

Research Article

Reduction of SO₂ to Elemental Sulfur in Flue Gas Using Copper-Alumina Catalysts

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This study aims to propose an advanced catalyst for the selective catalytic reduction of SO₂, as a sustainable process to mitigate the emission of this toxic gas, which is a significant environmental concern. The conversion of SO₂ through catalytic reduction with CH₄ to elemental sulfur was investigated using Al₂O₃-Cu catalysts. The reaction was conducted under atmospheric pressure and at a temperature range of 550–800°C. A remarkable 99.9% SO₂ conversion rate and 99.5% sulfur selectivity were achieved using the Al₂O₃-Cu (10%) catalyst at 750°C. The highest conversion rates of SO₂ to elemental sulfur, with minimal production of undesirable by-products such as H₂S and COS, were obtained when the SO₂/CH₄ molar feed ratio was set at 2, which is the stoichiometric ratio. Furthermore, the optimal catalyst exhibited excellent long-term stability for SO₂ reduction with methane.

1. Introduction

Today, SO_2 remains a critical airborne pollutant [1, 2]. Alongside nitrogen oxides, it remains a primary contributor to acid rain formation. The impact of sulfur dioxide on human well-being is substantial, causing detrimental health effects, diminishing agricultural output, leading to fish fatality by lowering river pH, and instigating numerous other hazardous consequences. Both stationary and mobile sources contribute to SO_2 emissions. Vehicles running on high-sulfur-content gasoline and diesel represent the mobile sources, while stationary sources encompass metallurgical facilities (such as copper, zinc, and lead roasting units), coal-fired power plants, oil and gas refineries, and petrochemical industries. Given the detrimental repercussions, the development of effective strategies to manage these emissions is imperative.

In general, flue gas desulfurization (FGD) techniques are categorized into two main groups: disposability and

regenerability [1, 2]. The primary disposability methods involve lime sorption, offering a major pathway for curbing atmospheric SO_2 emissions. Nonetheless, these techniques are better suited for treating modest quantities of SO_2 within flue gas, proving inadequate for large flows, which generate a substantial volume of nonuseable by-products, a challenge exacerbated by landfill disposal.

On the contrary, regenerative techniques are designed for handling higher SO_2 volumes, such as those found in copper converting and zinc roasting plants. Notably, the catalytic conversion of SO_2 into sulfuric acid and elemental sulfur is the cornerstone of regenerative methods. When a robust demand exists for sulfuric acid, it becomes justifiable to reduce SO_2 emissions while producing this substance. However, the corrosive nature of sulfuric acid poses significant challenges in terms of storage and transportation. In comparison, the selective catalytic reduction of SO_2 to sulfur, facilitating simpler transport and storage of solid sulfur, holds greater appeal and promise [3]. The reduction of sulfur dioxide to sulfur has been explored using both drybased and wet-based catalysts. Dry-based catalysts are of greater interest, primarily because of their applicability in industrial processes. [4]. Various reducing agents have been explored for this process, including CO [5], CH_4 , and H_2 [6] as the primary contenders, while syngas (CO + H_2) [7, 8] and carbon [9, 10] have also been tested.

Various catalysts, such as $CoMo/\gamma$ -Al₂O₃ [5], SnO₂ [11], Ir/CeO₂ [12], and Ce-Al-O_x composite oxide catalyst [13] for the reduction of SO₂ with carbon monoxide and NiO/ γ -Al₂O₃ [6], FeS₂/ γ -Al₂O₃ [14], and Al₂O₃/MoS₂ [15] for the reduction of SO₂ with hydrogen, have been investigated. The use of plasma for the catalytic reduction of sulfur dioxide has also been investigated [16, 17].

The advantage of CO and H_2 lies in their lower operating temperatures, although their production is notably expensive.

The use of CH_4 as a reducing agent has a drawback in its higher operating temperatures compared to H_2 and CO. However, CH_4 's affordability and accessibility make it an attractive option, particularly for nations endowed with substantial natural gas reserves, such as Iran, Russia, and others.

Catalysts for the reduction of SO₂ to elemental sulfur using CH₄ have included bauxite [18], alumina [19–21], metal oxides, and sulfides supported on alumina and activated carbon [22–26], along with transition metal sulfides [27], ferromanganese nodules [28], and cobalt oxide on different supports [29]. Cerium oxide has also demonstrated significant catalytic activity in this context [30–35]. The application of plasma for catalytic reduction of sulfur dioxide using FeS/Al2O3 has also been subject to investigation [17]. Although copper on ceria-based catalysts has exhibited reliable performance in CH₄-assisted SO₂ reduction, the industrialization of cerium is hindered by its high cost.

Therefore, alumina was selected as the catalyst support in this study, offering a well-established substrate. Moreover, its greater surface area, compared to ceria, is a pivotal factor in solid-gas reactions, rendering it a superior choice. Furthermore, our prior research has assessed the catalytic efficiency of nickel oxide, molybdenum oxide, and cobalt oxide catalysts supported on alumina [36–38].

