



Article

# Effect of CaO on NO<sub>x</sub> Reduction by Selective Non-Catalytic Reduction under Variable Gas Compositions in a Simulated Cement Precalciner Atmosphere

Ye Sun, Weiyi Fan, Tianle Zhu \* and Xiaowei Hong

School of Space and Environment, Beihang University, Beijing 100191, China; suny@buaa.edu.cn (Y.S.); fanweiyi1226@sina.com (W.F.); hongxiao86@126.com (X.H.)

\* Correspondence: zhutl@buaa.edu.cn; Tel.: +86-10-82314215

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**Abstract:** High-concentration CaO particles and gas compositions have a significant influence on NO<sub>x</sub> reduction by selective non-catalytic reduction (SNCR) in cement precalciner. The effect of gas composition on NO<sub>x</sub> reduction by SNCR with NH<sub>3</sub> was studied in a cement precalciner atmosphere with and without CaO at 700–1100 °C. It was found that CaO significantly lowers NO<sub>x</sub> reduction efficiency between 750 °C and 1000 °C, which is attributed to the catalytic oxidation of NH<sub>3</sub> to NO. Although increasing NH<sub>3</sub> concentration was advantageous to NO<sub>x</sub> reduction, the existence of CaO led to the opposite result at 750–900 °C. Adding H<sub>2</sub>O can suppress the negative effect of CaO on NO<sub>x</sub> reduction. Decreasing O<sub>2</sub> content from 10% to 1% shifts the temperature range in which CaO has a significant effect from 750–1000 °C to 800–1050 °C. CO has a variety of influences on the CaO effect under different experimental conditions. The influences of NH<sub>3</sub>, H<sub>2</sub>O, O<sub>2</sub>, and CO on the effect of CaO can be attributed to the impacts of the gas compositions on gas-phase NH<sub>3</sub> conversion, gas-solid catalytic NH<sub>3</sub> oxidation, or both processes. A proposed pathway for the effect of gas compositions on NO<sub>x</sub> reduction in CaO-containing SNCR process was developed that well predicted the CaO-containing SNCR process.

**Keywords:** CaO; NO<sub>x</sub> reduction; SNCR; cement precalciner atmosphere

## 1. Introduction

Air pollution is now one of the most serious environmental problems worldwide. Nitrogen oxides (NO<sub>x</sub>, including NO and NO<sub>2</sub>) emitted from cement rotary kilns are major contributors to acid rain, photochemical smog and haze [1]. In China, 1.7 Mt NO<sub>x</sub> was emitted by the cement industry in 2015, accounting for 9.1% of total NO<sub>x</sub> emissions from anthropogenic sources [2]. The cement industry has become the third-largest NO<sub>x</sub> emission source in China, after the thermal power industry and vehicles. Meanwhile, as the largest cement-producing country in the world, “Emission Standard of Air Pollutants for Cement Industry” (GB4915-2013), which is regarded as the strictest in history, has been issued by the Chinese government to reduce NO<sub>x</sub>, SO<sub>2</sub>, NH<sub>3</sub> and Hg<sup>0</sup> emissions.

Current NO<sub>x</sub> emission control technologies in the cement industry include low-temperature sintering, staged combustion, low NO<sub>x</sub> burners, over-fire air, SNCR and selective catalytic reduction (SCR) [3]. By far, SNCR is the predominant deNO<sub>x</sub> technology in cement rotary kilns due to its suitable, efficient, and cost-effective performance. Additionally, since SNCR is typically conducted in the cement precalciner, where the temperature ranges from 850 °C to 1200 °C and conforms to the temperature window of SNCR, some countries have introduced full-scale SNCR into the cement industry. However, as opposed to SNCR for electric power generation, NO<sub>x</sub> reduction efficiencies have

varied from 15% to 80% between projects, and even within individual projects, for cement kilns [4,5]. This variability is mainly due to the complicated environment in the cement precalciner, including temperature, gas composition and Ca-based particles (95% composed of CaO) from raw material calcinations. Therefore, the influences of multiple factors on  $\text{NO}_x$  reduction by SNCR in a simulated cement precalciner atmosphere have been researched extensively.

Previous researchers, including our team, have investigated the effects of  $\text{O}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{SO}_2$ ,  $\text{CO}$ , etc. on the SNCR process over various temperature ranges [6–9]. In addition to temperature and gas compositions, CaO particles of high concentration from raw material calcinations have a significant influence on  $\text{NO}_x$  reduction in a cement precalciner. Actually, catalytic reactions involving  $\text{NH}_3$  and  $\text{NO}$  can occur on the CaO surface [10,11]. To date, researchers have investigated catalytic  $\text{NH}_3$  decomposition,  $\text{NH}_3$  oxidation, and  $\text{NO}_x$  reduction on the CaO surface. In the absence of  $\text{O}_2$ , CaO can catalyze  $\text{NH}_3$  decomposition to  $\text{N}_2$  [12,13]. CaO also catalyzes reactions between  $\text{NH}_3$  and  $\text{NO}$  in an  $\text{O}_2$ -free atmosphere [5,14]. When  $\text{O}_2$  is present, these reactions do not apply, and the main effect of CaO is to catalyze  $\text{NH}_3$  oxidation with high  $\text{NO}$  selectivity [15,16].

Actually, gas-phase reactions coexist with the gas-solid catalytic reactions of the SNCR process in cement precalciners. However, previous research has only focused on the gas-solid catalytic reactions, not how these reactions interact with the gas-phase SNCR process. In addition, the temperature and gas conditions used in previous research did not match the conditions in cement precalciners. As a result, it is unclear how CaO affects overall  $\text{NO}_x$  reduction efficiency within the temperature range and under the variable gas conditions of a cement precalciner. Thus, the present work attempts to investigate the influence of CaO on  $\text{NO}_x$  reduction by SNCR with  $\text{NH}_3$  under variable gas compositions, using a fixed-bed reactor. Both gas-phase and gas-solid catalytic reactions were considered. The influences of gas compositions on the effect of CaO were also studied by varying  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{O}_2$ , and  $\text{CO}$  contents. Pathways for the effect of gas compositions on  $\text{NO}_x$  reduction in CaO-containing SNCR process were proposed.

## 2. Materials and Methods

### 2.1. Experimental Setup

The experimental setup consists of a gas feeding unit, a high-temperature fixed bed experimental system, and gas analytical instruments. A schematic diagram is shown in Figure 1.

