Performance for the catalytic CO oxidation over the Mo\textsubscript{0.5}Sn\textsubscript{9}Co\textsubscript{90.5}O\textsubscript{2} catalyst

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Abstract. In this study, carbon monoxide catalytic oxidant MoSnCoO\textsubscript{x} was prepared by coprecipitating method to investigate the effect of MoO\textsubscript{3} addition amount on catalyst activity. Meanwhile, the sulfur and water resistance of the catalysts were researched by simulating the industrial conditions of sintering smoke emission. The samples were studied using BET, XRD, SEM and H\textsubscript{2}-TPR techniques. The results revealed that catalyst added with 0.5% MoO\textsubscript{3} had better activity than the original Sn\textsubscript{9}Co\textsubscript{91}O\textsubscript{2} catalyst and its efficiency reached 98.04% at 70 °C. After 21 h reaction with sulfur and water in the flue gas, the catalyst efficiency only decreased to 89.75%. According to the results of characterization, Mo\textsubscript{0.5}Sn\textsubscript{9}Co\textsubscript{90.5}O\textsubscript{2} catalyst could better resist sulfur and water, because the presence of MoO\textsubscript{3} not only reduced the crystallinity of the catalyst, but it also increases the specific surface area and oxidation capacity.

1. Introduction
Nowadays, with the rapid progress of the society, people's quality of life is constantly improved along with demand for steel products is also increasing. As one of the pillar industries in China, the iron and steel industry exports a lot of steel products to the society, and also releases a huge amount of toxic pollutants into the atmosphere. In the process of producing steel, sintering process is not only a link with huge material flow, but also a link with high pollution emission coefficient. The mixture produces a wide variety of pollutants during sintering, producing a large amount of dust and soot (even containing heavy metal volatiles), CO\textsubscript{2}, CO, SO\textsubscript{2}, NO\textsubscript{x}, alkali metal chlorides, HCl, HF, CH compounds, as well as trace amounts of dioxins [1]. Among these pollutants, the high emission concentration of carbon monoxide (CO) can lead to the body tissue necrosis due to hypoxia after inhalation, or even endanger human life. What is more, CO is not easy to react with other substances in the atmosphere and stays for a long time, thus affecting the atmospheric climate. With the pressure from the environmental protection agency, as well as the importance of keeping the air clean, control of these pollutants is imminent. According to existing reports, many catalysts with good catalytic oxidation performance have been studied, such as Co-Fe\textsubscript{2}O\textsubscript{3}-CuO [2], CuO/Co\textsubscript{3}O\textsubscript{4} [3,4]. These catalysts could reduce carbon monoxide emissions effectively at low temperatures. Among them, Co-based catalysts had good catalytic activity [5]. The addition of Co\textsubscript{3}O\textsubscript{4} [6] to Pt/SnO\textsubscript{2} could provide additional adsorption sites for oxygen on the weakly bound CO molecules on the surface of Co\textsubscript{3}SnO\textsubscript{4} or the catalyst, and the catalyst had no inhibition on the transformation of high CO content. It was also found that Pt/SnO\textsubscript{2} [7–9] had good activity at a low temperature. Under the reduction treatment of 90 °C, activated oxygen on the surface of SnO\textsubscript{2} promoted the Pt on the oxidation reaction. However, one of the characteristics of sintering flue gas discharged by steel mills was the high moisture content in flue gas. The presence of H\textsubscript{2}O had a fatal effect on the catalytic oxidation of CO catalyst [10]. Cheap and highly active metal-oxide catalysts, such as Co\textsubscript{3}O\textsubscript{4}, rapidly deactivated in trace amounts of water (3-10 ppm water levels) in feed gas [11]. Another
serious problem was sintering also contains a certain amount of SO\textsubscript{2} in flue gases. Machida [12] mentioned in his study that a serious problem was deactivation due to sulfur poisoning. Several attempts have been made to address this problem, including introducing Pt oxides that are insensitive to SO\textsubscript{2} toxicity, using MgO as the preferred adsorption site for SO\textsubscript{2}, or looking for sulfur containing catalyst compositions. Hence, the preparation of a catalyst with good catalytic activity and resistance to sulfur and water is very important to solve the CO emission. It had been reported that NH\textsubscript{3}-SCR catalysts adding molybdenum could significantly improve the activities of vanadium and titanium, while reducing SO\textsubscript{2} adsorption in V/Mo-Ti catalyst, effectively improving the reaction between sulfur tolerance by inhibiting terminal V=O and SO\textsubscript{2} [13]. Redox-treated catalysts were composed of well-dispersed Pt particles on MoO\textsubscript{3}. Due to the interaction between Pt and MoO\textsubscript{3}, more active sites were formed, thus improving the catalytic activity of these systems and improving the performance of sulfur tolerance [14]. Meanwhile, molybdenum was relatively cheap and widely used metal, it could also improve the activity of electrocatalysts [15]. Therefore, the addition of Mo element made the CO catalytic oxidant have better efficiency and could be produced in large quantities due to its low cost.

