Effect of N (N=Fe, Co, Ni, Cu, Ce) Loaded on Blast Furnace Slag in Low-temperature NH_3 -SCR

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Abstract

Using low-value solid waste blast furnace slag as a catalyst carrier, the active component N (N = Fe, Co, Ni, Cu and Ce) was loaded by impregnation method to study its effect on the denitration and sulfur resistance of the Mn-based blast furnace slag catalyst. BET, XRD, XPS, SEM and FT-IR characterization methods were used to analyze the denitration mechanism. The results show that: (1) Mn-Ce/GGBS catalyst has better denitration and sulfur resistance; (2) Mn-Ce/GGBS catalyst has a significant denitration effect when load ratio is 2:1; (3) The catalyst can reduce the poisoning and deactivation of S and prolong the catalyst service life; (4) MnO, MnO₂, Mn₂O₃, CeO₂ and Ce₂O₃ play an important role; (5) The larger the ratio of Mn⁴⁺/Mn³⁺, Ce⁴⁺/Ce³⁺, O_α/O_β, the stronger the catalyst activity and the better denitration effect, and the introduction of SO₂ will increase the acid sites on the catalyst surface and increase the catalyst activity.

Highlights

- Blast Furnace Slag can be prepared as a good catalyst carrier.
- Ce can improve the denitration performance.
- Blast Furnace Slag catalyst is characterized by SEM, BET, XPS, FT-IR, XRD.
- Realize the comprehensive utilization of solid waste.
- The larger the ratio of Mn⁴⁺/Mn³⁺, Ce⁴⁺/Ce³⁺, O_α/O_β, the stronger the catalyst activity.

1. Introduction

Nitrogen oxides (NO_x) are one of the important root causes of smog and ozone pollution, and are important precursors of the main atmospheric pollutants PM_{2.5} and ozone (Zhang et al., 2020; Yang et al., 2018). Its main sources are caused by emissions from motor vehicle exhaust, coal-fired power plants, and industrial sources (steel, coking, cement, glass, and ceramics), among which industrial source emissions are the main source of atmospheric NO_x (Ashraf et al., 2019; Agbo et al., 2021; Dadi et al., 2021). In recent years, although motor vehicle exhaust and NO_x emissions from coal-fired power plants have been well controlled and reduced, industrial source NO_x emissions have not been effectively controlled (Ma et al., 2018).

SCR (Selective Catalytic Reduction) technology initially used a precious metal platinum catalyst to treat NO_x (Zhao et al., 2020). Although it can solve practical industrial problems, the cost of the catalyst is high and a large number of by-products of ammonium nitrate will be generated in the active temperature range (Vogel et al., 2020; Li et al., 2020; Chen et al., 2014). The highly active commercial SCR catalyst developed and improved afterwards has been effectively used in industrial production. However, the flue gas temperature in the non-electric power industry is low, so the existing mature SCR denitration technology cannot fully control NO_x (Zhang et al., 2021; Jaegers et al., 2019).

At present, the industrial flue gas denitration catalysts that are commercially used are mainly vanadium-titanium type, because they have higher NH_3 -SCR catalytic activity at 280–450°C, and the catalysts have higher toxicity and poor sulfur resistance (Theofanidis et al., 2018; Jablonska et al., 2018; Jogi et al., 2018). It is urgent to find a catalyst with low temperature activity, weak catalyst toxicity and sulfur resistance to replace the commercial vanadium titanium catalyst. The Mn-based catalyst has a wide distribution of valence states of active components, and manganese between different valence states can be converted to each other to produce redox, which can make NH_3 selectively reduce NO and promote the SCR reaction (Abazari et al., 2021; Schroeder et al., 2020). However, SO_2 in the flue gas will also poison the Mn-based catalyst and has not been applied in industry. When the multi-metal oxide catalyst shows more excellent low temperature activity, it also has certain sulfur resistance and longer service life (Italiano et al., 2016; Lei et al., 2020; Wang et al., 2018).

The active components dispersed on the surface of the carrier can optimize the performance of the catalyst (Wahiduzzaman et al., 2018; Tamura et al., 2018). The catalysts used in practice all have a certain shape, such as plate, honeycomb, spherical, etc. The shaped carrier will significantly improve the performance of the catalyst (Jun et al., 2020). Due to the relatively small amount of industrial flue gas in the non-power industry, the demand for plate and honeycomb catalysts is relatively small. For the demand for denitration technology and catalysts in glass furnaces, cement and other industries, the use of small catalysts can achieve energy saving and emission reduction and reduce the cost of investment (Chen et al., 2020; Faizullina et al., 2020). At present, industrially prepared denitration catalyst carriers mostly use industrially prepared oxides such as SiO_2 , TiO_2 and Al_2O_3 , etc., which is also an expensive investment for small enterprises (Abdelhamid et al., 2019; Chen et al., 2017). Therefore, choosing a carrier with low cost and wide source is essential to promote the full implementation of denitration technology in small industries (Han et al., 2019; Sun et al., 2018).

