Study on Denitration Performance of Solid Waste Blast Furnace Slag Catalysts under Different Preparation Processes

Zhao Lu, Zhang Lei,* Shu Hao, Jia Yang, Zhang Lei, Bai Fang, and Chen Xiaosheng

ABSTRACT: In this article, blast furnace slag, a high-yield industrial solid waste, was taken as the research object and it was used as the main material. Bentonite was used as the binder, and water was added to shape the blast furnace slag into a small column. The denitration catalyst was prepared using different methods, its denitration performances were compared and analyzed, and the best preparation method and process parameters were screened. Results showed that bentonite will clearly improve denitration performance, and 4:1 blast furnace slag and bentonite was selected as the molding ratio to reduce the effect of bentonite on its performance, combined with the hardness and surface adhesion of the prepared carrier. Separately, the catalysts were prepared using citric acid impregnation, hydrothermal decomposition, and mixing method, and active Mn was loaded. Among them, the hydrothermal decomposition method cannot completely decompose in a closed kettle, resulting in a lower denitration performance. The catalyst prepared using the mixing method is superior to that prepared using the impregnation method because the active component prepared by the former was more uniformly dispersed, and simple and easy to operate, which can meet the needs of the excess denitration catalysts of small enterprises.

1. INTRODUCTION
Nitrogen oxide (NO\textsubscript{x}) is one of the important causes of haze and ozone pollution. It is also an important precursor of PM\textsubscript{2.5} and ozone.\textsuperscript{1} It is mainly caused by emissions from motor vehicle exhaust, coal-fired power plants, and industrial sources (steel, coking, cement, glass, and ceramic industries), and industrial emissions are the main source of atmospheric NO\textsubscript{x}.\textsuperscript{2,3} In recent years, although the emission of NO\textsubscript{x} from motor vehicle exhaust and coal fired power plants has been well controlled and reduced, the emission of NO\textsubscript{x} from industrial sources has not been effectively controlled.\textsuperscript{3}

Selective catalytic reduction (SCR) technology is the most commonly used method to remove NO\textsubscript{x} from flue gas.\textsuperscript{5} Research on a low-temperature SCR denitration catalyst started late in China. Although domestic research has made some progress, a certain distance from the industrial application remains.\textsuperscript{6,7} Many problems need to be solved urgently. First, most of the domestic desulfurization systems use wet flue gas desulfurization technology.\textsuperscript{8} The flue gas temperature after desulfurization is below 150 °C, thus improving the low-temperature activity of the catalyst, especially the activity below 150 °C, is very important. Second, after desulfurization, some SO\textsubscript{2} remains in the flue gas. In a low-temperature environment, SO\textsubscript{2} will aggravate the poisoning of the catalyst, resulting in a substantial decrease in the catalyst's denitration effect. Therefore, the sulfur resistance of the SCR catalyst under low temperature conditions must be improved.\textsuperscript{9−11} Third, most of the domestic research is currently focused on the low-temperature activity and sulfur resistance of granular catalysts, and the industrial application of catalysts must be shaped catalysts.\textsuperscript{12,13} Molding preparation
influences catalytic activity and sulfur resistance. The mechanical properties, thermal stability, specific surface area, pore structure, pressure loss, and service life of the molded catalysts are problems that need to be solved. At present, most of the current low-temperature catalysts are supported catalysts, and most carriers such as molecular sieves and activated carbon have a large pore structure. Molecular sieve catalysts can only show activity at high temperatures, compared with other catalysts, they have good acid and corrosion resistance and are suitable for several specific nitrogen removal processes. Activated carbon catalysts and molecular sieve catalysts show higher catalytic activity for oxidizing NO at low temperatures, and even a greater conversion rate of NO at room temperature. The preparation methods of molecular sieves and activated carbon are complicated and costly. Therefore, it is a low-temperature denitration catalyst with high cost performance, high strength, easy molding, and low price, which can maintain a high denitration performance under high concentration conditions.

