

Selective catalytic reduction of sulfur dioxide by carbon monoxide over iron oxide supported on activated carbon

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Abstract: The selective reduction of sulfur dioxide with carbon monoxide to elemental sulfur was studied over AC-supported transition-metal oxide catalysts. According to the study, Fe₂O₃/AC was the most active catalyst among the 4 AC-supported catalysts tested. By using Fe₂O₃/AC, the best catalyst, when the feed conditions were properly optimized (CO/SO₂ molar ratio = 2:1; sulfidation temperature, 400 °C; Fe content, 20 wt%; GHSV = 7000 mL g⁻¹ h⁻¹), 95.43% sulfur dioxide conversion and 86.59% sulfur yield were obtained at the temperature of 350 °C. Catalyst samples were characterized by X-ray powder diffraction in order to relate the phase composition to the activation behavior and catalytic performance. The active phase of catalyst was detected as FeS₂, and the formation of FeS₂ was greatly dependent on the sulfidation temperature.

Key words: Sulfur dioxide, carbon monoxide, activated carbon, transition-metal oxide, selective catalytic

1. Introduction

Sulfur dioxide is a toxic and corrosive sulfur compound that damages health, corrodes equipment, generates acid rain, and pollutes and acidifies the soil.^{1,2} As recent environmental concern enforces more strict regulations of the emission of SO_x, the treatment of SO₂ in flue gas has attracted increasing attention. Numerous flue gas desulfurization processes have been commercialized, and most of them are throwaway types in which alkaline materials react with SO₂ to form alkaline metal sulfate that is often stockpiled. Because of the large amount of sulfur dioxide being produced, the disposal of the sulfate will lead to another environmental problem.^{3,4} Several regenerable sulfur dioxide scrubbing systems have been developed.⁵⁻⁷ In these regeneration processes, a direct sulfur recovery process, in which SO₂ is selectively reduced to elemental sulfur with a reductant over catalyst, has been proposed as the best choice for SO₂ treatment.⁸⁻¹⁷ The reductants include H₂, CO, CH₄, and C (carbon).

In previous studies, using fluid coke as the reducing agent, Bejarano et al.¹⁷ obtained a maximum sulfur yield (around 95%) at about 700 °ğ. By using CO as the reducing agent, the reaction temperatures could be reduced to somewhat lower levels (280–400 °ğ) than using carbon, while keeping the conversion at the same level. CH₄ was also employed, but the reaction temperature (550–840 °ğ) was not low enough for practical application.^{8,15} H₂ as another intensively investigated reducing agent has also been shown to effectively reduce SO₂ to elemental sulfur.¹²

So far, the catalytic reduction of SO₂ to form elemental sulfur with CO has been investigated over

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several types of catalysts, including mixed oxides,^{18–20} perovskite-type oxides,^{21–23} and supported transition metals. Jia et al.^{21,24} found that about 97% conversion of sulfur dioxide and 95% sulfur yield were achieved at a temperature of 500 °C over perovskite LaCoO₃.

Recently, carbon-supported catalysts have been used in a growing number of applications.^{25–27} As a catalyst support, carbon has a developed porous structure, electronic conductivity, weak acid on the surface, and weak interaction with metal.²⁸ Compared with oxides, carbon-supported catalysts often exhibit better activity, selectivity, and stability for some reactions.^{29,30} Liu et al.³¹ studied reduction of SO₂ to elemental sulfur using hydrogen over activated coke supported Co–Mo catalysts, and a sulfur yield of about 85% was achieved at the temperature of 300 °C under the optimal feed compositions (SO₂/H₂ mole ratio = 1:3). In this paper, it was found that AC-supported catalysts showed catalytic activity for the reduction of SO₂ by CO, and that Fe₂O₃/AC was the most active catalyst. We investigated the performance of Fe₂O₃/AC in terms of the effect of operating conditions, such as Fe content, CO/SO₂ molar ratio, and space velocity.