In this investigation, $Cu-Al_2O_3$ catalysts with varying concentrations were synthesized and characterized for CH₄-assisted SO₂ reduction. Subsequent reactor tests were performed and compared under stoichiometric molar feed ratios and within a temperature range of 550–800°C to identify the most effective catalyst.

Finally, the study delved into the impact of feed ratio, space velocity, and long-term stability (crucial for industrial applications) on Cu-Al₂O₃ (10%), identified as the optimal catalyst.

2. Experimental Section

2.1. Catalyst Preparation. This study employed the wet impregnation technique for catalyst preparation [39, 40]. An aqueous solution of copper nitrate trihydrate

(Cu(NO₃)₂.3H₂O, sourced from Merck) was employed as the copper precursor for impregnating onto a commercial γ -Al₂O₃ support with a particle size ranging from 2.5 to 3 mm. The well-impregnated catalyst was then allowed to stand for 1 hour, subjected to overnight drying at 120°C within an oven, and ultimately calcined at 550°C for a duration of 4 hours. The copper-alumina catalysts employed in this research were characterized by the loading of copper oxide onto γ -alumina, yielding copper weight percentages of 5%, 10%, and 15%. These catalysts are, respectively, denoted as Al₂O₃-Cu (5%), Al₂O₃-Cu (10%), and Al₂O₃-Cu (15%).

2.2. Catalyst Characterization. The BET-specific surface area, pore size distributions, and adsorption isotherms of the catalysts were assessed using the nitrogen adsorption method via the Autosorb-1-MP apparatus from Quantachrome, operating at 77 K. To determine phase composition, XRD patterns of the catalysts were captured using a diffractometer (PHILIPS-PW1730) operating at 40 kV and 30 mA, utilizing Cu K α radiation (λ = 1.5406 A°). The catalysts' morphology was examined using field-emission scanning electron microscopy (FE-SEM) with a TE-SCAN instrument from the Czech Republic.

The acidic properties of the catalysts were gauged through temperature-programmed ammonia desorption $(NH_3$ -TPD) analysis. To examine the catalyst's characteristics in the form of a TPO (temperature-programmed oxidation) test, thermogravimetric analysis was performed using a Rheometric Scientific instrument, as explicitly mentioned in the relevant section.

2.3. Catalyst Performance Tests. The experiments were conducted in a fixed-bed stainless steel tubular reactor with loading 1 g of the catalyst in each reactor test. The flow diagram of the system is shown in Figure 1.

At first, the reactor is purged by an inert gas stream (gas 1). Then, the system is heated to reach the desired temperatures under a mixture of reaction gases. The reacting gas (gas 2) is a combination of CH_4 , SO_2 , and inert (argon) streams with predefined concentrations.

SO₂, CH₄, and argon inlet concentrations in the mixture were adjusted by three mass flow controllers. The reaction outlet was analyzed online by a mass spectrometer (MS) from Leda Mass.

After converting base peak heights to partial pressures, it is possible to plot mole fractions of up to 12 different gases versus time with ppm sensitivity by the mass spectrometer [41].

3. Results and Discussion

3.1. Catalyst Characterization. XRD patterns of the alumina and Al₂O₃-copper catalysts are shown in Figure 2.

The alumina peaks (number 1) and copper oxide peaks (number 2) are distinguished in Figure 2. According to Figure 2(a), the major peaks of alumina are obvious while, by adding copper oxide (Figure 2(b)-2(d)) to the catalyst, the



FIGURE 1: Flow diagram of the reaction test system.



FIGURE 2: XRD patterns of the alumina (a), Al₂O₃-Cu (5%) (b), Al₂O₃-Cu (10%) (c), and Al₂O₃-Cu (15%) (d).

height of alumina peaks drops and copper oxide peaks arises which is fair clear for Al_2O_3 -Cu (15%) catalyst in Figure 2(d).

Table 1 shows the results of BET (Brunauer, Emmett, and Teller) surface area, total pore volume, and average pore diameter of γ -Al₂O₃ support and Al₂O₃-Cu catalysts. It was expected that the impregnation of CuO (as a promoter) on Al₂O₃ would decrease the surface area of the catalyst concurrent with its total pore volume due to the blockage of support pores.

Although the presence of CuO as an active species on the support pores would boost desired catalytic performances of the catalyst, N_2 adsorption isotherms of alumina and Al_2O_3 -Cu synthesized catalysts are given in Figure 3. With a similar trend to Table 1, alumina support shows the highest N_2 adsorption while, with increasing the amount of CuO on the support, the adsorbed N_2 by the catalysts decreases.

Specifically, through CuO impregnation of the Al_2O_3 support, copper precursor molecules penetrate into the support pores reducing the surface area, pore volume, and consequently N₂ adsorption ability. It should be noticed that smaller pores would be filled first which causes an ascending trend along with increasing CuO weight percent for the average pore diameter of the prepared catalysts according to

TABLE 1: BET surface area, total pore volume, and average pore diameter of synthesized catalysts.