In recent years, more domestic researchers hope to use the solid waste generated in the industry to prepare high-performance functional materials. Blast furnace slag is the waste slag discharged during blast furnace smelting, and its output accounts for 30−50% of the output of pig iron. If it cannot be processed or used in time, it will cause the accumulation of solid waste and even soil pollution. The composition of blast furnace slag is mainly affected by the source of iron ore and the process of smelting. Therefore, its chemical composition varies within a certain range. Blast furnace slag is mainly composed of alkaline oxides CaO and MgO and acidic oxides Al₂O₃ and SiO₂, in which CaO, MgO, Al₂O₃, and SiO₂ contents are 35.8−43.9, 7.4−13, 6.2−12.5, and 32.4−36.2%, respectively. In addition, blast furnace slag has a small amount of metal oxides and sulfides. The inherent rich oxide content of blast furnace slag determines that it can be used as a rich resource. However, slag is mainly made into cement or a vitreous substance, such that being rich in elements is a waste of resources. With the research and understanding of the performance of slag, people begin to study and use slag in multiple directions. Coupled with the demand for denitrification catalysts, this article selects the solid waste blast furnace slag as a catalyst carrier for denitrification.

Nowadays, many preparation methods including precipitation, impregnation, mixing, ion exchange, and melting are used for preparing denitrification catalysts. The precipitation method is carried out by adding a metal salt to a precipitant and reacting to form a precipitate and obtain a catalyst and a carrier. The impregnation method is obtained by immersing the carrier in a salt solution, followed by drying, roasting, and activating treatment. The mixing method is obtained by mixing, shaping, drying, roasting, and reducing the active component and fine material carrier through mechanical mixing. The ion exchange method has the characteristics of high dispersion and uniform distribution, and is often used in organic catalytic reactions. In the melting method, the active component is melted at a high temperature, and the degree of dispersion of the mixer far exceeds that of the general mixture. At present, few studies focus on the application of blast furnace slag to denitrification. Therefore, selecting a suitable blast furnace slag catalyst preparation method for subsequent research is important.

This article focuses on flue gas from nonelectric power industries, mainly steel, coking, cement, glass, and ceramics. A small columnar denitrification catalyst is prepared according to its characteristics. The temperature of flue gas in nonpower industries is between 120 and 180 °C, and the actual flue gas space velocity in industry is about 3000 h⁻¹. With NO as the main pollutant, its concentration is 500−600 ppm. In this experiment, different methods are used to prepare a blast furnace slag catalytic material and the best preparation method is selected and applied in local enterprises, which can expand the use of blast furnace slag and meet the emission reduction standard requirements of relevant enterprises so as to combine solid waste resource utilization and air pollution control.
2. RESULTS AND DISCUSSION

Owing to multiple valence states of manganese, the catalyst can show excellent redox performance, and the electrons are converted between Mn$^{3+}$ and Mn$^{4+}$, and can show excellent catalytic performance. Similarly, the MnO$_x$/$\gamma$-Al$_2$O$_3$ catalyst presents the best catalytic performance among these supported Mn-based catalysts because of its high dispersion, suitable reduction behavior, largest amount of acid sites, optimal NO$_x$ adsorption capacity, and abundant Mn$^{4+}$ content.$^{44,45}$ The blast furnace slag carrier is loaded with 5% Mn, and prepared by impregnation, hydrothermal decomposition, and mixing methods. Through different preparation techniques, the methods of simple preparation and easy operation are selected for subsequent research.

2.1. Effect of Preparation on the Blast Furnace Slag Catalyst. 2.1.1. Effect of Bentonite on Denitration Performance of the Blast Furnace Slag. Figure 1 shows the effect of different amounts of bentonite on the denitration performance of blast furnace slag. Figure 1a shows that the denitration rates of the carriers with different addition amounts of bentonite (6:1 to 2:1) at 1 min were 71.37, 74.31, 76.08, 79.80, and 83.73%, while that of the pure bentonite carrier was 86.47%. Figure 1b shows NO treatment capacity and the total NO conversion rate, the denitration rate of pure bentonite was still the best. The denitration rate of blast furnace slag with ratios of 2:1 and 3:1 was higher than that in the first 5 min. Therefore, 4:1 was selected as the optimal ratio of blast furnace slag molding to reduce the effect of added bentonite on the performance of the slag, combined with the roughness and adhesion of the surface of the carrier during the preparation of the carrier.

The catalyst carrier prepared by blast furnace slag mixing with bentonite changed its physical properties after roasting. The main performances were as follows. First, the color was changed from white to yellowish brown. Second, hardness increased. Third, after immersion in water, the roasted carrier could be immersed in water for a long time, whereas the nonroasted carrier would loosely collapse after a slight immersion, as shown in Figure 2.
Pure bentonite and the preferred 4:1 ratio of the formed blast furnace slag were selected to compare the denitration performance before and after roasting. The results are shown in Figure 3. Figure 3a shows that the denitration rate of pure bentonite before and after roasting hardly changed, indicating that heat treatment would not change the performance of bentonite. The preferred 4:1 ratio of formed blast furnace slag denitration performance considerably improved after roasting because the residual water in the blast furnace slag would evaporate to form more pore structures, and the water phase would lose moisture and become active sites, which was conducive to the adsorption of NH₃ and NO on the blast furnace slag. Figure 3b shows NO treatment capacity and the total NO conversion rate. Combined with Figure 3a, heat treatment could improve the performance of the material. Compared with the nonroasted carrier, roasting helped improve denitration performance. The lower the bentonite content was, the more evident the denitration increased after roasting. This finding indirectly indicated that the blast furnace slag would improve its performance with the increase of heat treatment.