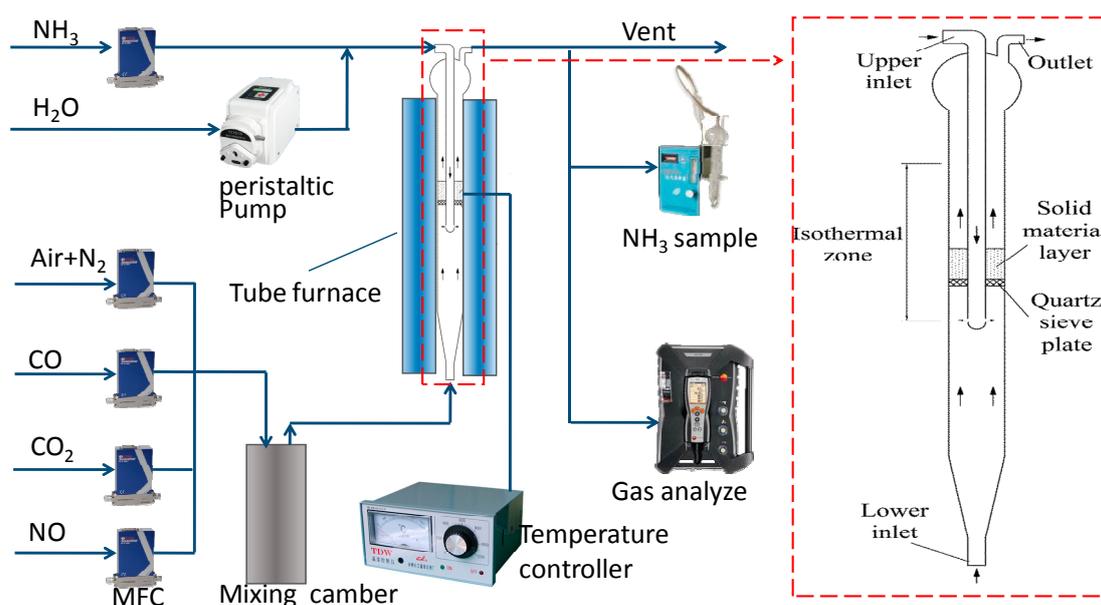


Figure 1. Schematic diagram of the experimental setup.

A quartz cylinder with a 25 mm inner diameter, 1100 mm length and two gas inlets was used as the SNCR reactor. A quartz sieve was correctly plated at the constant temperature zone of the electric furnace to support Ca-based particles. The inner temperature of the reaction zones was detected online by a thermal couple. The simulated cement precalciner gas stream containing N<sub>2</sub>, NO, CO, CO<sub>2</sub> and air was introduced into the reactor from the lower inlet, the secondary stream with NH<sub>3</sub> (diluted by N<sub>2</sub>) and water were fed into the reactor from the upper inlet. The two streams passed through respective preheating zones, and were then mixed in the reaction zones; the gas outlet was at the top of the reactor. The distance between the stream mixing point and the sieve plate was 50 mm.

## 2.2. Samples

CaO particles were prepared by decomposing analytical-grade CaCO<sub>3</sub> with a particle size of 38–45 μm. In the experiments without CaO, SiO<sub>2</sub> particles with a size of 38–45 μm were used as the background solid material due to its sluggishness. Prior to the experiments, SiO<sub>2</sub> or CaCO<sub>3</sub> was introduced into the reactor, distributed uniformly on the sieve plate, and then a preheating process was carried out: (1) The heating rate was set to 15 °C min<sup>-1</sup> and the solid materials were gradually heated from room temperature. Meanwhile, the air flow rate was set to 0.1 dm<sup>3</sup> min<sup>-1</sup> to take away the CO<sub>2</sub> generated from CaCO<sub>3</sub> calcinations. During this stage, the sintering of the solid particles proceeded gradually; (2) When the temperature of the solid material was about 850 °C, the air-flow rate was set to 0.5 dm<sup>3</sup> min<sup>-1</sup>; (3) When the temperature reached 1000 °C, the flow rate was set to 2 dm<sup>3</sup> min<sup>-1</sup>. This stage lasted for 30 min; (4) The heating process was stopped, and the solid materials were cooled down to the target experimental temperature in N<sub>2</sub> atmosphere. After the preheating process, CaCO<sub>3</sub> completely decomposed to CaO, and the particle materials were sintered to a porous block structure to avoid being blown out by the gas stream.

The properties of the CaO samples are listed in Table 1.

**Table 1.** Properties of pretreated CaO sample.

Morphology	Porous Block
Average particle diameter (μm)	38–45
Specific surface area (m <sup>2</sup> g <sup>-1</sup> )	37.162
Specific pore volume (cm <sup>3</sup> g <sup>-1</sup> )	0.091
Average pore diameter (nm)	11.302
Density (g cm <sup>-3</sup> )	3.35

## 2.3. Experimental Methods

The experiments were performed at atmospheric pressure. The basic cement precalciner gas was composed of 10% O<sub>2</sub>, 20% CO<sub>2</sub>, 3% H<sub>2</sub>O, 4000 ppm CO, 400 ppm NO, and 400 ppm NH<sub>3</sub> with N<sub>2</sub> used as balance gas, and the total flow rate was 2 dm<sup>3</sup> min<sup>-1</sup>. The effects of both CaO amount and basic gas composition on NO<sub>x</sub> reduction by SNCR were investigated. The concentrations of O<sub>2</sub>, CO, NO, and NO<sub>2</sub> were monitored by using a Testo 350-pro flue gas analyzer. NH<sub>3</sub> slip was sampled by a bubble column absorber containing dilute sulfuric acid solution and then analyzed by Nessler's reagent spectrophotometry.

