further increase of Fe content, the conversion and sulfur yield decreased. Hence, 20% is the optimum content of Fe on the γ-Al_2O_3 support, at which the synergistic effect between the Fe species and γ-Al_2O_3 would act best to catalytically reduce SO_2 with CO. Excess Fe content (beyond 20 wt %) will probably lead to a decreased dispersion degree of the active phase (FeS_2). When the Fe content was 20%, a 92.5% SO_2 conversion and a 91.8% sulfur yield were obtained at 340 °C over Fe_2O_3/γ-Al_2O_3.

3.4. The Effect of Feed Gas Composition. To obtain the optimal operating conditions, we investigated the effect of different feed ratios of CO/SO_2 on the efficiency of SO_2 reduction. Because the complete reduction of 1 mole of SO_2 needs 2 moles of CO ($2CO + SO_2 = 2CO_2 + S$), the feed ratio of CO/SO_2 was varied from 1:1 to 3:1, while the SO_2 concentration was fixed at 5000 ppm. From Figure 11, we can see that, when the feed ratio of CO/SO_2 is 1:1, that is, CO is insufficient, SO_2 conversion and the sulfur yield are less than 50%. When the feed ratio of CO/SO_2 is 3:1, that is, CO is in excess, SO_2 conversion is the highest while the sulfur yield is at the lowest below 400 °C because of a substantial amount of COS formed via the reaction between CO and S. Similar results were also observed by Zhuang et al.[19] and Chen and Weng.[14] Excess CO reacted with elemental sulfur to produce COS at low temperatures, while COS is unstable and decomposed into CO and S at higher temperatures. Therefore, the sulfur yield increased with the temperature. When CO/SO_2 is at a stoichiometric molar ratio of 2:1, the highest SO_2 conversion and sulfur yield can be obtained.

Knowing that the optimal ratio of CO/SO_2 is 2:1 and that the feed concentrations of CO and SO_2 may affect the efficiency of SO_2 reduction, four different feed concentrations (CO/SO_2 = 5000:2500, 10 000:5000, 15 000:7500, and 20 000:10 000, all in ppm) were employed to assess their influence. Figure 12 manifests that low feed concentrations of CO and SO_2 provide a higher reduction rate of SO_2 and a higher yield of elemental sulfur. SO_2 conversions under four different feed concentrations were 94.5%, 92.5%, 86.1%, and 79.3% at 340 °C, respectively. However, at a temperature of 380 °C, a high SO_2 conversion and sulfur yield (COS concentration in effluent gas was lower than 90 ppm) were all obtained whatever SO_2 inlet concentration was used.

Considering that O_2, H_2O, and CO_2 are often present in the flue gas, there is a necessity to investigate the effect of O_2, H_2O, or CO_2 on the performance of the catalysts. As shown in Figure 13, when the feed gas contained 0.5% oxygen, both the SO_2 conversion and the sulfur yield decreased sharply. The SO_2 conversion dropped down to 29.41% after 60 min of reaction time. An XRD analysis of the used catalyst revealed that FeS_2 had been transformed to Fe_2O_3. After the removal of O_2, the catalytic activity restored slowly. When the feed gas contained 4% water vapor, the SO_2 conversion decreased gradually from

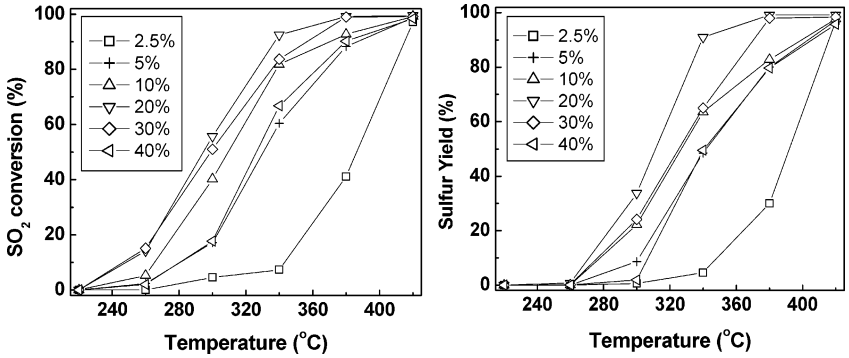

Figure 10. Effect of Fe content in Fe_2O_3/γ-Al_2O_3 on SO_2 conversion and sulfur yield. Feed compositions: 5000 ppm SO_2 and 10 000 ppm CO, SV = 18 000 mL/g h.

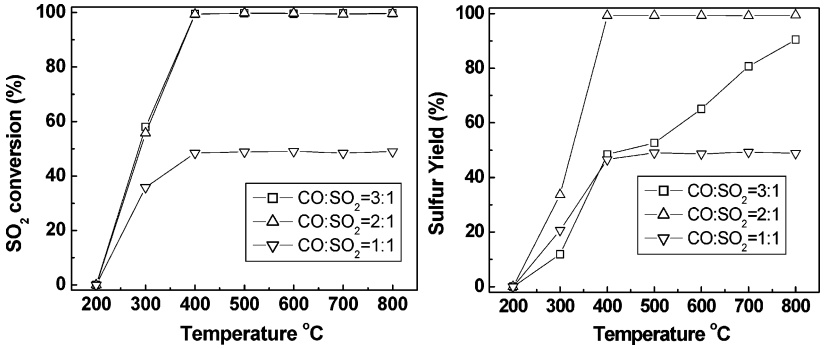

Figure 11. Effect of molar ratios of CO/SO_2 on SO_2 conversion and sulfur yield over Fe_2O_3/γ-Al_2O_3 (SV = 18 000 mL/g h).