2.1.2. Citric Acid-Impregnation Method. Figure 4 shows the influence of citric acid concentration on the performance of the catalyst prepared by the impregnation method. Figure 4a shows that under the condition of loading 5% Mn, adding different concentrations of citric acid could improve the denitration performance of the Mn-based blast furnace slag. At 1.5 min, the denitration rate was still 67.26%. Figure 4b shows NO treatment capacity and the total NO conversion rate. Combined with Figure 4a, the denitration efficiency decreased.
gradually. The performance of the Mn-based slag catalyst with 0.01% citric acid was better than that of the others, and the total NO treatment rate reached 41.03%. Citric acid could promote the combination of Mn on the surface of the carrier and the active site, but excessive citric acid would change the acidity of the catalyst surface and the distribution of active sites when the amount of citric acid was very large, resulting in decreased catalytic activity.46,47

2.1.3. Hydrothermal Decomposition Method. Figure 5 shows the effect of different hydrothermal times on denitration performance. Figure 5a shows that the denitration performance of blast furnace slag impregnated with active components and heated in a polytetrafluoroethylene hydrothermal kettle did not change substantially. Before 1 min, the denitration rate of blast furnace slag decomposed by hydrothermal decomposition was slightly higher than that of the carrier because the hydrothermal kettle was a closed container. A small amount of impregnated nitrate would decompose at a high temperature to produce part of gaseous substances, and the water would show a gaseous state at 180 °C. Manganese nitrate underwent limited decomposition in a hydrothermal kettle, and the generated gas was equivalent to gas activation of the carrier. Figure 5b shows that the total removal rate and the removal amount of the catalyst after hydrothermal decomposition were lower than those of the carrier. Because it cannot be completely decomposed in the sealed hydrothermal kettle, that was, the manganese nitrate was produced at the same time as the decomposition produces manganese oxide. Therefore, in the later stage of denitration, the completely decomposed manganese nitrate could not play a catalytic role, resulting in a lower effect than the carrier.

Figure 6. Effect of different loadings of manganese nitrate on denitration performance. (a) Denitration performance. (b) NO treatment capacity and the total NO conversion rate.

Figure 7. Effect of different preparation processes on denitration performance. (a) Denitration performance. (b) NO treatment capacity and the total NO conversion rate.
2.1.4. Mixing Method. Figure 6 shows the effect of different loadings of manganese nitrate on denitration performance. Figure 6a shows the denitration performance under mixing method. Figure 6b shows the total removal rate and the removal amount of the catalyst. It can be seen that as the concentration of manganese nitrate increased, the denitration performance of blast furnace slag increased. Under different loadings (1, 3, 5, 7, and 9%), the blast furnace slag with 5% loading showed a better denitration performance, and its denitration rate was higher than other loadings. The denitration rate of about 60% was still maintained at 2 min, and the denitration rates at 0.5, 1, and 1.5 min were 98.43, 92.75, and 76.28%, respectively. Because when the loading amount was too small, the distribution of active components on the surface of the catalyst was uneven, when the loading amount was too large, it would block the pores of the catalyst and reduce its denitration performance.

2.2. Comparison of Preparation of the Blast Furnace Slag Catalyst. Compared with three different preparation processes, the loading amount of active component Mn was 5%. The catalysts prepared using the impregnation, hydrothermal, and mixing methods were named Mn-BBGS(I), Mn-BBGS(H), and Mn-BBGS(M), respectively. Their denitration performances are compared in Figure 7.

