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Reduction of SO_2 by CO under plasma-assisted catalytic system induced by microwave

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Microwave plasma-assisted catalytic reduction of SO_2 by CO was studied over four catalysts. The activities of the four catalysts under microwave plasma decreased in the order of $CoO/\gamma\text{-}Al_2O_3 \gg SnO_2 >$ copper wires > iron wires, which was consistent with the results under conventional heating. By comparing the activity of $CoO/\gamma\text{-}Al_2O_3$ catalyst in the microwave plasma mode with that in the conventional mode, it is demonstrated that the temperature at which the full SO_2 conversion was obtained in the microwave plasma mode was about 200 °C lower than that under the conventional heating mode. Moreover, an increase of space velocity had little effect on SO_2 conversion and sulfur selectivity under microwave plasma; while under conventional heating mode, both SO_2 conversion and sulfur selectivity significantly decreased with an increase of space velocity.

KEY WORDS: microwave plasma; catalytic reduction; SO_2; CO.

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 (FGD) processes are mostly of the throwaway 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. An alternative approach to remove SO_2 is the catalytic reduction of SO_2 to elemental sulfur, which can be applied directly to flue gases containing a small amount of oxygen or to the case where SO_2 in the flue gas is isolated or concentrated using a proper adsorption/regeneration system [2]. Especially when CO is used as a reducing agent, both SO_2 and CO can be removed simultaneously from the flue gas. From this point of view, the catalytic reduction of SO_2 by CO to sulfur is desirable and has received much attention in recent years. Various types of catalysts have been investigated for this reaction under conventional furnace-heating, including alumina-supported transition metals [3–7], mixed oxides [8–10] and perovskite type oxides [11,12].

Recently, the concept of using plasma as an activation source for chemical reactions has been extensively studied. Plasma state is generated by the ionization process that occurs due to collision of ingoing molecules with electrons [13]. Since plasma is composed of highly excited atomic, molecular, ionic and radical species, it can offer a unique way to induce gas phase reactions, such as microwave plasma for methane decomposition [14] and dielectric barrier discharges (DBDs) plasma for ozone generation [15]. However, plasma processes are not always selective. In contrast, it is known that catalytic processes can be very selective but often require a certain gas composition and a sufficiently high temperature [16]. Thus, novel results have been obtained in many catalytic reactions by coupling the plasma process with heterogeneous catalysis. For example, Kunimori *et al.* found that nitrogen was chemisorbed on a Ru catalyst during a N_2 plasma discharge and the chemisorbed N species reacted with H to form NH_3 even at room temperature [17]. Heintze and Pietruszka compared purely catalytic process with plasma-assisted catalytic process to differentiate the effects of plasma activation from catalytic process in the partial oxidation of methane. They found that the catalyst alone was only active above 300 °C, whereas plasma induced partial oxidation of methane occurred in the entire temperature range investigated (100–400 °C) [18]. Similarly, the work of Mutel *et al.* indicated the use of low-pressure plasma in the synthesis of nitrogen oxide can lower the energy costs by 53% in comparison with the industrial process used at present [19]. In our laboratory, continuous

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microwave plasma was obtained at atmospheric pressure that does not require the use of electrodes and some attractive results have been achieved in NO_x removal by using this process [20–22].

Compared to other plasma technologies, such as AC (alternating current) and DC (direct current) discharge plasma, microwave discharge plasma is energy-efficient because a large amount of energy goes into the production of energetic electrons rather than into gas heating [22]. In this paper, the catalytic activities of four types of material were investigated under microwave plasma. At 311 °C, 99.7% of SO_2 conversion was obtained over $CoO/\gamma\text{-}Al_2O_3$ catalyst under microwave plasma, which is about 200 °C lower than that under conventional heating. Moreover, an increase of space velocity had little effect on SO_2 conversion and sulfur selectivity under microwave plasma.

