

# Manganese residue modified steel slag to improve low-temperature SCR of NO<sub>x</sub>

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## ABSTRACT

In this study, the denitrification performance of steel slag modified by manganese slag was studied. Different proportions of steel slag and electrolytic manganese anode mud mixtures were configured. The different proportions of the mixture would have varied physical and chemical properties. SS1+EMAM2 catalyst showed the nearly 100% NO<sub>x</sub> removal efficiency at 175°C. The specific surface area of steel slag is enhanced dramatically after modification by EMAM. Adding EMAM enhanced the weak acid sites and Brønsted-acid sites on the catalyst surface, resulting in a higher low-temperature SCR activity.

**Keywords:** industrial waste utilization, selective catalytic reduction, steel slag, electrolytic manganese anode mud

## NONMENCLATURE

### Abbreviations

SCR	selective catalytic reduction
EMAM	electrolytic manganese anode mud
SS	steel slag

## 1. INTRODUCTION

High-speed development of China's steel industry generates a large amount of steel slag (SS). Its emission about 150-200 million tons in China in 2019[1]. Electrolytic manganese anode mud (EMAM) also is a kind

of hazardous solid waste that comes from electrolytic manganese metal industry. EMAM contains many kinds of heavy metals, such as Mn, Pb, Co, Ni, Sn and Cr[2]. Making the best of these residues and reducing their risk on environmental protection was one of the important ways to reduce the carbon emission.

Nitrogen oxide (NO<sub>x</sub>) is one of the main precursors of acid rain and photochemical smog, causing environmental problems such as haze and tropospheric ozone[3-5]. NO<sub>x</sub> can also react with other substances to form particles. In the existing reports, MnO<sub>x</sub> is widely applied in SCR[6-8] due to their variable valence state and excellent redox properties, but its synthesis method usually adopts the hydrothermal synthesis method or impregnation method, which is a high cost of chemicals used and waste of time[9]. In this work, EMAM was used to modify the SS, so that it obtained excellent low temperature selective catalytic reduction of NO<sub>x</sub>. This not only makes the reaction more efficient but also makes it easier to use bulk industrial waste and has real-world industrial applications. There are also positive implications for carbon neutrality.

## 2. MATERIAL AND METHODS

### 2.1 Catalysts preparation

The NaCl (GR, ≥99.8%) used in the experiment was purchased by Sinopharm and has not been further purified. EMAM was acquired by an electrolytic manganese producer in Hunan province of China. SS was

provided by Ningbo Taiji Environmental Protection Equipment Co., LTD.

The catalyst was prepared according to the following procedure: (1) A certain concentration of NaCl solution (a mixture of 100mL deionized water and 25g NaCl) was configured; (2) Mix SS and EMAM in a certain proportion (1:1, 1:2, 2:1) and pour evenly into above solution; (3) Place the mixed solution in a magnetic stirrer with heating and stir for 6 hours; (4) The obtained mixed grout was pumped and filtered, solid-liquid separation, and the solid product was washed two or three times with hot water to make it neutral. Finally, the required denitration catalyst was obtained by drying at 105°C for 12 hours in the air blast drying oven.

## 2.2 Catalytic activity test

The denitration activity test device is shown in Fig. 1. A 0.1g catalyst was placed in a fixed-bed reactor, and simulated flue gas with a total gas flow of 150 ml/min was added, which contained 500 ppm of NO, 600 ppm of NH<sub>3</sub>, and 5% O<sub>2</sub>. The removal efficiency of NO<sub>x</sub> is shown in the following formula:

$$NO_x \text{ removal efficiency} = \frac{[NO_x]_{inlet} - [NO_x]_{outlet}}{[NO_x]_{inlet}} \times 100\%$$

Where, [NO<sub>x</sub>]<sub>inlet</sub> and [NO<sub>x</sub>]<sub>outlet</sub> represent the concentration of NO<sub>x</sub> before and after the reactor, ppm.