Figure 7a shows the denitration performance of different preparation processes. The performances of the impregnation and mixing method were much higher than those of hydrothermal decomposition. Figure 7b shows NO treatment capacity and the total NO conversion rate. It can be seen that the catalyst prepared by the mixing method exhibited a better denitration performance, and the total NO removal rate of the mixing method was 48.61% because the hydrothermal decomposition temperature was low, manganese nitrate cannot be completely decomposed, and its denitration performance was low. The catalysts prepared using the impregnation method and the mixing method showed good denitration performance. According to reports in the literature, the mixing method was similar to the excess impregnation method. Thus, their denitration curve trends are similar, and the excess impregnation method can make the active components more uniformly distributed.18,49

2.3. Characterization. 2.3.1. FT-IR Analysis. Figure 8 shows the infrared spectra of the optimal catalyst Mn/GGBS(ground granulated blast-furnace slag, 5%) prepared using the mixing method, which are recorded as Mn/GGBS(fresh) and Mn/GGBS(inactive) before and after denitration, respectively. The water added during molding would cause the hydration reaction of the slag. The tricalcium silicate in the slag reacts with water to form hydrated calcium silicate and calcium hydroxide. Therefore, the –OH stretching vibration peak in Ca(OH)₂ at 3625 cm⁻¹ is from hydration. The fresh catalyst has the –OH stretching vibration peak of crystal water at 3286 cm⁻¹, the catalyst loses part of crystal water at 150 °C in the denitrination device after the reaction, and the peak position shifts to 3422 cm⁻¹. The small peak at 1423 cm⁻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. The O–C–O stretching vibration peak in CO₁₋₂ is at 382 cm⁻¹. The blast furnace slag has a large peak at about 1000 cm⁻¹ caused by the stretching vibration of Si–O. The blast furnace slag has a large peak at about 971 cm⁻¹ caused by the stretching vibration of Si–O. After forming, this peak shifts to the direction of a high wave number. The slag at 708 cm⁻¹ is the Si–O–Si symmetrical stretching vibration peak in [SiO₄]⁶⁻, whereas the catalyst shifting the peak to a low wave number indicates that its degree of polymerization decreased and became active. The slag is the flexural vibration peak of Si–O–Si at 480 cm⁻¹. After the catalyst is prepared, the peak moves to a low wave number, and the absorption peak gradually becomes sharp. Because during catalyst preparation, mixing makes slag particle friction and collision between them, the particle size becomes smaller and activity increases.

2.3.2. X-ray Diffraction Analysis. Figure 9 shows that the raw material blast furnace slag is dominated by the nonmetal oxide crystal form. The prepared catalyst has a peak between 25° and 30°, because the main component of the added binder bentonite is SiO₂, which causes the main peak of the prepared catalyst to change. The Mn-based blast furnace slag catalyst prepared by the mixing method is referred to as Mn/GGBS(M). Figure 9 shows the X-ray diffraction (XRD) patterns of Mn/GGBS(fresh) and Mn/GGBS(inactive) before denitration.
and after denitration. In Mn/GGBS(fresh), 21.855° is the diffraction peak of manganese oxide Mn$_2$O$_7$ (PDF#79-0083) and 36.362° is the diffraction peak of manganese oxide Mn$_5$O$_8$ (PDF#72-1427). The diffraction peaks at 34.652 and 40.226° are attributed to MnO (PDF#72-1533) from skutterudite, 59.880° is the diffraction peak attributed to Mn$_3$O$_4$ (PDF#89-4837) from Ermenite, but MnO$_2$ and Mn$_2$O$_3$ have no obvious diffraction peaks. These two oxides are amorphous or uniformly dispersed on the catalyst surface. After denitration, the diffraction peaks of Mn/GGBS(inactive) are weakened to some extent. Only 37.263° is the newly formed diffraction peak of MnO$_2$ (PDF#89-5171). The catalyst after denitration formed a silicate crystal structure at 50.285°, and the main phase weakened causing a complicated side reaction.

2.3.3. Scanning Electron Microscopy Analysis. Blast furnace slag powder (GGBS) mainly presents an angular, irregular shape, with sharp edges, containing many fine debris-like particles of uneven size. Figure 10 shows the scanning electron micrograph of the Mn-based blast furnace slag catalyst Mn/GGBS(M), and the magnifications are 40,000, 20,000, 10,000, and 5000 times. The Mn-based blast furnace slag prepared by the mixing method has no sharp edges and small crumb-like particles. The surface of the particles is relatively rough, the edges of the particles are light in color, and appears layered at high magnification. After the manganese salt is etched and modified on the surface of the particles, the large particles tend to delaminate. The slag modified by manganese salt cannot adjust the gradation distribution of particles like the basic oxide-modified slag to increase its specific surface area. However, the multilayer structure can effectively increase the specific surface area of the particles, facilitate the combination of active components and slag particles, and improve the denitration performance of the slag.