NO<sub>x</sub> reduction efficiency, abbreviated as NO<sub>x</sub> reduction, is measured based on inlet and outlet NO<sub>x</sub> concentration. The temperature window is defined as the temperature region in which the NO<sub>x</sub> reduction efficiency exceeds 80% of the maximum value. The NO<sub>x</sub> reduction efficiency is defined as:

$$\text{NO}_x \text{ reduction} = \frac{C_{\text{NO}_x,\text{in}} - C_{\text{NO}_x,\text{out}}}{C_{\text{NO}_x,\text{in}}} \times 100\% \quad (1)$$

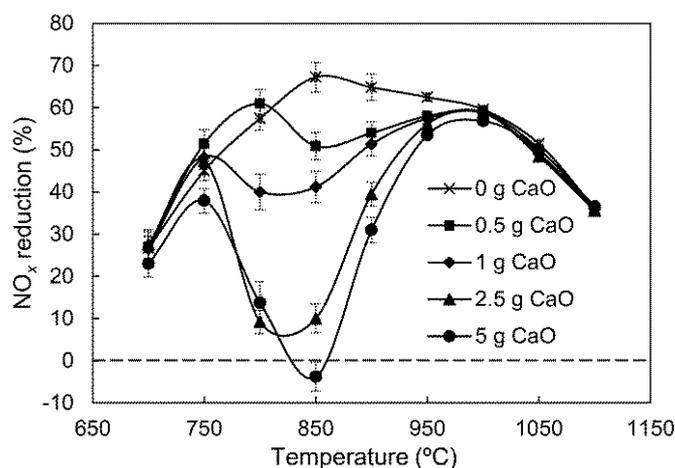
where  $C_{\text{NO}_x,\text{in}}$  and  $C_{\text{NO}_x,\text{out}}$  represent the inlet and outlet NO<sub>x</sub> concentrations, respectively.

### 3. Results

#### 3.1. Effect of CaO on SNCR

##### 3.1.1. Effect of CaO Amount on NO<sub>x</sub> Reduction

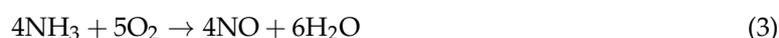
The effect of CaO amounts on NO<sub>x</sub> reduction by SNCR was studied under the basic gas compositions, and the results are illustrated in Figure 2.



**Figure 2.** Effect of CaO amount on NO<sub>x</sub> reduction by SNCR.

As shown in Figure 2, the NO<sub>x</sub> reduction curve without CaO is a unimodal shape. The maximum reduction efficiency of approximately 68% occurs at 850 °C. The temperature window of SNCR is 800–1050 °C. After CaO is added into the reactor, the NO<sub>x</sub> reduction efficiencies between 800 °C and 1000 °C decrease significantly, and these curves take on a bimodal shape. As CaO increases from 0.5 g to 5 g, the low-temperature peak value of NO<sub>x</sub> reduction drops from 61% to 38% with the corresponding temperature change from 800 °C to 750 °C. The high-temperature peak value, which is approximately 58% at 1000 °C, is hardly influenced by CaO content. The trough value of NO<sub>x</sub> reduction at 800–850 °C drops sharply with the increase of CaO content, and even a negative reduction efficiency, corresponding to the CaO of 5 g, appears at 850 °C.

As discussed in detail in our previous study [8], without CaO addition, the final NO<sub>x</sub> reduction efficiency by SNCR is determined by the competition between gas-phase NO<sub>x</sub> reduction and gas-phase NH<sub>3</sub> oxidation processes:



In a CaO-containing atmosphere, reactions (3) and (4) also occur catalytically on the CaO surface, which can lead to extra NO<sub>x</sub> formation, and may be responsible for the negative NO<sub>x</sub> reduction efficiency at 850 °C in the 5 g CaO group of Figure 2.

##### 3.1.2. Effect of CaO on NH<sub>3</sub> Oxidation

To investigate catalytic NH<sub>3</sub> oxidation on the CaO, experiments were conducted under the basic gas compositions without NO. The results are shown in Figure 3.

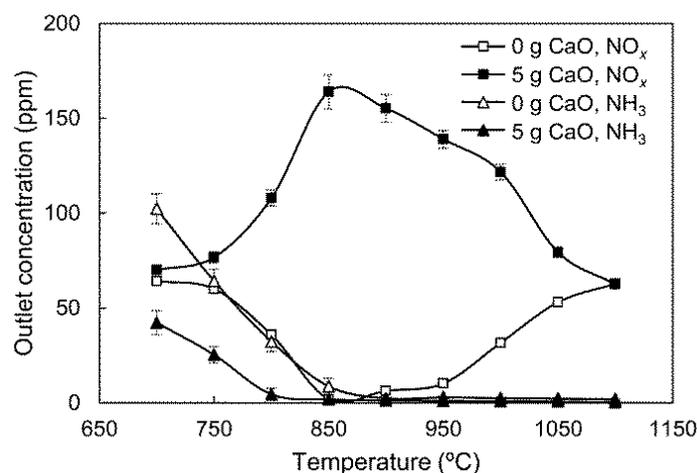
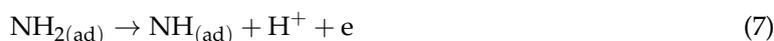


Figure 3. Effect of CaO amount on the oxidation of NH<sub>3</sub> to NO<sub>x</sub>.

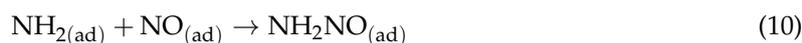
Figure 3 demonstrates that NH<sub>3</sub> can be oxidized to NO<sub>x</sub> by gas-phase reactions. In the 0 g CaO group, the outlet NO<sub>x</sub> concentration does not increase monotonically, as reported in other research [14], when temperature rises from 700 °C to 1100 °C. The relatively high level of outlet NO<sub>x</sub> at 700–800 °C can be attributed to the high concentration of CO in the gas stream. As stated in our previous study [8], CO can enhance the conversion of NH<sub>3</sub> to NH<sub>2</sub> and NH at low temperatures, thus promoting gas-phase NH<sub>3</sub> oxidation. As temperature rises, CO is gradually consumed by O<sub>2</sub> in the preheating zone of the reactor, which inhibits the oxidation of NH<sub>3</sub> to NO. When the temperature goes above 950 °C, the conversion of NH<sub>3</sub> to NH is accelerated without CO, raising the outlet NO<sub>x</sub> concentration. In the 5 g CaO group, the relationship of outlet NO<sub>x</sub> concentration with temperature is almost opposite from the group with no CaO. As temperature rises, the NO<sub>x</sub> concentration increases to its maximum at 850 °C and then gradually declines. There are two types of reaction process involving NH<sub>3</sub> in the 5 g CaO group, namely, gas-solid catalytic NH<sub>3</sub> oxidation and gas-phase NH<sub>3</sub> conversion. For gas-solid catalytic NH<sub>3</sub> oxidation, the initial and rate-determining step is the H-abstraction of adsorbed NH<sub>3</sub> [17,18]:



Then, deeper H-abstraction might occur with NH<sub>2(ad)</sub>, forming NH<sub>(ad)</sub>, generating NO:



In the presence of O<sub>2</sub> and NO, NH<sub>2(ad)</sub> can reduce adsorbed NO to form N<sub>2</sub>:



As such, the NO<sub>x</sub> selectivity of catalytic NH<sub>3</sub> oxidation is determined directly by the proportion of NH<sub>2(ad)</sub> involved in reactions (7) and (10).

