Article

Low Temperature Selective Catalytic Reduction Using Molding Catalysts Mn-Ce/FA and Mn-Ce/FA-30%TiO$_2$

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Abstract: Mn-Ce/FA (M) and Mn-Ce/FA-TiO$_2$ (M), using fly ash (FA) with and without TiO$_2$ as the carriers, were prepared by an integral molding technique. With the increase of TiO$_2$ content, the rates of NO conversion and denitration of Mn-Ce/FA-TiO$_2$ (M) increased, and the NO$_2$ and N$_2$O formation rates decreased. It is found that TiO$_2$ could effectively inhibit the excessive oxidation of NO and the generation of N$_2$O. The effects of space velocity, oxygen concentration and ammonia nitrogen ratio on three types of nitrogen oxides (NO, NO$_2$, N$_2$O) and denitration rates of the Mn-Ce/FA (M) and Mn-Ce/FA-30%TiO$_2$ (M) were further investigated. In addition, it is demonstrated that Mn-Ce/FA (M) and Mn-Ce/FA-30%TiO$_2$ (M) were more suitable to be used in the environment of low sulfur and less water.

Keywords: catalyst molding; Mn-Ce/FA (M); Mn-Ce/FA-30%TiO$_2$ (M); NO$_2$; N$_2$O; NO

Highlights:

- Mn-Ce/FA-30%TiO$_2$ (M) showed higher NO conversion than Mn-Ce/FA(M).
- Catalysts with higher TiO$_2$ content demonstrated lower formation rates of N$_2$O and NO$_2$.
- With the Mn-Ce/FA-30%TiO$_2$ (M), NO was mainly converted to N$_2$ and N$_2$O.
- SO$_2$ preferentially reacted with NH$_3$ to form ammonium sulfate to reduce the production of N$_2$O.
- The hydroxyl groups in H$_2$O inhibited the production of N$_2$O.

1. Introduction

In 2016, the total energy consumption including coal, oil, gas, hydro, nuclear, wind, etc. in China reached 4.36 billion tce (ton of standard coal equivalent) and coal consumption accounted for 62.0% [1]. Meanwhile, coal will be the dominant energy source in China for a long time. NOx emission will reach 29.34 million tons and the emission from thermal power plants will account for 17.51 million tons by 2020 in China [2]. NOx can pollute the atmosphere and cause photochemical smog, ozone hole and acid rain. In addition, it significantly affects the human central nervous system endangering human health. Thus reducing the nitrogen oxide pollution is an urgent task. At present, control methods of NOx emission can be divided into three categories: free nitrogen combustion, low NOx combustion and flue gas purification technology [3]. Among them, the flue gas NH$_3$-SCR (Selective Catalytic Reduction) denitration has become the mainstream technology for industrial applications because of its high removal efficiency of NOx.

The core of SCR technology is the development of a catalyst. Currently, commercial SCR catalysts are mainly vanadium based with an active temperature range of 350–450 °C [4]. In this case, the SCR device must be installed before air preheater and after fuel economizer, so this installation is usually accompanied by a high concentration of ash and SO_2 which can cause catalyst poisoning [5]. However, the exhaust temperature zone of most boiler systems in China is mainly 120–250 °C. If a vanadium catalyst is to be used, flue gas preheating device must be added, which increased the overall energy consumption and cost [6]. Therefore, low temperature SCR has attracted extensive attention. The excellent activity of manganese oxides and great oxygen carrying capacity of cerium oxides are very promising among the existing low temperature SCR catalysts. For example, Liao et al. [7] compared Mn-Ce/TiO_2 catalysts prepared by coprecipitation, impregnation and deposition, respectively. The results showed that the denitration rate of the Mn-Ce/TiO_2 could reach 90% at 100–160 °C. Chen et al. [8] prepared a modified Mn-Ce/TiO_2 denitration catalyst by impregnation. With the increase of Ce content, oxygen storage capacity of the catalyst was enhanced to promote the removal rate of NO. Meanwhile, the surface active acid sites and active oxygen quantity of the catalyst were increased with the doping of Co, which effectively improved the efficiency of De-NOx.

TiO_2 has a good chemical stability [9]. At present, research on low temperature SCR monolithic catalysts is mainly related to TiO_2 based catalysts. Sun et al. [10] studied the influence of additives on the denitration rate of Ce-Mn/TiO_2. It was found that a proper amount of glycerin could play a role of lubrication and the presence of glass fiber could increase the mechanical strength of the catalyst. Meanwhile, 2.5% active carbon could enhance the activity of the catalyst at low temperature and the removal rate of NO was increased by 16% at 80 °C compared to the catalyst without active carbon. Although the TiO_2 catalyst with different active components exhibit good denitration activity, it is difficult to be applied to actual industrial production due to the high cost. Thus, the research and development of a low cost and highly active low temperature molding catalyst have great significance in practical application.

Our previous work studied Mn- and Ce-based catalysts using activated carbon as support for low temperature SCR [11]. Fly ash (FA), which is much cheaper than activated carbon, is a solid waste collected and discharged by thermal power plant [12], which is generally alkaline and mainly consists of SiO_2, Al_2O_3 and Fe_2O_3. With the rapid development of thermal power, the amount of fly ash from coal-fired power plants has increased largely. Since 2012, China's annual emission amount of fly ash is about 0.3 billion tons, but the recovery utilization rate is less than 30%. FA is commonly used for road construction, brick making, cement and concrete mixing, etc. [13]. In recent years, FA has been used in the field of environmental protection because of its good adsorption properties, especially in the treatment of wastewater. Because FA is usually a powder of irregular size and shape with large specific surface area and many pores, which can be used as the support of the catalyst. For example, Zhang et al. [14] prepared a TiO_2-FA catalyst for the degradation of methyl orange wastewater. Xuan et al. [15] prepared a catalyst supported by FA for denitration. Transition metals such as Fe, Cu, V, Ni were used as active components. The results showed that the catalytic activity of FA as carrier was inferior to that of active carbon. When Cu was used as active component at 280 °C, the efficiency of denitration was the best and the conversion rate of NO could reach 92%. Shi et al. [16] used FA composite attapulgite (PG) as support for Fe and Mn. At a temperature range of 150–300 °C, the denitration rate of the Mn-Fe/PG catalyst could reach more than 80%, performing superior low temperature SCR activity.