Lag is a by-product of the blast furnace ironmaking process. In the ironmaking process, iron oxide is reduced to metallic iron at high temperatures. Impurities such as silica and alumina in the iron ore react with lime to form a melt with silicate and aluminosilicate as the main components. After being quenched into a loose, porous granular material, it is called blast furnace slag (BFS). It is waste slag discharged during blast furnace smelting, and its output accounts for 30–50% of pig iron output. A large amount of slag is produced every year. Without proper treatment, the residual products occupy a large amount of high-quality land resources, which will not only cause environmental pollution, but also cause serious waste of resources (Rahman et al., 2019; Selvamani et al., 2017). However, because the current slag is mainly based on the preparation of cement or vitreous, it is a waste of resources for the slag to be rich in elements. With the research and understanding of the performance of slag, people began to study and use slag in multiple directions. For the cement manufacturing industry and the glass furnace industry, blast furnace slag is one of the important raw materials used, coupled with the company's demand for denitration catalysts, so this article selects solid waste blast furnace slag as the carrier of denitration catalysts (Veerapandian et al., 2019; Vita et al., 2018).

In this paper, it is proposed to prepare denitration catalyst carrier with blast furnace slag, and load another active assistant on the basis of Mn based blast furnace slag at the same time. The modification of Mn based blast furnace slag can improve the denitration performance and obtain better sulfur resistance performance at the same time. It can not only expand the use of blast furnace slag, but also meet the needs of relevant enterprises to meet the emission reduction standards, so as to achieve the purpose of combining the utilization of solid waste resources with the control of air pollution.

2. Experimental

2.1. Experimental device

The activity evaluation of the catalyst is shown in Fig. 1.

2.2. Methods

2.2.1. Material

The blast furnace slag powder used in the experiment was produced in a steel plant in Hanzhong, Shaanxi. The chemical composition and elemental composition of the slag powder are shown in Table 1 and Table 2.

Table 1
Main chemical components of ground granulated blast furnace slag (%)

CaO	MgO	Al ₂ O ₃	SiO ₂	MnO	TiO ₂	SO ₃	K ₂ O	Fe ₂ O ₃	Total
41.46%	7.68%	13.34%	30.19%	0.52%	1.58%	2.55%	0.57%	1.27%	99.16%

Table 2
Main element components of ground granulated blast furnace slag (%)

Ca	Mg	Al	Si	Mn	Ti	S	K	Fe	Total
54.51%	6.16%	9.87%	20.88%	0.86%	2.00%	1.64%	0.81%	1.91%	98.64%

2.2.2. The preparation of the catalyst

(1) The metal Mn and the nitrate of different metals (Fe, Co, Ni, Cu, Ce) are mixed according to the load ratio of 2:1, then added to the blast furnace slag and placed in an ultrasonic cleaning machine, ultrasonic power 80W, ultrasonic time 20min, drying and forming.

(2) The dried and formed blast furnace slag catalyst is placed in an oven and dried at 100°C for 1h, and then transferred to a muffle furnace and roasted at 400°C for 2h to prepare a denitration catalyst. The prepared catalysts are denoted as Mn-Fe/BBFS, Mn-Co/BBFS, Mn-Ni/BBFS, Mn-Cu/BBFS, Mn-Ce/BBFS, respectively.

2.2.3. Flue gas analysis and evaluation system

In this experiment, the temperature of the reactor was set to 150°C, and the total amount of gas was 1000mL/min, in which nitrogen monoxide was 600ppm, oxygen was 6%, and the rest was nitrogen.

Different catalysts were placed in the temperature control tower, and the change of NO was detected and recorded by a flue gas analyzer (Testo 340). The calculation method of the denitration rate is:

Removalefficiency = $\frac{C_{NO_{inlet}} - C_{NO_{outlet}}}{C_{NO_{inlet}}} \times 100\%$	Eq. (1)
NO removal= $M_{NO} / 22.4 \times t \times C_{NO} \times Q_{total}$	Eq. (2)
Total NO removal rate= $\frac{\text{Removed NO}}{\text{Unremoved NO}}$	Eq. (3)

2.3. Experimental characterization

BET: In this experiment, the N₂ adsorption isotherm was mainly used to analyze at -196°C by JW-BK122W system and the specific surface area was calculated by BET equation.

XRD: The sample was tested by XD-3 X-ray diffraction analyzer to obtain an XRD pattern.

SEM: The SEM model was JSM-6460LV, the working voltage was 20kV, and the magnification was 5000 times.

XPS: The X-ray photoelectron spectrometer model used in this paper was: ESCALAB250 (manufactured by Thermo Fisher Scientific, USA). The instrument had a sensitivity of 180 KCPS, an energy resolution of 0.45eV (Ag), and an image resolution of 3μm. The results of the analysis were all corrected with C1s.

FT-IR: The Fourier infrared spectrometer is produced by Bruker, model is VERTEX 70.