For gas-phase NH<sub>3</sub> oxidation and NO<sub>x</sub> reduction, the rate-determining step is the conversion of NH<sub>3</sub> to NH<sub>2</sub> [19]:





Figure 3 also shows that the outlet  $\text{NH}_3$  concentration with CaO addition is lower than that without CaO below 850 °C. This indicates that reactions (5) and (6) proceed faster than reactions (12) and (13) below 850 °C. Because most  $\text{NH}_3$  is oxidized in the gas-solid reaction process, the  $\text{NO}_x$  concentration is mainly affected by the  $\text{NO}_x$  selectivity of catalytic  $\text{NH}_3$  oxidation. This leads to the escalation of outlet  $\text{NO}_x$  concentrations up to 850 °C. According to the kinetic parameters in previous research, when the temperature rises from 700 °C to 1100 °C, the rate constant of catalytic  $\text{NH}_3$  oxidation varies insignificantly [5], while the rate constants of gas-phase  $\text{NH}_3$  conversion increase significantly [19]. As a result, above 850 °C, the gas-phase  $\text{NH}_3$  conversion rate gradually surpasses the catalytic  $\text{NH}_3$  oxidation rate. More  $\text{NH}_3$  is oxidized in gas-phase reaction processes with a low  $\text{NO}_x$  selectivity, diminishing the outlet  $\text{NO}_x$  concentration. When the temperature rises to 1100 °C, the gas-phase  $\text{NH}_3$  conversion is fast enough to prevent  $\text{NH}_3$  involvement in catalytic reactions, and almost all  $\text{NH}_3$  is consumed by the gas-phase process. In this condition, the catalytic  $\text{NH}_3$  oxidation on the CaO surface can be ignored. When NO is introduced into the gas stream,  $\text{NH}_3$  consumption by the gas-phase  $\text{NO}_x$  reduction process further decreases the  $\text{NH}_3$  in the catalytic oxidation. This narrows the temperature range with significant CaO effect to 750–1000 °C.

### 3.2. Influences of Gas Compositions on the Effect of CaO

#### 3.2.1. Influence of Initial $\text{NH}_3$ Concentration

In Figure 2, there is a slight increase in  $\text{NO}_x$  reduction efficiency at 700–800 °C in the 0.5 g CaO group compared with the group with no CaO. This improvement may be related to the  $\text{NH}_3$  concentration involved in gas-phase  $\text{NH}_3$  oxidation and  $\text{NO}_x$  reduction. To verify this, the effect of initial  $\text{NH}_3$  concentrations on SNCR was investigated, and the results are shown in Figure 4.

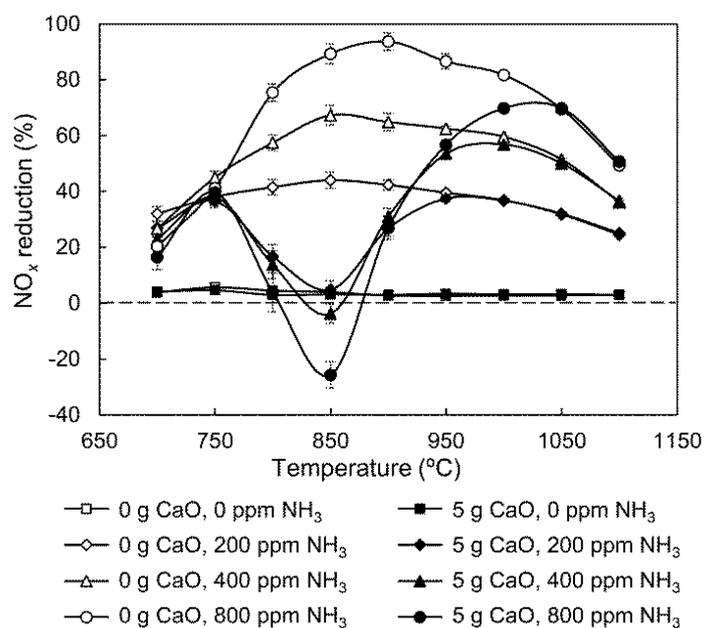


Figure 4. Effect of initial  $\text{NH}_3$  concentration on  $\text{NO}_x$  reduction.

The  $\text{NO}_x$  reduction efficiency without CaO increases with initial  $\text{NH}_3$  concentration above 750 °C. However, there is an adverse result below 750 °C, suggesting that the lower initial  $\text{NH}_3$  concentration improves  $\text{NO}_x$  reduction at low temperatures. Therefore, when 0.5 g CaO is added, the  $\text{NH}_3$  involved in gas-phase  $\text{NH}_3$  oxidation and  $\text{NO}_x$  reduction decreases due to  $\text{NH}_3$  consumption through catalytic reactions, resulting in a slight increase in  $\text{NO}_x$  reduction efficiency at 700–800 °C.

It can also be seen from Figure 4 that increasing the initial  $\text{NH}_3$  concentration results in lower  $\text{NO}_x$  reduction efficiencies at 750–900 °C when CaO is added. At this temperature, gas-solid catalytic  $\text{NH}_3$  oxidation is more sensitive to  $\text{NH}_3$  concentration changes than gas-phase SNCR process. The initial  $\text{NH}_3$  concentration has a minor influence on the low-temperature peak value of  $\text{NO}_x$  reduction, but significantly augments the high-temperature one. Conversely, as shown in Figure 2, CaO content affects the low-temperature peak value notably, but has almost no effect on the high-temperature one. In an actual SNCR operation in a cement precalciner,  $\text{NH}_3$  addition is more controllable than CaO, so the temperature range of 950–1050 °C is more favorable for obtaining high reduction efficiency.

### 3.2.2. Influence of $\text{H}_2\text{O}$

The influence of  $\text{H}_2\text{O}$  contents on the effect of CaO was investigated, and the results are shown in Figure 5.

