Elementary sulfur recovery by H_2-regeneration of SO_2-adsorbed CuO/Al_2O_3—Effect of operation parameters

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Abstract

CuO/Al_2O_3 is capable of removing SO_2 and NO_X from flue gas simultaneously at around $400\,°C$. After the SO_2 removal, the SO_2-adsorbed CuO/Al_2O_3 needs to be treated to regenerate its SO_2 removal capacity and to recover the removed sulfur. This paper reports recent research on direct formation of elementary sulfur during H_2-regeneration of the SO_2-adsorbed CuO/Al_2O_3 through recycling of the regeneration tail gas. In such a way, the SO_2 removal, the sorbent-catalyst's regeneration and elementary sulfur recovery can be carried out in a single reactor. The operating parameters studied include the amounts of H_2 fed into the reactor, H_2 feed strategy and O_2 treatment of the H_2-regenerated CuO/Al_2O_3. An intermittent H_2 feeding mode is found to give a higher elementary sulfur yield (91%), less residual sulfur-compounds in the system after the regeneration, and higher SO_2 capacity in the subsequent SO_2 removal process. An O_2 treatment after the H_2-regeneration improves the elementary sulfur yield further and results in a number of other advantages.
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1. Introduction

CuO/Al_2O_3 is an important sorbent-catalyst for simultaneous SO_2 and NO_X removal from flue gas. During the SO_2 removal CuO reacts with SO_2 in the presence of O_2 to form $CuSO_4$, some of the Al_2O_3 may also react with SO_2 to form $Al_2(SO_4)_3$ [1,2]. Upon saturation of the CuO/Al_2O_3 by SO_2, it subjects to a regeneration treatment to convert $CuSO_4$ back to CuO (elementary Cu in some case) and gaseous SO_2 by a reducing gas such as H_2, NH_3, or CO [3–5]. The SO_2 released is then processed to either produce sulfuric acid through oxidization, or elementary sulfur through reduction by H_2, or ammonium sulfate through reaction with NH_3, or liquid SO_2 through condensation. All these processes need additional reactors and most of them need catalysts [6,7], which results in an increase in cost.

Our preliminary research shows that the regeneration of a SO_2-adsorbed CuO/Al_2O_3 and recovery of elementary sulfur can be carried out in the same reactor as for SO_2 removal, if H_2 is used and the tail gas from the H_2-regeneration is recycled back. In this case, the Cu species on CuO/Al_2O_3 serves

as the sorbent for SO_2 during the SO_2 removal stage and the catalyst for reduction of the released SO_2 to elementary sulfur during the regeneration stage. This simplifies the overall process. For example, at a temperature of $400\,°C$, CuO/Al_2O_3 can adsorb SO_2 from flue gas efficiently with a long-term stable SO_2 removal capacity close to the stoichiometric amounts of Cu in the CuO/Al_2O_3 and gives an elementary sulfur yield of 80% in the H_2-regeneration at the same temperature. After the H_2-regeneration, the Cu species in the sorbent-catalyst include mainly elementary Cu and a lesser amount of CuS. The CuS is possibly the catalyst for the elementary sulfur recovery, but it has no ability to adsorb SO_2 in the subsequent SO_2 removal stage. Furthermore, the CuS reacts quickly with O_2 in flue gas, which results in a short-time surge in SO_2 release and in a bed temperature increase upon oxygen contact with flue gas [4]. These reaction steps seriously influence the SO_2 removal capacity and long-term stability of CuO/Al_2O_3 and make the process control difficult.

In principle, the amount of CuS or elementary Cu formed in the H_2-regeneration is not constant but depends on the regeneration conditions. Therefore, it is possible to reduce the amounts of CuS through adjustments in regeneration conditions. This study investigates the effects of operating conditions on the effectiveness of the H_2-regeneration of a SO_2-adsorbed CuO/Al_2O_3 with

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aims for higher elementary sulfur yield, less remnants of CuS, and smaller SO_2 release and temperature increase at the early stage of the SO_2 removal. The study includes effects of H_2 feed, H_2 feed strategy and O_2 treatment in the H_2-regeneration.