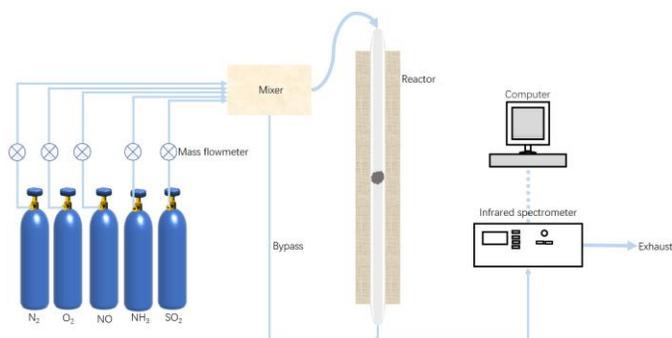


Fig. 1. Diagram of denitrification experimental facility

## 3. RESULTS AND DISCUSSION

### 3.1 Catalytic performance

Fig. 2 shows the denitrification activity test curve of SS+EMAM with different proportions. It can be observed that all samples show different denitrification activities under the same reaction conditions, among which the initial SS has the lowest denitrification activity, with an efficiency of 19% at 320°C, while the initial untreated EMAM shows better denitrification performance. With the increase of reaction temperature, it shows the highest denitration efficiency at 280°C, up to 91%, the

main reason is that EMAM contains more MnO<sub>2</sub>, according to most reports, the main active ingredient in denitration is MnO<sub>2</sub>. By comparing the SS and EMAM complexes after modification (NaCl leaching), it can be observed that the modified material significantly improves the activity of SCR at low temperature, and the denitrification efficiency of SS1+EMAM2 and SS1+EMAM1 reaches more than 90% at 120°C to 240°C. Compared with the SS modified by EMAM in different proportions, when the SS proportion increases, its denitrification activity is lower than the other two proportions, which may be because the specific surface area of the material decreases when the SS content is too high. However, when the ratio is 1:1 and 1:2, the denitrification efficiency is slightly different in the first 180 °C and nearly identical after 180 °C.

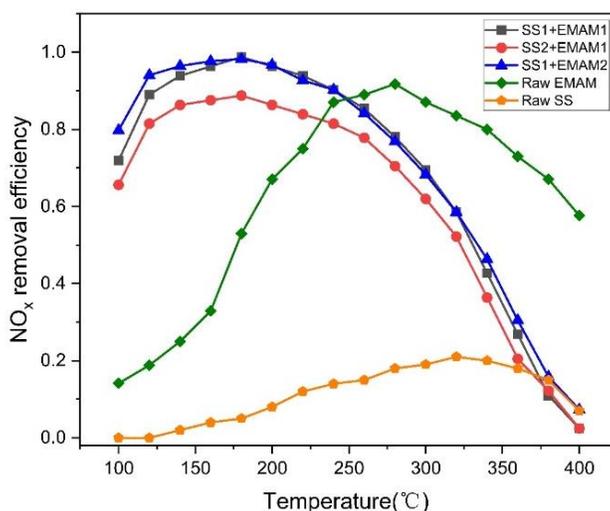


Fig. 2. Denitrification activity test of SS+EMAM with different ratio

### 3.2 Catalyst characterization

#### 3.2.1 BET

In order to study the specific surface area and pore size of SS composites modified with different proportions of EMAM, BET tests were performed on the materials, as shown in Fig. 3. By observing the obtained N<sub>2</sub>-adsorption and desorption curves, the three samples have a hysteresis loop when the relative pressure P/P<sub>0</sub> > 0.4, which is a typical type IV isotherm, and this phenomenon indicates that the prepared materials have a mesoporous structure. By comparing the amount of N<sub>2</sub> adsorption of the three different proportions of composites, it is found that the adsorption amount of SS1+EMAM2 is the largest, and the adsorption amount of SS2+EMAM1 is the least, so it can be concluded that the increase of EMAM content can increase the specific

surface area of the composite, and high BET surface area is beneficial to the progress of the SCR reaction. In Table 1, the maximum specific surface area of SS1+EMAM2 is 70.2m<sup>2</sup>/g, and the minimum specific surface area of SS2+EMAM1 is 37.7m<sup>2</sup>/g. Therefore, the addition of EMAM has a key influence on the specific surface area. The average pore size does not change much, but the total pore volume increases with the increase of the EMAM content, which is the same as the changing trend of the specific surface area. The RO phase and insoluble silicate in the SS lead to a small specific surface area of SS, and these substances are difficult to remove after washing with NaCl. The specific surface area of EMAM is relatively large compared to SS, so the addition of EMAM neutralizes the disadvantage of the small specific surface area of steel slag, thereby improving the denitration reaction activity.