Although extensive research of granular catalysts for low temperature SCR has been done and the denitration rate can be up to 90%, the granular catalyst cannot be directly installed for industrial applications because of its large bed resistance, poor fixation, poor mechanical, etc. Therefore, the development of the catalyst molding process is a necessary step to practical application using low temperature SCR technique.

At present, molding catalyst can be broadly divided into coating and integral types. The coating type adopts ceramic as carrier of active components loaded by impregnation method, but the catalyst

framework is easy to be washed by flue gas, leading to weak abrasive resistance, short life-span and poor denitration rate. Integral molding catalyst has attracted wide attention because of its honeycomb, homogeneous pores, strong mechanical properties, uniform distribution of active components and high denitration rate. However, the commercial available monolithic honeycomb catalysts are mostly used at medium temperature (350–450 °C), and cannot be directly applied to the existing boiler exhaust system where low temperature SCR is required. A new molding catalyst for low temperature SCR commercial application is required.

FA is a good catalyst support for low temperature SCR due to its low cost and its suitability. However, it has poor moldability. Thus a mixture of FA and TiO_2 was used in this work to improve the extrusion. MnOx and CeOx were used as active components. Mn-Ce/FA (M) and Mn-Ce/FA-30%TiO_2 (M) were prepared by the integral squeezing molding method. The effects of TiO_2 content, space velocity, oxygen concentration and ammonia nitrogen ratio on the performance of NO conversion and denitration were studied. In addition, the NO_2 and N_2O formation rates were investigated in relation to the resistance of the catalysts against water and sulfur.

2. Experimental

2.1. Catalyst Preparation

FA and FA-TiO_2 were used as catalyst supports. The active precursors ($Mn(NO_3)_2$, $Ce(NO_3)\cdot 6H_2O$) were dissolved in deionized water. The mass fraction of active components (Mn, Ce) was 8.5%, and the mole ratio of Mn:Ce was kept 1:1. The required amounts of carriers of FA and FA-30%wt TiO_2 were dry-mixed for 20 min with methylcellulose, respectively. After mixing evenly, the active component precursor and proper water were added, the mixture was stirred for 30 min, and then kneaded mud for 2.5 h and stayed for 24 h. The embryo of catalyst was obtained by squeezed molding with a mold. The embryo was dried at 80 °C for 4 h and 110 °C for 3 h, and finally calcined at 500 °C for 2.5 h in N_2 atmosphere. When the catalyst was cooled to room temperature in N_2 atmosphere, the required molding catalyst was obtained, namely Mn-Ce/FA (M) and Mn-Ce/FA-30%TiO_2 (M), respectively. The two cylindrical catalysts have the diameter of 23 mm and the length of 40 mm. And seven channels were evenly distributed in each molding catalyst.

2.2. Catalyst Characterization

The surface area and pore volume of the catalysts were analyzed by the method of Brunauer-Emmett-Teller (BET) (ASAP2020HD88). X-ray diffraction (XRD) (D8 FOCUS) with monochromatized Cu-Ka radiation and ceramic X tube (voltage 40 KV, current 40 mA) was used for phase analysis with scanning speed of $0.02°$ per 0.1 s from $10°$ to $60°$. The catalyst for characterization experiments was ground into 500 mesh powder, uniformly filled on the sample vessel and pressed with glass slides. The surface morphology of the catalyst was analyzed by scanning electron microscopy (SEM) with Hitachi S-3500N.

2.3. Experimental System

An NH_3-SCR test was carried out in a fixed bed reaction system. The simulated gases (NH_3, NO and O_2 balanced with N_2) were supplied by cylinders. The catalytic reaction conditions were 800 ppm NH_3, 800 ppm NO, 6% O_2, and gas total flow was 1200 mL/min (Figure 1). The gas was controlled by mass flow meters and entered a fixed bed reactor through a gas mixer. The NO content of the inlet and outlet was measured by a Fuel Gas Analyzer (J2KNpro (e-Com)), and recorded through a computer.
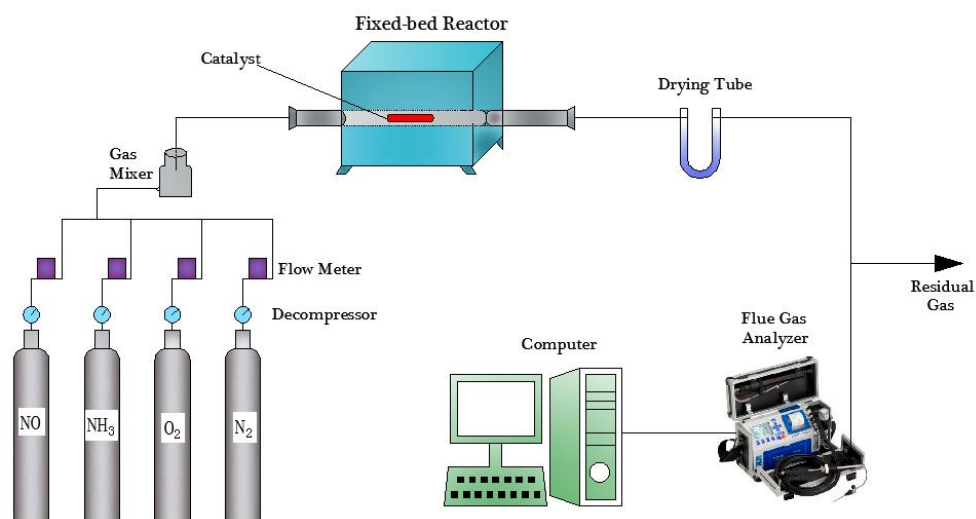
Figure 1. Schematic diagram of the reaction system.

2.4. Activity Evaluation Method

The NO conversion rate was calculated using Equation (1):

$$\eta_{\text{NO}}(\%) = \frac{\text{NO}_{\text{inlet}} - \text{NO}_{\text{outlet}}}{\text{NO}_{\text{inlet}}} \times 100\%, \tag{1}$$

The NO$_2$ formation rate was calculated using Equation (2):

$$\eta_{\text{NO}_2}(\%) = \frac{\text{NO}_{2\text{outlet}}}{\text{NO}_{\text{inlet}}} \times 100\%, \tag{2}$$

The N$_2$O formation rate was calculated using Equation (3):

$$\eta_{\text{N}_2\text{O}}(\%) = \frac{\text{N}_2\text{O}_{\text{outlet}}}{\text{NO}_{\text{inlet}}} \times 2 \times 100\%, \tag{3}$$

The denitration rate was calculated using Equation (4):

$$\eta_{de}(\%) = \frac{\text{NO}_{\text{inlet}} - \text{NO}_{\text{outlet}} - \text{NO}_{2\text{outlet}} - 2\text{N}_2\text{O}_{\text{outlet}}}{\text{NO}_{\text{inlet}}} \times 100\%, \tag{4}$$

where NO$_{\text{inlet}}$, NO$_{\text{outlet}}$, NO$_{2\text{outlet}}$, and N$_2$O$_{\text{outlet}}$ represent inlet NO concentration (ppm), outlet NO concentration (ppm), outlet NO$_2$ concentration (ppm), and outlet N$_2$O concentration (ppm), respectively.