2. Experimental

2.1. Catalyst preparation

Four types of material (copper wires, iron wires, SnO_2 and $CoO/\gamma\text{-}Al_2O_3$) that easily induce microwave plasma were used as catalysts in this study. Copper wires and iron wires (approximately 3 mm long and 0.5 mm in diameter) were polished with sand paper before use. $CoO/\gamma\text{-}Al_2O_3$ was prepared by impregnating $\gamma\text{-}Al_2O_3$ support (home-made, surface area 238 m^2/g, pore volume 0.35 cm^3/g) with an aqueous solution of $Co(NO_3)_2 \cdot 6H_2O$ (AR grade, Shenyang Agent Company, China) to give 10 wt.% Co loading that was calculated on the oxide basis. Tin dioxide (AR grade, Shenyang Agent Company, China) and $CoO/\gamma\text{-}Al_2O_3$ were both pelletized and sieved to 40–60 mesh before use.

2.2. Microwave plasma unit

The microwave plasma unit is shown in figure 1. It consists of a 200 W, 2.45 GHz magnetron microwave source, connected through a rectangular waveguide to a single-mode resonant cavity that was terminated with a tuning plunger. With this unit, the resonance of the microwave irradiation on the catalysts could be easily tuned. The cavity was equipped with taps to measure the incident and reflected power. A tubular quartz reactor with 6 mm i.d. was aligned vertically at the center of the cavity, so that it is positioned in the region of maximum microwave field intensity. Because the microwave is mainly absorbed by the catalyst located at the outer part of the reactor, the inner part of the quartz reactor was blanked such as empty torus [23]. The reactor was filled with 0.2 g catalyst for each run. An infrared pyrometer (Shanghai Institute of Technical physics, PR China) with temperature range of 150–1000 °C was used to measure the temperature of the catalyst bed.

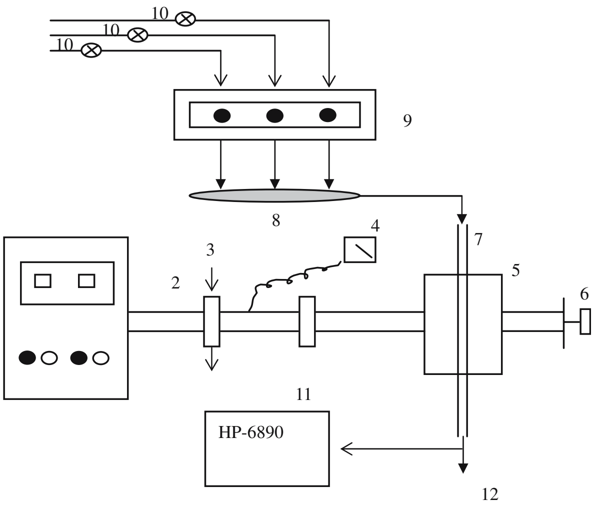

Figure 1. Schematic diagram of microwave plasma experiment: (1) microwave generator; (2) wave guide; (3) cooling water; (4) reflectometer; (5) resonant cavity; (6) tuning plunger; (7) quartz reactor; (8) mixing cylinder; (9) mass flowmeter; (10) valve; (11) gas chromatograph; (12) vent

2.3. Activity test

The catalytic reaction between SO_2 and CO was carried out in a fixed-bed flow reactor system under microwave plasma or conventional furnace-heating at atmospheric pressure. A mixture of 10,000 ppm CO and 5000 ppm SO_2 in balanced helium was used as reactant. Because metal sulfide was the active species for this reaction [6,10], $CoO/\gamma\text{-}Al_2O_3$ was presulfided with the reactant mixture at 500 °C for 2 h under conventional heating before reaction. The effluent gas passed through an ice-water trap, where elemental sulfur was condensed. SO_2 and COS in the effluent gas were separated by Gaspro Capillary and detected by FPD, while CO and CO_2 were separated by Porapack Q and detected by TCD. The percent conversion (X) of SO_2 and selectivity (S_{sulfur}) of elemental sulfur are defined as follows:

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

$$S_{\text{sulfur}} = \frac{[SO_2]_{\text{in}} - [SO_2]_{\text{out}} - [COS]_{\text{out}}}{[SO_2]_{\text{in}} - [SO_2]_{\text{out}}} * 100\%,$$

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

3. Results and discussion

3.1. Microwave plasma induced by four materials

In this study, we chose four types of material as the catalysts, including $CoO/\gamma\text{-}Al_2O_3$, iron wires and copper wires. Reduction of SO_2 by CO was performed by