Sample	$S_{\rm BET}$ (m ² /g)	V _{total} (pore volume) (cm ³ /g)	Average pore diameter (Å)
Al_2O_3	347.1	0.3786	43.62
Al ₂ O ₃ -Cu (5%)	237.6	0.3630	61.10
Al ₂ O ₃ -Cu (10%)	207.8	0.3499	67.35
Al ₂ O ₃ -Cu (15%)	191.4	0.3420	71.48

Figure 4 and data given in Table 1. BJH pore size distributions of various catalysts are shown in Figure 4.

3.2. Catalysts Activity Tests. The principal reaction for SO_2 reduction by CH_4 can be represented as follows:

$$CH_4 + 2SO_2 \longrightarrow 2S + CO_2 + 2H_2O \tag{1}$$

The main side reaction that may occur between SO_2 and CH_4 is as follows:

300

250

Volume (cc/g) 120 100

50

0

0

0.1

Al₂O₃-Cu (5%)

+ Al,O,

0.2

0.3

FIGURE 3: N_2 adsorption isotherms of synthesized catalysts.

0.4 0.5

 P/P_0

0.6

• Al₂O₃-Cu (10%)

▲ Al₂O₃-Cu (15%)

0.7

0.8

0.9

1



FIGURE 4: BJH pore size distribution of synthesized catalysts.

$$2CH_4 + SO_2 \longrightarrow H_2S + 2CO + 3H_2$$
(2)

While the first reaction produces a suitable sulfur product, the second reaction produces toxic H_2S and CO gases. SO_2 conversion was calculated from inlet and outlet SO_2 volume fractions through the following equation:

$$X_{\rm SO2} = \frac{V_{\rm SO2_{in}} - V_{\rm SO2_{out}}}{V_{\rm SO2_{in}}} * 100,$$
 (3)

 $V_{\rm SO2_{in}}$ and $V_{\rm SO2_{out}}$ are the volumetric velocity of SO₂ at the reactor inlet and outlet, respectively, while sulfur selectivity was estimated by the molar difference of the sum of all sulfur-containing products (including H₂S, COS, CS₂, and unreacted SO₂) from the reacted share of SO₂. Figure 5 shows SO₂ conversion plots for the prepared catalysts against operating temperatures.

At 550°C, the SO₂ conversation rate is very low. When the temperature increases, the SO₂ conversion rate extremely increases for all catalysts. This proves a strong dependency of the reaction to the temperature.

At temperatures higher than 550°C, the increasing rate of SO_2 conversion for Al_2O_3 -Cu (5%) and Al_2O_3 is lower than Al_2O_3 -Cu (10%) and Al_2O_3 -Cu (15%). At 600 and 650°C, Al_2O_3 -Cu (10%) performance is slightly better, but at higher



FIGURE 5: SO₂ conversion as a function of temperature for different catalysts (2% SO₂-1% CH₄-Ar; S.V. = 3000 mL/h^{-1}).

temperatures, both Al_2O_3 -Cu (10%) and Al_2O_3 -Cu (15%) catalysts show a similar performance.

Therefore, adding more than 10 percent of copper not only has no beneficial effect but also could increase the operating costs.

It is worth noting that all the Al_2O_3 -Cu catalysts presented a much better performance than alumina support in the temperature range of 550–800°C indicating CuO performance as a suitable active species for this process.

The partial pressure curves of H_2S , produced from reactions for different catalysts, are compared in Figure 6.

For all the catalysts, by increasing the temperature, the amount of produced H_2S decreases which is in contrast to the SO₂ conversion ascending trend. Seemingly, at lower temperatures, the conversion is incomplete, and there is a large share of unreacted CH₄ and SO₂. Subsequently, this unreacted CH₄ can be decomposed according to the following reaction:

$$CH_4 \longrightarrow C + 2H_2$$
 (4)

Thereafter, it is likely that produced H_2 could react catalytically with unreacted SO₂ to form H_2S and water via the following reaction:

$$3H_2 + SO_2 \longrightarrow H_2S + 2H_2O$$
 (5)

Given that no significant amount of hydrogen is produced and that H_2S decreases with increasing conversion rate, this possibility is confirmed [24]. It is noteworthy that, even at 550°C with maximum produced H_2S , its share is less than 0.35% of the outlet flow.

For temperatures over 700°C, the H_2S produced for Al_2O_3 -Cu (5%) is higher than that of alumina, while the amount of unreacted SO_2 is more significant for alumina. This can be due to the more active catalytic behavior of Al_2O_3 -Cu (5%) than alumina for methane decomposition



FIGURE 6: Partial pressures of H_2S versus temperature for different catalysts.

(reaction (4)), and the reaction of produced H_2 with SO_2 (reaction (5)) forming more H_2S .

COS partial pressure profiles from the reaction versus temperature are illustrated in Figure 7 for different catalysts.