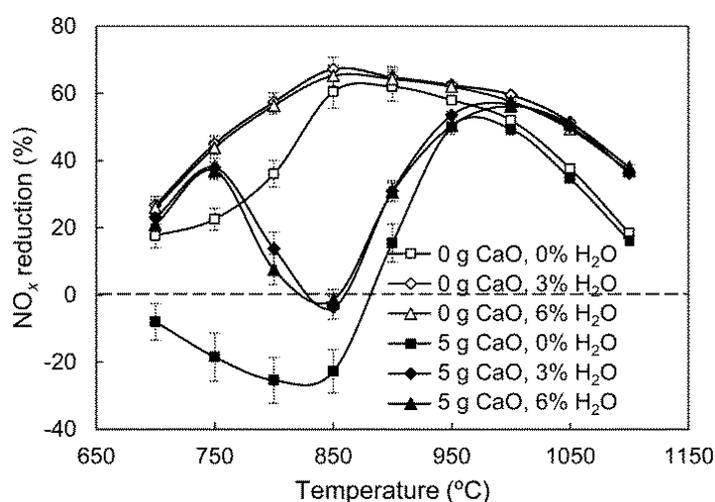


Figure 5. Influence of  $\text{H}_2\text{O}$  on the effect of CaO.

Figure 5 shows that when no CaO is present,  $\text{H}_2\text{O}$  has a positive effect on gas-phase SNCR process, which was discussed in our previous research [8]. In the 5 g CaO group, the  $\text{NO}_x$  reduction efficiency without  $\text{H}_2\text{O}$  remains negative up to approximately 870 °C. When  $\text{H}_2\text{O}$  is added, the efficiency increases significantly and the negative effect of CaO on  $\text{NO}_x$  reduction is suppressed to a certain extent. This may be because adding  $\text{H}_2\text{O}$  stimulates gas-phase  $\text{NH}_3$  conversion, decreasing  $\text{NH}_3$  involved in catalytic oxidation. Furthermore,  $\text{H}_2\text{O}$  can compete for active sites, adsorbing  $\text{NH}_3$  on the CaO surface, and thus inhibiting subsequent catalytic  $\text{NH}_3$  oxidation [16,20]. Therefore,  $\text{H}_2\text{O}$  addition benefits  $\text{NO}_x$  reduction not only in a gas-phase reaction system, but also in a CaO-containing atmosphere.

### 3.2.3. Influence of $\text{O}_2$

$\text{O}_2$  content is not uniform in cement precalciners, and generally ranges from 0% to 13%. Figure 6 shows the influence of  $\text{O}_2$  concentrations on the effect of CaO on SNCR.

As shown in Figure 6, the results without CaO coincide with our previous research. With CaO addition, when  $\text{O}_2$  content is reduced from 10% to 1%, the low-temperature peak, the trough, and the high-temperature peak of  $\text{NO}_x$  reduction curve shift to the higher temperatures of 800 °C, 950 °C, and 1050 °C, respectively. In addition, the trough value drops to a more negative one from -4% to -18%. This result suggests that decreasing  $\text{O}_2$  content shifts the temperature region in which CaO significantly impacts  $\text{NO}_x$  reduction from 750–1000 °C to the higher value range of 800–1050 °C, which shows that the gas-phase SNCR process is very susceptible to the change of  $\text{O}_2$  content, while the variation of  $\text{O}_2$  content between 1% and 10% fails to influence catalytic  $\text{NH}_3$  oxidation [11]. Hence,

when O<sub>2</sub> content decreases, the SNCR process slows and requires higher temperatures to proceed fast enough to dominate the whole process. As NO<sub>x</sub> selectivity of catalytic NH<sub>3</sub> oxidation rises with temperature, the minimum NO<sub>x</sub> reduction efficiency drops.

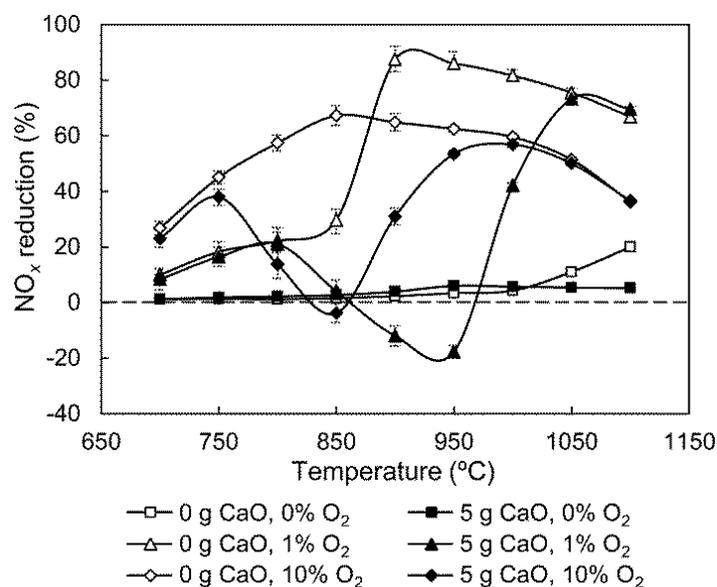


Figure 6. Influence of O<sub>2</sub> on the effect of CaO.

O<sub>2</sub> is necessary for the SNCR process, so when O<sub>2</sub> is not present, the NO<sub>x</sub> reduction efficiency without CaO is trivial below 1000 °C. The slight efficiency increase above 1000 °C is due to H radicals, which are generated from H<sub>2</sub>O pyrolysis and help NH<sub>3</sub> conversion [8]. In contrast, the NO<sub>x</sub> reduction efficiency of the 5 g CaO group remains trivial, even at high temperatures. Although CaO can catalyze NO reduction by NH<sub>3</sub> in the absence of O<sub>2</sub> [5,14], the catalyst cannot restore its activity without O<sub>2</sub> reoxidation [18]. On the other hand, the competitive adsorption of H<sub>2</sub>O by CaO not only inhibits the catalytic NH<sub>3</sub> + NO reaction, but also reduces gaseous H radicals. This weakens gas-phase NO<sub>x</sub> reduction in the absence of O<sub>2</sub>. Therefore, it is not possible to reduce NO<sub>x</sub> with NH<sub>3</sub> in an O<sub>2</sub>-free zone in a cement precalciner.

