Effect of Zr- La-TiO$_2$ Catalyst on Denitrification for Coal Combustion

Weiliang Cheng$^1$, Meng Liu$^2$, Yi Fu$^2$, Mingzhu Liu$^2$ and Shuqin Wang$^2$

$^1$ School of Energy Power and Mechanical Engineering, North China Electric Power University, Beijing 102206, China
$^2$ School of Environmental Science and Engineering, North China Electric Power University, Baoding, 071003, China

Email: wangshuqin1@126.com.

Abstract. Nanocomposites of TiO$_2$ co-doped with La and Zr were prepared using the microwave-assisted sol-gel method. The samples were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), X-ray photoelectron spectroscopy (XPS), energy dispersive spectroscopy (EDS) and specific surface area measurement (BET). The XRD results revealed that all the catalysts showed an anatase phase. It was found that the particle size of La-Zr-TiO$_2$ is much smaller than pure TiO$_2$. Moreover, the denitrification efficiency of La-Zr-TiO$_2$ was 65.77%, which was higher than that of the pure and mono-doped TiO$_2$ in the experiment.

Keywords. Co-combustion with biomass and coal; catalytic performance; doping TiO$_2$; denitrification.

1. Introduction

Recently, Zr-based catalysts have been reported for their excellent removal of NO$_x$ in selective catalytic reduction (SCR) [1-3]. It has been reported that ZrO$_2$ could improve oxygen storage capacity and thermal stability [4-5], which might be due to its ability to make the lattice unstable [6]. There might be a connection between oxygen storage capacity and SCR performance, which might be beneficial to denitrification for co-firing. The doping of La in the TiO$_2$ has been reported for the promotion of photocatalytic ability [7-9]. The enhanced visible light activity is primarily due to enhanced separation of light-induced carriers, low bandgap energy, strong visible light absorption, and high adsorption capacity [8]. The doping of the rare earth metal causes expansion of TiO$_2$ lattice formation, which results in more oxygen defects. Shojaei et al. [10] synthesized La$^{3+}$ and Zr$^{4+}$ co-doped anatase nano-TiO$_2$, which showed high photocatalytic activity on the degradation of 4-nitrophenol (4-NP). However, the denitrification performance of La or Zr doping TiO$_2$ has not been studied yet.

In our previous research, it was found that nano-TiO$_2$ plays a catalytic role in the combustion process [11]. Thereafter, the effect of V-TiO$_2$ on the denitrification efficiency of co-firing with biomass and coal was studied [12]. The results showed that V-TiO$_2$ can effectively reduce NO$_x$ emission, but the denitrification efficiency was not ideal. The catalytic effect of TiO$_2$ could be improved by changing the doping element of TiO$_2$. Rare earth and transition metal doping can inhibit the growth of particles and crystal transformation and improve the catalytic performance of TiO$_2$ [13, 14]. Transition metal elements can exhibit a variety of valence states, and more lattice defects can be formed in the TiO$_2$-doped transition metal ions, which is beneficial to the formation of Ti$^{3+}$ oxidation active centers and improve the catalytic effect of TiO$_2$. In this paper, the effect was studied of La-Zr-$...
TiO$_2$ prepared using the microwave-assisted sol-gel method on the denitrification efficiency of cofiring with biomass and coal, which could provide a theoretical basis for NO reduction in circulating fluidized bed boilers.

2. Experimental

2.1. Materials Preparation

All chemical reagents used in the present experiments were obtained from commercial sources and used without further purification.

Nanocomposites of doped TiO$_2$ were prepared using the microwave-assisted sol-gel method. Appropriate amounts of tetrabutyl titanate, glacial acetic acid, ethyl alcohol absolute and dopants (ZrOCl$_2$·8H$_2$O and La(NO$_3$)$_3$·6H$_2$O) were dissolved in deionized water and stirred at room temperature. Then the mixture solution was transferred to the microwave synthesizer and aged at 600W for 30 minutes. The obtained sol was placed under microwave irradiation for 20 minutes to get dry gel, and then calcined at 600°C to get the Zr-TiO$_2$ and La-Zr-TiO$_2$. For comparison purposes, the pure TiO$_2$ was prepared using the same method, but the calcination temperature was 500°C.

2.2. Catalyst Characterization

The XRD pattern was recorded using an X-ray diffractometer (Dandong, Y2000, China). The BET surface area and pore structure were determined on a surface area and pore size analyzer (Beckman Coulter, SA3100, USA). The morphology was analyzed using a SEM (QUANTA, F250, USA), equipped with the EDS system. XPS measurements were conducted using a Quantera Scanning X-ray Microprobe from Ulvac-Phi. Since the related work has been done beforehand, and some experience was gained, each catalyst with the best denitrification effect was selected for detection and characterization in this experiment.

