Effect of Co-combustion of Multiple Additives with Coal on NO Removal

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ABSTRACT: Denitrification experiments of co-combustion of coal and additives were carried out in a horizontal tube furnace. The results showed that calcium acetate limited the production of NO2. The optimum calcination temperature of CTAB-Zr-TiO2 was 673 K. The denitrification efficiency reached up to 72.27%, and desulfurization efficiency reached 83.03% when corncob, calcium acetate, and CTAB-Zr-TiO2 were added. Corncob, calcium acetate, and CTAB-Zr-TiO2 all promoted coal combustion. The specific surface area of CTAB-Zr-TiO2 (55.50 m²/g) was the largest, which was more than 4.5 times that of pure TiO2 (12.20 m²/g). The denitrification process in the co-combustion of coal with multiple additives included a homogeneous reaction and heterogeneous reaction. The homogeneous reaction was that NO and NO2 were reduced to N2 by reducing gases produced in combustion. The heterogeneous reaction involved the reduction of NO and NO2 by coal char. The additives increased the specific surface area of the coal char and enhanced the activity of the heterogeneous reduction of NO and NO2. At the same time, the catalysis of alkali metal oxides in corncob and CTAB-Zr-TiO2 promoted the heterogeneous reduction of NO and NO2 by the coal char.

1. INTRODUCTION

Energy is produced through the combustion of coal, and nitrogen oxides (NOx) are the main air pollutants produced in the process.1 Currently, the main technologies for reducing NOx emissions are flue gas denitrification and low-NOx combustion technology.2 The technology and equipment required for low-NOx combustion are not yet ready for comprehensive application. The main reduction methods used in coal-fired power plants are the SCR method and SNCR method,3−5 and only SNCR is suitable for high temperature. However, SNCR requires a large amount of reductant, and the treated nitrogen oxide still faces difficulty in meeting the ultralow emission requirements, so additional processing costs are required.4 Therefore, an economical and reliable technology must be developed for controlling NOx emissions in coal-fired processes. Many studies have indicated that NOx emissions can be controlled by adding chemical components such as carbon monoxide, ammonia, unburned hydrocarbons, and limestone.5,6 Using small amounts of chemical additives to limit NOx emissions is simple, highly efficient, and inexpensive.9 The desirability of new pollutant-treatment technologies based on clean energy sources has increased due to the serious environmental changes caused by the production of non-renewable energy. Some studies have indicated that the co-combustion of coal and biomass can increase the ignition point, enhance the ignition performance, and facilitate the complete combustion of coal in the furnace because of the low ignition temperature and abundant volatile content of biomass.10,11 In addition, the emission concentration of sulfur oxide (SOx), NOx, and other pollutant emissions is lower when coal is co-combusted with biomass.12,13 Zhang et al. found that the peanut shell burned at 800 °C with a denitrification efficiency of 41.58% and desulfurization efficiency of 10.25%.14 Liu et al.15 found a synergistic effect of bituminous coal with corncob or hardwood. Moreover, they found that the combustion of a mixture of biomass and coal outperforms that of coal alone. However, the abundant alkali metals (e.g., potassium and sodium) and chlorine in biomass can easily cause slagging in fluidized bed combustion.16 Calcium-based additives are effective flue-gas desulfurization agents.17 Studies have shown that organic calcium compounds (OCCs) decompose easily and produce numerous hydrocarbons (CmHn) at high temperature. These hydrocarbons can reduce NO. The CaO produced by OCCs at high temperatures catalyzes the heterogeneous reduction of NO by coal.
char; thus, the production of CaO reduces the NO released. Consequently, the addition of OCCs and biomass in coal combustion reduces the slagging in biomass and coal combustion and the NO\textsubscript{x} emitted in flue gas. Daood et al.\textsuperscript{19} proposed that additives (such as SiO\textsubscript{2}, TiO\textsubscript{2}, and Fe\textsubscript{2}O\textsubscript{3}) added in small quantities to the co-combustion of coal and biomass can enhance the decomposition of volatile hydrocarbons to promote the reduction of NO and reduce NO\textsubscript{x} emissions. Because of the small specific surface area of pure TiO\textsubscript{2}, its catalytic activity is limited. Some studies have indicated that doping a few transition metal ions (such as Mn, Ce, etc.) into TiO\textsubscript{2} can inhibit lattice growth, increase the specific surface area, and improve catalytic efficiency.\textsuperscript{20} These studies have shown that the addition of a rare earth element can significantly enhance the activity of the catalyst. In addition, the doping of Zr at low temperature has been studied,\textsuperscript{21–23} but there are few studies at high temperature. Therefore, Zr was doped into TiO\textsubscript{2} as a doping element in this paper. The pore volume, specific surface area, and adsorption capacity of TiO\textsubscript{2} can be increased by adding a pore-forming agent. Yi et al.\textsuperscript{24} used ultrasonically assisted pore-forming agents [cetyltrimethylammonium bromide (CTAB), NH\textsubscript{4}NO\textsubscript{3}, and urea] to modify the surface of the adsorbent Al\textsubscript{2}O\textsubscript{3}@TiO\textsubscript{2}–Ce. In their study, the CTAB-modified adsorbent exhibited the most effective denitrification. Therefore, CTAB was used in this study as a pore-forming agent in the preparation of TiO\textsubscript{2}.

