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Recovery of elemental sulphur via selective catalytic reduction of SO_2 over sulphided CoMo/γ-Al_2O_3 catalysts

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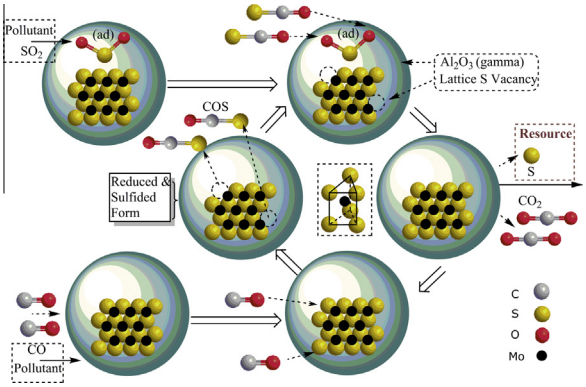
HIGHLIGHTS

- Sulphided CoMo/γ-Al_2O_3 catalysts were prepared based on orthogonal design.
- Near 100% efficiency was achieved for the removal of SO_2 from flue gas.
- SO_2 is completely converted into elemental S by the Al-S_{400}-0.31 catalyst.
- Mechanism for selective catalytic reduction of SO_2 to elemental S was proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

This study aimed to develop sulphided CoMo/γ-Al_2O_3 catalysts to recover elemental sulphur via selective reduction and to understand the catalytic mechanism of the selective catalytic reduction (SCR) of SO_2 into sulphur when CO is used as the reducing agent. A series of catalysts were prepared based on Taguchi's L_9 orthogonal array and were evaluated in terms of their SO_2 conversion efficiency, selectivity of SO_2 reduction to elemental sulphur, elemental sulphur yield, and selectivity of COS formation. It is found that the catalyst sulphided at 400 °C with a ratio of Co/(Co + Mo) = 0.31 and supported on γ-Al_2O_3 had the best performance among all the catalysts studied. In addition, the physical–chemical properties and catalytic activities of this catalyst were studied systematically. The mechanism of selective reduction of SO_2 to elemental sulphur using CO as the reducing agent was therefore proposed.

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1. Introduction

Sulphur dioxide (SO_2) together with nitrogen oxides (NO_x) are the major pollutants in coal-fired flue gas [1]. The emission of these gaseous pollutants by coal-fired power plants has caused severe environmental problems, such as haze, acid rain and soil acidification [2]. The development of cost-effective technologies for the removal of these pollutants in flue gas is therefore of great importance and has attracted significant attention worldwide. Currently, limestone-scrubbing process is widely used in coal-fired power plants for SO_2 removal. However, this process has some drawbacks, such as inevitable solid wastes disposal, high water consumption, the need of waste water treatment, dust emission etc. [3].

In the past few decades, much effort had been made to develop selective catalytic reduction catalysts for the selective reduction of NO_x in flue gas [4,5]. However, in recent years, the selective reduction of SO_2 to its elemental form to avoid associated environmental

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problems as well as to recover elemental sulphur as a saleable product has gained more and more attentions [6]. The major challenges to achieve this include to develop novel catalysts for selective reduction and to find suitable reducing agents for the reduction reaction(s). Various reactants, such as H_2 [7], CO [8], carbon [9], CH_4 [10] and C_2H_4 [11], have been tested as the reducing agents for the reduction reaction. Among these potential reducing agents for commercial use, CO is a choice of better potential not only because it co-exists with SO_2 in flue gas [12,13], but also because the reaction is thermodynamically favoured.

Several catalysts, such as Pt-Au bimetallic catalyst [12,14], La_2O_2S catalyst [15,16], were developed for the selective reduction of SO_2. In spite of good catalytic performance in SO_2 reduction to elemental sulphur using CO as an agent, the use of expensive noble metals and rare earth metals as the active components limits the large-scale use of these catalysts. Therefore, transition metals become obvious cost-effective alternatives. For these transition metal-based catalysts, it is their sulphided phase rather than their oxided phase that plays a key role in their catalytic performance [17–19]. To date, catalysts with sulphided CoMo, NiMo, etc as active components have already been widely used for the catalytic removal of sulphur from petroleum products in hydrodesulphurization (HDS) processes [20–22].