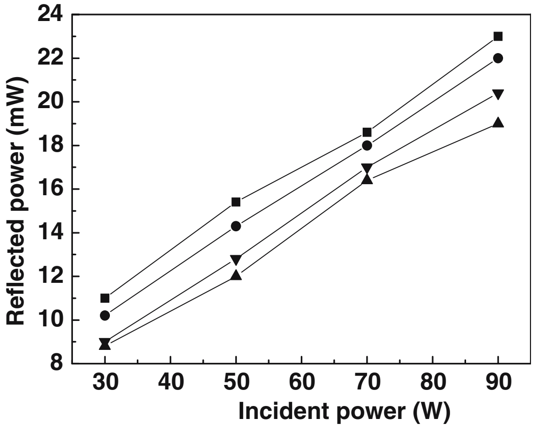

Figure 2. Effect of incident power on reflected power. (▼) CoO/γ-Al_2O_3; (▲) SnO_2; (●) copper wires; (■) iron wires

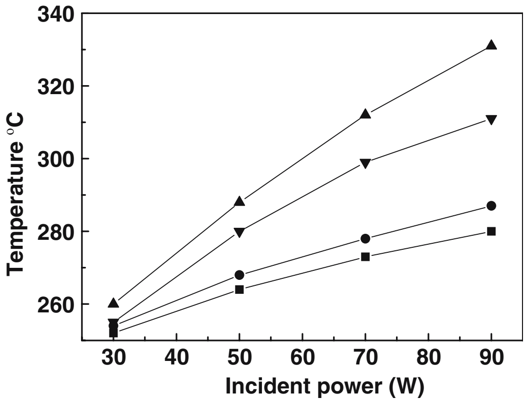

Figure 3. Effect of incident power on temperature. (▼) CoO/γ-Al_2O_3; (▲) SnO_2; (●) copper wires; (■) iron wires

means of microwave plasma in a controlled manner. Prior to plasma generation, the catalysts were treated in He flow (flow rate: 60 ml/min) under 60 W microwave irradiation for a few minutes. Microwaves were coupled to the catalyst bed, and reflected power was minimized by adjusting the tuning plunger. When plasma was formed, the reflected microwave power dropped rapidly to the smallest value and stable plasma was obtained over the catalyst bed in atmospheric condition. After irradiation for 40 min, the He flow was switched to the feed gas. The reflected power was measured at different input power for the four catalysts, and the values are shown in figure 2. It can be seen that the reflected power almost linearly increased with the incident power and its value was very low with respect to the incident power (less than 0.04%), indicating that the microwave efficiency induced by the four materials was very high. Moreover, the reflected power of the four catalysts decreased in the order of iron wires > copper wires > CoO/γ-Al_2O_3 > SnO_2. Besides inducing microwave plasma, the catalysts can also absorb part of the microwave energy, thus increasing the temperature of the catalyst bed. As shown in figure 3, the temperatures of the catalyst bed increased with the input power, and varied with the catalyst material in the order of iron wires < copper wires < CoO/γ-Al_2O_3 < SnO_2. Tin dioxide and Co species absorbs microwave energy more efficiently than iron wires and copper wires, which results in much higher temperatures for SnO_2 and CoO/γ-Al_2O_3 than the other two at the same incident power.

Microwave plasma displays a certain color. Tang *et al.* [21] observed red plasma over Fe/HZSM-5, while Roh *et al.* [23] reported light blue-colored plasma was formed over Co_3O_4/SiC. In our experiment, we noted that the color of plasma varied with the gas composition and the catalysts used. Table 1 lists the colors of the microwave plasma that were induced by the four catalysts under different gas compositions. The different color of plasma may be due to the different excited species that were produced from the collisions of molecules or ions with energetic electrons.

Table 1
Color of microwave plasma induced by four materials in different atmosphere

Catalyst	He	5000 ppm SO_2 + 10,000 ppm CO + He
Iron wires	White	Green
Copper wires	White	Green
SnO_2	Red	Blue
CoO/γ-Al_2O_3	Red	Purple

3.2. *Plasma-assisted catalytic performances*

To discriminate between the effects of plasma activation and catalytic process in the SO_2 reduction by CO, the performances of the four catalysts were first studied under conventional heating, and the results are illustrated in figure 4. It can be seen that neither iron wires nor copper wires showed any catalytic activity for SO_2 reduction by CO, while SnO_2 only had a very low catalytic activity. In contrast, CoO/γ-Al_2O_3 showed a much higher catalytic activity, with a 100% SO_2 conversion at 540 °C.