3. CONCLUSIONS

Blast furnace slag and bentonite are formed in a certain proportion to prepare a catalyst carrier. Different methods are used to prepare a denitration catalyst. The denitration performance of the catalyst prepared using the mixing method is superior to others, and the operation is relatively simple, which can provide theoretical support for small industrial enterprises.

(1) The addition of bentonite can improve the molding effect, but also influence its denitration performance. Therefore, the best molding ratio of blast furnace slag and bentonite is 4:1, and the amount of water is 30 wt% to reduce the influence of bentonite on its denitration performance.

(2) The denitration catalyst is prepared using three methods: citric acid impregnation, hydrothermal decomposition, and mixing. The catalyst prepared using the mixing method shows the best performance and highest denitrification efficiency, and the preparation method is relatively simple.

(3) The active components of the catalyst prepared using the mixing method are more uniform than those prepared using the impregnation method. The XRD pattern shows no evident diffraction peaks of MnO$_2$ and Mn$_2$O$_3$ on the catalyst surface, indicating that these two oxides are amorphous or uniformly dispersed on the catalyst surface.

4. MATERIALS AND METHODS

4.1. Materials. 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 2.

Table 1. Main Chemical Components of Ground Granulated Blast Furnace Slag (%)

| Element | CaO | MgO | Al$_2$O$_3$ | SiO$_2$ | MnO | TiO$_2$ | SO$_3$ | K$_2$O | Fe$_2$O$_3$ | Total |
|---------|-----|-----|-------------|--------|------|--------|-------|-------|-----------|-------|
| CaO     | 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 (%)

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

Figure 10. Electron micrographs of the Mn/GGBS(M) catalyst at different magnifications.
4.2. Preparation of Catalyst. 4.2.1. Preparation of Blast Furnace Slag Catalyst Carrier Using Extrusion Molding. The formed carrier needs to be roasted to increase the hardness and strength before it can be used to prepare the catalyst using the impregnation method. Therefore, the formed carrier must be continuously roasted in a muffle furnace at 400 °C for 1 h. Different ratios of slag and bentonite were selected (2:1, 3:1, 4:1, 5:1, and 6:1). The slag and bentonite were mixed according to the ratio. Next, 30 wt % of distilled water was added, and stirred evenly, it is extruded and extruded into a strip, dried in a drying cabinet at 100 °C for 1 h, cut into sections, and roasted in a muffle furnace at 400 °C for 1 h.

4.2.2. Preparation of Denitration Catalyst Using Citric Acid Impregnation Method. Manganese nitrate was dissolved in water. A certain amount of citric acid (0, 0.01, 0.03, 0.05, 0.07, and 0.09%) was added, mixed evenly, and impregnated on the preferred blast furnace slag carrier (4:1 roasting). It was taken out after sealing and standing for 24 h, dried in a drying cabinet at 100 °C for 1 h, and placed in a muffle furnace at 400 °C for 2 h.

4.2.3. Preparation of Denitration Catalyst Using Hydrothermal Decomposition. First, 40 g of the shaped and roasted carrier was weighed and immersed in the active component manganese nitrate solution, and then put into a polytetrafluoroethylene hydrothermal kettle. The oven temperature was set to 180 °C, and the catalyst was heated for 2, 4, 6, 8, and 10 h.
4.2.4. Preparation of Denitration Catalyst Using Mixing Method. The manganese nitrate solution with different contents (1, 3, 5, 7, and 9%) was weighed and dissolved in a beaker with water. After adding the blast furnace slag powder, it was mechanically stirred for 1 h. The blast furnace slag powder modified by manganese nitrate was dried and formed, and finally it was roasted in a muffle furnace at 400 °C for 2 h to produce the Mn-based blast furnace slag catalysts, which were denoted as Mn/GGBS(1%), Mn/GGBS(3%), Mn/GGBS(5%), Mn/GGBS(7%), and Mn/GGBS(9%).

4.3. Catalytic Activity Evaluation. The activity evaluation of the catalyst is shown in Figure 11.

4.4. 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 1000 mL/min, in which nitrogen monoxide was 510 ppm, 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 using a flue gas analyzer (Testo 340).