The amount of produced COS for Al_2O_3 -Cu catalysts at temperatures lower than 700°C is less than that of alumina while at higher temperatures is in contrast. This may be due to the fact that the amount of CS₂ production increases [33] with increasing temperature and its further reaction with CO₂ to produce COS, indicated in reaction (6). No CS₂ was detected at the reactor outlet during the experiments.

$$CS_2 + CO_2 \longrightarrow 2COS$$
 (6)

Additionally, according to Figure 7, it could be seen that despite larger values of produced COS for Al_2O_3 -Cu (5%) than the others, Al_2O_3 -Cu (10%) and Al_2O_3 -Cu (15%) catalysts present similar performances with much lower toxic COS. Generally, the important thing is that the total amount of undesirable H_2S and COS is negligible resulting in an outstanding catalyst selectivity of more than 99.5% for Al_2O_3 -Cu (10%) which was chosen as the best catalyst. The temperature-programmed desorption plots of ammonia (NH₃-TPD) for Al_2O_3 and Al_2O_3 -Cu (10%) are illustrated in Figure 8 with related results of weak, moderate, and strong acid sites as given in Table 2.

Accordingly, the density of moderate and weak acid sites was increased significantly by adding CuO to alumina support, and alumina's weak acid sites were converted into very weak acid sites (first peak) and weak acid sites (second peak) [42–44].

The density of strong acid sites is decreased because of replacing CuO with Brønsted strong acid sites. In other words, CuO has weak and moderate acidity leading to an increase in weak and moderate acid sites after support modification with CuO [42–44] to achieve a more active catalyst for selective catalytic reduction of SO₂ with CH₄.



FIGURE 7: Partial pressures of COS versus temperature for different catalysts.

The FE-SEM images shown in Figure 9 illustrate the placement of copper nanoparticles on the surface and pores of Al_2O_3 -Cu (10%) catalysts fairly well. This causes the reduction of pores and the specific surface area of the Al_2O_3 -Cu (10%) than the Al_2O_3 (Table 1). However, these copper nanoparticles create very active sites for reaction.

3.3. Effects of Feed Gas Composition. The effect of changing the SO_2/CH_4 molar ratio on SO_2 conversion and H_2S -COS production is shown in Figure 10.

It can be seen that high conversion values were attained for SO_2/CH_4 molar ratios below 2 when CH_4 is in excess and larger than the stoichiometric ratio. Substantially, entering SO_2 more than the stoichiometric ratio required for reaction (1) leads to a conversion drop and a remarkable unreacted SO_2 , same as the case with SO_2/CH_4 ratio of 3 with a reported SO_2 conversion of 71%.

However, when the SO_2/CH_4 ratio is less than the stoichiometric ratio (excess methane), H_2S and COS production greatly increase as a result of reacting SO_2 with CH_4 through reaction (2) which is now more favorable than reaction (1). Moreover, the excess methane could be decomposed through reaction (4) to produce further H_2 with its share via reaction (2). Total produced H_2 could react with SO_2 to form H_2S according to reaction (5).

In addition, CH_4 can react with S_2 to produce CS_2 through reaction (8). Then, the produced CS_2 reacts with H_2O and produces H_2S and COS according to reaction (9). In the next step, COS reacts with water (product of reaction (1)) in reaction (10) and produces more H_2S . The drastic increase in H_2 at low ratios of SO_2/CH_4 confirms the possibility.

$$CH_4 + S_2 \longrightarrow CS_2 + 2H_2 \tag{7}$$

$$CS_2 + H_2O \longrightarrow COS + H_2S$$
 (8)

$$COS + H_2O \longrightarrow CO_2 + H_2S$$
 (9)



FIGURE 8: NH₃-TPD profiles of Al_2O_3 and Al_2O_3 -Cu (10%) catalysts.

TABLE 2: The amount of total, weak, moderate, and strong acid sites of Al₂O₃ and Al₂O₃-Cu (10%) catalysts.

Catalyst	Al_2O_3	Al ₂ O ₃ -Cu (10%)
Weak acid sites (mmol/g)	0.0416	0.0880
Moderate acid sites (mmol/g)	0.1084	0.137
Strong acid sites (mmol/g)	0.2356	0.188
Total acid sites (mmol/g)	0.3857	0.414



FIGURE 9: FE-SEM images of Al_2O_3 (a) and Al_2O_3 -Cu (10%) (b).



FIGURE 10: Effects of feed gas composition on SO₂ conversion and H₂S, COS, and H₂ production for Al₂O₃-Cu (10%) catalyst (S.V. = 3000 mL/h^{-1}).

For COS, except the mentioned mechanism, the generated CS_2 according to reaction (8) could produce COS through reaction (6). Hence, the amount of COS greatly increases with decreasing SO_2/CH_4 ratio.

3.4. Effects of Space Velocity. The effect of space velocity is shown in Figure 11.

When space velocity increased from 3000 to 12000 ml/h, SO_2 conversion decreased from 99.8% to 70%. H₂S and COS production showed no significant change, and finally, selectivity in the same value remained high. The sharp decline in conversion can be due to reducing contact time between the reactants and the catalyst while the dependency of sulfur selectivity is independent of the space velocity increment.