Figure 5 presents the results of SO_2 reduction by CO under microwave plasma over the four catalysts. Both iron and copper wires can induce plasma easier than CoO/γ-Al_2O_3 and SnO_2. Plasma can be achieved over iron wires and copper wires when input power was as low as 10 W. Whereas 30 W was required for CoO/γ-Al_2O_3 and SnO_2 to induce microwave plasma. However, for the plasma-assisted catalytic reaction between SO_2 and CO, the activity trend is not consistent with the capability of plasma generation. For instance, over copper wires and iron wires, SO_2 conversion maintained constantly at a low level (13–15%) regardless of input microwave power. Over SnO_2, SO_2 conversion was only slightly higher than that over copper and iron wires, but still below 30%. In contrast, for CoO/γ-Al_2O_3, once the plasma is generated, it can provide high SO_2 conversion

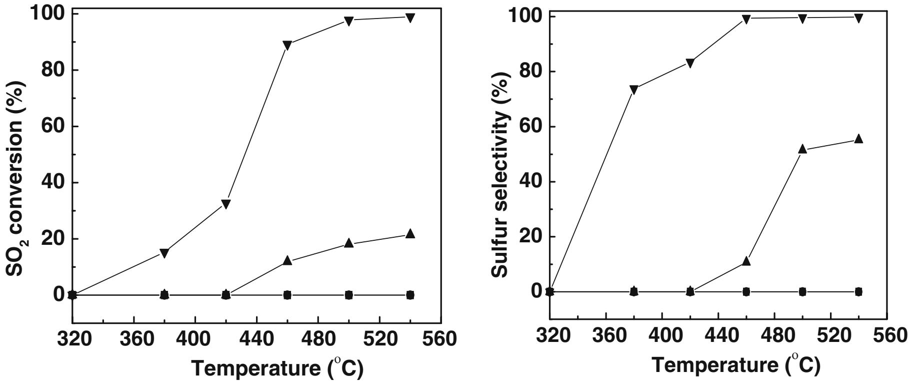

Figure 4. Effect of temperature on SO_2 conversion and sulfur selectivity under conventional heating (Feed compositions: 5000 ppm SO_2 and 10,000 ppm CO, SV = 18,000 ml/g. h). (▼) CoO/γ-Al_2O_3; (▲) SnO_2; (●) copper wires; (■) iron wires.

and sulfur selectivity. Moreover, SO_2 conversion increased with the microwave power. The sulfur selectivity had a similar trend to the SO_2 conversion within the investigated power range. Table 2 lists the results of plasma-assisted catalytic reaction over the four catalysts at a power of 90 W. 98.7% of SO_2 conversion and 100% of sulfur selectivity were obtained over CoO/γ-Al_2O_3 at a power of 90 W, which is corresponding to the reaction temperature of 311 °C. It is worthwhile to note that under conventional heating mode (see figure 4), the CoO/γ-Al_2O_3 catalyst did not exhibited any catalytic activity at the same reaction temperature and only at above 500 °C, the same activity can be obtained. More importantly, iron and copper wires, which were completely inactive under the conventional heating mode, exhibited some activity for SO_2 reduction with CO, though their activity level was much lower than that of CoO/γ-Al_2O_3. This result is similar to that obtained by Tang *et al.* [20], and strongly suggests that plasma play a significant role in activating the reactant molecules. Assuming that the activity of iron and copper is due to the pure contribution of microwave plasma, the superior activity of CoO/γ-Al_2O_3 can be attributed to the synergism of catalyst and plasma.

Table 3 lists the activity change with the variation of space velocity over CoO/γ-Al_2O_3 under two different reaction modes. It can be seen that under microwave plasma an increase of space velocity had little effect on SO_2 conversion and sulfur selectivity. However, under conventional heating mode, both SO_2 conversion and sulfur selectivity significantly decreased with an increase of space velocity. For instance, when the space velocity increased from 18,000 to 36,000 ml/g h, SO_2 conversion and sulfur selectivity almost decreased to half of the initial values. Such a capability of retaining high catalytic performances even at very high space velocity is an outstanding feature of microwave plasma-assisted catalysis.