3. Results And Discuss

3.1. Effect of bimetal modification on denitration and sulfur resistance of blast furnace slag

Figure 2(a) is the effect of bimetallic modification on the denitration performance of blast furnace slag. Through comparison, it is found that the denitration rate of Mn-Ce bimetal modified blast furnace slag is much higher than that of other catalysts. And compared with the single metal Mn-based blast furnace slag catalyst, the deactivation time is doubled, and its denitration rate is still above 60% at 4 min. It shows that active additive Ce can promote the denitration. This is because the metal oxide formed by the Ce has a strong oxygen storage capacity, and various Ce oxides formed on the surface of the catalyst can be converted by reaction. The redox reaction activity of $\text{Ce}^{3+}/\text{Ce}^{4+}$ can greatly improve the denitration performance of blast furnace slag, and the crystalline structure formed on the blast furnace slag after muffle roasting will reduce the activation energy of the reaction and promote the NH_3 -SCR reaction.³²

Fig. 2(b) shows that after a certain amount of SO_2 was introduced into the system, the denitration efficiency of all catalysts decreased slightly. The Mn-Ce/GGBS catalyst still showed better denitration rate and stability than others, and the total NO removal rate of the best catalyst is 63.24%. The reason why SO_2 can accelerate the deactivation is that SO_2 will react on the catalyst surface to form ammonium sulfate. When SO_2 gathers too much, a large amount of ammonium sulfate will be produced and cover the catalyst surface, which will block the catalyst channel and reduce the catalytic activity. The reason why the catalyst denitration has been improved is that the generated NH_4^+ will react with NO on the catalyst surface, and then the ammonium sulfate will not gather. The added reducing gas SO_2 can increase the oxidation-reduction ability, which is conducive to the reduction of NO. Therefore, the introduction of SO_2 has both inhibition and improvement effects on the activity of the catalyst. When a certain content of SO_2 is introduced, the active component Mn in the catalyst will react with S to form manganese sulfide and manganese sulfate, which will reduce the activity of Mn. At this time, the active component Ce in the catalyst has a more active electronic layer structure than Mn, so it first reacts with SO_2 to generate cerium sulfide or cerium sulfate to protect the denitration performance of the active component Mn.

3.2 Characterization

3.2.1 BET analysis

Table 3 is the average pore size, pore volume and specific surface area of blast furnace slag GGBS and the prepared catalysts Mn-Ce/GGBS(fresh), Mn-Ce/GGBS(inactivated) and Mn-Ce/GGBS(desulfurization). It can be seen that the prepared catalysts are smaller than raw material GGBS. This is due to the cavitation effect of ultrasonic waves, which causes the slag powder and solution in the blast furnace to squeeze and expand, promotes the formation of tiny bubble cavities inside the slag after the droplets impregnated

into the slag escape, and the physical and chemical properties of cavitation can improve its pore size distribution, etc. Therefore, the specific surface area and pore volume of the catalyst can be increased to a certain extent. However, due to ultrasonic vibration and friction, the pore size of the catalyst becomes smaller. After the catalyst undergoes denitration and sulfur resistance, the pore structure becomes smaller and the specific surface area decreases due to the accumulation of ammonium nitrate or sulfate on the catalyst surface to block the pores.

Table 3
BET and pore size in different catalysts

Catalyst	Pore size(nm)	Pore volume(cm ³ ·g ⁻¹)	A _{BET} (m ² ·g ⁻¹)
GGBS	4.289	0.007	1.517
Mn-Ce/GGBS(fresh)	4.179	0.053	21.795
Mn-Ce/GGBS(inactived)	3.914	0.043	16.278
Mn-Ce/GGBS(desulfurization)	3.823	0.040	18.331

Figure 3 shows that N₂ adsorption and desorption of GGBS and Mn-Ce/GGBS(desulfurization) catalysts. Both the GGBS and the sulfur resistant catalysts have H3-type hysteresis rings, indicating that both are mesoporous structures. And the pore size of the prepared catalyst is reduced after sulfur resistance, because the ultrasonic cavitation improves the pore size distribution of the catalyst.

3.2.2. FT-IR analysis

Figure 4 is the infrared spectrum of Ce-modified Mn/GGBS catalysts Mn-Ce/GGBS (fresh), Mn-Ce/GGBS (inactived) and Mn-Ce/GGBS (desulfurization). The water added during the molding process will cause hydration reaction of the slag. The tricalcium silicate in the slag reacts with water to form hydrated calcium silicate and calcium hydroxide. Therefore, at 3649cm⁻¹ and 3615cm⁻¹ are -OH stretching vibration peaks in Ca(OH)₂ produced by the hydration of the three catalysts. GGBS at 3302cm⁻¹, Mn-Ce/GGBS(fresh) at 3310cm⁻¹ is -OH stretching vibration peak of crystallization water, denitration catalyst and anti-sulfur catalyst lose crystal water at 150°C in denitration device. The small peak at 1427cm⁻¹ is caused by the stretching vibration of the Si-O bond of the amorphous SiO₂ in the slag, and the peak is weakened after the catalyst is prepared. At 1381cm⁻¹ is the O-C-O stretching vibration peak in CO₃²⁻. The blast furnace slag has a large envelope peak around 1000cm⁻¹ due to the stretching vibration of Si-O. After being modified by the metal salt, this peak shifts to the direction of high wave number. The slag is the symmetric stretching vibration peak of Si-O-Si in [Si₂O₇]⁶⁻ at 708cm⁻¹, and the shift of the catalyst peak to a low wave number indicates that its polymerization degree has decreased and become active. The slag contains a large amount of CaO, so the vibration absorption peak of the gypsum phase is at 678cm⁻¹. The slag is the bending vibration peak of Si-O-Si at 480cm⁻¹. After the catalyst is prepared, the

peak moves to a low wave number, and the absorption peak gradually becomes sharp. The reason is that during the modification process of the ultrasonic-assisted metal salt, due to cavitation, frictional collision occurs between the slag particles, the particle size becomes smaller, and the activity increases.