3.5. Stability of Catalyst. The stability of Al_2O_3 -Cu (10%) as the best catalyst was tested at 750°C for 20 hours. As illustrated in Figure 12, in the first 9 hours, the conversion rate was constant. In this initial period, the amount of H_2S byproduct was almost constant. Afterward, the conversion rate started to diminish.

The SO_2 conversion rate experienced only a slight 3% decrease between 9 and 12 hours, while, for durations exceeding 13 hours, the conversion rate remained relatively constant.

In this regard, SO_2 conversion reduction is consistent with H_2S production ascending trend, as a result of increasing unreacted CH_4 which could be decomposed to H_2 with further reactions according to the scenario discussed earlier. Therefore, Al_2O_3 -Cu (10%) showed a good stability for SO_2 reduction with CH_4 .

The main threat at high temperatures for catalyst deactivation is coke production which can be produced by CH_4 decomposition according to reaction (4). However, in the main reaction per each consumed mole of SO2, two moles of water vapor are produced that could prevent coke deposition through reaction (10) as an additional advantage.



FIGURE 11: Effect of space velocity on SO₂ conversion and sulfur selectivity for Al_2O_3 -Cu (10%) (2% SO₂-1% CH₄-Ar).

$$C + H_2 O \longrightarrow CO + H_2$$
 (10)

To investigate Al_2O_3 -Cu (10%) changes during the reactor test, the catalyst after 40 hours of reactor lifetime test was analyzed by thermogravimetric (TG) analysis in an air environment by connecting its outflow to the mass spectrometer (MS) device for a better understanding of the phenomena.

The changes in the catalyst weight and SO_2 MS peaks obtained from TG-MS analysis are indicated in Figure 13. For this test, the temperature was increased to 1000°C with a constant rate and then for a few minutes was maintained isothermally at 1000°C.

According to Figure 13, it can be seen at first some weight loss appeared due to the loss of the adsorbed water by the catalyst. At temperatures about 300°C, the catalyst weight increased rapidly while at the temperature range of 400–700°C decreased slowly, and finally at temperatures more than 700°C decreased again sharply.

It could be deduced that during the reactor lifetime test, CuO is sulfided and converted into copper sulfide [45, 46]. This copper sulfide would be sulfated in temperatures more than 300°C forming copper sulfate and causing the catalyst weight gain at these temperatures. Thereafter, at temperatures more than 700°C, the copper sulfate is decomposed to copper oxide and the catalyst weight decreases [45, 46].

The sharp increase for SO_2 in output at 700°C was fully confirmed by copper sulfate decomposition. It should be noted that a small increase in SO_2 and a small decrease in the catalyst weight at a temperature range of 400–700°C could be due to the oxidization of sulfur product trapped in the catalyst cavities.

The TG-MS analysis shows the sulfidation of CuO changes the catalytic performance of Al_2O_3 -Cu (10%) over time which results in decreasing SO₂ conversion and increasing improper by-product (H₂S). These results also show that CuO is more suitable than copper sulfide for the selective catalytic reduction of SO₂ with CH₄.



FIGURE 12: Effect of reaction time on SO₂ conversion and H₂S production over Al₂O₃-Cu (10%) (2% SO₂-1% CH₄-Ar; S.V. = 3000 mL/h⁻¹).



FIGURE 13: Changes in catalyst weight and SO₂ MS peaks obtained from thermogravimetric analysis for Al₂O₃-Cu (10%).

In general, Al_2O_3 -Cu (10%) showed a reliable performance for this process and with further modifications against sulfidation could be more applicable in terms of industrialization.

 $\log(k_i) = \log(A_i) - \frac{E_i}{kT}.$ (11)

3.6. Determining Activation Energies. Activation energies are determined by assuming Arrhenius's dependency on the temperature for the reaction constants [47].

While $k = 8.6173324 \times 10^5$ eV/K is the Boltzmann constant, *T* is the absolute temperature and A_i is preexponential factor. Arrhenius plot obtained from SO₂ conversion values for Al₂O₃-Cu (10%) is given in Figure 14.



FIGURE 14: Arrhenius plot of SO_2 conversion values for Al_2O_3 -Cu (10%) catalyst.

According to Figure 14, Al_2O_3 -Cu (10%) activation energy equals 0.2690 eV in the temperature range of 550–800°C, while it was calculated 0.33 eV for Al_2O_3 -Mo (% 10) catalyst [37] and 0.228 eV for Al_2O_3 -Co (%15) [38] catalyst in a same operating condition. However, with respect to the work by Guiance et al. [47], the activation energy for the Al2O3-Cr2O3 catalyst is calculated at 0.43 eV at temperatures between 25°C and 45°C.