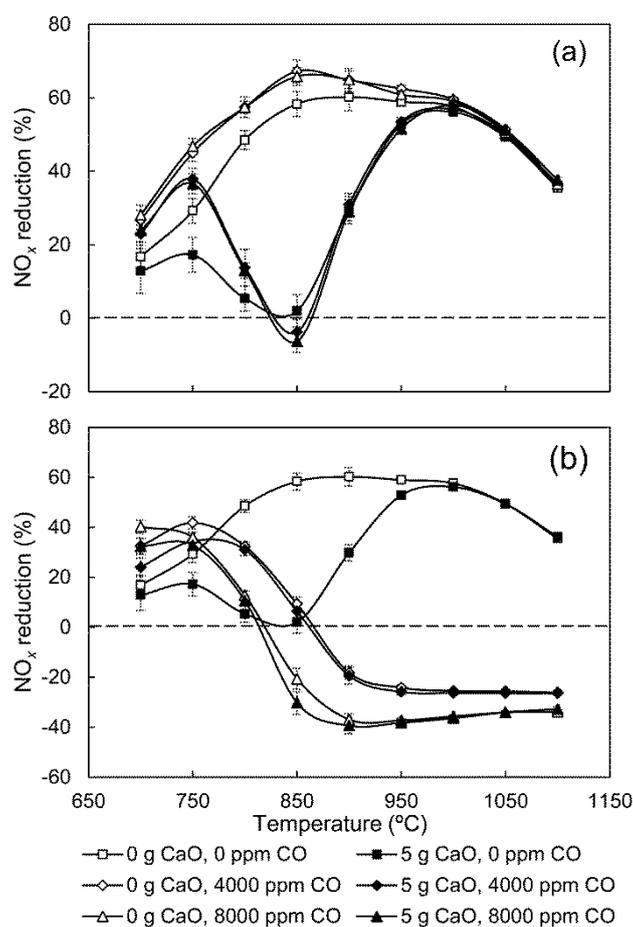
#### 3.2.4. Influence of CO

CO is an important constituent of flue gas in a cement precalciner. Similar to O<sub>2</sub>, it varies with location and operation conditions. It has been reported that CaO can catalyze NO reduction by CO, but the catalysis becomes negligible in the presence of either O<sub>2</sub> or a high concentration of CO<sub>2</sub> [21]. Previous research has investigated the influence of CO on gas-phase NO<sub>x</sub> reduction [8,22,23]; however, it remains unclear how CO influences the effect of CaO on NO<sub>x</sub> reduction with NH<sub>3</sub>. Therefore the influence of CO concentrations in a multi-phase reaction system was studied, and the results are seen in Figure 7.

Figure 7a shows an improvement of gas-phase NO<sub>x</sub> reduction when adding CO at low temperatures. In the 5 g CaO group, the increase of CO content leads to a slight decrease of NO<sub>x</sub> reduction efficiency between 820 °C and 900 °C, implying that the effect of CaO is enhanced. This may be attributed to H<sub>2</sub>O consumption by CO [24]:



This series of reactions weakens the inhibitory effect of H<sub>2</sub>O on catalytic NH<sub>3</sub> oxidation, engaging more NH<sub>3</sub> in catalytic oxidation, leading to incremental NO<sub>x</sub> generation. During the experiments, it was observed that the outlet CO concentration with the addition of CaO was lower than that without CaO under the same conditions. This is because CaO can catalyze CO oxidation [14], which suggests that there exist active sites adsorbing CO onto the CaO surface. If the active sites for CO are the same as those for NH<sub>3</sub>, CO should inhibit the negative effect of CaO on NO<sub>x</sub> reduction similarly to H<sub>2</sub>O. However, the results suggest that the active sites adsorbing CO and NH<sub>3</sub> are distinct, and that CO does not directly influence catalytic NH<sub>3</sub> oxidation. Therefore, the only reason that adding CO would enhance NO<sub>x</sub> reduction efficiency below 820 °C in the 5 g CaO group is that CO can promote the gas-phase SNCR process. The influence of CO can be ignored above 1000 °C in the group with no CaO, due to CO consumption by O<sub>2</sub> in the reactor's preheating zone. In the 5 g CaO group, because CO oxidation is promoted by CaO, the influence of CO is already negligible at 900 °C.



**Figure 7.** Influence of CO concentrations on the effect of CaO (a) when CO is introduced into the reactor with the main stream; and (b) when CO is introduced into the reactor with the secondary stream.

As can be seen from Figure 7b, when CO is introduced into the reactor with the secondary stream, NH<sub>3</sub> is actually injected into an O<sub>2</sub>-free atmosphere with a high CO content before mixing with the stream containing O<sub>2</sub>. In this case, a large amount of NH<sub>3</sub> is converted to NH<sub>2</sub> and NH radicals, which shifts the temperature window of SNCR to lower values and causes negative NO<sub>x</sub> reduction efficiencies at high temperatures [8]. Additionally, except that the NO<sub>x</sub> reduction efficiency of 5 g CaO group is a little lower than that of the 0 g CaO group below 800 °C, there is little difference between the results of the two groups with CO addition. This means that the negative effect of CaO on NO<sub>x</sub> reduction is almost completely suppressed. Consequently, it can be inferred that NH<sub>2</sub> and NH radicals

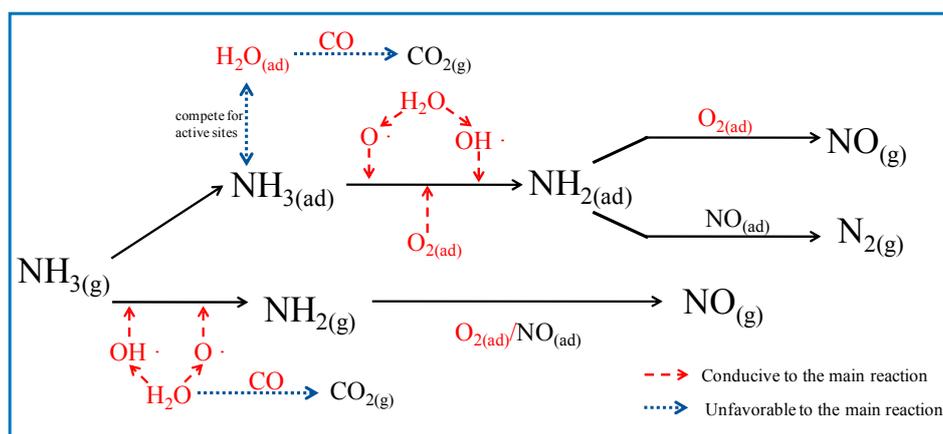
generated from gas-phase  $\text{NH}_3$  conversion cannot be adsorbed by CaO to join in the catalytic reactions. The catalytic oxidation of  $\text{NH}_3$  must be initiated by the adsorption of molecular  $\text{NH}_3$ .