3. Results and Discussion

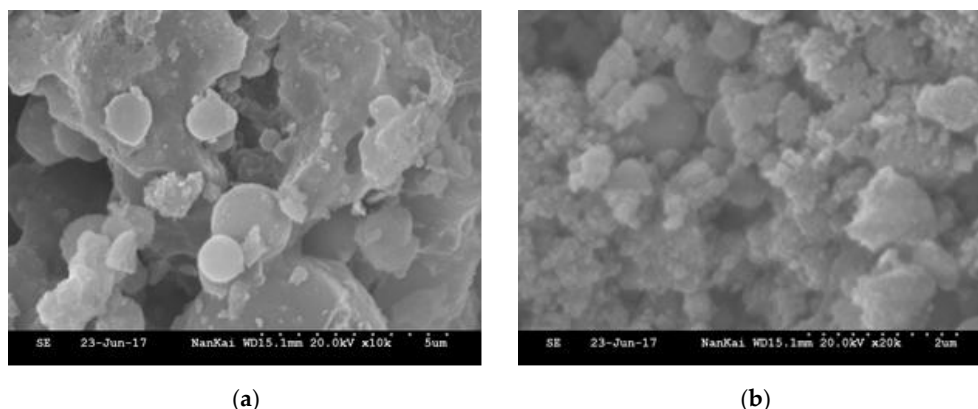### 3.1. Characterization of Catalysts

3.1.1. BET Analysis

The Mn-Ce/FA (M) and Mn-Ce/FA-30%TiO$_2$ (M) were characterized by BET. As shown in Table 1, the surface area and pore volume of the Mn-Ce/FA-30%TiO$_2$ (M) were about twice as much as those of the Mn-Ce/FA (M). This indicates that the surface area and pore volume of the catalysts can greatly increase by the addition of TiO$_2$. In general, a larger surface area can improve gas adsorption capacity of catalysts, which increases the contact area and reaction rate of reactants.

Table 1. BET analyses of the prepared catalysts.

Catalysts	Surface Area (m^2/g)	Pore Volume (cm^3/g)
Mn-Ce/FA (M)	10.56	0.034
Mn-Ce/FA-30%TiO$_2$ (M)	17.40	0.076

3.1.2. SEM Analysis

The molding Mn-Ce/FA (M) and Mn-Ce/FA-30%TiO$_2$ (M) were characterized by SEM. The results were shown in Figure 2.

(a)   (b)

Figure 2. SEM micrographs of the prepared catalysts. (**a**) Mn-Ce/FA (M); (**b**) Mn-Ce/FA-30%TiO$_2$ (M).

FA is an excellent carrier of catalysts due to the irregular micro-spherical structure, developed porous porosity, smooth surface, substantial pore channel and large pore size. Figure 2a is SEM picture of the Mn-Ce/FA (M). The large pore channels and holes of molding catalyst with binder decreased significantly, and the bonding state of a spongy surface appeared, but still retained a portion of pore space. Figure 2b is SEM picture of the Mn-Ce/FA-30%TiO$_2$ (M). The surface of the catalyst formed TiO$_2$ clusters. The active component directly loaded on the surface of FA and combined with TiO$_2$ [17]. Most of the holes and spherical structure of the Mn-Ce/FA-30%TiO$_2$ (M) disappeared, and pore channels of the surface were difficult to be observed. The addition of binder results in the aggregation of the active component to block the pore channels of the carrier.

3.1.3. XRD Analysis

From the XRD spectra, the Mn-Ce/FA (M) had obvious SiO$_2$ diffraction peaks at 27.8°, and no diffraction peaks of Al$_2$O$_3$ or other materials were observed clearly. Two peaks simultaneously appeared on the Mn-Ce/FA-30%TiO$_2$ (M), namely anatase TiO$_2$ and SiO$_2$ diffraction peaks, indicating that adding TiO$_2$ did not change the crystal structure of the original carrier. No characteristic peaks of MnOx and CeOx were found on the catalysts. There might be no crystalline metal oxides, or MnOx and CeOx highly disperses on the supports [17], leading to low crystallinity and amorphous non-crystalline structure. Liu et al. [18] reported manganese oxide phase state could affect denitration activity and increase the dispersion, promoting the generation of amorphous manganese oxide and significantly improving denitration rate. As shown in Figure 3, the relative intensity of SiO$_2$ diffraction peak of the catalyst doped with TiO$_2$ was lower than that of the catalyst based on FA alone. The unique electronic cloud structure of anatase TiO$_2$ and the highly dispersed active component are beneficial for catalytic activity. After the impregnation of metals, the active component can interact with anatase TiO$_2$ and SiO$_2$, resulting in the reduction of carrier crystallinity.
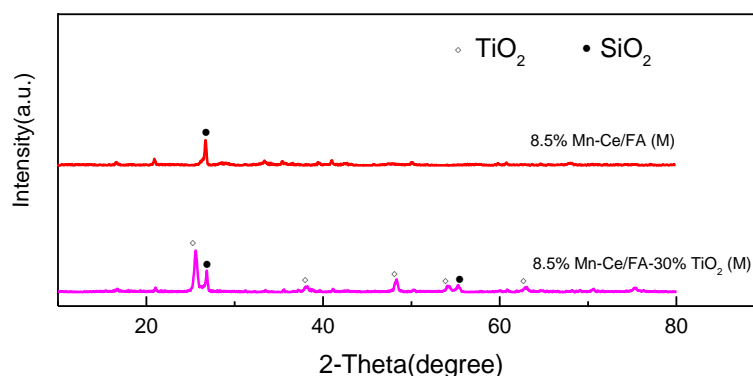
Figure 3. XRD analyses of the prepared catalysts.