2. Experimental

2.1. Sorbent preparation

A γ-Al_2O_3 support (30–60 mesh, BET surface area of 185 $m^2 g^{-1}$) is impregnated with an aqueous $Cu(NO_3)_2$ $3H_2O$ solution and then calcined at 500 °C for 8 h in a muffle furnace after drying at 50 °C for 8 h and at 110 °C for 5 h. The final sample contains about 8 wt.% CuO.

2.2. Experimental procedure

Fig. 1 is the flow chart of the overall process. First, the SO_2 removal step (the dot lines in Fig. 1) is carried out at 400 °C by feeding a simulated flue gas, containing 2200 ppm SO_2, 6% O_2 and balance N_2, to the fixed-bed reactor of 15 mm in diameter with 4 g CuO/Al_2O_3. When the SO_2 removal rate decreases from the initial 100% to 80%, the feed flue gas is switched to pure N_2 to purge the reactor for 30 min. The reactor is then fed with H_2, at a flow rate of 4 ml/min, and the recycled tail gas from the reactor at a flow rate of 400 ml/min, to start the regeneration and the elementary sulfur recovery steps (the solid lines in Fig. 1). The elementary sulfur formed is collected in the cold trap.

The compositions of the inlet and the outlet of the reactor (during the SO_2 removal stage) and the recycled gas composition (during the H_2-regeneration and elementary sulfur recovery stages) are all determined on-line by a Blazers QMG 422 quadrupolar mass spectrometer. The H_2 feeding rate and cumulative H_2 fed are controlled and measured by a mass flow controller. To prevent elementary sulfur condensation prior to the cold trap, the tubing between the reactor and the cold trap is maintained at 250 °C with a heating tape while the cold trap is maintained at room temperature. The regeneration and elementary sulfur recovery stages are terminated when the amount of elementary sulfur collected in the cold trap does not increase further. The elementary sulfur is then dried and weighed. The

yield of elementary sulfur is defined as:

$$Y_T(\%) = \frac{m_T}{M_T}$$

where Y_T is the sulfur yield at the regeneration temperature of T, m_T the mass of elementary sulfur collected at the regeneration temperature of T, and M_T is the mass of regenerable sulfur adsorbed on CuO/Al_2O_3 which equals the amount of elementary sulfur adsorbed in the subsequent SO_2 removal stage.

2.3. Characterization of the sorbent-catalyst

The amount of CuS is determined by the difference in water-soluble Cu (measured by ICP-AES, model Atomscan 16, manufactured by TJA, America) in the sorbent-catalyst before and after the conversion of CuS to $CuSO_4$. Sulfur content of the sorbent-catalyst samples are measured by elementary analysis (KZDL-3B, China). Chemical morphology of S and Cu in the sorbent-catalyst is characterized by X-ray photoelectron spectroscopy measurement, which is carried out on a PHI-5300 ESCA system using Al Kα radiation (1486.6 eV) at a residual pressure in the vacuum chamber of 10^{-10} Torr.