Although the injection method in Figure 7b can suppress the negative effect of CaO on  $\text{NO}_x$  reduction,  $\text{NH}_3$  is apt to be oxidized to  $\text{NO}_x$  via gas-phase reactions. Therefore, in an actual SNCR operation for cement precalciners,  $\text{NH}_3$  should not be injected into an  $\text{O}_2$ -free area with high CO and then mixed with an  $\text{O}_2$ -containing gas stream.

#### 4. Discussion

Homogeneous reactions (gas-phase) play a predominant role in non-CaO SNCR in cement precalciners, and the rate-determining step is the conversion of  $\text{NH}_3$  to  $\text{NH}_2$ . For heterogeneous catalytic reactions (gas-solid), the rate-determining step is the H-abstraction of adsorbed  $\text{NH}_3$  [17,18]. CaO has an inhibitory effect on the SNCR process, especially in the middle temperature zone of 750–1000 °C; the CaO contents are closely related to the inhibitory effect of CaO. CaO can catalyze  $\text{NH}_3$  decomposition. Moreover, CaO catalyzed  $\text{NH}_3$  oxidation in the presence of  $\text{O}_2$ , which can lead to extra  $\text{NO}_x$  formation.

The effects on  $\text{NO}_x$  reduction efficiency in the presence of CaO with the increase of  $\text{H}_2\text{O}$ ,  $\text{O}_2$ , and CO concentration are different. The addition of  $\text{H}_2\text{O}$  benefits  $\text{NO}_x$  reduction in homogeneous reactions, and suppresses the negative effect of CaO on  $\text{NO}_x$  reduction to a certain extent. The thermal decomposition of  $\text{H}_2\text{O}$  results in the regeneration of O and OH radicals [8]; these radicals then stimulate gas-phase  $\text{NH}_3$  conversion, decreasing the  $\text{NH}_3$  involved in catalytic oxidation. Furthermore,  $\text{H}_2\text{O}$  can compete for  $\text{NH}_3$  active sites on the CaO surface, and thus reducing the occurrence of heterogeneous reactions;  $\text{O}_2$  is indispensable for  $\text{NO}_x$  reduction by SNCR, as  $\text{O}_2$  is the primary reactant of NO production from the reaction of  $\text{NH}_2$  with  $\text{O}_2$  in the CaO-containing SNCR process, which causes a negative effect of CaO on  $\text{NO}_x$  reduction. CO leads to a slight decrease of  $\text{NO}_x$  reduction efficiency between 820 °C and 900 °C, and enhances the effect of CaO, which may be attributed to  $\text{H}_2\text{O}$  consumption by CO [24]. The influence of CO is already negligible above 900 °C. The results of this study could provide a reference for engineering applications for optimizing  $\text{NO}_x$  reduction processes by  $\text{NH}_3$ -SNCR in cement precalciners. A pathway for the effect of gas compositions on  $\text{NO}_x$  reduction in CaO-containing SNCR processes, based on conclusions derived from the experimental results and acknowledged reactions, is given in Figure 8.



**Figure 8.** Proposed pathways for the effect of gas compositions on  $\text{NO}_x$  reduction in CaO-containing SNCR process.

#### 5. Conclusions

CaO in a cement precalciner can inhibit  $\text{NO}_x$  reduction by the SNCR process between 750 °C and 1000 °C due to the catalytic oxidation of  $\text{NH}_3$  to NO on the CaO surface. When CaO is added,

NO<sub>x</sub> reduction efficiency follows a bimodal distribution against temperature. The low-temperature peak changes with CaO content, while the high-temperature peak is hardly influenced by CaO content. The trough value between the two peaks decreases significantly as CaO increases. With a high CaO content, the trough value of NO<sub>x</sub> reduction at 850 °C is even negative. In CaO-containing cement precalciner, gas-phase NH<sub>3</sub> conversion coexists with gas-solid catalytic NH<sub>3</sub> oxidation. Below 750 °C, the NO<sub>x</sub> selectivity of catalytic NH<sub>3</sub> oxidation is low, so CaO does not significantly impact NO<sub>x</sub> reduction efficiency. Above 1000 °C, the gas-phase NH<sub>3</sub> conversion proceeds fast enough to prevent NH<sub>3</sub> from being oxidized catalytically. Although NO<sub>x</sub> reduction performance appears to improve by adding CaO at low temperatures, the improvement is slight, and likely results from the loss of NH<sub>3</sub> involved in gas-phase NH<sub>3</sub> conversion.

NH<sub>3</sub>, H<sub>2</sub>O, O<sub>2</sub>, and CO influences the effect of CaO by affecting gas-phase NH<sub>3</sub> conversion, or gas-solid catalytic NH<sub>3</sub> oxidation, or both processes. Although increasing NH<sub>3</sub> concentration is advantageous to NO<sub>x</sub> reduction, increasing NH<sub>3</sub> results in a decrease in NO<sub>x</sub> reduction efficiency at 750–900 °C when CaO is added. H<sub>2</sub>O can significantly suppress the negative effect of CaO on NO<sub>x</sub> reduction. As O<sub>2</sub> content decreases from 10% to 1%, the temperature region for a significant CaO effect shifts higher. With the addition of CO, the effect of CaO is reduced below 820 °C, while it is slightly enhanced at approximately 850 °C. When NH<sub>3</sub> is injected into an O<sub>2</sub>-free atmosphere with a high CO content, it is apt to be oxidized to NO<sub>x</sub> after mixing with an O<sub>2</sub>-containing stream. In this case, the effect of CaO on NO<sub>x</sub> reduction is almost eliminated.

Considering the effect of CaO on NO<sub>x</sub> reduction under variable gas compositions, it is recommended that NH<sub>3</sub> be injected into the O<sub>2</sub>-containing area with a low CaO concentration in the temperature range of 950–1100 °C to obtain a high NO<sub>x</sub> reduction efficiency by SNCR in a cement precalciner.