3.2.3. XRD analysis

It can be seen from Fig. 5 that after the denitration and sulfur resistance of the Mn-Ce/GGBS catalyst, the main crystal structure has not changed much, and the crystal form mainly based on manganese oxide and cerium oxide. The Mn mainly exists as oxides of Mn_3O_4 and Mn_5O_8 , and the other valence manganese oxides do not exist in the crystal structure, indicating that MnO , MnO_2 , and Mn_2O_3 are amorphous or uniformly dispersed on the catalyst surface. The Ce element is mainly present in the oxides of Ce_6O_{11} and CeO , indicating that CeO_2 and Ce_2O_3 exist in an amorphous or uniformly dispersed form.

On the Mn-Ce/GGBS (fresh) catalyst, the diffraction peaks at 18.111° and 31.531° are Mn_5O_8 (PDF#39-1218), and the diffraction peaks at 60.024° are Mn_3O_4 (PDF#18-0803). The diffraction peaks at 27.857° and 45.960° are Ce_6O_{11} (PDF#32-0196). After inactivation, the diffraction peak of the manganese oxide of Mn-Ce/GGBS (inactivated) catalyst has decreased, and the diffraction peak of Mn_3O_4 at 60.024° is not obvious. The intensity of the diffraction peak of Ce_6O_{11} (PDF#32-0196) at 27.857° has decreased. Compared with the fresh catalyst, the Mn-Ce/GGBS (desulfurization) catalyst has a decrease in the diffraction peak of Ce_6O_{11} at 27.857° , 36.696° is the newly emerging diffraction peak of Ce_6O_{11} (PDF#32-0196), and 50.703° is the newly emerging CeO diffraction peak (PDF#33-0334). The characteristic peak of Mn_2SiO_4 appeared at 50.269° both before and after denitration and after sulfur resistance (PDF#35-0748).

Compare the XRD comparison chart of Mn-Ce/GGBS(fresh), Mn-Ce/GGBS(inactivated), Mn-Ce/GGBS(desulfurization). It can be seen that, comparing Mn-Ce/GGBS (inactivated) and Mn-Ce/GGBS (fresh) catalysts, there is almost no significant change in the XRD peak shape. It shows that the crystal structure of Mn-Ce/GGBS is not destroyed, and the structure of the catalyst remains stable after the reaction. When SO_2 is introduced, the peak shape of Mn-Ce/GGBS (desulfurization) changes slightly. The reason is that SO_2 reacts preferentially with the active components of the catalyst, occupying active sites, introducing new impurities, and consistent with the corresponding reduction in denitration effect.

3.2.4. XPS analysis

Figure 6(a) is the XPS full spectrum and peaks of Ce-modified Mn/GGBS catalysts Mn-Ce/GGBS (fresh), Mn-Ce/GGBS (inactivated) and Mn-Ce/GGBS (desulfurization). Table 4 is the proportion of different elements in the catalyst. It can be seen from Fig. 8(a) that the spectrum contains the peaks of multiple elements Ca, Mg, Si, Ti, C, O, Mn and Ce. Among Ca, Mg and Si. Ti and C are the main components of

blast furnace slag, and Mn, Ce and O will be introduced through the preparation of the catalyst. Therefore, the comparative analysis of the three elements Mn, Ce and O is mainly carried out. Near 950eV is the auger electron peak of the element O. The loading of Mn and Ce is relatively small, so the corresponding peak value is low.

Figure 6(b) and Table 4 that the binding energy of Mn2p of the three catalysts is composed of Mn2p_{1/2} and Mn2p_{3/2}. Fitting the Mn2p_{3/2} sub-peaks can obtain the binding peak positions of Mn with different valence states. The binding energy of Mn-Ce/GGBS (fresh) catalyst on the peak of Mn2p_{3/2} is 644.11eV, the binding energy of Mn³⁺ is 643.22eV, the binding energy of Mn²⁺ is 642.11eV; the ratio of Mn⁴⁺/Mn³⁺ is 7.15. The binding energy of Mn-Ce/GGBS (inactivated) catalyst on the peak of Mn2p_{3/2} is 644.27eV, the binding energy of Mn³⁺ is 642.88eV, the binding energy of Mn²⁺ is 641.72eV; the ratio of Mn⁴⁺/Mn³⁺ is 1.21. The binding energy of Mn-Ce/GGBS (desulfurization) catalyst on Mn2p_{3/2} peak is 643.47eV, the binding energy of Mn³⁺ is 642.29eV, the binding energy of Mn²⁺ is 641.47eV; the ratio of Mn⁴⁺/Mn³⁺ is 1.65. The greater the ratio of Mn⁴⁺/Mn³⁺ the stronger the activity of the catalyst, so Mn-Ce/GGBS (fresh) catalyst has the strongest denitration activity, and the activity decreases after denitration and sulfur resistance. The Mn⁴⁺/Mn³⁺ ratio of the catalyst after sulfur resistance is larger than that after denitration, the reason is that SO₂ forms competitive adsorption with reactants through the intermolecular force on the catalyst surface, After the SO₂ adsorbed on the catalyst surface is oxidized by O₂ to SO₃, it further reacts with the reactant NH₃ to produce (NH₄)₂SO₄ or NH₄HSO₄.