3.2. Effects of TiO$_2$ Content on Catalyst Activity

The temperature of experiment ranged from room temperature to 250 °C. The other conditions were: NO inlet 800 ppm, ammonia nitrogen ratio 1:1, space velocity 3000 h^{-1}, and N$_2$ as equilibrium gas. In Figure 4a,c, with the increase of TiO$_2$ content at different temperature, the NO conversion rate increased and N$_2$O formation rate decreased. At 250 °C, the NO conversion rate and N$_2$O formation rate of the Mn-Ce/100%TiO$_2$ (M) were 95% and 4.8%, respectively. Compared with the Mn-Ce/FA (M), NO conversion was increased by 16.8% and N$_2$O formation was decreased by 8.3%. N$_2$O originated from the direct oxidation of NH$_3$ and the reactions of NH$_3$ and NO. At 100–150 °C, the formation of N$_2$O follows the Langmuir-Hinshelwood mechanism, while it follows the Eley–Rideal mechanism at 250 °C [19]. The results show that the doping of TiO$_2$ has obvious inhibitory effect on the formation of N$_2$O. It is probable that the unique electronic cloud structure and a large amount of hydroxyl of nanophase TiO$_2$ avoid excessive NH$_3$ dehydrogenation. It results in the reduction of NH groups on the surface of the catalyst, effectively inhibiting the production of N$_2$O and improving the selectivity of N$_2$.

Meanwhile, with the increase of TiO$_2$ content at the same reaction temperature, the amount of NO$_2$ decreased (Figure 4b). It is indicated that the existence of TiO$_2$ reduced the excessive oxidation of NH$_3$ and O$_2$. Figure 4d shows the denitration rates using different catalysts. At 250 °C, the denitration rates of catalysts with different TiO$_2$ contents (10%, 30%, 50%, 80% and 100%) were 71.4%, 79.0%, 84.5%, 88.4% and 90.1%, respectively. It is demonstrated that when the TiO$_2$ content was more than 30%, the denitration rates of catalysts were similar. Considering the economy and efficiency, the Mn-Ce/FA-30%TiO$_2$ (M) is suggested to be optimal for low temperature SCR in this work. The surface of TiO$_2$ has a large number of Lewis acid sites, which can greatly promote the adsorption capacity of NH$_3$ at low temperature to improve the NO conversion rate. Chmielarz et al. [20] prepared the catalysts Mn-Ce/TiO$_2$ and NH$_3$-TPD was carried out. It was found that the surface of TiO$_2$ had massive Lewis acid sites, and the number of acid sites directly determined the activity of catalysts. At low temperature, the obvious desorption peak of NH$_3$ appeared. This might be due to desorption of NH$_3$ which adsorbed on a large number of Lewis acid sites of TiO$_2$.
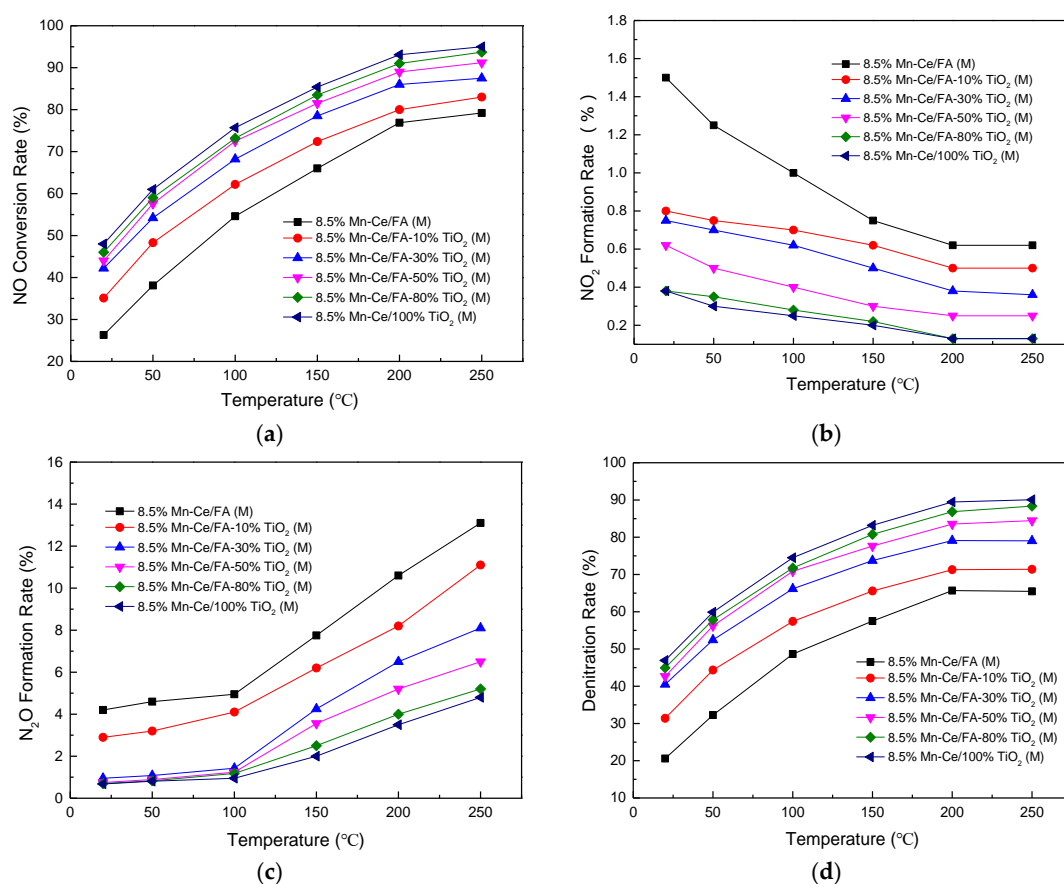
Figure 4. Nitrogen oxides analysis of different catalysts under different TiO_2 contents. (**a**) NO conversion; (**b**) NO_2 formation rate; (**c**) N_2O formation rate; (**d**) Denitration rate.