From above results, we can see that plasma-assisted CoO/γ-Al_2O_3 catalyst showed remarkably high activity for the reduction of sulfur dioxide by carbon monoxide in comparison with conventional reaction mode. It is likely that the catalytic reaction pathways in the microwave plasma are different from those in the conventional heating. In the conventional heating mode, reactant molecules were first adsorbed on the surface of catalyst, and were activated when enough energy was obtained. Then the activated molecules reacted on the

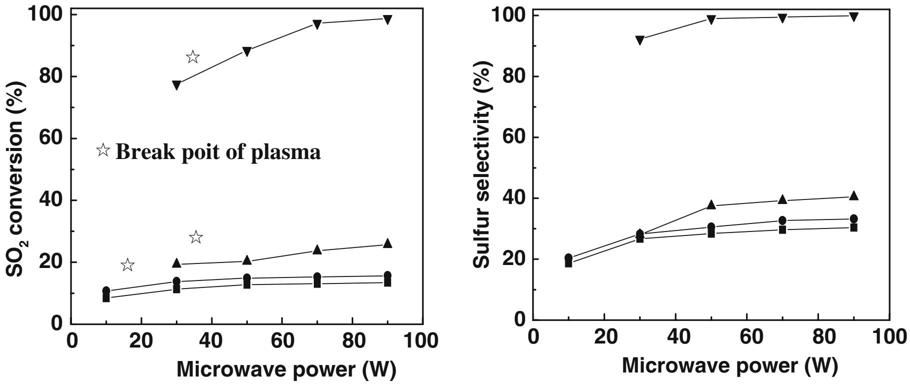

Figure 5. Effect of microwave power on SO_2 conversion and sulfur selectivity (Feed compositions: 5000 ppm SO_2 and 10,000 ppm CO, SV = 18,000 ml/g h). (▼) CoO/γ-Al_2O_3; (▲) SnO_2; (●) copper wires; (■) iron wires.

Table 2

SO_2 reduction by CO over four different microwave plasma-assisted catalytic systems[a]

Catalyst	SO_2 conversion (%)	Sulfur selectivity (%)	Temperature (°C)	Reflected power (mW)
Iron wires	13.4	30.4	280	23
Copper wires	15.6	33.2	287	22
SnO_2	25.8	99.96	311	20

[a] Reaction conditions: $CO/SO_2 = 2$; SV = 18,000 ml/g h; microwave power = 90 W.

Table 3

Effect of space velocity on SO_2 conversion and sulfur selectivity under different reaction mode over $CoO/\gamma\text{-}Al_2O_3$

Reaction mode	SV (ml/g h)	SO_2 conversion (%)	Sulfur selectivity (%)
Microwave plasma-assisted catalytic[a]	18,000	98.72	99.96
	27,000	98.42	99.75
	36,000	98.04	99.43
Conventional heating[b]	18,000	97.85	99.61
	27,000	77.44	80.37
	36,000	51.84	59.13

[a] Input microwave power: 90 W.

[b] Reaction temperature: 500 °C.

catalyst surface. In the case of the conventional heating, reactant molecules gain energy by thermal conduction, thus high reaction temperature is required. However, in the microwave plasma mode, a large amount of high-energy electrons are provided by He gas which suffers the microwave irradiation [22]. The difference between the electrons and the heavy ions is large, and the average temperature of the reacting gas is comparatively low [24]. These electrons with high energy and long lifetime can transfer energy to the reactant molecules by collision, and the reactant molecules are activated easily and fast by this mode. Over the catalytically inert iron and copper wires, the reaction between activated SO_2 and CO is mainly dependent on the probability of collision; hence SO_2 conversion and sulfur selectivity is limited. However, when the $CoO/\gamma\text{-}Al_2O_3$ that is catalytically active for SO_2 reduction by CO was located in the microwave plasma reactor, the reactant molecules activated by microwave plasma can be adsorbed on the surface of the catalyst and subsequently react selectively by catalytic function.

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