2. Experimental

2.1. Activated carbon pretreatment

The AC used in this study was purchased from the Gongyi Songshan Filter Media Activated Carbon Factory (P. R. China). The size of the particles in these samples ranged from 40 to 60 meshes. Prior to use, samples were washed with distilled water several times with the aim of removing some ash and impurities. After that, they were dried in air at 110 °C for 12 h. The appropriate amount of AC was pretreated with 5% (mass fraction) HNO₃ at 90 °C for 6 h, and then the samples were washed with distilled water until no further change in pH was detected (around pH 6). Finally, the samples were dried at 110 °C for 12 h. Such pretreated samples are referred to as AC (HN).

2.2. Catalyst preparation

The preparation of all catalysts by incipient impregnation was as follows. AC (HN) (surface area 1897 m²/g, pore volume 0.96 cm³/g) was used as catalyst supports. The supports were impregnated in a reaction container with appropriate aqueous solution of Fe(NO₃)₃·9H₂O. The well-impregnated samples were placed at room temperature for 2 h. Then the required amount of urea (Fe/urea mole ratio = 5:3) was slowly added to the samples, with thorough stirring at room temperature for 0.5 h. The mixed system was then heated at 90 to 95 °C. After the samples were continually stirred for 4.5 h, the reaction container was taken out and quenched in an ice-water bath. Afterwards, the precipitates were separated from the solution by filtration, washed 3 times with deionized water and once with anhydrous ethanol, and dried at 110 °C overnight. Finally, the catalyst precursors obtained were calcined under an inert atmosphere (nitrogen flow) at 500 °C for 5 h. In the tests for the influence of Fe content, the loading of Fe that was calculated on the basis of Fe₂O₃ was varied from 2.5 to 40 wt%, while Fe loading was fixed at 20 wt% for other tests.

2.3. Activity measurements

The catalytic reaction between SO₂ and CO was carried out in a fixed-bed flow reactor system at atmospheric pressure. A total of 0.5 g of the catalyst was packed in the middle part of a quartz reactor (9 mm i.d.). After being purged in a N₂ flow (36 mL/min) at 500 °C for 2 h, the catalyst was then presulfided with a mixture of reaction gas containing 2% (mole fraction) CO and 1% (mole fraction) SO₂ in N₂ at a flow rate of 58 mL/min

at 500 °C for 2 h. Note that, in order to study the presulfiding effect, a series of temperatures (300, 400, or 500 °C) was employed. After being presulfided, the catalyst was cooled to the reaction temperature (about 200 °C) for activity tests. Sulfur dioxide and carbon monoxide (supplied by Qingdao Heli Gas Co., Ltd, P. R. China), used as reactants, were mixed and diluted in N₂ by use of mass flow controllers. The feed gas typically consisted of 2% CO and 1% SO₂ except for the one used in the test of the effect of feed concentration. The effluent gas was passed through an ice-water trap, where elemental sulfur was condensed. When the steady state was attained, SO₂ in the inlet and outlet gases and COS in the effluent gas were separated by the OV-1701 column, and the concentration of each component was detected by flame photometric detector (FPD), and meanwhile CO and CO₂ were separated by GDX-502 column and detected by thermal conductivity detector (TCD).

2.4. X-ray diffraction analysis (XRD) measurements

X-ray diffraction patterns (XRD) of samples were collected in the 2θ angle from 10° to 90°, at a step width of 0.02° and by counting 1 s at each step with a Rigaku (D/max 2500/PC) diffract meter equipped with an online computer. Nickel-filtered Cu K α radiation was used.