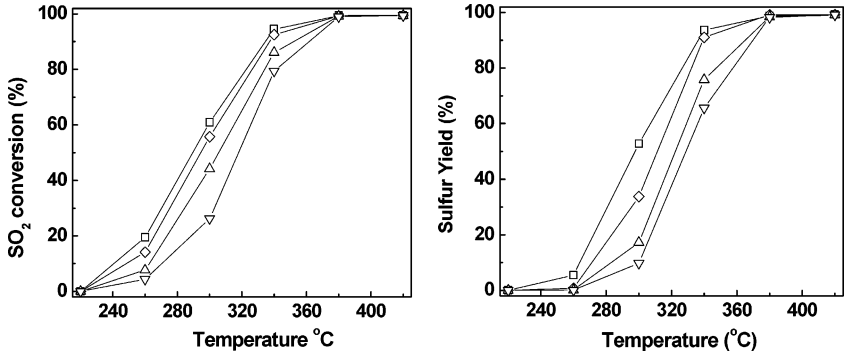

Figure 12. Effect of feed concentration ($CO:SO_2$, ppm) on SO_2 conversion and sulfur yield over Fe_2O_3/γ-Al_2O_3. (□) 5000:2500, (◇) 10 000:5000, (△) 15 000:7500, and (▽) 20 000:10 000.

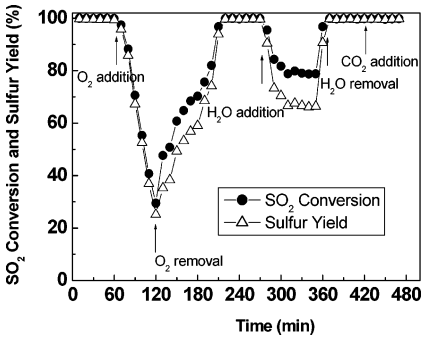

Figure 13. Effect of O_2, H_2O, or CO_2 addition on SO_2 conversion and sulfur yield over Fe_2O_3/γ-Al_2O_3 at 400 °C. Feed compositions: 5000 ppm SO_2, 10 000 ppm CO, 0.5% O_2 or 4% H_2O or 10% CO_2, SV = 18 000 mL/g h.

99.83% to 79.01% and was maintained unchanged. It was also found that the SO_2 conversion could be recovered in a very short time when the water vapor was removed from the feed gas. Ma et al.[28] reported a similar result over the lanthanum oxysulfide catalyst. In contrast, when 10% CO_2 was added to the feed gas, no decay in catalytic activity was found.

3.5. Stability of the Fe_2O_3/γ-Al_2O_3. The time dependence of the CO−SO_2 reaction over presulfided 20% Fe_2O_3/γ-Al_2O_3 was investigated at 380 °C and 400 °C, respectively. As illustrated in Figure 14, the conversion of SO_2 and the sulfur yield dropped only about 2% after a 30 h run at 380 °C, while no deactivation was observed at 400 °C, showing a good stability of the Fe_2O_3/γ-Al_2O_3.

3.6. Comparison with Other Catalysts. According to the literature, CoMo/γ-Al_2O_3[19] and Cr_2O_3/nano-CeO_2[14] were the most active catalysts reported so far for SO_2 reduction with CO. However, the high cost of nano-CeO_2 greatly limits its application on a large scale. As for CoMo/γ-Al_2O_3, complete conversion of SO_2 was achieved at 300 °C, which was lower than that over the Fe_2O_3/γ-Al_2O_3 catalyst we employed in the present work. But the different textural properties of γ-Al_2O_3, especially the surface area, would have a great influence on the catalytic activity. The surface area of the γ-Al_2O_3 used in CoMo/γ-Al_2O_3 was 333 m^2/g,[19] while it is only 238 m^2/g in our Fe_2O_3/γ-Al_2O_3.

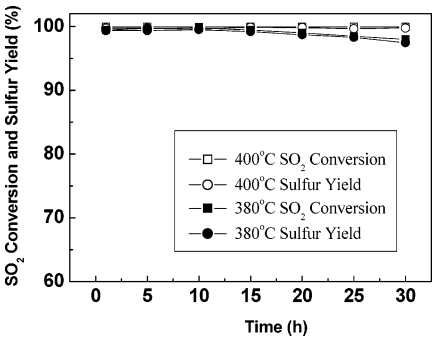

Figure 14. Stability of Fe_2O_3/γ-Al_2O_3 catalyst under 380 °C and 400 °C. Feed compositions: 5000 ppm SO_2 and 10000 ppm CO, SV = 18 000 mL/g h.

Moreover, our latest results show that a full SO_2 conversion can be obtained at 300 °C when the high-surface-area γ-Al_2O_3 (448 m^2/g) is used. Therefore, we believe that Fe_2O_3/γ-Al_2O_3 is one of best catalysts for the catalytic reduction of SO_2 to sulfur with CO.

4. Conclusions

Among the four different supported iron oxide catalysts, both Fe_2O_3/γ-Al_2O_3 and Fe_2O_3/ZSM-5 exhibited good performance for the reduction of sulfur dioxide by carbon monoxide. Presulfidation is necessary and important. FeS_2 is the key active phase for this reaction, and its formation depends not only on the acidic nature of the support but also on the presulfidation conditions employed. In addition, the acidity of the support can speed up the reaction between COS and SO_2. Under the optimal conditions, that is, an Fe content of 20 wt %, presulfidation at 500 °C for 2 h, and a CO/SO_2 ratio of 2:1, a 99.31% SO_2 conversion and a 99.17% sulfur yield were obtained at 380 °C over Fe_2O_3/γ-Al_2O_3.

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