In recent years, we found that adding multiple additives in the process of coal combustion can promote the removal of NO\textsubscript{x}, SO\textsubscript{2}, Hg, and other pollutants.\textsuperscript{25–27} The results showed that the modified TiO\textsubscript{2} increased combustion efficiency, promoted calcium oxide desulfurization, and effectively alleviated the slagging problem of the boiler caused by desulfurizers and biomass.\textsuperscript{25,26} We found that multiple additives effectively improved the efficiency of mercury removal and desulfurization, but the denitrification efficiency was only about 43%.\textsuperscript{27} Therefore, to improve the efficiency of denitrification, this paper continued to study the effects of various additives such as biomass corncob, desulfurizer, and modified TiO\textsubscript{2} on the denitrification and denitrification mechanism during coal combustion. This study provides theoretical guidance for the resource utilization of biomass and the feasibility of co-combustion technology in the circulating

Table 1. Proximate and Ultimate Analysis Results for Coal and Biomass (wt %, Air-Dry Basis)

| samples     | moisture | ash   | volatiles | fixed carbon | carbon | hydrogen | oxygen | nitrogen | sulfur |
|-------------|----------|-------|-----------|--------------|--------|----------|--------|----------|--------|
| coal        | 3.14     | 18.29 | 27.60     | 50.97        | 56.69  | 3.86     | 14.81  | 1.04     | 2.17   |
| corncob     | 3.78     | 0.02  | 76.00     | 20.20        | 44.43  | 6.25     | 44.82  | 0.62     | 0.08   |

Figure 1. (a) FT-IR spectra of corncob, (b) XRD patterns of TiO\textsubscript{2} and CTAB-Zr-TiO\textsubscript{2}, (c,d) N\textsubscript{2} adsorption isotherm (c) and pore distributions (d) of pure TiO\textsubscript{2} and CTAB-Zr-TiO\textsubscript{2}, and (e,f) SEM images of CTAB-Zr-TiO\textsubscript{2} (e) ×5000, (f) ×50 000.
fluidized bed, decreases the use of the reductant, and reduces the cost of the subsequent treatment of the flue gas.

2. RESULTS AND DISCUSSION

2.1. Characterizations of Samples. Table 1 presents the results for the ultimate and proximate analyses of coal and corncob. Table 1 indicates that the nitrogen content of the coal (fuel-N of 1.04%) was higher than that of the biomass (fuel-N of 0.62%). In addition, the volatile-matter content of coal (27.60%) was lower than that of corncob (76.00%). Plenty of volatile matter in the biomass precipitated rapidly at a reaction temperature of 1123 K. Consequently, an oxygen-inadequate zone formed in the local combustion area of the coal, promoting conversion of HCN to N₂ and reducing the generation of NO.