3.3. Effects of Reaction Conditions on Catalytic Activity

3.3.1. Effect of Space Velocity

The Mn-Ce/FA (M) and Mn-Ce/FA-30%TiO$_2$ (M) catalysts were studied for the influences of space velocities (3000 h^{-1}, 5000 h^{-1}, 7000 h^{-1}, 9000 h^{-1}, 11,000 h^{-1}), while the reaction conditions were at 250 °C, NO inlet concentration 800 ppm, ammonia nitrogen ratio 1:1, oxygen concentration of six percent and N_2 as balanced gas. As shown in Figure 5a,c,d, the rates of NO conversion, N_2O formation and denitration of the two catalysts were decreased with the increase of space velocity. At 3000 h^{-1}, the denitration rates using the Mn-Ce/FA (M) and the Mn-Ce/FA-30%TiO$_2$ (M) were 65.3% and 78.7%, NO conversion rates were 79.2% and 87.5%, and N_2O formation rates were 13.1% and 8.1%, respectively. With the increase of space velocity to 7000 h^{-1}, the rates of NO conversion, N_2O formation and denitration of the Mn-Ce/FA (M) and the Mn-Ce/FA-30%TiO$_2$ (M) decreased slowly. But among the three types of nitrogen oxides, NO_2 formation changed slightly with the variation of space velocity (Figure 5b).

The space velocity can affect mass transfer of reactants and products during SCR reactions. With the increase of space velocity, the flow rate of gases increases resulting in an enhanced gas diffusion. However, high flow rate of gases can reduce the contacts with catalytic sites. It was reported that excessive space velocity would decrease contact time between reaction gas and catalysts, which decreased the activity of the catalyst [21].
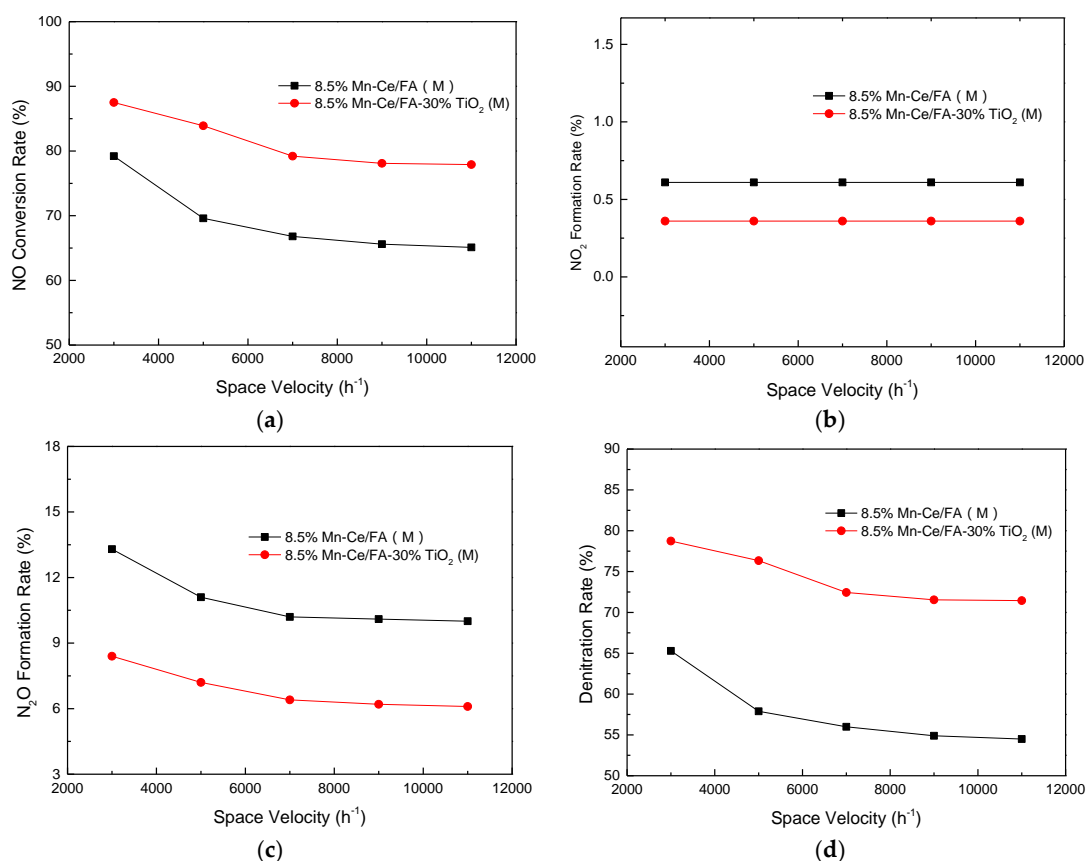
Figure 5. Effects of space velocity on catalytic activity. (**a**) NO conversion; (**b**) NO_2 formation rate; (**c**) N_2O formation rate; (**d**) Denitration rate.

3.3.2. Effect of Oxygen Concentration

Oxygen concentration plays an important role on the activity of catalyst. At 250 °C, NO inlet concentration 800 ppm, ammonia nitrogen ratio 1:1, space velocity 3000 h^{-1}, and N_2 as balanced gas, the effects of oxygen concentrations (1%, 3%, 6%, 9%, and 12%) on NOx were investigated using the Mn-Ce/FA (M) and Mn-Ce/FA-30%TiO_2 (M) catalysts. Under the condition of one percent oxygen concentration, the NO conversion rates of the Mn-Ce/FA (M) and the Mn-Ce/FA-30%TiO_2 (M) were 61.9% and 73.2%, and the NO_2 formation rates were 1.1% and 0.63%, respectively. With the increase of oxygen concentration to six percent, the NO conversion and NO_2 formation rates of the two catalysts gradually increased. This shows that the presence of oxygen greatly improved the catalytic reaction. However, with the increase of oxygen content, the dehydrogenation of NH_3 was also promoted to produce more N_2O. Although the amount of N_2O increased, the rates of NO conversion and denitration of the Mn-Ce/FA (M) and the Mn-Ce/FA-30%TiO_2 (M) were not affected greatly (Figure 6a,d). At 6% O_2, the denitration rates of the Mn-Ce/FA (M) and the Mn-Ce/FA-30%TiO_2 (M) were 65.3% and 78.6%, respectively. When the oxygen concentration increased from 6% to 12%, slight changes are observed for the rates of NO conversion, N_2O formation, and denitration. It was reported that oxygen of adsorbed state was firstly adsorbed on the surface of catalyst, and then diffused inside the catalyst to participate in catalytic reaction. On the one hand, the existence of oxygen is more conducive to oxidize NO to NO_2, and NO_2 is easier to react with ammonia to generate nitrogen and water. On the other hand, O_2 promotes dehydrogenation of NH_3 to NH_2 on the catalyst, which can enhance the SCR reaction by L-H mechanism. When oxygen is at saturated adsorption state on the catalyst, the surface of catalyst is not vacant for excess oxygen. As reported by other researchers, there