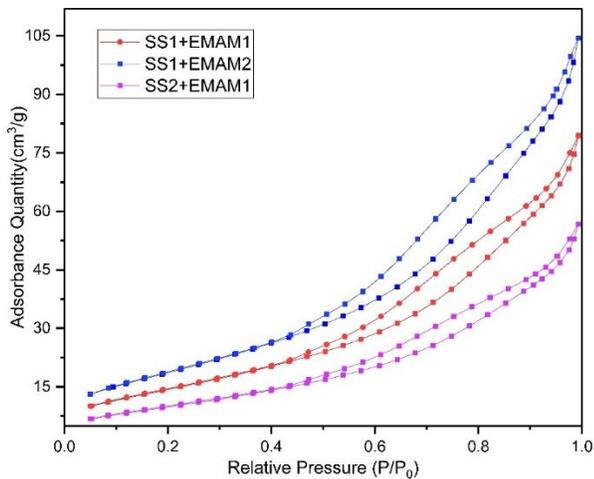


Fig. 3. N<sub>2</sub> adsorption and desorption curves of different proportions of SS and EMAM

Table 1 Surface properties of EMAM with different proportions of SS

Catalyst	BET surface area(m <sup>2</sup> /g)	Pore volume/(cm <sup>3</sup> /g)	Pore size/(nm)
SS1+EMAM1	54.3	0.12	8.7
SS1+EMAM2	70.2	0.16	8.9
SS2+EMAM1	37.7	0.08	9.0

### 3.2.2 SEM

Fig. 4 shows the SEM images of EMAM and SS with different proportions. It could be observed that the catalyst surface was obviously different. The three catalysts had an obvious massive structure, and many needle-like fibers appeared on the surface of the catalysts with the addition of EMAM, and these fibers also increase with the increase of EMAM content. These

fibers may be the main active substance in the reaction process and the active site of SCR.

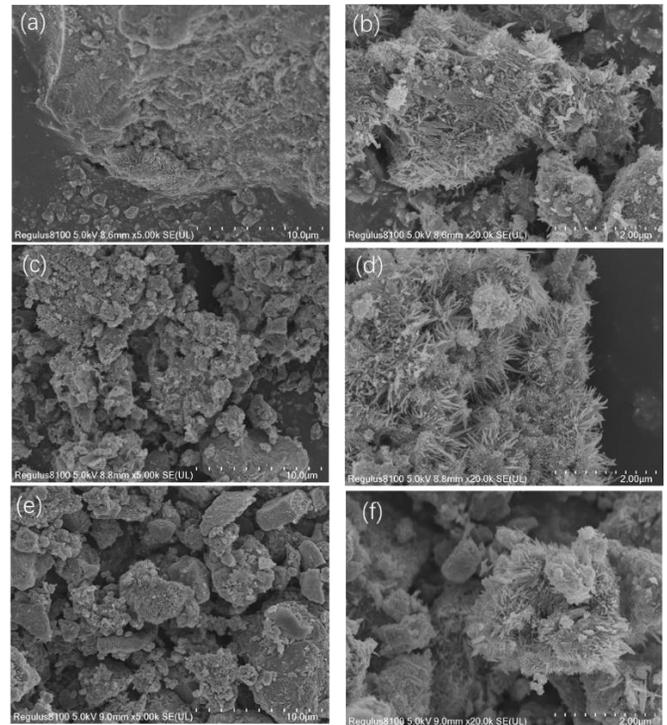


Fig. 4. SEM images of materials with different proportions. (a,b) SS1+EMAM1, (c,d) SS1+EMAM2, (e,f) SS2+EMAM1

### 3.2.3 XRD

The catalytic denitration activity of EMAM modified SS is not only related to its physical properties, but also related to the crystal phase, electronic state, and crystal structure of the active components on the surface of the material. The research used XRD characterization technology to analyze the modified SS with different proportions of EMAM. The experimental results are shown in Fig. 5. The XRD patterns of SS modified with different proportions of EMAM have similar diffraction peaks. By comparing with the standard PDF card (#44-0141), it is found that the crystal phase is mainly  $\alpha$ -MnO<sub>2</sub>. Dicalcium ferrite and dicalcium silicate have distinct peaks at 30-35°. By comparing the characteristic peaks of three different proportions of EMAM modified SS composites, it can be seen that as the proportion of SS increases, the characteristic peaks of dicalcium ferrite and dicalcium silicate are also gradually enhanced, indicating that their content is also increasing. However, the denitrification activity of dicalcium silicate is weak, which is also the main reason for the reduction in denitrification efficiency when the SS content is high. The results of XRD characterization technique didn't detect the oxides of other species. The reason may be that the

content of other species is less than the detection range of the equipment and the distribution in the EMAM+SS composite is relatively uniform, so their characteristic peaks cannot be determined.