3. Results and discussion

3.1. The effect of sulfidation temperature

In general, a catalyst used in a reductive desulfurization process should have undergone presulfiding. From the above XRD results, we can see that Fe₂O₃ is transformed to active species FeS₂ in the process of presulfidation. Therefore, sulfidation is the key step to activate the catalyst for SO₂ reduction with CO. It has been reported that presulfidation using a reaction gas mixture containing 0.3% CO and 0.1% SO₂ in He was completed within 2 h at 500 °C.¹¹ In this work, we investigated in detail the effect of the sulfidation temperature on the catalytic behavior of Fe₂O₃/AC. The conversion rates of SO₂ and sulfur yield are shown in Figure 1. The results showed that, no matter what sulfidation temperature was utilized, SO₂ conversion and sulfur yield increased rapidly at first and nearly leveled off then. Among those tests on temperature, catalyst presulfided at 500 °C had

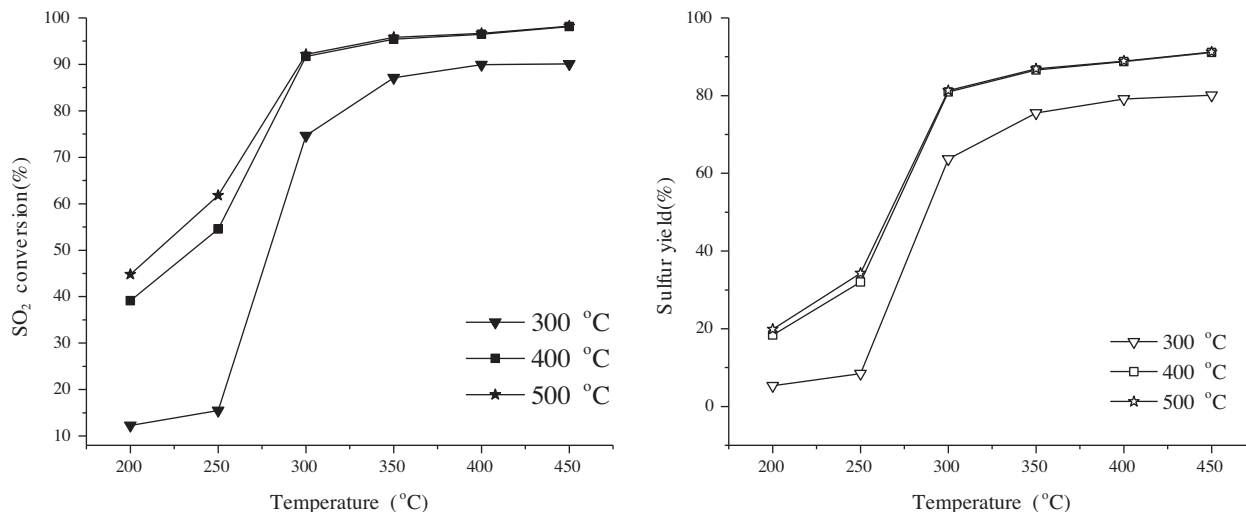


Figure 1. Effect of sulfidation temperature on SO₂ conversion and sulfur yield on Fe₂O₃/AC.

the fastest increasing rate and the highest SO_2 conversion and sulfur yield. The catalyst presulfided at $400\text{ }^\circ\text{C}$ showed activity similar to that of the one presulfided over $400\text{ }^\circ\text{C}$, whereas the catalyst presulfided below that temperature showed much lower activity. A total of 95.43% SO_2 conversion and 86.59% sulfur yield were obtained over $\text{Fe}_2\text{O}_3/\text{AC}$ catalyst in a reaction temperature of $350\text{ }^\circ\text{C}$ after the catalyst was presulfided at $400\text{ }^\circ\text{C}$.