was a negative influence for further NO removal, and the excessive oxygen would diffuse in the reactor to oxidize NO to NO_2 [22].
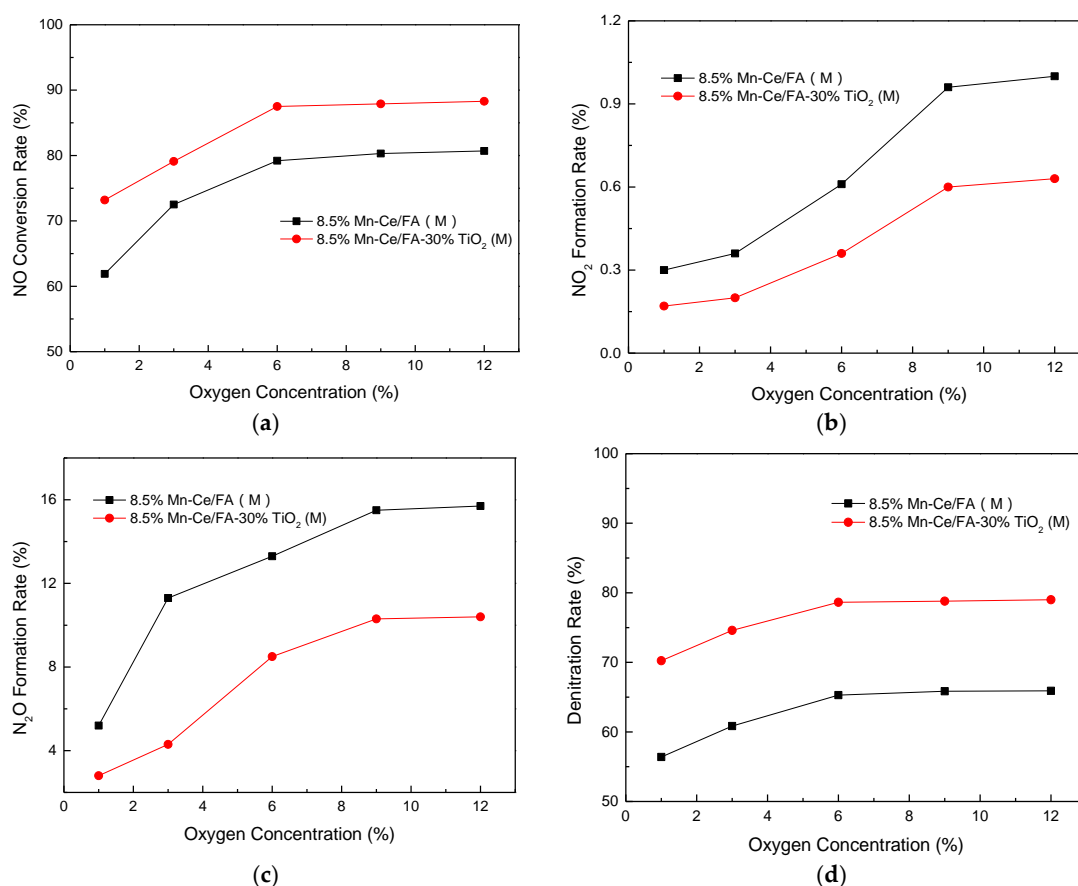

Figure 6. Effects of oxygen concentration on catalytic activity. (**a**) NO conversion; (**b**) NO_2 formation rate; (**c**) N_2O formation rate; (**d**) Denitration rate.

3.3.3. Effect of Ammonia to Nitrogen Ratio

In engineering applications, the ammonia nitrogen ratio is generally controlled between 1.0 and 1.2. In this experiment, the ratios of ammonia to nitrogen were 0.5, 0.8, 1, 1.2, and 1.5. As shown in Figure 7a,d, with the increase of ammonia nitrogen ratio, the rates of NO conversion and denitration of the Mn-Ce/FA (M) and the Mn-Ce/FA-30%TiO$_2$ (M) increased. When the ammonia nitrogen ratio was higher than 1, NO conversion rate and denitration rate increased slowly and remained at a stable level. Figure 7b shows that the amount of NO_2 remained constant. It is indicated that the change of ammonia nitrogen ratio did not affect the NO_2 formation rate. But the N_2O formation rates of the two catalysts increased with the increase of ammonia nitrogen ratio (Figure 7c). When the amount of ammonia increased, NH_3 was automatically dehydrogenated to generate a large amount of NH. Then NH was oxidized to form NHNO by oxygen, and NHNO combined with NO to generate N_2O [23]. However, when the ammonia ratio was higher than 1, the increase of N_2O was not obvious. Because the NO adsorption sites of catalyst reach saturation, the ammonia of dehydrogenation cannot react with NO to produce N_2O. Ammonia is firstly adsorbed on the acid site of catalyst according to the L-H mechanism. When ammonia is overloaded, acid adsorption on the surface of catalyst reaches saturation. Excessive ammonia would cause ammonia slip. García-Bordejé et al. [24] studied NH_3 transient experiment on carbon coated cordierite catalyst. It was found that NH_3 with high adhesion adsorbed on the surface of the catalyst, and excessive ammonia would replace the vacancy of active substances, leading to the decrease of denitration rate.
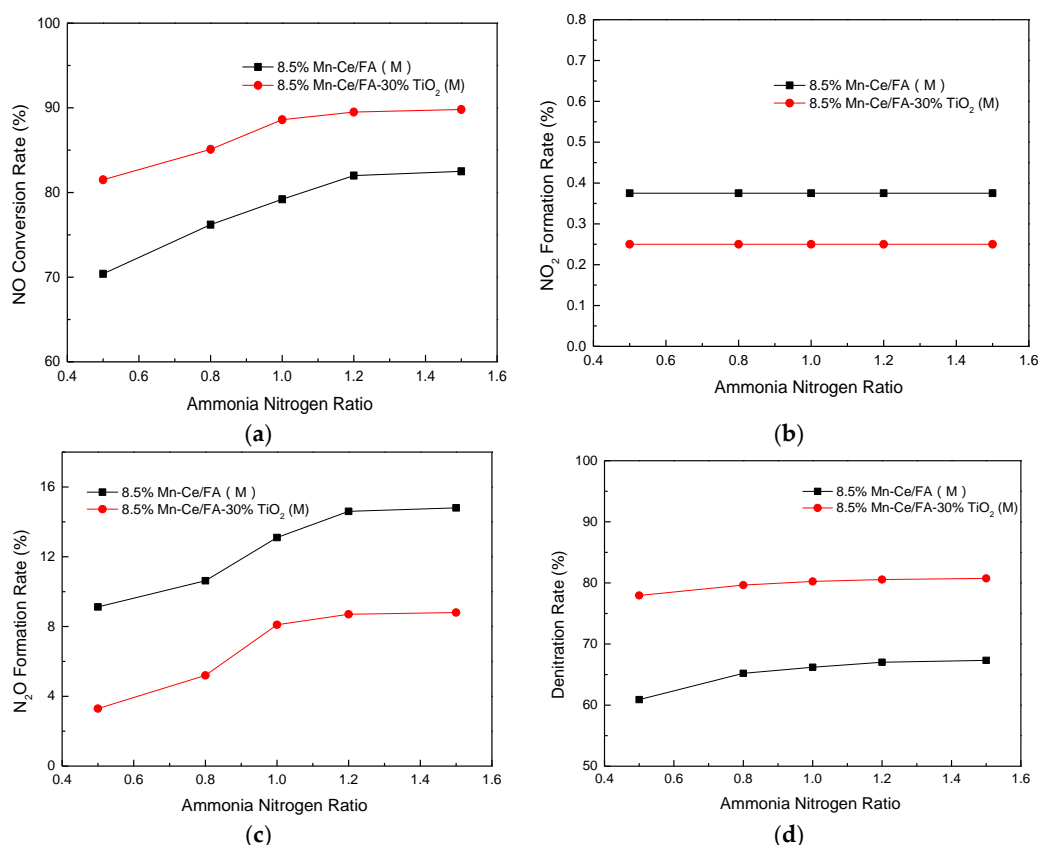
Figure 7. Effects of ratio of ammonia to nitrogen on catalytic activity. (**a**) NO conversion; (**b**) NO_2 formation rate; (**c**) N_2O formation rate; (**d**) Denitration rate.