3. Results and discussion

3.1. Effect of H_2 feed

Fig. 2A shows the mass of elementary sulfur collected in millimole per gram of sorbent-catalyst at various total amounts of H_2 fed into the reactor at a regeneration temperature of 400 °C. Fig. 2B shows representative MS curves of SO_2 and H_2S obtained during one of the runs. The results show that SO_2 is the primary gas product of the H_2-regeneration as evidenced by the high SO_2 concentration at low H_2/Cu molar ratios. At a H_2/Cu ratio of 4.2 the SO_2 concentration starts to decrease and elementary sulfur starts to appear in the cold trap. The amount of elementary sulfur collected increases then with an increase in H_2/Cu ratio. These phenomena indicate conversion of SO_2
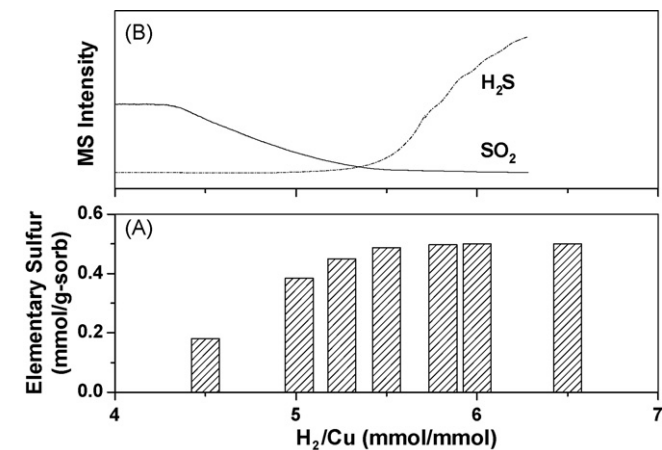

Fig. 1. Experimental apparatus.

Fig. 2. Effect of H_2 feed on elementary sulfur moles: data in A are obtained for different total amount of H_2; data in B show the changes of sulfur-gases during one of the run. Regeneration conditions: 400 °C, continuously fed H_2.
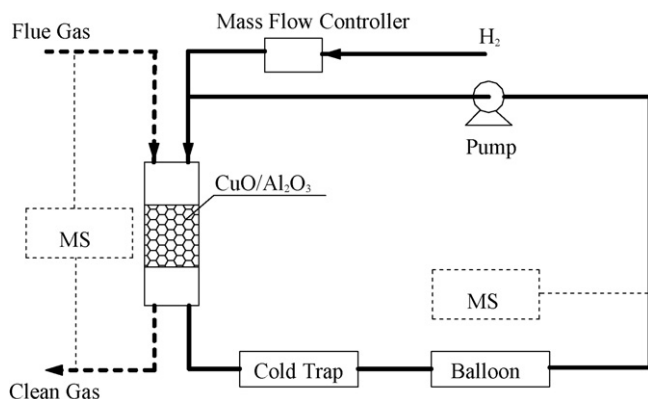
to elementary sulfur. The amount of elementary sulfur reaches a maximum at H_2/Cu ratios of around 5.7, where SO_2 concentration drops to the baseline. At a H_2/Cu ratio of 5.1 H_2S starts to appear in the gas phase, and its concentration increases with an increase in H_2/Cu ratio. These data suggest that H_2S is a secondary product of the regeneration, resulting from hydrogenation of SO_2 and the elementary sulfur formation is possibly affected by the concentration ratio of H_2S and SO_2. It is important to note that the retention time of the sorption reactor (Fig. 1) under the experimental conditions is about 11 min, corresponding to a superficial H_2/Cu ratio of 0.5, and the recycle always contains residual sulfur-containing gases during the regeneration. In this regard the starting and the ending point in H_2/Cu ratio for the elementary sulfur formation are about 3.7 and 4.7, respectively. These values seem to agree with the reaction stoichiometry for the formation of elementary sulfur and CuS under the H_2 atmosphere:
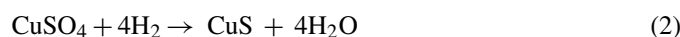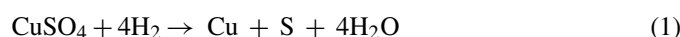
$$CuSO_4 + 4H_2 \rightarrow Cu + S + 4H_2O \tag{1}$$

$$CuSO_4 + 4H_2 \rightarrow CuS + 4H_2O \tag{2}$$

Fig. 3 shows the residual CuS content after completion of the H_2-regeneration at various H_2/Cu ratios and the amount of SO_2 released upon interaction of the newly regenerated sorbent-catalyst with the flue gas (with 6% O_2). The difference between CuS and SO_2 is the amount of $CuSO_4$ formed in the same time due to the reaction of SO_2 and CuO. Clearly the amount of residual CuS increases with an increase in H_2/Cu ratio, and a higher CuS content corresponds to a higher SO_2 release. These data suggest that about 37% SO_2 adsorbed on the CuO/Al_2O_3 stays on the sorbent-catalyst in the form of CuS and the rest of the SO_2 is converted to elementary sulfur. This amount of CuS is obviously too high if H_2 is fed continuously in the regeneration.