4. Conclusion

The current investigation focused on the selective catalytic reduction of SO₂ using CH₄ over CuO alumina-based catalysts. The catalysts were prepared using the wet impregnation technique. Four distinct catalysts were synthesized, featuring copper loadings of 0%, 5%, 10%, and 15% by weight on γ -Al₂O₃ support. These catalysts were subjected to testing within a fixed-bed pilot reactor. Notably, all CuO-containing catalysts, Al₂O₃-Cu (10%) demonstrated the most favorable outcomes in terms of catalytic activity and sulfur selectivity. Interestingly, the inclusion of additional CuO did not impart any discernible advantageous effects.

The optimal catalyst showcased remarkable performance, achieving a remarkable SO2 conversion of 99.9% coupled with a sulfur selectivity exceeding 99.5% at a temperature of 750°C. Furthermore, a meticulous assessment of the influence of the SO₂/CH₄ molar feed ratio revealed that the peak catalytic efficiency was achieved at the stoichiometric ratio pertinent to the primary reaction (reaction (1)). The minimal presence of undesirable by-products such as H₂S and COS indicated the prominence of reaction (1) as the predominant reaction pathway. However, over the course of the lifetime test, a reduction in catalytic activity by approximately 30% was observed due to the conversion of CuO into copper sulfide species, a phenomenon unveiled through TG-MS analysis. Ultimately, the activation energy for Al₂O₃-Cu (10%) was computed to be 0.1355 eV within the temperature spectrum spanning 550-800°C.

Data Availability

All the data and results have been presented in the manuscript and supplementary documents, and they can be published as a public report.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

References

- D. Davis and D. Kemp, Kirk-Othmer Encyclopedia of Chemical Technology, Wiley, Hoboken, NJ, USA, 1991.
- [2] R. R. Lunt and J. D. Cunic, Profiles in Flue Gas Desulfurization, Wiley-AIChE, Hoboken, NJ, USA, 1st edition, 2000.
- [3] M. M. X. Lum, K. H. Ng, S. Y. Lai et al., "Sulfur dioxide catalytic reduction for environmental sustainability and circular economy: a review," *Process Safety and Environmental Protection*, vol. 176, pp. 580–604, 2023.
- [4] K. H. Ng, S. Y. Lai, N. F. M. Jamaludin, and A. R. Mohamed, "A review on dry-based and wet-based catalytic sulphur dioxide (SO₂) reduction technologies," *Journal of Hazardous Materials*, vol. 423, Article ID 127061, 2022.
- [5] H. Zhao, X. Luo, J. He, C. Peng, and T. Wu, "Recovery of elemental sulphur via selective catalytic reduction of SO 2 over sulphided CoMo/γ-Al2O3 catalysts," *Fuel*, vol. 147, pp. 67–75, 2015.
- [6] C.-L. Chen, C.-H. Wang, and H.-S. Weng, "Supported transition-metal oxide catalysts for reduction of sulfur dioxide with hydrogen to elemental sulfur," *Chemosphere*, vol. 56, no. 5, pp. 425–431, 2004.
- [7] Y. Jin, Q. Yu, and S. G. Chang, "Reduction of sulfur dioxide by syngas to elemental sulfur over iron-based mixed oxide supported catalyst," *Environmental Progress*, vol. 16, no. 1, pp. 425431–425438, 1997.
- [8] T. Ge, C. Zuo, H. Chen, Y. Muhammad, L. Wei, and C. Li, "Catalytic activity and molecular behavior of lanthanum modified CoS_x/γ -Al₂O₃ catalysts for the reduction of SO₂ to sulfur in smelter off-gas using CO-H₂ mixture as reductant," *Industrial & Engineering Chemistry Research*, vol. 58, no. 9, pp. 3595–3605, 2019.
- [9] X. Wang, A. Wang, X. Wang, and T. Zhang, "Microwave plasma enhanced reduction of SO2 to sulfur with carbon," *Energy and Fuels*, vol. 21, no. 2, pp. 867–869, 2007.
- [10] X. Pi, F. Sun, Z. Qu et al., "Producing elemental sulfur from SO2 by calcium loaded activated coke: enhanced activity and selectivity," *Chemical Engineering Journal*, vol. 401, Article ID 126022, 2020.
- [11] G. B. Han, N.-K. Park, S. H. Yoon, and T. J. Lee, "Catalytic reduction of sulfur dioxide with carbon monoxide over tin dioxide for direct sulfur recovery process," *Chemosphere*, vol. 72, no. 11, pp. 1744–1750, 2008.
- [12] C. Jinyan, L. Yutao, S. Tianrun et al., "The positive role of Ir0 and OV on the reduction of SO2 by CO over Ir/CeO2," *Applied Surface Science*, vol. 620, Article ID 156826, 2023.
- [13] Q. Jin, X. Meng, W. Ji et al., "SO2 reduction for sulfur production by CO over Ce-Al-Ox composite oxide catalyst," *Catalysis Communications*, vol. 174, Article ID 106587, 2023.
- [14] S. C. Paik and J. S. Chung, "Selective hydrogenation of SO₂ to elemental sulfur over transition metal sulfides supported on Al₂O₃," *Applied Catalysis B: Environmental*, vol. 8, no. 3, pp. 267–279, 1996.
- [15] Y. Yang, J. Yu, Y. Chen et al., "A novel synthetic method of porous and nanoflower-like Al2O3/MoS2 catalyst for reduction of SO2 to elemental sulfur," *Nano Research*, vol. 16, no. 5, pp. 6076–6084, 2023.
- [16] M. S. AlQahtani, X. Wang, J. L. Gray, S. D. Knecht, S. G. Bilén, and C. Song, "Plasma-assisted catalytic reduction of SO2 to elemental sulfur: influence of nonthermal plasma and

temperature on iron sulfide catalyst," *Journal of Catalysis*, vol. 391, pp. 260-272, 2020.