In this study, MoSnCoO\textsubscript{x} catalysts added MoO\textsubscript{3} was prepared by co-precipitation method, which could better remove CO from the flue gas containing sulfur and water (0.024\% SO\textsubscript{2} and 13\% H\textsubscript{2}O). The CO catalyst evaluation device was built to simulate the low-concentration of CO (0.8\% CO) in the practical sintering flue gas. The effects of the amount of MoO\textsubscript{3} on the performance of SnO\textsubscript{2}-Co\textsubscript{3}O\textsubscript{4} composite catalytic oxidation catalyst was studied. The sulfur and water resistance of the catalyst were also investigated in this study.

2. Experimental section

2.1 Materials
Cobalt acetate (C\textsubscript{4}H\textsubscript{6}O\textsubscript{4}CoO\textsubscript{4}·4H\textsubscript{2}O), stannic chloride (SnCl\textsubscript{2}·2H\textsubscript{2}O), ammonium molybdate (NH\textsubscript{4})\textsubscript{6}Mo\textsubscript{7}O\textsubscript{24}·4H\textsubscript{2}O, anhydrous sodium carbonate (Na\textsubscript{2}CO\textsubscript{3}), AR grade, Tianjin Fuchen chemical reagent factory. Testo 350, Detu instrument international trade co. LTD, range 0 - +10000 ppm, resolution 1 ppm.

2.2 Catalysts preparation
The MoSnCoO\textsubscript{x} composite catalytic oxidation catalyst was prepared by coprecipitating. A certain amount of cobalt acetate, tin chloride and ammonium molybdate were weighed in proportion, and the reagents were added to the beaker. Added 200 mL of deionized water to dissolve the reagents and stirred constantly. The prepared sodium carbonate solution (1 mol/L) was added under the condition of 70 \( ^\circ \)C water bath to form a precipitate, and the pH value of the end point of the precipitate was 10. After that, continued the ultrasound and stirred for 3 h. After standing for a certain time, the ions were removed by filtration until no sodium ions were present. Finally, the drained sediment was put into oven and dried at 110 \( ^\circ \)C for 12 h, and roasted at 400 \( ^\circ \)C in muffle furnace for 3h. The calcined catalyst was naturally cooled and ground, and 20-40 mesh particles were sifted out for later use. Using this preparation method, Sn\textsubscript{0.5}Co\textsubscript{0.5}O\textsubscript{2}, Mo\textsubscript{0.05}Sn\textsubscript{0.5}Co\textsubscript{0.75}O\textsubscript{2}, Mo\textsubscript{0.75}Sn\textsubscript{0.25}Co\textsubscript{0.05}O\textsubscript{2}, Mo\textsubscript{1}Sn\textsubscript{0.0}Co\textsubscript{0.0}O\textsubscript{2}, Mo\textsubscript{2}Sn\textsubscript{0.0}Co\textsubscript{0.0}O\textsubscript{2} catalysts were prepared respectively.