3.2. Effect of H_2 feed strategy

To reduce the CuS content, an intermittent H_2 feeding mode is tested in the regeneration. Fig. 4 shows changes in SO_2, H_2S and H_2 profile in the system during the regeneration. In Stage I,
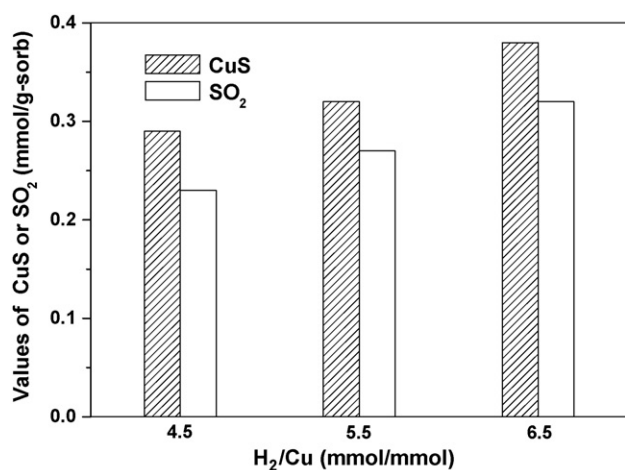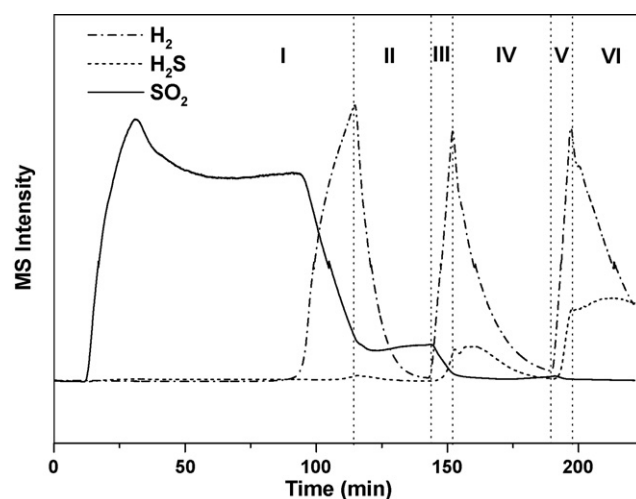

Fig. 4. Effect of intermittent H_2 feeding mode on gaseous composition: H_2 is fed continuously in stages of I, III and V; H_2 is stopped in stages of II, IV and VI. Regeneration conditions: 400 °C, H_2 feeding rate of 4 ml/min.

H_2 is fed continuously to the reactor at a flow rate of 4 ml/min. After about 11 min on stream, SO_2 starts to appear in a fast rate and reaches the maximum in 20 min, which is followed by a 20% decrease to a stable value. During this time period no elementary sulfur is found in the cold trap. At time on stream of 95 min H_2 breakthrough and SO_2 decrease are observed simultaneously, which are accompanied by elementary sulfur deposition in the cold trap. No H_2S is detected in Stage I. Stage II starts when H_2S is observed in the gas phase, and the feed H_2 is stopped. A fast decrease in H_2 concentration and a slight increase in SO_2 concentration are observed in this stage, indicating consumption of H_2. The H_2 feed is resumed in Stage III for 8 min. An immediate increase in H_2 concentration, an immediate decrease in SO_2 concentration and a delayed increase in H_2S concentration are observed. The Stage IV starts when H_2 feed is stopped again. Different from Stage II, SO_2 concentration shows no increase and H_2S concentration shows a slow decrease in this stage. In Stage V the H_2 feed is again resumed. Apparently, H_2S concentration increases in a much faster rate in this stage than does in Stage III. In Stage VI, the stop of the H_2 feed does not reduce H_2S concentration. The information contained in Fig. 4 suggests that (1) the regeneration consumes all the fed H_2 in the early state and yields only SO_2 before elementary sulfur is collected, indicating consumption of H_2 for SO_2 formation in this early state of regeneration; (2) when elementary sulfur is being formed, H_2S show the same trend as H_2, indicating its formation from hydrogenation of SO_2; (3) SO_2 shows an opposite trend in comparison to H_2 and H_2S, indicating its consumption involving a reaction with H_2S; (4) the formation of elementary sulfur is likely associated with the direct reaction between H_2S and SO_2.