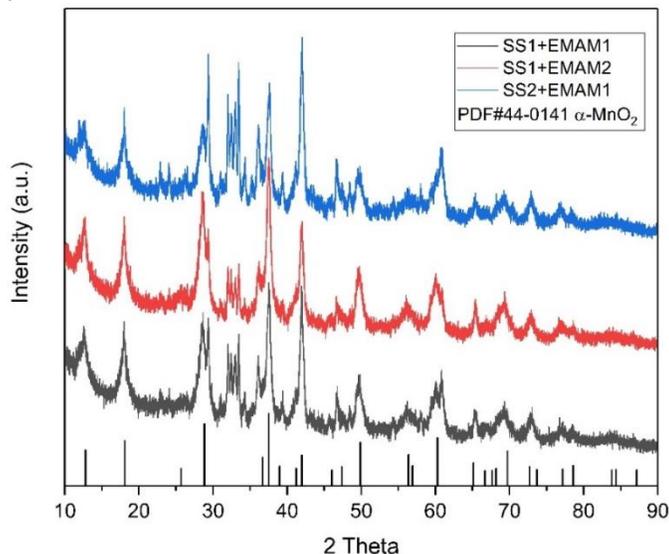


Fig. 5. XRD patterns of SS modified with different proportions of EMAM

### 3.2.4 NH<sub>3</sub>-TPD

The adsorption behavior of NH<sub>3</sub> on the acid sites of the catalyst surface is a key indicator for evaluating the NH<sub>3</sub>-SCR reaction. The NH<sub>3</sub>-TPD characterization analysis was performed in order to evaluate the amount and strength of the acid on the catalyst surface. Fig. 6 shows the NH<sub>3</sub>-TPD spectrum of SS modified by EMAM in different proportions. From the figure, we can observe that the three samples show different degrees of desorption peaks in the range of 100-800°C, which are specifically expressed as the desorption of NH<sub>3</sub> in acidic sites with different acidities. It can be seen from Fig.6 that the three samples all have weak acid sites to varying degrees, and the obvious desorption peaks in the range of 500-700°C indicate that NH<sub>3</sub> is adsorbed on the strong acid sites of the three samples. According to relevant literature reports[10, 11], the low-temperature desorption peak is formed due to the combination of NH<sub>3</sub> and Lewis acid sites, while the high-temperature desorption peak is attributed to the combination of NH<sub>3</sub> on Brønsted acid sites. In addition, the desorption peak area is also related to the amount of acidic sites. Table 2 quantitatively calculates the acid content of the three catalysts in different temperature ranges, in which the total acid content of the SS1+EMAM2 sample reaches 1.26mmol/g. The results showed that the SS1+EMAM2 catalyst had more acidic sites, which was beneficial to the SCR performance of the catalyst, which was

consistent with the results of the activity test. Therefore, the higher specific surface area and abundant Brønsted acid sites of the SS1+EMAM2 sample are the main reasons for its improved catalytic performance.

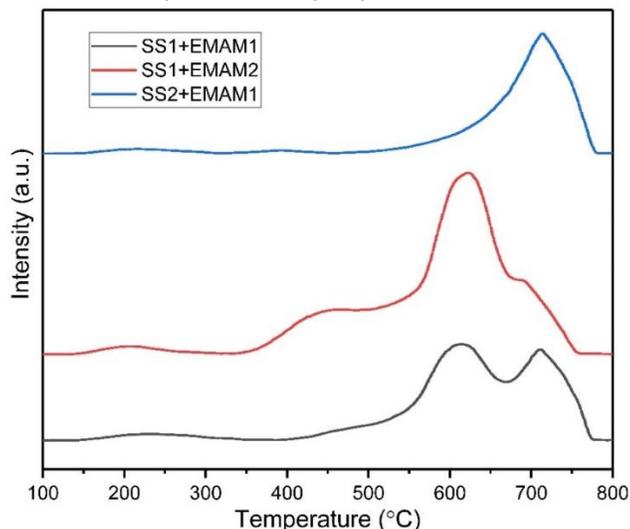


Fig. 6. NH<sub>3</sub>-TPD spectrum of SS modified by EMAM in different proportions

Table 2 Comparison of acid content of SS modified with different proportions of EMAM

Samples	Temperature range (°C)	Acid amount (mmol/g)
SS1+EMAM1	100-385	0.037
	385-670	0.486
	670-800	0.302
SS1+EMAM2	100-330	0.034
	330-485	0.178
SS2+EMAM1	485-800	1.048
	100-325	0.021
	325-460	0.010
	460-800	0.538