Figure 1a displays the Fourier-transform infrared spectra of corncob. The peaks at 3418, 1375, and 896 cm⁻¹ corresponded to the stretching vibrations of the hydroxyl group. The peaks at 2920 cm⁻¹ can be assigned to aromatic CH₃ group stretching. Under combustion in the oxygen atmosphere, the carboxyl, C=O, and aromatic CH₃ groups in the cellulose, hemicellulose, and lignin of corncob were easily oxidized to CO₂ and H₂O, which competed with nitrogen in coal for oxygen and inhibited nitrogen oxidation to NO.

The crystal structures of the CTAB-Zr-TiO₂ and pure TiO₂ catalysts were analyzed using XRD patterns. Figure 1b displays the wide-angle XRD patterns of various catalysts. Compared with pure TiO₂, no additional diffraction peak was observed for CTAB-Zr-TiO₂. Characteristic peaks corresponding to the (101), (004), (200), (105), and (204) planes were observed for anatase TiO₂. These characteristic peaks for CTAB-Zr-TiO₂ were shifted slightly to the right, and the characteristic peaks of anatase became higher and narrower. The results indicated that the modifiers changed the octahedral structure of TiO₂ and distorted its lattice. Lattice distortion increased the oxygen vacancies on the catalyst surface, thereby enabling adsorption of additional oxygen atoms.

Through the line-width analysis of the (101) diffraction peak of anatase, the average crystal sizes of CTAB-Zr-TiO₂ and pure TiO₂ were estimated to be 9.80 and 10.24 nm, respectively, by using the Scherrer equation. The crystal size of TiO₂ decreased with CTAB and Zr doping, indicating that the modiﬁers supported combustion. The smaller the grain is, the larger is the speciﬁc surface area.

The surface area and pore structure of catalysts were investigated through N₂ adsorption–desorption measurement. As displayed in Figure 1c, all the catalysts exhibited a reversible type IV isotherm, which is a vital characteristic of mesoporous materials. Both CTAB-Zr-TiO₂ and TiO₂ catalysts exhibited the H₁ hysteresis loop, which indicated the ordered mesoporous structure. Figure 1d indicates that the CTAB-Zr-TiO₂ and TiO₂ catalysts exhibited the concentrated pore size in the range of mesopores. The most probable common radius of pure TiO₂ and CTAB-Zr-TiO₂ was 8.63 and 4.65 nm, respectively.

Table 2 presents the pore volume, pore size, and specific surface area per the BET model for various catalysts. The specific surface area of CTAB-Zr-TiO₂ (55.50 m²/g) was more than 4.5 times that of pure TiO₂ (12.20 m²/g). The pore volume of pure TiO₂ was 0.02 m³/g and that of CTAB-Zr-TiO₂ was increased to 0.09 m³/g. However, the pore size of pure TiO₂ was 7.91 nm and that of CTAB-Zr-TiO₂ was reduced to 3.15 nm. The results were consistent with the XRD results. Therefore, CTAB and Zr doping promoted TiO₂ grain dispersion.

Table 2. Pore Volume, Pore Width, and Specific Surface Area of Different Catalysts

| samples          | S_{BET} (m²/g) | r̅ (nm) | V_p (cm³/g⁻¹) |
|------------------|----------------|--------|---------------|
| TiO₂             | 12.20          | 7.91   | 0.02          |
| CTAB-Zr-TiO₂     | 55.50          | 3.15   | 0.09          |

As seen from Figure 2b, after corncob was added, a typical double peak appeared. The first peak represented the biomass volatilization reaction zone (approximately 670–780 K), and the second peak was related to coal combustion (approximately 820–970 K). The decomposition rate in the first stage of the severe weight-loss region was higher with corncob than with pure coal without corncob. The phenomenon occurred because of the decomposition of hemicellulose and cellulose and the softening and decomposition of the lignin in the biomass. However, lignin is highly stable and more difficult to decompose than hemicellulose or cellulose. It is speculated that the third peak at approximately 1000 K is related to the decomposition of lignin. The sample mass decreased, and the combustion rate increased after the addition of calcium acetate to the coal and biomass. Therefore, calcium acetate promotes the co-combustion of coal and biomass. The addition of corncob increased the rate of the
first stage of combustion and decreased the rate of the second stage, making the combustion more stable.