Figure 6(c) and Table 4 that the binding energies of Ce3d (Ce3d_{3/2} and Ce3d_{5/2}) of the three catalysts are not divided into two peaks due to the influence of other impurities. Fitting the location is divided into 8 peaks, Ce is dominated by Ce⁴⁺ and Ce³⁺ elements, where u₃ and v₃ are the binding energy positions of Ce³⁺, and the rest are the binding energy positions of Ce⁴⁺. The binding energy of Mn-Ce/GGBS(fresh) catalyst at different positions is u₁, u₂, u₃, u₄, v₁, v₂, v₃ and v₄, the ratio of Ce⁴⁺/Ce³⁺ is 3.91. The binding energy of Mn-Ce/GGBS (inactivated) catalyst at different positions is u₁, u₂, u₃, u₄, v₁, v₂ and v₃, the binding energy intensity of v₄ is significantly weakened after denitration; the ratio of Ce⁴⁺/Ce³⁺ is 2.07. The binding energy of Mn-Ce/GGBS(desulfurization) catalyst at different positions is u₁, u₂, u₃, u₄, v₁, v₂ and v₃, the binding energy strength of sulfur-resistant catalyst v₄ has also been significantly reduced; the ratio of Ce⁴⁺/Ce³⁺ is 2.51. The greater the ratio of Ce⁴⁺/Ce³⁺, the greater the content of Ce⁴⁺ and the stronger its oxidation ability. Therefore, strengthening the conversion between Ce⁴⁺ and Ce³⁺ and improving the mobility of oxygen can improve the activity of the catalyst, and can also increase the activity of the catalyst by changing the valence state of Mn through the oxidation of Ce⁴⁺. The addition of the active additive Ce can improve the redox capacity of the catalyst, and it can interact with the multivalent Mn and generate electron transfer: $\text{Mn}_2\text{O}_3 + 2\text{CeO}_2 \rightarrow 2\text{MnO}_2 + \text{Ce}_2\text{O}_3$, $\text{Ce}_2\text{O}_3 + 1/2\text{O}_2 \rightarrow 2\text{CeO}_2$. And the introduction of SO₂ will increase the acid sites on the catalyst surface and increase the catalyst activity.

Table 4
Element rate on the different catalysts surface

Catalyst	Mn ⁴⁺ /Mn ³⁺	Ce ⁴⁺ /Ce ³⁺	O _α /O _β
Mn-Ce/GGBS(fresh)	7.15	3.91	27.62
Mn-Ce/GGBS(inactivated)	1.21	2.07	8.34
Mn-Ce/GGBS(desulfurization)	1.65	2.51	1.50

Fig. 6(d) O sub-peak diagram and Table 4 that there are peaks of chemically adsorbed oxygen (O_α) and surface lattice oxygen (O_β) in the three catalysts. The binding energy of Mn-Ce/GGBS(fresh) catalyst for adsorbed oxygen and lattice oxygen is 532.00eV and 529.77eV, respectively, and the ratio of O_α/O_β is 27.62. The Mn-Ce/GGBS(inactivated) catalysts are 532.05eV and 530.12eV, respectively, and the ratio of O_α/O_β is 8.34. The Mn-Ce/GGBS(desulfurization) catalysts are 532.23eV and 531.11eV, respectively, and the ratio of O_α/O_β is 1.50. Chemically adsorbed oxygen is relatively active and plays a major role in the oxidation reaction. It can promote the reaction between NO and O₂ to form NO₂, and then the SCR

reaction occurs: $2\text{NO}_2 + 4\text{NH}_3 + \text{O}_2 \xrightarrow{\text{cat}} 3\text{N}_2 + 6\text{H}_2\text{O}$ or

3.2.5. SEM analysis

Figure 7 is an electron micrograph of different magnifications (20000, 10000 times) of Mn-Ce/GGBS catalyst before and after denitration and after sulfur resistance. Figure 7(a) is Mn-Ce/GGBS(fresh) catalyst, Fig. 7(b) is Mn-Ce/GGBS(inactivated) catalyst, and Fig. 7(c) is Mn-Ce/GGBS(desulfurization) catalyst.

After the denitration of the catalyst Mn-Ce/GGBS(inactivated), the gap between the particles is reduced, and there is a phenomenon of particle agglomeration on the surface of the catalyst. The reason is that the ammonium sulfate generated during the SCR reaction accumulates on the surface of the catalyst, so that it covers the surface of the catalyst, reducing the voids between the particles and the pore structure of the catalyst, which reduces the denitration performance of the catalyst and deactivates it. After introducing a certain amount of SO₂, the active component Mn in the catalyst will react with the S element to produce manganese sulfide and manganese sulfate, which reduces the activity of the Mn element. At this time, since the active component Ce in the catalyst has a more active electron layer structure than Mn, it first reacts with SO₂ to generate cerium sulfide or cerium sulfate to protect the denitration performance of the

active component Mn. Therefore, there are still small particles on the surface of the catalyst like Mn-Ce/GGBS(fresh), and the reduction of the gap between the particles comes from the accumulation of sulfide and sulfate.