3.4. Research on Sulfur and Water Resistances of Catalysts

3.4.1. Sulfur Resistance

The sulfur resistance using the Mn-Ce/FA (M) and Mn-Ce/FA-30%TiO$_2$ (M) was studied under the conditions of 250 °C, NO 800 ppm, NH$_3$ 800 ppm, six percent O$_2$ and 3000 h^{-1}. SO$_2$ with the concentration of 100 ppm and 200 ppm was added into the reaction at 90 min lasting for a period of time, then stopped at 270 min, respectively. When the addition of 100 ppm SO$_2$ was stopped, the rates of NO conversion and denitration of the Mn-Ce/FA (M) recovered to 74.4% and 58.3%, and the two rates of the Mn-Ce/FA-30%TiO$_2$ (M) recovered to 83.5% and 75.1%, respectively. Compared with the SCR without SO$_2$, the two rates decreased by only about 5% while decreased by about 10% at 200 ppm SO$_2$ (Figure 8a,d). It is indicated that the Mn-Ce/FA (M) and the Mn-Ce/FA-30%TiO$_2$ (M) were relatively suitable for low sulfur environment. Figure 8b showed that SO$_2$ had almost no significant effect on NO$_2$ formation. However, the N$_2$O formation rate became slightly lower as SO$_2$ was added and then higher than the initial value after SO$_2$ was stopped (Figure 8c). It is suggested that the added SO$_2$ first reacted with ammonia to form ammonium sulfite, which effectively inhibited the dehydrogenation of NH$_3$. When the dehydrogenation of NH$_3$ was inhibited, the NH group from NH$_3$ also decreased. This resulted in the decrease of generation of N$_2$O, which was from the reaction of NO and NH. However, when the addition of SO$_2$ was stopped, NH$_3$ was dehydrogenated to produce more N$_2$O. SO$_2$ may aggravate the deposition of ammonium sulfate on the surface of catalyst at low temperature. You et al. [25] studied Mn and Ce catalysts for SCR. Their FTIR results proved that the deposition of ammonium sulfate hindered the adsorption of NO and cut off the L-H path in SCR reaction to accelerate the poisoning of catalyst. Wei et al. [26] found that SO$_2$ reacted with MnOx to form sulfate. The generated sulfate not only consumed active components of catalysts, but also

deposited on the surface of the catalyst, which inhibited adsorption and desorption of the reaction gas and decreased denitration rate.
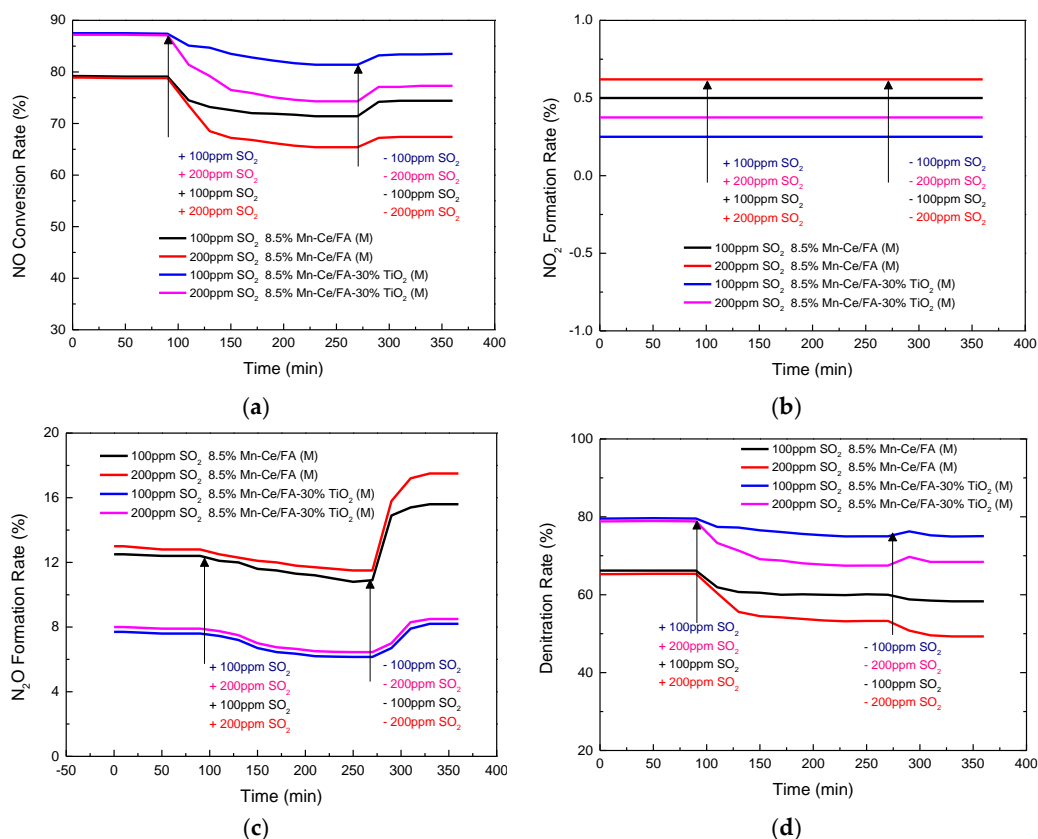