Oladejo et al.28 found that a synergistic effect occurs when coal is combined with oat straw. Therefore, we speculate that such a synergistic effect may result from the co-combustion of multiple additives with coal. That is, a co-combustion process cannot be considered a simple superposition of multiple combustion processes.

To further explore the denitration mechanism for the co-combustion of corncob and coal, we analyzed the components of coal ash and coal + corncob ash after combustion. Table 3

Table 3. Main Components of the Residual Ash Obtained after Combustion (%)

| samples                  | SiO₂   | Al₂O₃ | Fe₂O₃ | CaO  | MgO  | K₂O  | Na₂O |
|--------------------------|--------|-------|-------|------|------|------|------|
| coal                     | 46.62  | 21.64 | 12.34 | 5.38 | 1.32 | 0.68 | 0.58 |
| coal + corncob           | 38.18  | 14.68 | 15.02 | 8.08 | 1.81 | 3.04 | 0.75 |

lists the main components in the ash. The contents of CaO, MgO, K₂O, Fe₂O₃, and other alkaline oxides were higher in the coal + corncob ash than in the pure coal ash, indicating the abundance of alkaline compounds in corncob. Studies have shown that alkaline substances such as Fe₂O₃ can catalyze NO reduction.32

The rate of the temperature increase on the surface of coal and additives was very high when it underwent sudden combustion in the tubular furnace at 1123 K. Thus, the combustion processes of the volatiles and coal char had a common time overlap. In the initial stage of volatilization and combustion, much oxygen was consumed. Moreover, the oxygen content on the coal char surface was almost 0, which was conducive to heterogeneous NO reduction. To clarify the denitration mechanism of the co-combustion of coal with multiple additives, we conducted an experiment to investigate the removal of NO from the coal char. This experiment was also conducted in the horizontal tubular furnace. First, 0.2 g of coal char was pushed into the furnace at 1123 K. NO gas was subsequently introduced at 40 mL/min, and the reaction time was 15 min. The masses of the coal char and porcelain boat were recorded before and after the reaction. These masses were used to calculate the mass lost during the reaction. The difference in the NO concentration after the addition of the coal char was calculated. The ratio between the difference and the initial NO concentration was considered the denitration efficiency.

Five types of coal chars were used in the experiment: (a) coal, (b) coal + corncob, (c) coal + corncob + CTAB-Zr-TiO₂, (d) coal + corncob + calcium acetate, and (e) coal + corncob + calcium acetate + CTAB-Zr-TiO₂.

As presented in Table 4, the coal chars exhibited favorable denitrification performance. The denitrification efficiency of all char samples was more than 82%. The sample containing corncob, calcium acetate, and CTAB-Zr-TiO₂ exhibited the highest denitrification efficiency and mass-loss rate and the largest specific surface area. The mass-loss rate of the coal char increased with the denitrification efficiency, suggesting that a chemical reaction occurred during denitrification. The denitrification efficiency of sample b (coal + corncob) was 7.13% higher than that of sample a (coal). A comparison of the denitrification efficiencies of samples c (coal + corncob + CTAB-Zr-TiO₂) and d (coal + corncob + calcium acetate) indicated that CTAB-Zr-TiO₂ and calcium acetate were beneficial for the denitrification reaction of the coal char. Moreover, CTAB-Zr-TiO₂ promoted the combustion of the coal char and augmented the specific surface area. The residual mass of the samples decreased after the addition of the additives in the TG analysis was identified by the results mentioned above.

Combined with the above characterization results, it can be speculated as follows: reducing gases were produced during the combustion of corncob and calcium acetate. On the one hand, a large amount of the reducing gas formed the anoxic zone in the local combustion zone, which inhibited the production of HCN, the precursor of NO. On the other hand, the reducing gas reduces NO to N₂ homogeneously. The catalytic action of alkaline metal compounds, such as Fe₂O₃ in corncob, can accelerate the heterogeneous reduction of NO in the coal char; all additives can increase the specific surface area of the coal char, enhance the reactivity of the coal char in heterogeneous reduction of NO, and promote the heterogeneous reduction of NO. To verify this conjecture, the denitrification experiments of co-combustion of coal and additives were carried out.