4. Conclusion

(1) The denitration rate of Mn-Ce bimetal modified blast furnace slag is much higher than other catalysts. Compared with the single metal Mn-based blast furnace slag catalyst, the deactivation time has doubled, and its denitration rate is still above 60%.

(2) When a certain amount of SO₂ is introduced, the denitration trend of all catalysts except Mn-Ni/GGBS decreases first and then increases slightly. The Mn-Ce/GGBS catalyst still shows better denitration performance than others. And the total NO removal rate of the best catalyst is 63.24%.

(3) Using solid waste blast furnace slag as a catalyst carrier, comprehensive utilization makes it a usable secondary resource, which not only reduces pollution to the environment, but also achieves the utilization of solid waste resources.

Declarations

Authors Contributions

Conceptualization, Zhang Lei(F) and Zhang Lei(M); Methodology, Shu Hao; Software, Wang Yusu; Validation, Jia Yang; Investigation, Shu Hao; Data Curation, Shu Hao; Writing-Original Draft Preparation, Jia Yang; Writing-Review & Editing, Jia Yang and Wang Yusu.

Competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

All data generated or analyses during this study are included in this published article.

Ethical approval: Not applicable

Consent to participate: Not applicable

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References

1. Abazari, R., Esrafil, L., Morsali, A., Wu, YH., Gao, JK., 2021. PMo12@UiO-67 nanocomposite as a novel non-leaching catalyst with enhanced performance durability for sulfur removal from liquid fuels with exceptionally diluted oxidant. *Appl. Catal. B-Environ.* 283, 119582. <https://doi.org/10.1016/j.apcatb.2020.119582>.
2. Abdelhamid, H.N., 2019. Surfactant assisted synthesis of hierarchical porous metal-organic frameworks nanosheets. *Nanotechnology.* 30, 43. <https://doi.org/10.1088/1361-6528/ab30f6>.
3. Agbo, KE., Walgraeve, C., Eze, JI., Ugwoke, PE., Ukoha, PO., Van Langenhove, H., 2021. Household indoor concentration levels of NO₂, SO₂ and O₃ in Nsukka, Nigeria. *Atmos. Environ.* 244, 117978. <https://doi.org/10.1016/j.atmosenv.2020.117978>.
4. Ashraf, A., Butt, A., Khalid, I., Alam, R.U., Ahmad, S.R., 2019. Smog analysis and its effect on reported ocular surface diseases: A case study of 2016 smog event of Lahore. *Atmos. Environ.* 198, 257-264. <https://doi.org/10.1016/j.atmosenv.2018.10.029>.
5. Chen, J.C., Zhang, J.H., Liu, J.Y., Yao, H., Evrendilek, F., Buyukada, M., Xie, W.M., Sun, S.Y., 2020. Co-pyrolytic mechanisms., kinetics., emissions and products of biomass and sewage sludge in N₂, CO₂ and mixed atmospheres. *Chem. Eng. J.* 397, 125372. <https://doi.org/10.1016/j.cej.2020.125372>.
6. Chen, M., Jin, L., Liu, Y., Guo, X.R., Chu, J.W., 2014. Decomposition of NO in automobile exhaust by plasma–photocatalysis synergy. *Environ. Sci. Pollut. R.* 21, 1242-1247. <https://doi.org/10.1007/s11356-013-2021-2>.
7. Chen, M.Y., Zhao, M.M., Tang, F.S., Ruan, L., Yang, B., 2017. Effect of Ce doping into V2O5-WO₃/TiO₂ catalysts on the selective catalytic reduction of NO_x by NH₃. *J. Rare. Earth.* 35 (2017) 1206-1215. <https://doi.org/10.1016/j.jre.2017.06.004>.
8. Dadi, RK., Daya, R., Kumar, A., Joshi, SY., An, HM., Cunningham, MJ., Currier, NW., 2021. A modeling and experimental study on hydrothermal aging deactivation of NO oxidation activity on Pt-Pd catalyst. *Appl. Catal. B-Environ.* 283, 119655. <https://doi.org/10.1016/j.apcatb.2020.119655>.
9. Faizullina, LK., Galimova, YS., Salikhov, SM., Valeev, FA., 2020. Michael Adducts of Levoglucosenone with alpha-Ethoxycarbonyl- and alpha-Nitrocyclododecanones: Transformation into Chiral Macrolides. 56(11) 1434-1439. <https://doi.org/10.1007/s10593-020-02834-x>.
10. Han, J., Kim, T., Jung, H., Pyo, S., Cho, G., Oh, Y., Kim, H., 2019. Improvement of NO_x reduction rate of urea SCR system applied for an non-road diesel engine. *Int. J. Auto. Tech-Kor.* 20 (2019) 1153-1160. <https://doi.org/10.1007/s12239-019-0108-6>.
11. Italiano, C., Balzarotti, R., Vita, A., Latorrata, S., Fabiano, C., Pino, L., Cristiani, C., 2016. Preparation of structured catalysts with Ni and Ni Rh/CeO₂ catalytic layers for syngas production by biogas reforming processes. *Catal. Today.* 273, 3-11. <https://doi.org/10.1016/j.cattod.2016.01.037>.