The calculation method is:

\[
\text{NO conversion rate} = \frac{C_{\text{NO, inlet}} - C_{\text{NO, outlet}}}{C_{\text{NO, inlet}}} \times 100\% (1)
\]

\[
\text{NO removal amount} = M_\text{NO} \times 22.4 \times t \times C_{\text{NO}} \times Q_{\text{total}} (2)
\]

\[
\text{total NO removal rate} = \frac{\text{removed NO}}{\text{unremoved NO}} (3)
\]

4.5. Experimental Characterization. 4.5.1. Fourier Transform Infrared. A general analysis method that can be used to observe and analyze the molecular structure of a compound can be used to determine and identify the nature and quantity of the compound. The Fourier infrared spectrometer used in this work was produced by Bruker, and the model is VERTEX 70.

4.5.2. X-ray Diffraction. The sample was tested using a XD-3 X-ray diffraction analyzer to obtain an XRD pattern. The composition of grains and materials formed on the surface of the catalyst was observed, and the denitration mechanism was studied from the viewpoint of catalyst crystallites and dispersion.

4.5.3. Scanning Electron Microscopy. Secondary electron signal imaging was used to capture the characteristics of the surface of the sample, that was, the sample was scanned with a particularly narrow electron beam, causing the two to interact and produce an effect. The secondary electrons magnify the topography of the sample surface, which was created chronologically as the sample scanned. The scanning electron microscopy model used in this study was JSM-6460LV, the working voltage was 20 kV, and the magnification was 5000 times.

**Authors**

Zhao Lu — School of Geology and Environment, Xi’an University of Science and Technology, Xi’an 710054, China; Shu Hao — Institute of Water Resources and Hydro-Electric Engineering, Xi’an University of Technology, Xi’an 710048, China; Jia Yang — Institute of Water Resources and Hydro-Electric Engineering, Xi’an University of Technology, Xi’an 710048, China; Zhang Lei — China National Heavy Machinery Research Institute Co, Ltd, Xi’an 710032, China; Bai Fang — CAS Key Laboratory of Green Process and Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China; Chen Xiaosheng — Shenniu Hongliulin Coal Mine of Shanxi Coal Industry Co., Ltd., Shenniu 719300, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c03672

**Author Contributions**

Z.L. (F) and Z.L. (M) conceptualized the work, S.H., J.Y. assisted in software programming, Z.L. and S.H. validated the experiments, Z.L. (F) helped in conducting the investigation, S.H. assisted in data curation, Z.L. assisted in writing the original draft, and Z.L., B.F., and C.X. assisted in writing, reviewing, and editing.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was supported by the National Natural Science Foundation of China [grant number 51704230]; Key Laboratory of Coal Resources Exploration and Comprehensive Utilization, Ministry of Natural Resources in P.R. China [grant number KF2019-7]; Shanmxi Key Research and Development Project [grant number 2019ZDLSF05-05-01]; 2019 Shaanxi Provincial Natural Science Basic Research Program Enterprise Joint Fund Project [grant number 2019JL-01]; Open Fund of Shanmxi Key Laboratory of Geological Support for Coal Green Exploitation [no. DZBZ2020-08]; and Xi’an Science and Technology Plan Project [grant number 2019217714GXRC013CG014-GXYD134].

**REFERENCES**

(1) Ashraf, A.; Butt, A.; Khalid, I.; Alam, R. U.; Ahmad, S. R. Smog analysis and its effect on reported ocular surface diseases: A case study of 2016 smog event of Lahore. Atmos. Environ. 2019, 198, 257–264.

(2) Zhang, L.; Jia, Y.; Zhang, L.; He, H. B.; Yang, C.; Luo, M.; Xiao, J. T. Preparation of soybean oil factory sludge catalyst by plasma and the kinetics of selective catalytic oxidation denitrification reaction. J. Clean. Prod. 2019, 217, 317–323.

(3) Zhao, H.; Song, Q.; Liu, S.; Li, Y.; Wang, X.; Shu, X. Study on catalytic co-pyrolysis of physical mixture/staged pyrolysis characteristics of lignite and straw over an catalytic beds of char and its mechanism. Energy Convers. Manage. 2018, 161, 13–26.

(4) Song, Q.; Zhao, H.; Jia, J.; Zhang, F.; Wang, Z.; Lv, W.; Yang, L.; Zhang, W.; Zhang, Y.; Shu, X. Characterization of the products obtained by pyrolysis of oil sludge with steel slag in a continuous pyrolysis-magnetic separation reactor. Fuel 2019, 255, 115711.

(5) Jaegers, N. R.; Lai, J. K.; He, Y.; Walter, E.; Dixon, D. A.; Vasiliiu, M.; Chen, Y.; Wang, C.; Hu, M. Y.; Mueller, K. T.; Wachs, I. E.; Wang, Y.; Hu, J. Z. Mechanism by which Tungsten Oxide Promotes the Activity of Supported V₂O₅/TiO₂ Catalysts for NOX Abatement.
Structural Effects Revealed by V-51 MAS NMR Spectroscopy. Angew. Chem., Int. Ed. 2019, 58, 12609–12616.