Table 1 and Fig. 5 compare the results of the two H_2 feeding mode. Obviously, compared to the continuous H_2 feeding mode the intermittent H_2 feeding mode (1) converts more $CuSO_4$ into SO_2, resulting in a higher SO_2 removal capacity in the subsequent SO_2 removal process; (2) yields more elementary sulfur (91%) and less residual sulfur-containing gases in the system after the regeneration; (3) yields less CuS in the sorbent after

Fig. 3. Residual CuS in CuO/Al_2O_3 after H_2-regeneration with different H_2/Cu and the released SO_2 amounts in subsequent initial sulfation stage.

Table 1
Effect of H_2 feed mode on the released SO_2 and SO_2 removal capacity in the subsequent sulfation process

H_2 feeding mode	SO_2 capacity (mmol/g-sorb)	Elementary sulfur (mmol/g-sorb)	Released SO_2 (mmol/g-sorb)	Residual sulfur-gases (mmol/g-sorb)
Intermittent	0.64	0.56	0.25	0.08
Continuous	0.60	0.50	0.30	0.10
Continuous with O_2 treatment	0.56	0.53	0	0

SO_2 capacity = SO_2 absorbed in the total sulfation − SO_2 released in the initial sulfation.

the regeneration, corresponding to less SO_2 released from oxidation of CuS; (4) consumes less H_2 in the regeneration. These results show that the amounts of CuS and H_2S can be controlled and the elementary sulfur yield can be significantly improved simply by adjustment in H_2 feeding strategy.

3.3. Effect of O_2 treatment after the H_2-regeneration

The residual sulfur-containing gases in the system are mainly H_2S and H_2 (no SO_2) after the continuous regeneration mode, while the solid sulfur in the sorbent is mainly CuS. Thus, an input of some amounts of O_2 may transform CuS into CuO and SO_2 and result in more reaction between H_2S and SO_2 to form elementary sulfur. Fig. 6 shows SO_2 and H_2S profiles during the continuous regeneration mode followed by replacement of the H_2 feed by an air feed at 10 ml/min at a time on stream of 140 min. It is interesting to note that the O_2 in the air completely disappeared from the gas phase for 50 min of the air introduction. The O_2 breakthrough occurs only when H_2S in the gas phase undergoes fast decreases to the baseline, and no SO_2 is observed in the gas during the whole air treatment. These phenomena are accompanied by a slight increase in bed temperature, from 400 °C to 408 °C, and a significant increase in elementary sulfur yield, from 83% to around 95%. Fig. 7 shows MS signals of SO_2 during the early stage of the SO_2 removal process using a sorbent-catalyst regenerated with the O_2 treatment (Fig. 7A) and without the O_2 treatment (Fig. 7B). The absence of SO_2 peak in

Fig. 7A suggests the absence of CuS in the sorbent-catalyst after the O_2 treatment. The bed temperature in these two cases is also different, no visible change for the sample with the O_2 treatment but a fast increase from 400 °C to 435 °C for the sample without the O_2 treatment. It is to be noted that the temperature change may also result from the reaction between Cu and O_2, in addition to that between CuS and O_2.