Figure 8. The experiment of SO_2 stability. (**a**) NO conversion; (**b**) NO_2 formation rate; (**c**) N_2O formation rate; (**d**) Denitration rate.

3.4.2. Water Resistance

Figure 9 showed the water stability of the Mn-Ce/FA (M) and the Mn-Ce/FA-30%TiO_2 (M) during low temperature SCR reactions. A concentration of three or six percent H_2O was added into the reaction at 90 min lasting for a period of time, then stopped at 270 min. When the addition of three percent water was terminated, the rates of NO conversion and denitration of the Mn-Ce/FA and the Mn-Ce/FA-30%TiO_2 decreased by about five percent, compared to the SCR process without water addition. The reduction of SCR efficiency was about 10% in the presence of six percent H_2O. It is indicated that the Mn-Ce/FA and Mn-Ce/FA-30%TiO_2 were more suitable to be used in less water environment.

Figure 9b shows that H_2O had almost no significant effect on the amount of NO_2 production. H_2O competes with reactive gas NH_3 for the active sites on the surface of catalyst. The adsorption of water molecules produces hydroxyl groups, resulting in a reduction of active sites of catalyst. Although the addition of water decreased denitration rate, it also inhibited the production of N_2O. It was reported that water could reduce active sites of catalysts, but would be adsorbed on the surface of catalysts to produce massive hydroxyl in free state [27]. Huang [28] reported that the presence of steam in the flue gas inhibited SCR reaction of NH_3 and NO which adsorbed on the Lewis acid sites, and the effect of inhibition increased with the increase of H_2O concentration.
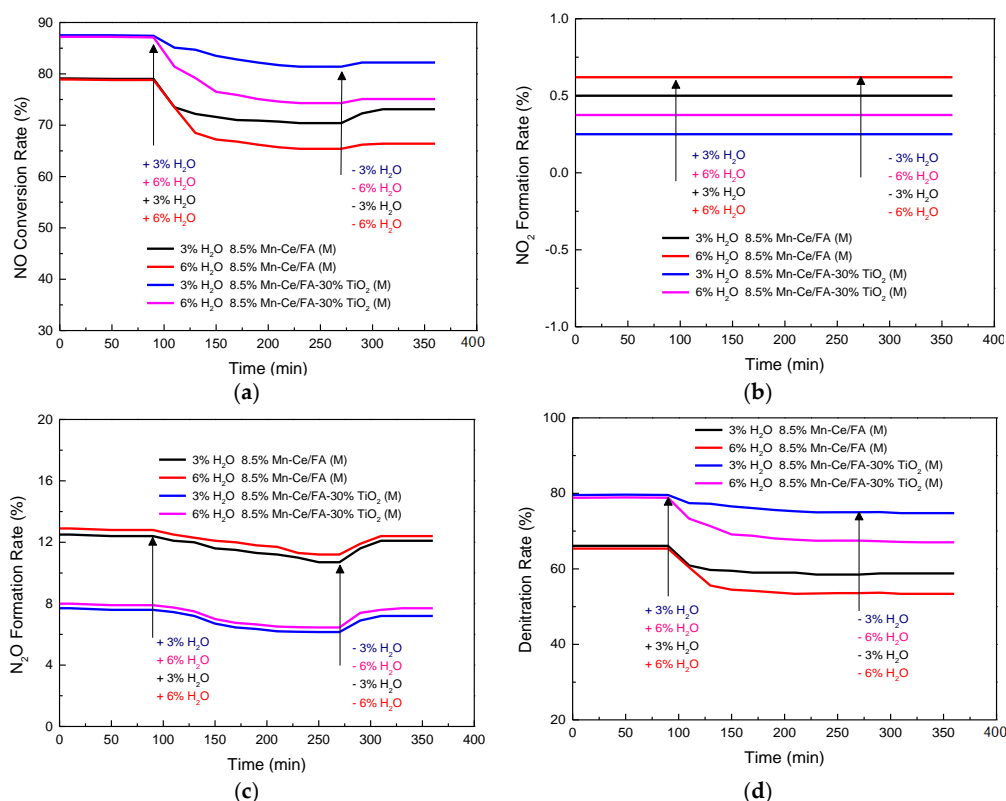
Figure 9. The experiment of H_2O stability. (**a**) NO conversion; (**b**) NO_2 formation rate; (**c**) N_2O formation rate; (**d**) Denitration rate.

4. Conclusions

A cost-effective molding fly ash-based catalyst was investigated in this work for low temperature SCR process. The main conclusions are:

(1)　With the increase of TiO_2 content, the NO conversion and denitration rates of catalysts increased, and the amount of NO_2 and N_2O decreased.

(2)　The rates of NO conversion, denitration and N_2O formation of the Mn-Ce/FA (M) and the Mn-Ce/FA-30%TiO_2 (M) increased with the increase of oxygen concentration and ammonia nitrogen ratio, and the decrease of space velocity. The NO_2 formation rate was not affected by the change of space velocity and ammonia nitrogen ratio, but increased with the increase of oxygen concentration.

(3)　In the experiments of water and sulfur resistances, the rates of NO conversion and denitration of Mn-Ce/FA (M) and Mn-Ce/FA-30%TiO_2 (M) under 100 ppm SO_2 and three percent H_2O conditions decreased by about five percent, respectively, compared with water and sulfur free environment. It was found that H_2O and SO_2 had almost no effect on the production of NO_2. The presence of SO_2 could inhibit the excessive dehydrogenation of NH_3 and decreased production of N_2O. The hydroxyl groups in H_2O could also inhibit the formation of N_2O.

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