(6) Lei, Z.; Hao, S.; Yang, J.; Zhang, L.; Fang, B.; Wei, K.; Lingbo, Q.; Jin, S.; Wei, C. Study on denitration and sulfur removal performance of Mn-Ce supported fly ash catalyst. Chemosphere 2020, 128646.

(7) Huang, Y.; Liu, S.; Zhang, J.; Syed-Hassan, S. S. A.; Hu, X.; Sun, H.; Zhu, X.; Zhou, J.; Zhang, S.; Zhang, H.; Zhang, H. Volatile-char interactions during biomass pyrolysis: Cleavage of C-C bond in a β-5 lignin model dimer by amino-modified graphitized carbon nanotube. Bioresour. Technol. 2020, 307, 123192.

(8) Ma, Y.; Yuan, D.; Mu, B.; Gao, L.; Zhang, X.; Zhang, H. Synthesis, properties and application of double salt (NH4)2Mg(SO4)2·6H2O in wet magnesium-ammonia FGD process. Fuel 2018, 219, 12–16.

(9) Bergman, S. L.; Dahlin, S.; Meslov, V. V.; Xiao, Y.; Englund, J.; Xi, S.; Tang, C.; Skoglundh, M.; Pettersson, L. J.; Bernasek, S. L. In situ studies of oxidation/reduction of copper in Cu-CHA SCR catalysts: Comparison of fresh and SO2-poisoned catalysts. Appl. Catal., B 2020, 269, 118722.

(10) Zhang, Y.; Zheng, C.; Hu, F.; Zhao, H.; Liu, S.; Yang, Z.; Zhu, Y.; Gao, X. Field test of SO3 removal in ultra-low emission coal-fired power plants. Environ. Sci. Pollut. Res. 2020, 27, 4746–4755.

(11) Park, J.-H.; Ahn, J.-W.; Kim, K.-H.; Son, Y.-S. Historic and future review of electron beam technology for the treatment of SO2 in flue gas. Chem. Eng. J. 2019, 355, 351–366.

(12) Xu, Z.; Li, Y.; Guo, J.; Xiong, J.; Lin, Y.; Zhu, T. An efficient and sulfur resistant K-modified activated carbon for SCR denitration compared with acid- and Cu-modified activated carbon. Chem. Eng. J. 2020, 395, 125047.

(13) Yan, D.; Li, Q.; Zhang, H.; Zhou, X.; Chen, H. A highly dispersed mesoporous zeolite@TiO2 supported Pt for enhanced sulfur-resistance catalytic CO oxidation. Catal. Commun. 2020, 142, 106042.

(14) Vignesh, R.; Ashok, B. Critical interpretative review on current outlook and prospects of selective catalytic reduction system for NOx strategy in combustion: Emission, kinetic and ash conversion patterns. Int. J. Engine Res. 2020, 21, 1542–1565.

(15) Selvamani, A.; Shanthi, K.; Santhanaraj, D.; Babu, C. M.; Srinivasan, V. V.; Thirukumar, P.; Ramkumar, V.; Shalikaparveen, A.; Balasubramanian, R. Effective removal of automobile exhausts over flower-like Ce1-xCuxO2 nanocatalysts exposed active {100} planes. J. Rare Earths 2018, 36, 603–612.

(16) Zhao, H.; Li, Y.; Song, Q.; Liu, S.; Ma, Q.; Ma, L.; Shu, X. Catalytic reforming of volatiles from co-pyrolysis of lignite blended with corn straw over three different structures of iron ores. J. Aanal. Appl. Pyrol. 2019, 2019, 144, 104714.

(17) Song, Y.; Hu, J.; Liu, J.; Evrendilek, F.; Buyukada, M. Catalytic effects of CaO, Al2O3, Fe2O3, and red mud on Pteris vittata combustion: Emission, kinetic and ash conversion patterns. J. Cleaner Prod. 2020, 252, 119646.

(18) Yu, J. C.-C.; Nguyen, V.-H.; Lasek, J.; Wu, J. C. S. Titania nanosheet photocatalysts with dominantly exposed {001} reactive facets for photocatalytic NOx abatement. Appl. Catal., B 2017, 219, 391–400.