Sulfidation is one of the most important steps in catalyst preparation. Figure 2 showed the XRD patterns of $\text{Fe}_2\text{O}_3/\text{AC}$ after sulfidation at different temperatures. When the space velocity was fixed at $7000\text{ mL}/(\text{g h})$ and the CO/SO_2 molar ratio was set at 2.0, the sulfidation temperature was varied from 300 to $500\text{ }^\circ\text{C}$. From the pattern, it can be seen that both Fe_2O_3 ($2\theta = 35.6^\circ$) and FeS_2 ($2\theta = 33.0^\circ, 37.1^\circ, 47.5^\circ, \text{ and } 56.3^\circ$) were observed when sulfidation took place at $300\text{ }^\circ\text{C}$ for 2 h. However, FeS_2 was the only Fe species when sulfidation occurred at above $400\text{ }^\circ\text{C}$. The result of XRD analysis showed that the phase transformation from Fe_2O_3 to FeS_2 would not be complete when sulfidation occurred at $300\text{ }^\circ\text{C}$, and as long as catalysts were presulfided above $400\text{ }^\circ\text{C}$, Fe_2O_3 would be completely transformed to FeS_2 .

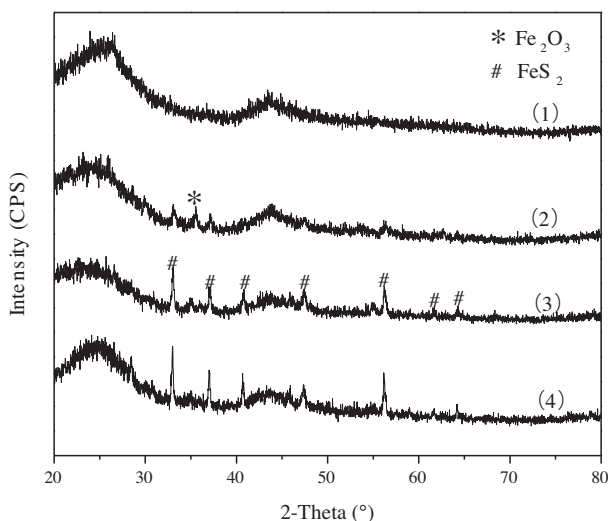


Figure 2. X-ray diffraction patterns of AC and $\text{Fe}_2\text{O}_3/\text{AC}$ under different sulfidation temperature. (1) AC; (2) $\text{Fe}_2\text{O}_3/\text{AC}$ presulfided at $300\text{ }^\circ\text{C}$; (3) $\text{Fe}_2\text{O}_3/\text{AC}$ presulfided at $400\text{ }^\circ\text{C}$; (4) $\text{Fe}_2\text{O}_3/\text{AC}$ presulfided at $500\text{ }^\circ\text{C}$.

3.2. The effect of supported metals

Different metal species were supported on AC to assess the effect on catalytic activity. The metal species supported were common metals. Each metal oxide/AC catalyst was presulfided at $500\text{ }^\circ\text{C}$ for 2 h, and then a gas mixture with a constant molar ratio of $\text{CO}:\text{SO}_2 = 2:1$ (CO , 2 wt%; SO_2 , 1 wt%) was fed into the reaction container. The space velocity (gas hourly space velocity (GHSV)) was fixed at $7000\text{ mL}/(\text{g h})$. Results of the reaction tests with different supported metals, including conversion of SO_2 and sulfur yield, are shown in Figure 3. The results showed that the $\text{Fe}_2\text{O}_3/\text{AC}$ catalyst possessed the best catalytic activity, and ZnO/AC was the second most active catalyst. At the same time, the reactivity of all catalysts increased with elevation of reaction temperature. As the temperature was increased from 200 to $300\text{ }^\circ\text{C}$, SO_2 conversion and sulfur yield of $\text{Fe}_2\text{O}_3/\text{AC}$ abruptly increased, whereas those of ZnO/AC , CuO/AC , and NiO/AC varied less. At the reaction temperature of $350\text{ }^\circ\text{C}$, 95.43% SO_2 conversion and 86.59% sulfur yield were obtained over $\text{Fe}_2\text{O}_3/\text{AC}$