The O_2 treatment also eliminates the residual gaseous sulfur in the system, a portion of it is transformed into elementary
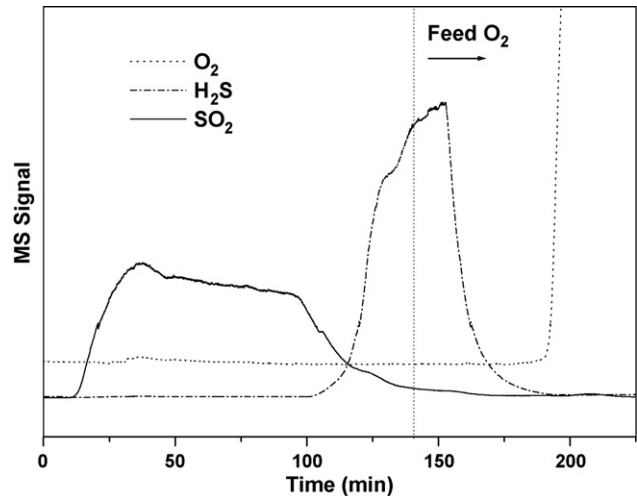

Fig. 6. Changes of gaseous composition in the system with O_2 treatment after continuous H_2-regeneration. Regeneration temperature: 400 °C.
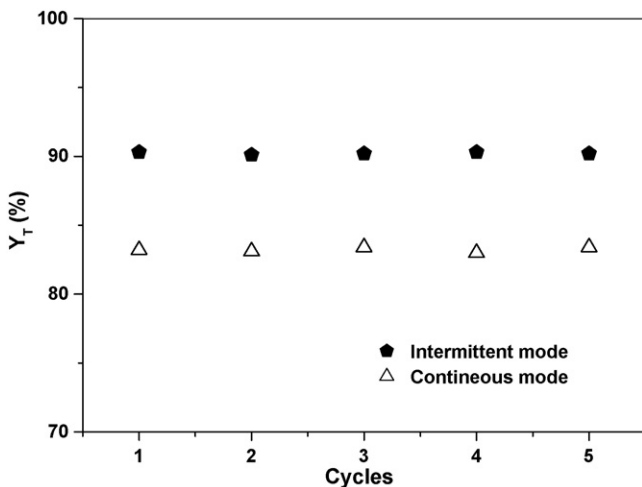

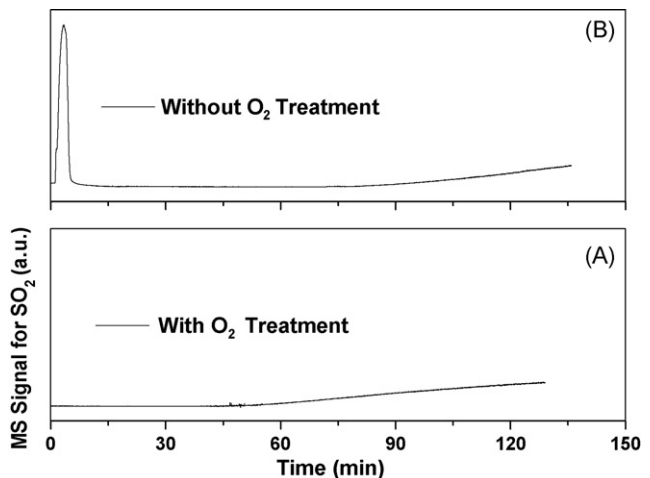Fig. 5. Effect of H_2 feeding mode on elementary sulfur yield. Regeneration temperature: 400 °C.