2.3 Catalyst activity evaluation
The catalyst catalytic oxidation of carbon monoxide experiment was conducted in a fixed bed glass reaction tube (ϕ19×250 mm), with the temperature of the reaction tube controlled by heating an electric furnace. The test temperature was 40 \( ^\circ \)C-120 \( ^\circ \)C. Among them, H\textsubscript{2}O was added to a mixing cylinder by an injection pump, heated with tropical coil and controlled by temperature, so that H\textsubscript{2}O was mixed with other gases in a gaseous manner. CO flue gas analyzer (Testo 350, Germany) was used to detect the CO concentration in the import and export reaction.

2.4 Catalyst characterization
The pore structure of catalyst was determined by Micrometritics Gemini V. The sample was pretreated at 110 °C for 1 h, specific surface area was calculated according to BET method, pore volume and aperture were calculated according to BJH theory.

Scanning electron microscope (SEM) was tested by JSM7610F field emission electron microscope (Hitachi, Japan). Microimaging could be performed on samples with a working voltage of 10 kV.

X-ray diffraction (XRD) test used the D8 Advance type powder diffractometer (Bruker company) characterization of the catalyst crystal phase structure, \( \lambda = 1.5406 \) (Å) with Cu Ka radiation source, tube voltage of 40 kV, current of 35 mA, scanning range was 10 ° to 80 °, scan rate of 7.2 °/ min.

H2 program temperature reduction analysis (H2-TPR) was performed on Micrometritics Auto Chem II 2920s chemical adsorption instrument. The mixture of 10 vol% H2/Ar was passed in, and then the temperature was raised to 820 °C at 10 °/min.

3. Results and discussion

3.1 Influence of MoO3 addition amount on catalyst activity

In the existing V/Mo-Ti SCR denitrification catalysts, molybdenum showed excellent sulfur resistance and could improve the activity of catalysts [16]. However, there are few catalysts used to remove CO in sintering flue gas containing sulfur and water in industry. It can be clearly seen from figure 1 that the catalyst activity of adding MoO3 was superior to that of Sn0.9Co0.1O2 catalyst without adding MoO3. The catalyst activity was best when MoO3 content was 0.25%. The catalyst efficiency reached 99.91% at 70°C, and the CO conversion efficiency reached 100% at 80°C. With the increase of MoO3 content in catalyst components, the activity of catalyst gradually decreases. When MoO3 content was 0.5%, the Mo0.5Sn0.5Co0.5O2 catalyst efficiency could reach 98.04% at 70 °C, and CO could be completely transformed at 90 °C. The conversion temperature was low enough to meet the needs of industry.

![Figure 1. The effect of MoO3 content on the activity of catalyst.](image)

3.2 BET analysis

| MoO3 content /% | Specific surface area / m²·g⁻¹ | Pore volume / cm³·g⁻¹ | Pore size /nm |
|-----------------|-------------------------------|----------------------|---------------|
| 0.0             | 93                            | 190.4                | 26.2          |
| 0.25            | 95                            | 0.43                 | 12.1          |
| 0.5             | 100                           | 0.36                 | 8.6           |
| 0.75            | 108                           | 0.35                 | 7.2           |
| 1.0             | 102                           | 0.28                 | 6.1           |
| 2.0             | 72                            | 0.22                 | 8.2           |

Table 1 showed the microstructure of MoSnCoO x catalysts with different MoO3 content. According to the data in the table, the specific surface area gradually increases with the MoO3 content increasing in the range of 0-1%, indicating that the addition of MoO3 could indeed increase the specific surface area.
of catalyst. With the increase of MoO3 content, the pore volume and pore diameter of the catalyst showed a trend of gradually decreasing. In this series, the Mo0.5Sn9Co90.5O2 catalyst with the best sulfur and water resistance had a large surface area of 100 m²/g. It could be considered that the pore structure and large specific surface area ensured the stability of the catalyst structure and good oxygen storage and released capacity in the process of catalytic oxidation [17]. This also enabled CO to spread rapidly in the pore of the catalyst and contacted with O2 more fully, eventually leading to the improvement of catalytic activity of the catalyst. However, the larger the pore volume and pore diameter of the catalyst, the better the activity of the catalyst [18].