catalyst. The experimental results were somewhat different from those reported by Chen et al.,¹² in which the activity of γ -Al₂O₃-supported Ni was found to be superior to that of Fe₂O₃/ γ -Al₂O₃ by using H₂ as a reducing agent. This may be due to the different specific surface area between AC and γ -Al₂O₃, leading to varying adsorption capability of H₂ or CO onto these metal species. As a comparison, Figure 3 also shows the catalytic performance of Fe₂O₃ without the use of support. Both the SO₂ conversion and the sulfur yield were much lower than those of Fe₂O₃/AC. Facilitating to form active-phase FeS₂ was one possible reason for the difference in their catalytic performance. Another reason was that activated carbon could speed up the reaction between COS and SO₂.

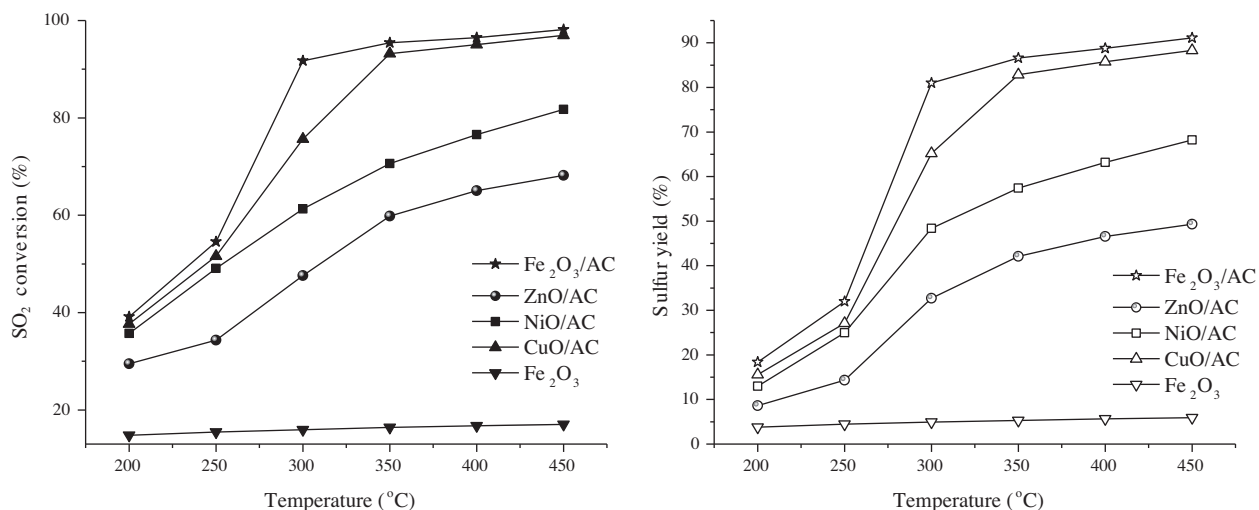


Figure 3. Effect of different supported metals on SO₂ conversion and sulfur yield.

3.3. The effect of Fe content

The EDS elemental analysis for Fe₂O₃/AC before sulfidation is shown in Figure 4, which shows that iron was detected, confirming that iron was supported onto activated carbon. Figure 5 shows the effect of iron content on the SO₂ conversion and sulfur yield over Fe₂O₃/AC. It was found that Fe content had a significant influence on