### 3.2.5 H<sub>2</sub>-TPR

H<sub>2</sub>-TPR analysis was used to study the reducibility of SS1+EMAM1, SS1+EMAM2 and SS2+EMAM1 samples. As shown in Fig. 7, a series of characteristic peaks can be observed as the temperature increases. The peaks of the three samples at about 349°C are attributed to the Mn<sup>4+</sup> to Mn<sup>3+</sup> transformation[12]. The peak of the SS1+EMAM2 sample moves towards low temperature relative to SS1+EMAM1 and SS2+EMAM1, indicating that the reduction temperature required is lower, which is also the reason why SS1+EMAM2 has higher SCR efficiency compared with the other two samples at low temperature.

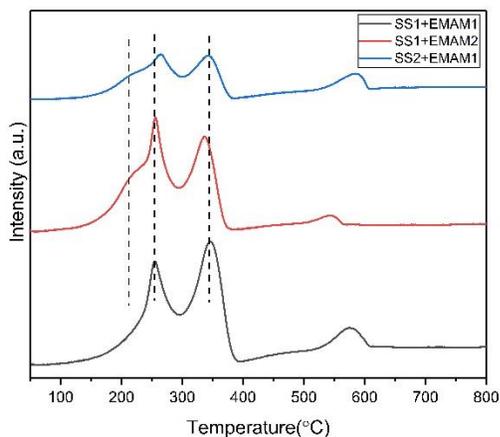


Fig. 7. H<sub>2</sub>-TPR spectrum of SS modified with different proportions of EMAM

### 3.2.6 XPS

The XPS spectrum of the SS modified with different proportions of EMAM was shown in Fig. 8. Researchers have clarified that chemisorbed oxygen plays an important role in catalytic redox reactions[13]. The O1s peak near 531.8 eV is attributed to chemisorbed oxygen ( $O_{\alpha}$ ), and the O1s peak near 530.3 eV is attributed to lattice oxygen ( $O_{\beta}$ ). In general, catalyst reactivity is proportional to the relative percentage concentration of chemisorbed oxygen, i.e.,  $O_{\alpha}/(O_{\alpha}+O_{\beta})$ . The  $O_{\alpha}/(O_{\alpha}+O_{\beta})$  ratios of the catalysts are listed in Table 3. According to the deconvolution peak area of Fig.8 (a) O1s, the concentrations of SS1+EMAM1, SS1+EMAM2 and SS2+EMAM1 are 67.83%, 56.27 and 77.16%, respectively. This is not in line with the SCR performance of the three catalysts, so it shows that the chemisorbed oxygen concentration ratio is not the main reason why SS1+EMAM2 is so good.

In Fig.8 (b), Mn 2p<sub>3/2</sub> belongs to Mn<sup>4+</sup> and Mn<sup>3+</sup>, which are located near 644.1 and 642.3 eV, respectively. The peak area represents the relative content of species. Mn<sup>4+</sup>/Mn in SS1+EMAM1, SS1+EMAM2 and SS2+EMAM1 are 48.34%, 48.34% and 49.14% respectively by calculating the area of deconvolution peak, indicating that the addition of EMAM didn't change the Mn<sup>4+</sup> content.

Fig. 8 (c) is the Fe 2p spectrum of Fe<sub>2</sub>O<sub>3</sub>. Two peaks can be observed at 711.2 and 725.7 eV, which are assigned to Fe 2p<sub>3/2</sub> and Fe 2p<sub>1/2</sub> respectively. It is worth noting that the peak intensities of the three catalysts are significantly different, indicating the difference in the content of iron oxide. The changing trend of iron content is the same as that in Table 3. The reason may be that MnO<sub>x</sub> occupies the surface of the catalyst in the EMAM, thus blocking the spectrum signal of Fe. In Table 3, it can be seen that with more EMAM added, the number of Mn

atoms on the surface of the catalyst also rises, which is in line with previous research.