3.3 H2-TPR analysis

Figure 2 showed the H2-TPR spectra of Sn9Co91O2 (a), Mo0.5Sn9Co90.5O2 (b), Mo0.75Sn9Co90.25O2 (c), Mo1Sn9Co90O2 (d) catalysts prepared by co-precipitation. From the figure, it can be observed that the H2-TPR spectrum of Sn9Co91O2 catalyst had two reduction peaks, namely low-temperature reduction peak /g302/g3 and high-temperature reduction peak /g533/g3 respectively, which were speculated to be the reduction process from Co3+/g314/g38/g82 to Co2+/g314/g38/g82/g3 [19]. After 0.5% MoO3 was supported on Sn9Co91O2 catalyst, the number and position of peaks observed by comparing (a) and (b) did not change significantly. It is speculated that MoO3 was uniformly supported on the surface of Sn9Co91O2 catalyst. (b) the peak of high-temperature reduction peak was higher than that of (a), which indicated that the addition of MoO3 could improve the redox capacity of Sn9Co91O2 catalyst to a certain extent, so as to better promoted the catalytic oxidation reaction of CO. With the increase of MoO3 content in the catalyst, the curve (c) and (d) in the figure proved that there was no significant change in the low-temperature reduction peak α, but a new peak appeared around 520 ° at the high-temperature reduction peak β, which might be the reduction peak of MoO3 according to literature [20]. After the content of MoO3 increased, MoO3 could not be well dispersed on the catalysts, leading to the gradual decrease of the activity of catalyst Mo0.75Sn9Co90.25O2 and Mo1Sn9Co90O2.

3.4 XRD analysis

Figure 3 showed the XRD spectra of the Sn9Co91O2 catalysts without MoO3 and the Mo0.5Sn9Co90.5O2 catalyst with 0.5% MoO3. It can be seen from the XRD spectrum that the positions of diffraction peaks were basically the same, with characteristic diffraction peaks of Co3O4 appearing in 2θ = 19 °, 31 °, 37 °, 39 °, 45 °, 59 °, 65 ° and 79 °, and the crystal state was good. Among them, the strongest diffraction line was Co3O4 (311) 2θ = 37 °, which was consistent with that mentioned by Dziembaj [21] in the paper. The diffraction peaks of other substances were not detected in the test, which could be considered that other components were highly dispersed or in an amorphous state on the surface of Co3O4, or were not detected below the detection limit. By comparing the diffraction peaks, the intensity of the two diffraction peaks was obviously different. The diffraction peak strength of the Mo0.5Sn9Co90.5O2 catalyst doped with 0.5% MoO3 was significantly weaker than that without addition,
indicating that the presence of MoO$_3$ reduced the crystallinity of the catalyst. The catalyst obtained by this method had small particle size and good precipitation effect.

### 3.5 Influence of SO$_2$ and H$_2$O on catalyst efficiency

The sulfur and water resistance properties of the catalyst were investigated under the condition of sintering flue gas in industry. It can be seen from figure 4 that the catalyst with MoO$_3$ content of 0.5% had the best sulfur and water resistance, and the catalyst efficiency was maintained at 100% in the first 150 min. Later, it was speculated that the catalyst efficiency began to decline slowly due to the formation of sulfate on the surface of the catalyst [22]. When the experiment reached 360 min, the CO removal efficiency only dropped to 98.43%. For comparison, the catalyst efficiency of Sn$_x$Co$_{90}$O$_2$ without MoO$_3$ was measured and gradually decreased from the 0 min of the test, and the CO removal efficiency was reduced to 82.42% at the 360 min of the test. By comparison, the sulfur and water resistance of the MoSnCoO$_x$ catalysts added with MoO$_3$ were better than that of the Sn$_x$Co$_{90}$O$_2$ catalyst without MoO$_3$, which indicated that the addition of MoO$_3$ could help inhibit the formation of sulfate on the surface of the catalyst under the condition of sulfur and water, and extended the service life of the catalyst to some extent.