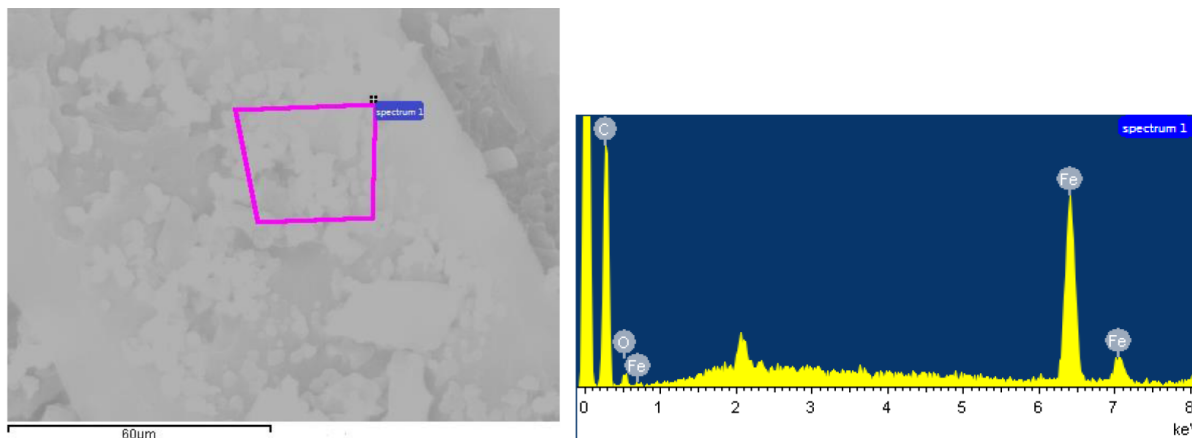


Figure 4. EDS elemental analysis for Fe₂O₃/AC (Fe content, 20 wt%).

the desulfurization performance of catalysts. With an increase in iron content from 2.5% to 20%, both the SO₂ conversion and the sulfur yield increased, and reached their maximum at the iron content of 20%. Catalytic activity of catalysts decreased with a further increase in iron content. Therefore, it was considered that 20% was the optimum content of iron.

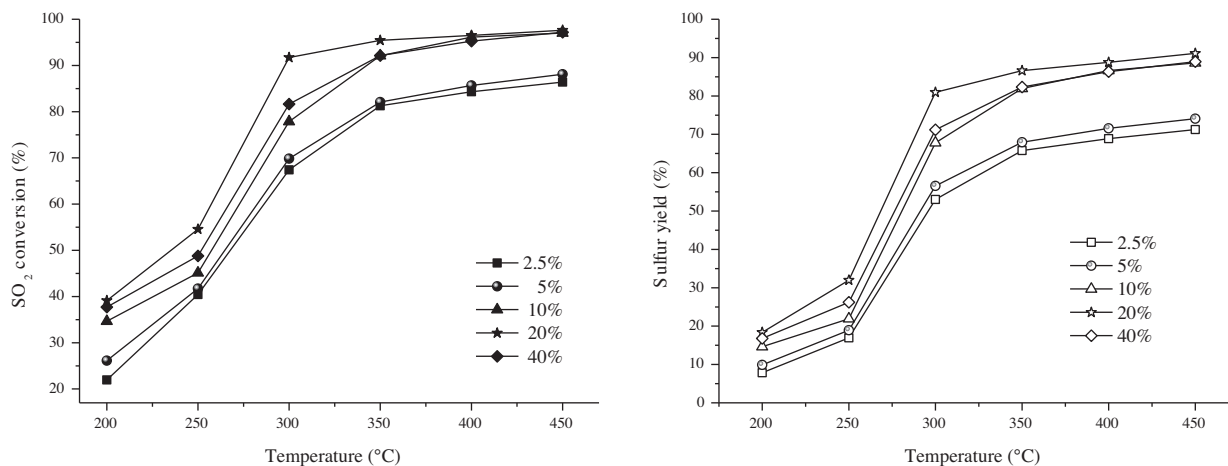


Figure 5. Effect of Fe content on SO₂ conversion and sulfur yield over Fe₂O₃/AC.

3.4. The effect of the CO/SO₂ molar ratio

To obtain the optimum reaction conditions, we further investigated the effect of different feed ratios of CO/SO₂ on SO₂ reduction. From Figure 6, we can see that the conversion of SO₂ increased with the elevation in CO/SO₂ molar ratio. When the feed ratio of CO/SO₂ was 1:1, that is, CO was insufficient, SO₂ conversion was less than 50%. When the feed ratio of CO/SO₂ was 3:1, which means CO was in excess, SO₂ conversion was highest while the sulfur yield decreased sharply above 250 °C because of a substantial amount of COS formed via the reaction between CO and S.