12. Jablonska, M., Wolkenar, B., Beale, A.M., Pischinger, S., Palkovits, R., 2018. Comparison of Cu-Mg-Al-O-x and Cu/Al₂O₃ in selective catalytic oxidation of ammonia (NH₃-SCO). *Catal. Commun.* 110, 5-9. <https://doi.org/10.1016/j.catcom.2018.03.003>.
13. Jaegers, N. R., Lai, J.K., He, Y., Walter, E., Dixon, D.A., Vasiliu, M., Chen, Y., Wang, C.M., Hu, M.Y., Mueller, K.T., Wachs, I.E., Wang, Y., Hu, J.Z., 2019 Mechanism by which Tungsten oxide promotes the activity of supported V₂O₅/TiO₂ catalysts for NO_x abatement: structural effects revealed by V-51 MAS NMR spectroscopy. *Angew. Chem. Int. Edit.* 58, 12609-12616. <https://doi.org/10.1002/anie.201904503>.
14. Jogi, I., Erme, K., Levoll, E., Raud, J., Stamate, E., 2018. Plasma and catalyst for the oxidation of NO_x. *Plasma. Sources. Sci. T.* 27. <https://doi.org/10.1088/1361-6595/aaae3c>.
15. Jun, HZ., Sun, G., Liu, J.Y., Evrendilek, F., Buyukada, M., 2020. Co-combustion of textile dyeing sludge with cattle manure: Assessment of thermal behavior., gaseous products., and ash Characteristics. *J. Clean. Prod.* 253 (2020) 119950. <https://doi.org/10.1016/j.jclepro.2019.119950>.
16. Lei, Z., Hao, S., Lei, Z., Yang, J., 2020. Gas modified pyrolysis coke for in-situ catalytic cracking of coal tar. *ACS. Omega.* 5(25), 14911-14923. <https://doi.org/10.1021/acsomega.0c00055>.
17. Li, S.C., Zhai, Y., Wei, X.X., Zhang, Z., Kong, X.F., Tang, F.S., 2020. Catalytic Performance of MIL-88B(V) and MIL-101(V) MOFs for the Selective Catalytic Reduction of NO with NH₃. *Chemcatchem.* <https://doi.org/10.1002/cctc.202001622>.
18. Ma, S.J., Wang, XW., Chen, T., Yuan, ZH., 2018. Effect of surface morphology on catalytic activity for NO oxidation of SmMn₂O₅ nanocrystals. *Chem. Eng. J.* 354, 191-196. <https://doi.org/10.1016/j.cej.2018.07.197>.
19. Meng, D.M., Xu, Q., Jiao, Y.L., 2018. Spinel structured CoMnO_x mixed oxide catalyst for the selective catalytic reduction of NO_x with NH₃. *Appl. Catal. B-Environ.*, 221, 652-663.
20. Rahman, M., Rooney., Hara, K., Nakatani, S., 2019. Measurement of automobile NO from bag and continuous stream by quantum cascade laser spectroscopy. *Int. J. Engine. Res.* 20, 261-273. <https://doi.org/10.1177/1468087417750937>.
21. Schroeder, C., Schroeder, W., Yang, S.S., Nystrom, A., Cai, Z., Subramanian, S., Li, S.J., Gundersen, M.A., Cronin, S.B., 2020. Plasma-enhanced NO_x remediation using nanosecond pulsed discharges in a water aerosol matrix. *Fuel. Process. Technol.* 208, 106521. <https://doi.org/10.1016/j.fuproc.2020.106521>.
22. Selvamani, A., Shanthi, K., Santhanaraj, D., Babu, C.M., Srinivasan, V. V., Thirukumaran, P., Ramkumar, V., Shakilaparveen, A., Balasubramanian, R., 2017. Effective removal of automobile exhausts over flower-like Ce_{1-x}Cu_xO₂ nanocatalysts exposed active {100} plane. *J. Rare. Earth.* 36, 603-612. <https://doi.org/10.1016/j.jre.2017.12.006>.
23. Sun, X., Guo, RT., Liu, SW., Liu, J., Pan, WG., Shi, X., Qin, H., Wang, ZY., Qiu, ZZ., Liu, XY., 2018. The promoted performance of CeO₂ catalyst for NH₃-SCR reaction by NH₃ treatment. *Appl. Surf. Sci.* 462, 187-193. <https://doi.org/10.1016/j.apsusc.2018.08.114>.