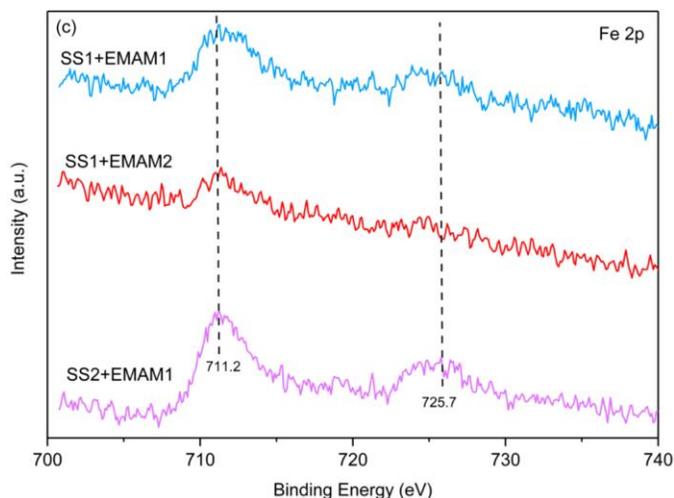
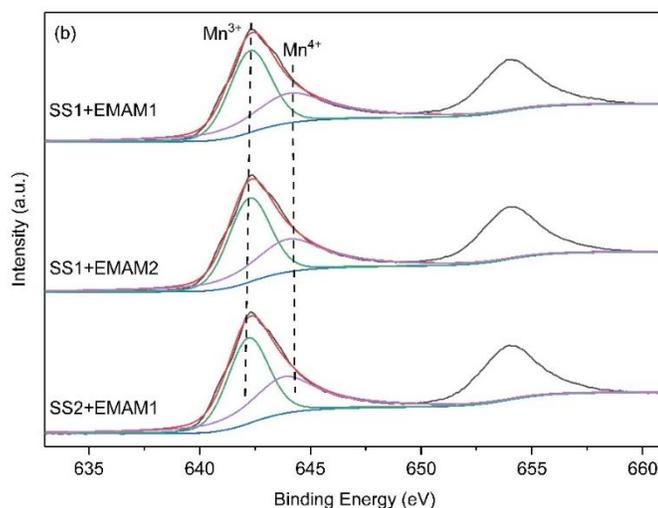
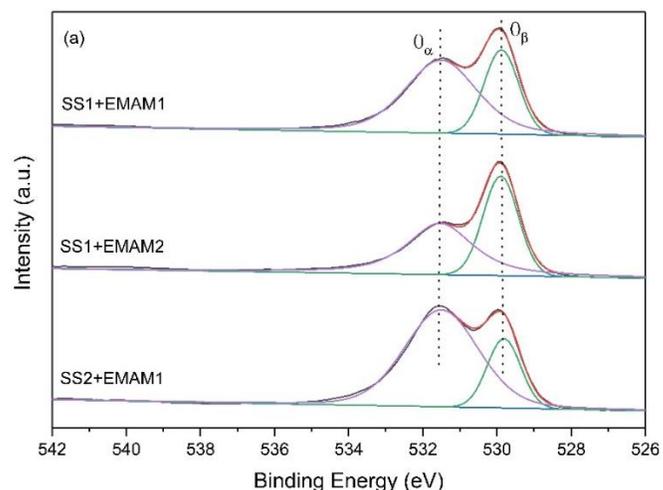


Fig. 8. XPS spectrum of SS modified with different proportions of EMAM; (a) O 1s; (b) Mn 2p; (c) Fe 2p

Table 3 Fe, Mn atom concentration and O<sub>α</sub> atom ratio on catalyst surface

Samples	Atomic concentration (%)			Atomic ratio (%)
	Fe	O	Mn	O <sub>a</sub> /(O <sub>a</sub> +O <sub>b</sub> )
SS1+EMAM1	1.51	76.33	22.16	67.83
SS1+EMAM2	0.71	71.88	27.41	56.27
SS2+EMAM1	2.04	81.03	16.93	77.16

#### 4. CONCLUSION

In this study, electrolytic manganese anode mud was used to modify the bof steel slag to improve the SCR activity. Through characterization analysis, the addition of manganese slag improved the specific surface area of the composite, and the main crystal phase after modification was MnO<sub>2</sub>, which is the active substance in the SCR process. At the same time, the addition of manganese slag can also increase the weak acid sites on the surface of the catalyst, further improving the low-temperature SCR process. However, experiments on sulfur resistance showed that SO<sub>2</sub> would irreversibly inactivate the three materials, possibly because the generated sulfate occupied the catalytic active site. Therefore, the subsequent work should be optimized for sulfur resistance.

#### ACKNOWLEDGEMENT

Following funding bodies are acknowledged for sponsoring this research: National Key R&D Program of China (2017YFB0603202), Ningbo 'Science and Technology Innovation 2025' Major Project (2018B10091) and Zhejiang Provincial Key Laboratory Programme (2020E10018).

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