2.2. Denitrification Experiments. The effect of desulfurizer types on denitrification was investigated. Figure 3 a indicates that the addition of calcium acetate promoted
denitrification, whereas the addition of inorganic calcium compounds inhibited denitrification. These findings are consistent with those of Zhang14 and Niu.18 Calcium acetate decomposed to form CaO and hydrocarbons (C\textsubscript{n}H\textsubscript{m}), which reduced some NO to N\textsubscript{2}. However, when inorganic calcium compounds were added, the CaO produced by combustion catalyzed the conversion of hydrocarbon nitrogen (HCN) and nitrogen hydrogen (NH\textsubscript{i}) compounds to NO and thus reduced the denitrification efficiency.

To further study the influence of the desulfurizer on NO\textsubscript{X} emission, the influence of the desulfurizer on NO\textsubscript{2} emission was also studied. Figure 3b indicates that inorganic calcium compounds catalyzed the conversion of HCN and NH\textsubscript{i} to NO\textsubscript{X} and increased NO\textsubscript{2} emissions. This catalytic effect made NO\textsubscript{2} easily reduced by the coal char. The reduction product was mainly NO, and very little N\textsubscript{2} was released. Thus, the addition of CaO not only increased the NO\textsubscript{2} emissions but also decreased NO-removal efficiency.

Therefore, compared with inorganic calcium compounds, calcium acetate is a more suitable denitrification additive. Therefore, calcium acetate was used as a desulfurizer additive in later experiments.

Figure 3c compares the effects of different catalysts on NO-removal efficiency. Figure 3c indicates that the denitrification efficiency was higher with than without a catalyst. The activity of pure TiO\textsubscript{2} was like that of without a catalyst, suggesting that pure TiO\textsubscript{2} was useless for the removal of NO. However, the incorporation of Zr in the TiO\textsubscript{2} framework considerably enhanced the catalytic activity. Moreover, the addition of a pore-forming agent (SDS or CTAB) in Zr-TiO\textsubscript{2} further improved the activity of the catalyst. The order of the catalytic activity was CTAB-Zr-TiO\textsubscript{2} > SDS-Zr-TiO\textsubscript{2} > Zr-TiO\textsubscript{2} > TiO\textsubscript{2}. The CTAB-Zr-TiO\textsubscript{2} catalyst exhibited the highest activity, with a NO-removal efficiency of 72.27%, which was approximately 2 times higher than that without a catalyst (36.33%). The results were mainly due to the lattice expansion of TiO\textsubscript{2} caused by Zr\textsuperscript{4+} doping. Moderate lattice expansion increases the oxygen defects, thereby enhancing the catalytic effect of TiO\textsubscript{2}. In the preparation of the TiO\textsubscript{2}, the pore-forming agents acted as dispersants. Adding a pore-forming agent significantly increased the adsorption capacity, pore volume, and specific surface area of nano-TiO\textsubscript{2}; thus, the catalytic performance and denitrification efficiency improved.

Figure 3d indicates that the optimal calcination temperature was different for different modified TiO\textsubscript{2} catalysts. The optimal calcination temperatures of Zr-TiO\textsubscript{2}, SDS-Zr-TiO\textsubscript{2}, and CTAB-Zr-TiO\textsubscript{2} were 873, 773, and 673 K, respectively. Incomplete growth of catalyst particles and low catalytic activity were observed when the calcination temperature of Zr-TiO\textsubscript{2} was lower than 873 K. When SDS or CTAB was added to the catalyst Zr-TiO\textsubscript{2}, the pore-forming agent dispersed well into the catalyst system at low temperatures; thus, the catalytic activity and denitrification efficiency increased. However, at higher temperatures, the framework of the pore-forming agent collapsed, the TiO\textsubscript{2} particles agglomerated, and plenty of grains increased. Thus, the specific surface area of TiO\textsubscript{2} and the denitrification efficiency decreased. Because SDS required a higher volatilization temperature than CTAB, the optimal calcination temperature for SDS-Zr-TiO\textsubscript{2} was higher than that for CTAB-Zr-TiO\textsubscript{2}.