Fig. 7. MS signals of SO_2 in subsequent sulfation of CuO/Al$_2$O$_3$ with or without O_2 treatment in H_2-regeneration. Temperature: 400 °C.
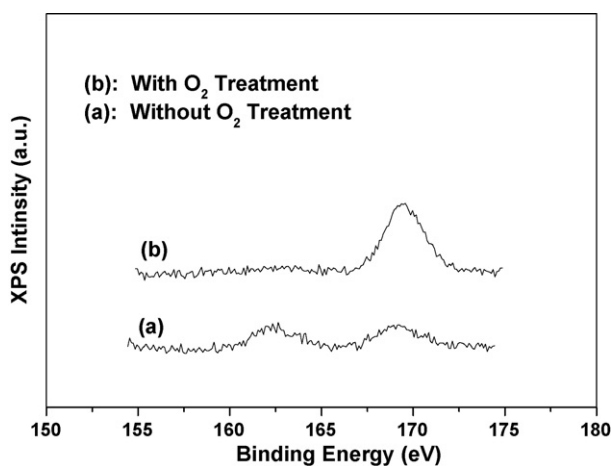
Fig. 8. XPS spectra of S 2p in CuO/Al$_2$O$_3$ with or without O$_2$ treatment after H$_2$-regeneration.

sulfur and the rest of it is being adsorbed by the sorbent-catalyst in the form of CuSO$_4$.

Fig. 8 shows XPS spectra of S 2p of CuO/Al$_2$O$_3$ subjected to the regeneration with and without the O$_2$ treatment. For the case without the O$_2$ treatment (Fig. 8a), the sample shows two peaks at 163 eV and 169 eV, which can be assigned to S^{2-} and S^{6+}, corresponding to the sulfur in CuS and Al$_2$(SO$_4$)$_3$, respectively. For the case with the O$_2$ treatment (Fig. 8b), the sample shows only one stronger peak at 169 eV indicating the absence of S^{2-} and increased S^{6+}. These results agree with the earlier discussion that the O$_2$ treatment converts CuS into CuSO$_4$.

4. Conclusions

After flue gas SO$_2$ removal at around 400 °C, the SO$_2$-adsorbed CuO/Al$_2$O$_3$ can be regenerated in H$_2$ at the same temperature to recover its SO$_2$ removal activity and obtain elementary sulfur simultaneously if the tail gas from the regeneration is recycled back to the reactor. The amount of H$_2$ fed and the H$_2$ feeding strategy are important parameters that determine the concentrations of SO$_2$ and H$_2$S in the system, and in turn the elementary sulfur yield and the SO$_2$ capacity in the subsequent SO$_2$ removal process. Intermittent H$_2$ feeding mode is preferred due to its ability to adjust the SO$_2$ to H$_2$S ratio for high elementary sulfur yields. Under the conditions used in this paper an elementary sulfur yield of 91% is obtained. An O$_2$ treatment of the regenerated CuO/Al$_2$O$_3$ after the H$_2$-regeneration increases the elementary sulfur yield further, eliminates the residual sulfur-containing gases in the system, and converts CuS and Cu into CuO and CuSO$_4$, which is very important for the long-term stability of CuO/Al$_2$O$_3$ since SO$_2$ and temperature peaks during the early stage of the SO$_2$ removal process are safely eliminated.

Acknowledgement

References

[1] M. Waqif, O. Saur, J.C. Lavalley, S. Perathoner, G. Centi, J. Phys. Chem. 95 (1991) 4051.
[2] K.S. Yoo, S.D. Kim, S.B. Park, Ind. Eng. Chem. Res. 33 (1994) 1786.
[3] K.S. Yoo, S.M. Jeong, S.D. Kim, S.B. Park, Ind. Eng. Chem. Res. 35 (1996) 1543.
[4] G.Y. Xie, Z.Y. Liu, Z.P. Zhu, Q.Y. Liu, J.R. Ma, Appl. Catal. B 45 (2003) 213.
[5] G. Centi, N. Passarini, S. Perathoner, A. Riva, Ind. Eng. Chem. Res. 31 (1992) 1947.
[6] S.C. Paik, J.S. Chung, Appl. Catal. B 5 (1995) 233.
[7] S.C. Paik, J.S. Chung, Appl. Catal. B 8 (1996) 267.