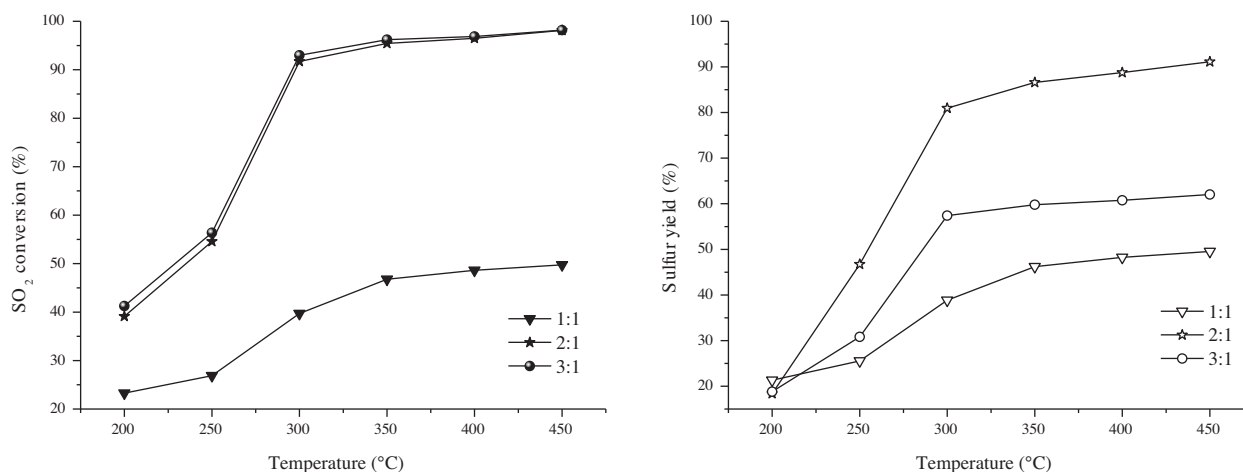


Figure 6. Effect of molar ratios of CO/SO₂ on SO₂ conversion and sulfur yield over Fe₂O₃/AC.

3.5. The effect of space velocity

Figure 7 shows the effect of gas velocity on the SO₂ reduction by CO over Fe₂O₃/AC catalyst. The result showed that there was little effect on the SO₂ conversion in the range 5000 to 7000 mL/(g h), whereas the SO₂ conversion decreased sharply with the increase in the space velocity over 7000 mL/(g h). This was because the contact time between the reactants and catalyst surface might be reduced. However, the tendency of the sulfur yield was inconsistent with the elevation of space velocity. The sulfur yield rose with the increase in elevation of the space velocity below 7000 mL/(g h) and reached 88.76% at 400 °C, whereas it decreased gradually above 7000 mL/(g h). The main reasons for the change in sulfur yield were that the sulfur selectivity increased at a space velocity below 7000 mL/(g h), whereas the SO₂ conversion decreased significantly with the growth in space velocity above 7000 mL/(g h).

3.6. Stability test of the Fe₂O₃/AC

The stability of the Fe₂O₃/AC, whose Fe content was 20%, was tested at 400 °C for 25 h. As illustrated in Figure 8, the SO₂ conversion and sulfur yield were low initially, but then grew to 96% and 88%, respectively. The catalyst seemed to be very stable: the conversion of SO₂ and the sulfur yield dropped less than 2.5% after a 24-h run at 400 °C.