2.3. Denitrification Experiment

The catalytic activities of TiO$_2$ were evaluated by means of the denitrification experiment carried out in a tube furnace. The combustion process was performed at 850°C for 60 minutes, until completion. The amount of released NO was measured by ethylene diamine dihydrochloride spectrophotometric method (HJ479-2009) to detect nitrogen oxides in ambient air. The efficiency of denitrification was calculated as per equation (1):

$$\eta = \frac{C_0 - C}{C_0} \times 100\%$$  \hspace{1cm} (1)

$C_0$—The NO concentration produced by coal combustion alone.

$C$ —The NO concentration produced by the catalyst blend.

3. Results and Discussion

3.1. X-ray Diffraction

The XRD patterns of the prepared TiO$_2$, mono-doped TiO$_2$ and La-Zr-TiO$_2$ catalysts are shown in figure 1. It shows the pattern data match with the anatase phase. The (101) face of La-TiO$_2$ has a noticeable left shift at about 0.12° (from 2θ=25.46° to 25.34°); this is probably due to the lattice distortion of the TiO$_2$ structure. In addition, the diffraction peak (101) of La-Zr-TiO$_2$ broadened with La doping, which also indicates that the crystallite size decreases. Moreover, no peaks are found that correspond with the ZrO$_x$ or LaO$_x$ phases, which indicates that Zr/La ions are well doped into the TiO$_2$ lattice.
3.2. BET Surface Area
The textural properties of prepared catalysts are listed in Table 1. The specific surface area of the prepared catalysts was determined, and the results were analyzed by BET method. The crystallite sizes shown in Table 1 were calculated using the Scherrer formula:

\[ D = \frac{k\lambda}{\beta \cos \theta} \]

Table 1. Structural and chemical characteristics of the different prepared catalysts.

| Samples      | Specific surface area (m² g⁻¹) | Average pore diameter (nm) | Pore volume (cm³ g⁻¹) | Crystallite size (nm) |
|--------------|--------------------------------|---------------------------|-----------------------|----------------------|
| TiO₂         | 12.20                          | 7.91                      | 0.0241                | 26.26                |
| Zr-TiO₂      | 25.17                          | 10.12                     | 0.0637                | 22.33                |
| La-Zr-TiO₂   | 36.20                          | 8.25                      | 0.0747                | 14.33                |

With the co-doping of La and Zr, the crystallite size decreased from 22.33 nm of Zr-TiO₂ to 14.33 nm of La-Zr-TiO₂. Compared to the surface area of 12.20 m² g⁻¹ (TiO₂) and 25.17 m² g⁻¹ (Zr-TiO₂), Zr-La-TiO₂ showed a higher value of 36.20 m² g⁻¹. Therefore, it can be inferred that, relative to Zr doping, La doping further inhibits grain growth.

3.3. SEM and EDS
The SEM micrographs of TiO₂, Zr-TiO₂ and La-Zr-TiO₂ are shown in Figure 2. The morphology and size of pure TiO₂ are uniform, and the cubic column particle morphology is exhibited. The Zr-TiO₂ and La-Zr-TiO₂ particles exhibit an irregular shape. The lattice is distorted due to the doping of La and Zr. As shown in Figure 3: the EDS measurements revealed that the La-Zr-TiO₂ sample contained O, Ti, Zr and La; the Zr-TiO₂ sample contained O, Ti and Zr. This indicates that the elements Zr and La were doped into TiO₂.

3.4. XPS Analysis
The surface composition and chemical state of the La-Zr-TiO₂ material was examined by XPS. As shown in Figure 4, the Ti, O, Zr, La and C elements were present on the surface of the nanocomposite. The Zr3d spectrum clearly shows two peaks at about 181eV and 183.3eV; these correspond with the Zr3d5/2 and Zr3d3/2, respectively, which is consistent with the reported Zr⁴⁺ data [15].

![XRD patterns of catalysts.](image)
**Figure 2.** SEM images of different catalysts: (a) TiO₂; (b) Zr-TiO₂; (c) La-Zr-TiO₂.