24. Tamura, M., Matsuda, K., Nakagawa, Y., Tomishige, K., 2018. Ring-opening polymerization of trimethylene carbonate to poly(trimethylene carbonate) diol over a heterogeneous high-temperature calcined CeO₂ catalyst. *Chem. Commun.* 54, 14017-14020. <https://doi.org/10.1039/c8cc08405j>.
25. Theofanidis, S.A., Galvita, V.V., Poelman, H., Batchu, R., Buelens, L.C., Detavernier, C., Marin, G.B., 2018. Mechanism of carbon deposits removal from supported Ni catalysts. *Appl. Catal. B-Environ.* 239, 502-512. <https://doi.org/10.1016/j.apcatb.2018.08.042>.
26. Veerapandian, S.K.P., Ye, Z.P., Giraudon, J.M., De, Geyter. N., Morent, R., Lamonier, J.F., 2019. A plasma assisted Cu-Mn mixed oxide catalysts for trichloroethylene abatement in moist air. *J. Hazard. Mater.* 379, 120781. <https://doi.org/10.1016/j.jhazmat.2019.120781>.
27. Vita, A., Italiano, C., Ashraf, M.A., Pino, L., Specchia, S., 2018. Syngas production by steam and oxy-steam reforming of biogas on monolith-supported CeO₂-based catalysts. *Int. J. Hydrogen. Energ.* 43, 11731-11744. <https://doi.org/10.1016/j.ijhydene.2017.11.140>.
28. Vogel, D.J., Lee, Z.R., Hanson, C.A., Henkelis, S.E., Smith, C.M., Nenoff, T.M., Dixon, D.A., Rimsza, J.M., 2020. Predictive Acid Gas Adsorption in Rare Earth DOBDC Metal-Organic Frameworks via Complementary Cluster and Periodic Structure Models. *J. Phys. Chem. C.* 124, 26801-26813. <https://doi.org/10.1021/acs.jpcc.0c08282>
29. Wahiduzzaman, M., Lenzen, D., Maurin, G., Stock, N., Wharmby, M.T., 2018. Rietveld Refinement of MIL-160 and Its Structural Flexibility Upon H₂O and N₂ Adsorption. *Eur. J. Inorg. Chem.* 32, 3626-3632. <https://doi.org/10.1002/ejic.201800323>.
30. Wang, H., Zhong, H.Y., Bo, G.Z., 2018. Existing forms and changes of nitrogen inside of horizontal subsurface constructed wetlands. *Environ. Sci. Pollut. R.* 25, 771-781. <https://doi.org/10.1007/s11356-017-0477-1>.
31. Yang, Y.R., Wang, M.H., Tao, Z.L., Liu, Q., Fei, Z.Y., Chen, X., Zhang, Z.X., Tang, J.H., Cui, M.F., Qiao, X., 2018. Mesoporous Mn-Ti amorphous oxides: a robust low-temperature NH₃-SCR catalyst. *Catal. Sci. Technol.* 8, 6396-6406. <https://doi.org/10.1039/c8cy01313f>.
32. Zhang, L., Shu, H., Jia, Y., Lei, Z., Bai, F., Kuang, W., Qi, L.B., Shang, J., Chao, Wei., 2021. Study on denitration and sulfur removal performance of Mn-Ce supported fly ash catalyst. *Chemosphere.* 128646. <https://doi.org/10.1016/j.chemosphere.2020.1286>.
33. Zhang, L., Shu, H., Jia, Y., Zhang, L., Xu, D., 2020. Study on Solid Waste Pyrolysis Coke Catalyst for Catalytic Cracking of Coal Tar. *Int. J. Hydrogen. Energ.* 45(38), 19280-19290. <https://doi.org/10.1016/j.ijhydene.2020.05.075>.
34. Zhao, Q., Chen, B.B., Li, J., Wang, X.B., Crocker, M., Shi, C., 2020. Insights into the structure-activity relationships of highly efficient CoMn oxides for the low temperature NH₃-SCR of NO_x. *Appl. Catal. B-Environ.* 277, 119215. <https://doi.org/10.1016/j.apcatb.2020.119215>.

Figures

Figure 1

Catalyst activity evaluation experimental process.

(a). Effect of bentonite on denitration performance of blast furnace slag

(b). Effect of bimetal modification on sulfur resistance of blast furnace slag

Reaction condition: $[\text{NO}]=500\text{ppm}$, $[\text{NH}_3]=500\text{ppm}$, $[\text{SO}_2]=500\text{ppm}$, $[\text{O}_2]=6\%$, N_2 balance

Figure 2

Effect of bimetal modification on denitration and sulfur resistance of blast furnace slag

Figure 3

N₂ adsorption and desorption of GGBS and Mn-Ce/GGBS(desulfurization) catalysts

Figure 4

FT-IR spectrum of Mn-Ce/GGBS catalysts.

Figure 5

XRD patterns of Mn-Ce/GGBS catalysts.

(a) XPS full spectrum

(b) Mn sub-peak diagram

(c) Ce sub-peak diagram

(d) O sub-peak diagram

Figure 6

XPS patterns of Mn-Ce/GBS catalysts.

Image not available with this version

Figure 7

Is an electron micrograph of different magnifications (20000, 10000 times) of Mn-Ce/GGBS catalyst before and after denitration and after sulfur resistance. Fig. 7(a) is Mn-Ce/GGBS(fresh) catalyst, Fig. 7(b) is Mn-Ce/GGBS(inactivated) catalyst, and Fig. 7(c) is Mn-Ce/GGBS(desulfurization) catalyst.

Figure 8

SEM micrographs of Mn-Ce/GGBS catalysts

Supplementary Files

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