- [17] M. S. AlQahtani, S. D. Knecht, X. Wang, S. G. Bilén, and C. Song, "One-step low-temperature reduction of sulfur dioxide to elemental sulfur by plasma-enhanced catalysis," *American Chemical Society Catalysis*, vol. 10, no. 9, pp. 5272–5277, 2020.
- [18] J. J. Helstrom and G. A. Atwood, "The kinetics of the reaction of sulfur dioxide with methane over a bauxite catalyst," *Industrial and Engineering Chemistry Process Design and Development*, vol. 17, no. 2, pp. 114–117, 1978.
- [19] S. E. Mousavi, H. Pahlavanzadeh, M. Khani, H. A. Ebrahim, and A. Mozaffari, "Selective catalytic reduction of SO₂ with methane for recovery of elemental sulfur over nickel-alumina catalysts," *Reaction Kinetics, Mechanisms and Catalysis*, vol. 124, no. 2, pp. 669–682, 2018.
- [20] A. Bobrin, V. Anikeev, A. Yermakova, V. I. Zheivot, and V. A. Kirillov, "Kinetic studies of high-temperature reduction of sulfur dioxide by methane," *Reaction Kinetics and Catalysis Letters*, vol. 40, no. 2, pp. 357–362, 1989.
- [21] J. Sarlis and D. Berk, "Reduction of sulfur dioxide with methane over activated alumina," *Industrial & Engineering Chemistry Research*, vol. 27, no. 10, pp. 1951–1954, 1988.
- [22] D. J. Mulligan and D. Berk, "Reduction of sulfur dioxide over alumina-supported molybdenum sulfide catalysts," *Industrial* & Engineering Chemistry Research, vol. 31, no. 1, pp. 119–125, 1992.
- [23] D. J. Mulligan, K. Tam, and D. Berk, "A study of supported molybdenum catalysts for the reduction of SO2 with CH4: effect of sulphidation method," *Canadian Journal of Chemical Engineering*, vol. 73, no. 3, pp. 351–356, 1995.
- [24] J. Sarlis and D. Berk, "Reduction of sulphur dioxide by methane over transition metal oxide catalysts," *Chemical Engineering Communications*, vol. 140, no. 1, pp. 73–85, 1995.
- [25] T. S. Wiltowski, K. Sangster, and W. S. O'Brien, "Catalytic reduction of SO₂ with methane over molybdenum catalyst," *Journal of Chemical Technology and Biotechnology*, vol. 67, no. 2, pp. 204–212, 1996.
- [26] X. Zhang, D. O. Hayward, C. Lee, and D. P. Mingos, "Microwave assisted catalytic reduction of sulfur dioxide with methane over MoS 2 catalysts," *Applied Catalysis B: Environmental*, vol. 33, no. 2, pp. 137–148, 2001.
- [27] D. J. Mulligan and D. Berk, "Reduction of sulfur dioxide with methane over selected transition metal sulfides," *Industrial & Engineering Chemistry Research*, vol. 28, no. 7, pp. 926–931, 1989.
- [28] N. Shikina, S. Khairulin, S. Yashnik, T. N. Teryaeva, and Z. R. Ismagilov, "Direct catalytic reduction of SO2 by CH4 over Fe-Mn catalysts prepared by granulation of ferromanganese nodules," *Eurasian Chemico-Technological Journal*, vol. 17, no. 2, pp. 129–136, 2015.
- [29] J.-J. Yu, Q. Yu, Y. Jin, and S. G. Chang, "Reduction of sulfur dioxide by methane to elemental sulfur over supported cobalt catalysts," *Industrial & Engineering Chemistry Research*, vol. 36, no. 6, pp. 2128–2133, 1997.
- [30] T. Zhu, A. Dreher, and M. Flytzani-Stephanopoulos, "Direct reduction of SO2 to elemental sulfur by methane over ceriabased catalysts," *Applied Catalysis B: Environmental*, vol. 21, no. 2, pp. 103–120, 1999.
- [31] T. Zhu, L. Kundakovic, A. Dreher, and M. Flytzani-Stephanopoulos, "Redox chemistry over CeO 2-based catalysts: SO2

reduction by CO or CH4," *Catalysis Today*, vol. 50, no. 2, pp. 381-397, 1999.