Although much effort was made to understand the catalytic reduction of $CoMo/Al_2O_3$ catalyst, there are still needs for the development of better catalysts as well as for the understanding of the mechanism for the recovery of elemental sulphur from flue gas. In this research, a series of $CoMo/\gamma\text{-}Al_2O_3$ catalysts were prepared and studied to convert SO_2 in flue gas into elemental sulphur. Systematic characterisation of selective reduction of SO_2 was conducted to understand the mechanism of SO_2 reduction into elemental sulphur.

2. Experimental

2.1. Orthogonal design of catalysts

A taguchi's orthogonal array L_9 was used for the screening of sulphided $CoMo/\gamma\text{-}Al_2O_3$ catalysts. Co loading, Mo loading and the temperature for sulphurization were selected as the control parameters, which were previously found to have significant influence on the performance of desulphurization catalysts [17,18,23]. Table 1 shows the examined factors and selected levels of the catalysts. The catalysts are designated as Al–S_t–λ, where **Al** represents $\gamma\text{-}Al_2O_3$, $\mathbf{S_t}$ represents sulphurization temperature of the catalyst and λ represents the mass ratio of Co/(Co + Mo). Because of this experimental design, to screen a good candidate catalyst, the number of catalysts to study is effectively reduced from 27 runs to 9 runs.

2.2. Preparation of catalysts

Sulphided $CoMo/\gamma\text{-}Al_2O_3$ catalysts were prepared using a combination of incipient wetness impregnation (IWI) and sulphur-chemical vapour deposition (S-CVD) methods. A commercial $\gamma\text{-}Al_2O_3$ (V-SK Co., Ltd., with a size range of 1.18 mm to 1.70 mm and a surface area of around 200 m^2/g) was used as the support whilst $Co(NO_3)_2{\cdot}6H_2O$ and $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (99.0% analytical grade, Sinopharm Chemical Reagent Co, Ltd.) were used as the metal precursors. A similar preparation procedures are described elsewhere [17,18].

2.3. Examination of catalytic activity

In this study, CO was used as the reducing agent. A mixture of SO_2, N_2 and CO in a desired molar ratio was used to simulate flue gas emitted at coal-fired power plants. Catalyst was loaded into a fixed-bed reactor with an inner diameter of 12 mm. The simulated flue gas with a flow rate of 1200 ml/min was introduced into the reactor. Concentrations of SO_2, CO and O_2 for both inlet and outlet gases were measured using a flue gas analyser (Testo 350 Pro, Germany). The concentration of COS was determined using a gas chromatograph (Shimadzu GC-2014, Japan). Each catalyst was tested at a desired reaction temperature ranging from 200 °C to 450 °C under atmospheric pressure. The results of SO_2 conversion efficiency, selectivity of SO_2 reduction to elemental sulphur, elemental sulphur yield and selectivity of COS formation are determined as follows (Eqs. (1)–(4)):

$$SO_2\text{conversion efficiency}\ (\%) = \frac{[SO_2]_{in} - [SO_2]_{out}}{[SO_2]_{in}} \times 100 \quad (1)$$

$$\text{Selectivity of } SO_2\text{ reduction to S}\ (\%) = \frac{[SO_2]_{in} - [SO_2]_{out} - [COS]_{out}}{[SO_2]_{in} - [SO_2]_{out}} \times 100 \quad (2)$$

$$\text{Elmental sulphur yield}\ (\%) = \frac{[SO_2]_{in} - [SO_2]_{out} - [COS]_{out}}{[SO_2]_{in}} \times 100 \quad (3)$$

$$\text{Selectivity of COS formation}\ (\%) = \frac{[COS]_{out}}{[SO_2]_{in} - [SO_2]_{out}} \times 100 \quad (4)$$

2.4. Characterisation of catalysts

Micromeritics ASAP 2020 was used to measure the specific surface area, pore volume and pore width. The existence of elements

Table 1
Catalyst design based on an L_9 orthogonal array.

Factors	*A* (Co/wt%)	*B* (Mo/wt%)	*C* (Sulphurization/°C)	*D* (Co/(Mo + Co) ratio)
Level				
Level 1	3	10	350	–
Level 2	6	15	400	–
Level 3	9	20	450	–
Catalysts				
Cat. 1	3	10	350	0.23
Cat. 2	3	15	400	0.17
Cat. 3	3	20	450	0.13
Cat. 4	6	10	400	0.38
Cat. 5	6	15	450	0.29
Cat. 6	6	20	350	0.23
Cat. 7	9	10	450	0.47
Cat. 8	9	15	350	0.38
Cat. 9	9	20	400	0.31

Cat. 1 – Cat.9 are the code used for 9 catalysts identification in the array.

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