(19) Karamitros, D.; Koltatsakis, G. Model-based optimization of catalyst zoning on SCR-coated particulate filters. Chem. Eng. Sci. 2017, 173, 514–524.

(20) Lei, Z.; Hao, S.; Zhang, L.; Yang, J.; Yusu, W. MnOx-CuOx cordierite catalyst for selective catalytic oxidation of the NO at low temperature. Environ. Sci. Pollut. Res. 2020, 27, 23695–23706.

(21) Chang, G.; Yang, H.; Ju, C.; Yang, Y. Novel selection of environment-friendly cementitious materials for winter construction: Alkali-activated slag/Portland cement. J. Cleaner Prod. 2020, 258, 120592.

(22) Abdelhamid, H. N. Surfactant assisted synthesis of hierarchical porous metal-organic frameworks nanosheets. Nanotechnology 2019, 30, 435601.

(23) Song, Q.; Zhao, H.; Jia, J.; Yang, L.; Lv, W.; Gu, Q.; Shu, X. Effects of demineralization on the surface morphology, microcrystalline and thermal transformation characteristics of coal. J. Aanal. Appl. Pyrol. 2020, 145, 104716.

(24) Zhang, L.; Shu, H.; Li, Y.; Guo, X.; Chen, H.; Zhang, H. Synthesis, properties and application of double salt (NH4)2Mg(SO4)2·6H2O in wet magnesium-ammonia FGD process. Fuel 2018, 219, 12–16.

(25) Bergman, S. L.; Dahlin, S.; Meslov, V. V.; Xiao, Y.; Englund, J.; Xi, S.; Tang, C.; Skoglundh, M.; Pettersson, L. J.; Bernasek, S. L. In situ studies of oxidation/reduction of copper in Cu-CHA SCR catalysts: Comparison of fresh and SO2-poisoned catalysts. Appl. Catal., B 2020, 269, 118722.

(26) Zhang, Y.; Zheng, C.; Hu, F.; Zhao, H.; Liu, S.; Yang, Z.; Zhu, Y.; Gao, X. Field test of SO3 removal in ultra-low emission coal-fired power plants. Environ. Sci. Pollut. Res. 2020, 27, 4746–4755.
(42) Zhang, L.; Shu, H.; Jia, Y.; Zhang, L.; Kuang, W. Study on in-situ catalytic cracking of coal tar by plasma preparation of pyrolysis coke catalyst. ACS Omega 2020, 5, 14924–14932.
(43) Li, X.; Feng, J.; Xu, Z.; Wang, J.; Wang, Y.; Zhao, W. Cerium modification for improving the performance of Cu-SSZ-13 in selective catalytic reduction of NO by NH3. React. Kinet., Mech. Catal. 2019, 128, 163–174.
(44) Qi, Y.; Shan, X.; Wang, M.; Hu, D.; Song, Y.; Ge, P.; Wu, J. Study on low-temperature SCR denitration mechanisms of manganese-based catalysts with different carriers. Water, Air, Soil Pollut. 2020, 231, 289.
(45) Yao, X.; Kong, T.; Yu, S.; Li, L.; Yang, F.; Dong, L. Influence of different supports on the physicochemical properties and denitration performance of the supported Mn-based catalysts for NH3-SCR at low temperature. Appl. Surf. Sci. 2017, 402, 208–217.
(46) Wang, B.; Yan, X.; Zhang, X.; Zhang, H.; Li, F. Citric acid-modified beta zeolite for polyoxymethylene dimethyl ethers synthesis: The textural and acidic properties regulation. Appl. Catal., B 2020, 266, 118645.
(47) Liu, Y.; Zhang, R.; Ren, H.; Liu, Y.; Ling, S.; Zhang, H.; Liu, B.; Cheng, R. CrV bimetallic philips catalyst prepared by citric acid-assisted impregnation on ethylene polymerization. Macromol. Chem. Phys. 2020, 221, 2000010.
(48) Bararpour, S. T.; Karami, D.; Mahinpey, N. Post-combustion CO2 capture using supported K2CO3: Comparing physical mixing and incipient wetness impregnation preparation methods. Chem. Eng. Res. Des. 2018, 137, 319–328.
(49) Antlimova, T.; Lie-Andersen, T.; Jensen, E. P.; Prag, C. B.; Nielsen, U. G.; Sørensen, D. R.; Skou, E. M.; Christensen, E.; Bjerrum, N. J.; Li, Q. The effect of preparation method on the proton conductivity of indium doped tin pyrophosphates. Solid State Ionics 2015, 278, 209–216.