The optimal catalyst in this study was CTAB-Zr-TiO\textsubscript{2}, which not only exhibited the highest improvement in denitrification efficiency versus pure TiO\textsubscript{2} but also has a low optimal calcination temperature and thus a low energy cost. Therefore, CTAB-Zr-TiO\textsubscript{2} was used in the subsequent experiments.
The denitrification results of the samples in Section 2.1 and the additives in Section 2.2, the mechanism of denitrification of co-combustion of coal and additives was proposed. According to the characterization results of the samples in Section 2.1 and the denitrification experimental results of co-combustion of coal and additives in Section 2.2, the mechanism of denitrification of co-combustion of coal and additives was proposed.

We believe that volatile-N in coal after combustion is oxidized to NO, and a small part of NO is oxidized to NO₂. The denitrification process in the co-combustion of coal with multiple additives (i.e., calcium acetate, corn cob, and CTAB-Zr-TiO₂) included a homogeneous reaction and heterogeneous reaction. The homogeneous reaction involved two processes: CₙHₘ and NH₃ were formed during the combustion of calcium acetate and corn cob, which easily reduce NO and NO₂ to N₂ and reduce a part of NO₂ to NO. Also, then, plenty of volatile matter separated from corn cob resulting in the formation of an oxygen-inadequate zone in coal which inhibited the oxidation of fuel nitrogen and reduced the production of NO and NO₂.

The heterogeneous reaction was the conversion of NO and NO₂ to N₂ by the coal char formed during combustion. The heterogeneous reduction of NO and NO₂ by the coal char was promoted by two approaches. One was that the additives (calcium acetate, corn cob, and CTAB-Zr-TiO₂) increased the surface area of the coal char, thus increasing the possibility of the heterogeneous reduction reaction. The other was that the catalysis of alkali metal oxides (such as Fe₃O₄) in biomass and CTAB-Zr-TiO₂ promoted the heterogeneous reduction of NO and NO₂ by the coal char.

The denitrification mechanism for the co-combustion of coal with multiple additives is illustrated in Scheme 1.

3. CONCLUSIONS

Calcium acetate with good desulfurization, TiO₂ with good denitrification performance, and corn cob chosen as mixed burning biomass were selected. The desulfurization efficiency of calcium acetate reached 83.03%. The denitrification efficiency was 72.27%, which was higher than the denitrification efficiency (43%) of the previous work (corn cob, calcium oxide, and V-TiO₂). The optimum calcination temperature of CTAB-Zr-TiO₂ was 673 K, which was lower than that of Zr-TiO₂ (873 K) and SDS-Zr-TiO₂ (773 K). CTAB and Zr doping augmented the specific surface area and enhanced the pore structure of TiO₂. The specific surface area of CTAB-Zr-TiO₂ (55.50 m²/g) was more than 4.5 times that of pure TiO₂ (12.20 m²/g).

Both calcium acetate and CTAB-Zr-TiO₂ support combustion, and the corn cob makes the combustion more stable. The denitrification process in the co-combustion of coal with multiple additives included a homogeneous reaction and heterogeneous reaction. The formation of CₙHₘ and NH₃ reduced NO and NO₂ to N₂ in the combustion. In the meantime, plenty of volatile matter were separated from corn cob resulting in the formation of an oxygen-inadequate zone in coal which inhibited the oxidation of fuel nitrogen and reduced the production of NO and NO₂. The heterogeneous reaction was the heterogeneous reduction of NO and NO₂ to N₂ by the coal char formed during combustion. Additives synergistically increased the surface area of the coal char, thus increasing the possibility of the heterogeneous reduction reaction. The catalysis of alkali metal oxides in biomass identified by the ash analysis and CTAB-Zr-TiO₂ promoted the heterogeneous reduction of NO and NO₂ by the coal char.

Finally, this study probes into the influence of additives on coal combustion, reveals the mechanism of denitrification of various additives in the co-combustion process, and provides guidance for energy saving and emission-reduction technology of a circulating fluidized bed.