- [32] M. Flytzani-Stephanopoulos, T. Zhu, and Y. Li, "Ceria-based catalysts for the recovery of elemental sulfur from SO 2-laden gas streams," *Catalysis Today*, vol. 62, no. 2-3, pp. 145–158, 2000.
- [33] S. E. Mousavi, H. A. Ebrahim, and M. Edrissi, "Preparation of high surface area Ce/La/Cu and Ce/La/Ni ternary metal oxides as catalysts for the SO2 reduction by CH4," Synthesis and Reactivity in Inorganic Metal-Organic and Nano-Metal Chemistry, vol. 44, no. 6, pp. 881–890, 2014.
- [34] S. Ebrahim Mousavi, H. Pahlavanzadeh, and H. Ale Ebrahim, "Preparation, characterization and optimization of high surface area Ce-La-Cu ternary oxide nanoparticles," *E-Journal* of Surface Science and Nanotechnology, vol. 15, pp. 87–92, 2017.
- [35] A. Hossein Khangah, M. Javad Sarraf, H. Ale Ebrahim, and M. Tabatabaee, "Preparing and optimization of cerium-lanthanum-cobalt ternary mixed oxide as catalyst for SO2 reduction to sulfur," *E-Journal of Surface Science and Nanotechnology*, vol. 17, pp. 16–26, 2019.
- [36] R. Khalighi, F. Bahadoran, M. H. Panjeshahi, A. Zamaniyan, and N. Tahouni, "High catalytic activity and stability of X/CoAl₂O₄ (X = Ni, Co, Rh, Ru) catalysts with no observable coke formation applied in the autothermal dry reforming of methane lined on cordierite monolith reactors," *Microporous and Mesoporous Materials*, vol. 305, Article ID 110371, 2020.
- [37] M. Khani, S. E. Mousavi, H. Pahlavanzadeh, H. Ale Ebrahim, and A. Mozaffari, "Study of MoO₃-γAl₂O₃ catalysts behavior in selective catalytic reduction of SO₂ toxic gas to sulfur with CH4," *Environmental Science and Pollution Research*, vol. 26, no. 10, pp. 9686–9696, 2019.
- [38] M. Khani, S. E. Mousavi, R. Khalighi et al., "Cobalt oxidealumina catalysts for the methane-assisted selective catalytic reduction of SO2 to sulfur," *Heliyon*, vol. 9, no. 11, Article ID 21269, 2023.
- [39] V. O. Stoyanovskii, A. A. Vedyagin, A. M. Volodin et al., "Peculiarity of Rh bulk diffusion in La-doped alumina and its impact on CO oxidation over Rh/Al2O3," *Catalysis Communications*, vol. 97, no. 1, pp. 18–22, 2017.
- [40] T. K. R. de Oliveira, M. Rosset, and O. W. Perez-Lopez, "Ethanol dehydration to diethyl ether over Cu-Fe/ZSM-5 catalysts," *Catalysis Communications*, vol. 104, no. 1, pp. 32–36, 2018.
- [41] H. Ale Ebrahim and E. Jamshidi, "Synthesis gas production by zinc oxide reaction with methane: elimination of greenhouse gas emission from a metallurgical plant," *Energy Conversion* and Management, vol. 45, no. 3, pp. 345–363, 2004.
- [42] S. Karnjanakom, G. Guan, B. Asep et al., "A green method to increase yield and quality of bio-oil: ultrasonic pretreatment of biomass and catalytic upgrading of bio-oil over metal (Cu, Fe and/or Zn)/γ-Al 2O3," RSC Advances, vol. 5, no. 101, pp. 83494–83503, 2015.
- [43] H. Tang, C. Gunathilake, X. Zhou, and M. Jaroniec, "Polymertemplated mesoporous hybrid oxides of Al and Cu: highly porous sorbents for ammonia," *RSC Advances*, vol. 6, no. 45, pp. 38662–38670, 2016.
- [44] Y. Shi, E. Xing, K. Wu, J. Wang, M. Yang, and Y. Wu, "Recent progress on upgrading of bio-oil to hydrocarbons over metal/ zeolite bifunctional catalysts," *Catalysis Science and Technology*, vol. 7, no. 12, pp. 2385–2415, 2017.

- [45] M. Nafees, M. Ikram, and S. Ali, "Thermal behavior and decomposition of copper sulfide nanomaterial synthesized by aqueous sol method," *Digest Journal of Nanomaterials and Biostructures*, vol. 10, no. 2, pp. 635–641, 2015.
- [46] C. M. Simonescu, V. Teodorescu, O. Carp, L. Patron, and C. Capatina, "Thermal behaviour of CuS (covellite) obtained from copper-thiosulfate system," *Journal of Thermal Analysis* and Calorimetry, vol. 88, no. 1, pp. 71-76, 2007.
- [47] S. Hernández Guiance, I. D. Coria, I. M. Irurzun, and E. E. Mola, "Experimental determination of the activation energies of CH4, SO2 and O2 reactions on Cr2O3/γ-Al2O3," *Chemical Physics Letters*, vol. 660, no. 1, pp. 123–126, 2016.