**Figure 3.** EDS of: Zr-TiO₂ (left); La-Zr-TiO₂ (right).
The ionic radius of the Zr$^{4+}$ ion (0.072 nm) is closer to that of the Ti$^{4+}$ ion (0.068 nm); therefore, the Ti$^{4+}$ ions in the TiO$_2$ lattice can be easily replaced by Zr$^{4+}$ ions during the doping reaction. However, the presence of La oxidation was not detected by XRD, probably due to the lower doping amount of La, which resulted in La$^{4+}$ being doped into the TiO$_2$ lattice. The La3d spectrum shows four peaks. Electron binding energy values are observed at 833.6 eV and 838.6 eV; this corresponds with the main peaks of La3d5/2 and La3d3/2 (3d04f configuration), where the vibrational peak (3d04f1 configuration) is located at 854.1 eV and 850.5 eV, which corresponds to La (III) oxidation state [16]. The O1s spectrum of the sample shows two peaks at 531.38 eV and 529.05 eV, which are related to the oxygen species being adsorbed and the oxygen in the surface lattice. La doping promoted the formation of Ti$^{3+}$ oxidation active centers; therefore, the ability of La-Zr-TiO$_2$ to adsorb oxygen increased, which is beneficial for the denitrification effect.

3.5. The Effect of the Zr-La-TiO$_2$ Preparation Conditions
The influence of the preparation conditions of Zr-La-TiO$_2$ on denitrification is shown in figure 5. The variables are: (a) microwave power; (b) calcination temperature; (c) doping amount. The results show that when the doping amount is 1%, the microwave power is 600W and the calcination temperature is 600°C, denitrification efficiency reaches the optimum value of the experiment.

La doping could inhibit grain growth, increase the surface area of TiO$_2$, and significantly improve the catalytic activity of TiO$_2$. However, excessive doping could reduce the surface-active sites in the catalyst, cause aggregation of particles, and ultimately reduce the specific surface area of TiO$_2$. In addition, the calcination temperature is also an important factor affecting the activity of the catalyst. A higher temperature will result in the conversion of anatase to rutile, and aggregation of crystal particles, which will reduce the catalyst activity of TiO$_2$. 

Figure 4. XPS spectra of La-Zr-TiO$_2$ high resolution: (a) survey spectra; (b) O1s spectra; (c) Zr3d spectra; (d) La3d spectra.
3.6. Effect of Zr and La Doping on Denitrification

The denitrification efficiency of different catalysts for the combustion of sample C was studied. In this experiment, the microwave-assisted sol-gel method was used to prepare: TiO$_2$ (pure, 500°C); Zr-TiO$_2$ (1% Zr doping, 600°C, marked 1#); La-TiO$_2$ (1% La doping, 600°C); La-Zr-TiO$_2$ (1% Zr doping, 1% La doping, 600°C). In addition, in order to compare the effect of the different preparation methods, Zr-TiO$_2$ (1% Zr doping, 700°C, marked 2#) was prepared by means of the sol-gel method without the microwave-assisted, as shown in figure 6, the denitrification efficiency of all doped TiO$_2$ is higher than that of pure TiO$_2$. This may be due to Zr and La doping, which inhibits grain growth, relatively increases the specific surface area of the catalyst, and promotes the denitrification reaction. The denitrification performance of 1# Zr-TiO$_2$ is higher than that of 2# Zr-TiO$_2$, which indicates an effect of microwave on the preparation of TiO$_2$. This may be because the microwave can heat the solution in a short time, and the growth of the TiO$_2$ particle size is suppressed. In the experiment, the denitrification efficiency of La-Zr-TiO$_2$ was 65.77%, which was higher than that of the pure and mono-doped TiO$_2$ in the experiment, and higher than the V-TiO$_2$, which showed the best denitrification efficiency in our previous work (46.6%) [12]. Since the highest efficiency was obtained in the La-Zr-TiO$_2$ denitrification experiment, and more oxygen vacancies and a larger specific surface area was exhibited, the experimental data were consistent with the catalyst characterization results.

![Figure 5](image-url)  
Figure 5. The effect of preparation conditions on denitrification efficiency.
4. Conclusions
In this paper, Zr-La-TiO₂ Catalyst was prepared by the microwave-assisted sol-gel method. The Catalyst was characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), X-ray photoelectron spectroscopy (XPS), energy dispersive spectroscopy (EDS) and specific surface area measurement (BET). The main results are as follows:

The characterization results showed that Zr-La-TiO₂ had a large surface area, which indicates that the rare earth metal La doping further inhibited grain growth on the basis of Zr doping. La doping greatly increases the oxygen vacancy, so the ability of Zr-La-TiO₂ to adsorb oxygen is increased.

The optimum preparation conditions for Zr-La-TiO₂ were obtained. When the Zr doping amount was 1%, the optimum doping amount of La was 1%, the optimum calcination temperature was 600°C, and the obtained Zr-La-TiO₂ had the highest denitrification efficiency. Zr-La-TiO₂ in coal ash remained active and could be re-used.

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