Scheme 1. Mechanism Diagram of Denitrification by Co-combustion of Multiple Additives and Coal: (a) Effect of Co-combustion of Multiple Additives and Coal on Denitrification and (b) Possible Denitrification Mechanism
4. MATERIALS AND METHODS

4.1. Materials. All the chemicals were of analytical grade (AR) and used without any further refinement. The following support materials were used: tetrabutyl titanate (C4H10O4Ti; AR, ≥99.0%, Tianjin Kemiu Chemical Reagent), absolute ethanol (C2H5OH; AR, ≥99.7%, Tianjin Huilang Chemical Technology), glacial acetic acid [CH3COOH; AR, ≥99.5%, Fuchen (Tianjin) Chemical Reagent], zirconium oxychloride (ZrOCl2·8H2O; AR, ≥99.0%, Tianjin Kemiu Chemical Reagent), cetyltrimethylammonium bromide (CTAB; AR, ≥99.0%, Shanghai McLean Biochemistry), and sodium dodecyl sulfate (SDS; AR, ≥99.0%, Tianjin Kemiu Chemical Reagent).

4.2. Catalyst Preparation. CTAB-Zr-TiO2 was prepared by a microwave-assisted sol–gel method. First, 10 mL of absolute ethanol, 40 mL of C16H36O4Ti, and 0.86 g of CTAB were mixed to create solution A. Then, 10 mL of absolute ethanol, 0.38 g of zirconium oxychloride, 3 mL of deionized water, and 2 mL of glacial acetic acid were mixed to create solution B. Subsequently, solution B was slowly added to solution A in a microwave synthesizer at room temperature (298 K) and a power of 200 W. After solution B was added, the temperature was increased to 333 K, and the power was increased to 600 W. The mixture was stirred until a transparent gel was formed. The gel was aged at room temperature (298 K) for 24 h and then dried by a microwave. Finally, the obtained xerogel was calcined in a muffle furnace for 3 h at a constant temperature. The mass of Shanxi coal was 0.5 g, the mass of corncob was 0.33 g (a corncob: Shanxi coal mass ratio of 4:6), and the mass of the catalyst was 0.04 g (the mass of the catalyst was 8% that of Shanxi coal). Calcium acetate chosen as a desulfurizer was added such that the Ca: S molar ratio was 2.3.

4.3. Coal-Char Preparation. Five types of coal chars were prepared: (a) coal, (b) coal + corncob, (c) coal + corncob + CTAB-Zr-TiO2, (d) coal + corncob + calcium acetate, and (e) coal + corncob + calcium acetate + CTAB-Zr-TiO2. The coal samples were placed into capped nickel crucibles. The samples were subsequently heated in the muffle furnace for 10 min at 1123 K without oxygen. Finally, the samples were ground into powder after cooling.

4.4. Experimental Methods. The coal used in the experiment was Shanxi coal, which was produced in the Shanxi province of China. Shanxi coal and corncob were first dried for 2 h at 378 K and then pulverized. The particle size was between 0.075 and 0.095 mm.

The denitrification experiment of co-combustion of coal and additives, which consist of a desulfurizer, catalyst, and biomass, was carried out in a horizontal tube furnace on the premise of ensuring the desulfurization efficiency (the desulfurization efficiency was obtained by the iodine titration method (HJ/T 56-2000) and reached 83.03%). The reaction temperature and pure-oxygen flow rate were set at 1123 K and 40 mL/min, respectively. Then, the fuel (pure Shanxi coal or Shanxi coal with additives) was evenly spread on a small porcelain boat. Finally, the boat was pushed into the middle reaction zone of the ceramic tube of the furnace and burned for 1 h at a constant temperature. The mass of Shanxi coal was 0.5 g, the mass of corncob was 0.33 g (a corncob: Shanxi coal mass ratio of 4:6), and the mass of the catalyst was 0.04 g (the mass of the catalyst was 8% that of Shanxi coal). Calcium acetate chosen as a desulfurizer was added such that the Ca: S molar ratio was 2.3.

The flow chart of the experiment is shown in Scheme 2.

The concentration of NO emitted was determined through naphthalene ethylenediamine hydrochloride spectrophotometry (HJ 479-2009). The concentration of NO released during the combustion of Shanxi coal without additives was used as a reference value (C0). The concentration of NO released during the combustion of mixed coal with additives was denoted as C.

The removal efficiency η can be calculated using the following formula: η = (C0 − C)/C0.

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Scheme 2. Flow Diagram of the Denitrification Experiment
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Notes

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