![Figure 4. The effect of SO$_2$ and H$_2$O on the efficiency of MoSnCoO$_x$ catalyst.](image)

![Figure 5. The effect of SO$_2$ and H$_2$O on the efficiency of Mo$_{0.5}$Sn$_9$Co$_{90.5}$O$_2$ catalyst for a long time.](image)

In order to detect the use of catalysts under such conditions in practical industrial applications, Mo$_{0.5}$Sn$_9$Co$_{90.5}$O$_2$ catalyst with the best effect in this series was selected in figure 5 to test the sulfur and water resistance of the catalyst for a long time. The SO$_2$ content was 0.024%, and the H$_2$O content was 13%. As can be seen from the experimental results, the catalyst efficiency only decreased from 100% to 98.34% before the experimental test of 720 min, with a slow rate of decline. It was possible that the co-existence of H$_2$O and SO$_2$ in the flue gas led to the formation of SO$_3^-$ or SO$_4^{2-}$, and it was most likely that a small amount of sulfate were generated with the active component of the catalyst, blocking the active site on the catalyst surface and reducing the activity of the catalyst [22]. The addition of MoO$_3$ has slowed the process down. However, due to the limited addition of MoO$_3$, the poisoning of the catalyst was more serious during the period from 720 min to 1260 min, and the decline rate of catalyst activity was accelerated. Even after 21 h of testing, the catalyst efficiency was still 89.75%.

### 3.6 Comparison of catalyst microstructure before and after poisoning

Table 2 showed the comparison of the microstructures between the fresh Sn$_x$Co$_{90}$O$_2$ catalyst and the catalyst after sulfur and water treatment for 6 h, and the comparison of the microstructures between the fresh Mo$_{0.5}$Sn$_9$Co$_{90.5}$O$_2$ catalyst and the Mo$_{0.5}$Sn$_9$Co$_{90.5}$O$_2$ catalyst after sulfur and water treatment for 6 h. According to the comparison of data in the table, the specific surface area and pore volume of Mo$_{0.5}$Sn$_9$Co$_{90.5}$O$_2$ catalyst decreased after it was poisoned. The specific surface area was reduced from 100 m$^2$/g to 94 m$^2$/g. This might be because in ventilation with sulfur and water reaction after 6 h, the generated sulfate could plug hole, or it might on account of some changes in porous catalysts [23]. This greatly reduced the contact frequency between the reaction gas and the active component of the catalyst,
which made the activity of the catalyst decrease. Meanwhile, we can notice that the Mo\textsubscript{0.5}Sn\textsubscript{9}Co\textsubscript{90.5}O\textsubscript{2} catalyst with good sulfur and water resistance was similar to the initial specific surface area after poisoning, while the specific surface area of the Sn\textsubscript{9}Co\textsubscript{91}O\textsubscript{2} catalyst without MoO\textsubscript{3} was greatly reduced after poisoning. It was speculated that the addition of MoO\textsubscript{3} might inhibit the formation of sulfate \cite{14}.

### Table 2. Comparison of catalyst microstructure before and after poisoning.

| Catalysts content                          | Specific surface area / m\textsuperscript{2} \cdot g\textsuperscript{-1} | Pore volume / cm\textsuperscript{3} \cdot g\textsuperscript{-1} | Pore size / nm |
|--------------------------------------------|---------------------------------------------------------------------|-----------------------------------------------------------------|--------------|
| Sn\textsubscript{9}Co\textsubscript{91}O\textsubscript{2} (fresh catalyst) | 43                                                                  | 0.37                                                            | 25.1         |
| Sn\textsubscript{9}Co\textsubscript{91}O\textsubscript{2} (H\textsubscript{2}O+SO\textsubscript{2}) | 27                                                                  | 0.34                                                            | 27.1         |
| Mo\textsubscript{0.5}Sn\textsubscript{9}Co\textsubscript{90.5}O\textsubscript{2} (fresh catalyst) | 100                                                                 | 0.36                                                            | 8.6          |
| Mo\textsubscript{0.5}Sn\textsubscript{9}Co\textsubscript{90.5}O\textsubscript{2} (H\textsubscript{2}O+SO\textsubscript{2}) | 94                                                                  | 0.34                                                            | 9.1          |