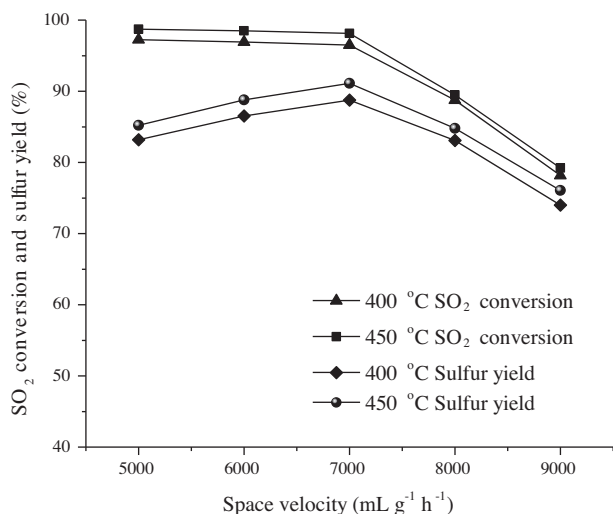


Figure 7. Effect of gas velocity on SO₂ conversion and sulfur yield over Fe₂O₃/AC.

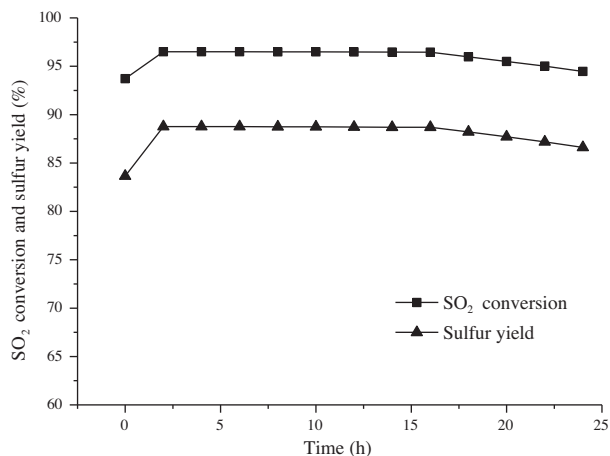


Figure 8. Effect of reaction time on SO₂ conversion and sulfur yield over Fe₂O₃/AC.

In this work, it was found that AC-supported transition-metal oxide catalysts were active for the reduction of SO₂ by CO to elemental sulfur. Among the 4 different supported catalysts, Fe₂O₃/AC was the most active one. Presulfidation was necessary and important. The active phase of catalyst was detected as FeS₂, and the formation of FeS₂ was greatly dependent on the sulfidation temperature. Using Fe₂O₃/AC, the best catalyst, the optimal feed molar ratio of CO/SO₂ was 2:1 and the best sulfidation temperature was 400 °C. When Fe content was 20 wt%, SO₂ conversion of 95.43% and sulfur yield of 86.59% were obtained at 350 °C on Fe₂O₃/AC.

3.7. Comparison with other catalysts

According to the literature, fluid coke and CH_4 could be employed as reducing agent, but the reaction temperature (550°C) was not low enough for practical application. H_2 as another intensively investigated reducing agent has also been shown to effectively reduce SO_2 to elemental sulfur,¹¹ but H_2 has several disadvantages, such as high cost in production, and inconvenience in transportation and storage. To date, the catalytic reduction of SO_2 to form elemental sulfur with CO has been investigated over several types of catalysts, including mixed oxides,^{18–20} perovskite-type oxides,^{21–23} and supported transition metals. Regarding mixed oxides, for ZrO_2 and perovskite LaCoO_3 catalyst, 95% conversion of SO_2 was achieved at 500°C , which was higher than that over the $\text{Fe}_2\text{O}_3/\text{AC}$ catalyst we employed in the present work.^{1,19} Over the Fe_2O_3 -only catalyst, SO_2 conversion was less than 20%, even at 450°C . Therefore, $\text{Fe}_2\text{O}_3/\text{AC}$ is thought to be one of the best catalysts for the catalytic reduction of SO_2 with CH_4 to elemental sulfur.

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