### 4. Conclusion

A series of MoSnCo\textsubscript{x} carbon monoxide catalytic oxidants with different MoO\textsubscript{3} content were prepared by coprecipitating. The results indicated that Mo\textsubscript{0.5}Sn\textsubscript{9}Co\textsubscript{90.5}O\textsubscript{2} catalyst showed good catalytic activity, its efficiency reached 98.04\% at 70 °C, and CO could be completely transformed at 80 °C. At the same time, this catalyst has the best sulfur and water resistance. After the reaction for 21 h with sulfur and water, the catalyst efficiency only drops to 89.75\%. XRD test confirmed that the presence of MoO\textsubscript{3} reduced the crystallinity of the catalysts and made the precipitation dispersive. The characterization of BET and H\textsubscript{2}-TPR proved that the addition of MoO\textsubscript{3} could increase the specific surface area of the catalysts and improved the oxidation capacity as well. The presence of sulfur and water might lead to the formation of sulfate in the reaction. However, Mo\textsubscript{0.5}Sn\textsubscript{9}Co\textsubscript{90.5}O\textsubscript{2} catalyst could slow down the decline rate of catalyst activity effectively, so that it could play a better role in removing CO from the flue gas.

### 5. References

[1] Anderson D and Fisher R 2002 Chemosphere 46 371–381
[2] Rezaei P, Rezaei M and Meshkani F 2019 Ultrason. Sonochem. 57 212–222
[3] Hossain S, Azeeva E, Zhang K, Zell E, Bernard D, Balaz S and Wang R 2018 Appl. Surf. Sci. 455 132–143
[4] Zedan A, Polychronopoulou K, Asif A, AlQaradawi S and AlJaber A 2018 Surf. Coat. Technol. 354 312–323
[5] Ghiasi M and Malekzadeh A 2014 Acta Metall. Sin. (Engl. Lett.) 27(4) 635–641
[6] Gürdag G, Boz I, Ebiller S and Gürkaynak M 2004 React. Kinet. Catal. Lett. 83(1) 47–54
[7] Nobutada Y, Naoto K, Hiroki M, Toshiaki M and Koichi E 2011 Catal. Today 164 169–175
[8] Shinde V and Madras G 2012 Catal. Sci. Technol. 2 437–446
[9] Massong H, Wang H, Samjeské G and Baltruschat H 2000 Electrochim. Acta 46 701–707
[10] Biemelt T, Wegner K, Teichert J, Lohe M, Martin J, Grothe J and Kaskel S 2016 Appl. Catal. B-Environ. 184 208–215
[11] Chen C, Njagi E, Sun S, Genuino H, Hu B and Suib S 2010 Chem. Mater. 22 3313–15
[12] Machida M, Ochiai K, Ito K and Ikeue K 2006 Catal. Today 117 584–587
[13] Kwon D, Park K, Ha H and Hong S 2019 Appl. Surf. Sci. 481 1166–67
[14] Zosimova P, Smirnov A, Nesterenko S, Yuschenko V, Sinkler W, Kocal J, Holmgren J and Ivanova I 2007 J. Phys. Chem. C 111 14790–98
[15] Pillai S, Sonawane S, Gumfekar S, Suryawanshi P, Ashokkumar M and Potoroko I 2019 Mater. Chem. Phys. 237 121854
[16] Beretta A, Lanza A, Lietti L, Clave S, Collier J and Nash M 2019 Chem. Eng. J. 359 88–89
[17] Dhal G, Mohan D and Prasad R 2019 J. Sci. Adv. Matel. Dev. 4 47–56
[18] Jampaiah D, Velissoju V, Devaiah D, Singh M, Mayes E, Coyle V, Reddy B, Bansal V and Bhargava S 2019 Appl. Surf. Sci. 437 209–221
[19] Fattah Z, Rezaei M, Ravandi A and Irankhah A 2014 Process Saf. Environ. Prot. 92 948–956
[20] Mobini S, Meshkani F and Rezaei M 2019 *Chem. Eng. Sci.* **197** 37–51
[21] Dziembaj R, Chojnacka A, Piwowarska Z, Gajewska M, Świętosławski M, Górecka S and Molenda M 2019 *Catal. Today* **333** 196–207
[22] Pereira C and González E 2014 *Fuel* **118** 137–147
[23] Ryou Y, Lee J, Lee H, Choung J and Yoo S 2015 *Catal. Today* **258** 518–524

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