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## References

1. Yang, B.; Shen, Y.S.; Su, Y.; Li, P.W.; Zeng, Y.W.; Shen, S.B.; Zhu, S.M. Removal characteristics of nitrogen oxides and particulates of a novel Mn-Ce-Nb-O<sub>x</sub> /P84 catalytic filter applied for cement kiln. *J. Ind. Eng. Chem.* **2017**, *50*, 133–141. [[CrossRef](#)]
2. MEPPRC. China Environment Statistical Annual Report 2013. 2014. Available online: [http://zls.mep.gov.cn/hjtj/nb/2013tjnb/201411/t20141124\\_291867.htm](http://zls.mep.gov.cn/hjtj/nb/2013tjnb/201411/t20141124_291867.htm) (accessed on 24 November 2014).
3. Li, B.; Zhao, J.Y.; Lu, J.F. Numerical study of the simultaneous oxidation of NO and SO<sub>2</sub> by ozone. *Int. J. Environ. Res. Public Health* **2015**, *12*, 1595–1611. [[CrossRef](#)] [[PubMed](#)]
4. Ba-Shammakh, M.S. A decision support tool for multi-pollutants reduction in cement industry using analytic hierarchy process (AHP). *Can. J. Chem. Eng.* **2011**, *89*, 1508–1515. [[CrossRef](#)]
5. Fu, S.L.; Song, Q.; Tang, J.S.; Yao, Q. Effect of CaO on the selective non-catalytic reduction deNO<sub>x</sub> process: Experimental and kinetic study. *Chem. Eng. J.* **2014**, *249*, 252–259. [[CrossRef](#)]
6. Daood, S.S.; Yelland, T.; Nimmo, W. Selective non-catalytic reduction Fe-based additive hybrid technology. *Fuel* **2017**, *208*, 353–362. [[CrossRef](#)]
7. Javed, M.T.; Nimmo, W.; Mahmood, A.; Irfan, N. Effect of oxygenated liquid additives on the urea based SNCR process. *J. Environ. Manag.* **2009**, *90*, 3429–3435. [[CrossRef](#)] [[PubMed](#)]
8. Fan, W.Y.; Zhu, T.L.; Sun, Y.F.; Lv, D. Effects of gas compositions on NO<sub>x</sub> reduction by selective non-catalytic reduction with ammonia in a simulated cement precalciner atmosphere. *Chemosphere* **2014**, *113*, 182–187. [[CrossRef](#)] [[PubMed](#)]

9. Fu, S.L.; Song, Q.; Yao, Q. Mechanism study on the adsorption and reactions of NH<sub>3</sub>, NO, and O<sub>2</sub> on the CaO surface in the SNCR deNO<sub>x</sub> process. *Chem. Eng. J.* **2016**, *285*, 137–143. [[CrossRef](#)]
10. Zijlma, G.J.; Jensen, A.D.; Johnsson, J.E.; van den Bleek, C.M. NH<sub>3</sub> oxidation catalysed by calcined limestone: A kinetic study. *Fuel* **2002**, *81*, 1871–1881. [[CrossRef](#)]
11. Fu, S.L.; Song, Q.; Yao, Q. Influence of CaO on urea pyrolysis in the selective non-catalytic reduction deNO(x) process. *J. Anal. Appl. Pyrolysis* **2017**, *126*, 397–404. [[CrossRef](#)]
12. Yang, X.; Zhao, B.; Zhuo, Y.Q.; Guo, Y.; Chen, C.H.; Xu, X.C. DRIFTS study of ammonia activation over CaO and sulfated CaO for NO reduction by NH<sub>3</sub>. *Environ. Sci. Technol.* **2011**, *45*, 1147–1151. [[CrossRef](#)] [[PubMed](#)]
13. Shimizu, T.E.; Karahashi, T.; Yamaguchi, T.; Inagaki, M. Decomposition of NH<sub>3</sub> over calcined and uncalcined limestone under fluidized bed combustion conditions. *Energy Fuels* **1995**, *9*, 962–965. [[CrossRef](#)]
14. Lin, W. *Interactions between SO<sub>2</sub> and NO<sub>x</sub> Emissions in Fluidised Bed Combustion of Coal*; Delft University of Technology: Delft, The Netherlands, 1994.
15. Li, T.J.; Zhuo, Y.Q.; Chen, C.H.; Xu, X.C. Effect of CaO on NH<sub>3</sub> + NO + O<sub>2</sub> reaction system in the absence and presence of high concentration CO<sub>2</sub>. *Asia-Pac. J. Chem. Eng.* **2010**, *5*, 287–293. [[CrossRef](#)]
16. Zijlma, G.J.; Jensen, A.; Johnsson, J.E.; van den Bleek, C.M. Influence of H<sub>2</sub>O and CO<sub>2</sub> on the reactivity of limestone for the oxidation of NH<sub>3</sub>. *Fuel* **2000**, *79*, 1449–1454. [[CrossRef](#)]
17. Ramis, G.; Yi, L.; Busca, G.; Turco, M.; Kotur, E.; Willey, R.J. Adsorption, activation, and oxidation of ammonia over SCR catalysts. *J. Catal.* **1995**, *157*, 523–525. [[CrossRef](#)]
18. Liu, Q.; Liu, Z.; Li, C.Y. Adsorption and Activation of NH<sub>3</sub> during Selective Catalytic Reduction of NO by NH<sub>3</sub>. *Chin. J. Catal.* **2006**, *27*, 636–646. [[CrossRef](#)]
19. Miller, J.A.; Bowman, C.T. Mechanism and modeling of nitrogen chemistry in combustion. *Prog. Energy Combust. Sci.* **1989**, *15*, 287–338. [[CrossRef](#)]
20. Shimizu, T.; Hasegawa, M.; Inagaki, M. Effect of water vapor on reaction rates of limestone-catalyzed NH<sub>3</sub> oxidation and reduction of N<sub>2</sub>O under fluidized bed combustion conditions. *Energy Fuels* **2000**, *14*, 104–111. [[CrossRef](#)]
21. Dam-Johansen, K.; Hansen, P.F.B.; Rasmussen, S. Catalytic reduction of nitric oxide by carbon monoxide over calcined limestone: Reversible deactivation in the presence of carbon dioxide. *Appl. Catal. B-Environ.* **1995**, *5*, 283–304. [[CrossRef](#)]
22. Sang, W.B.; Roh, S.A.; Sang, D.K. NO removal by reducing agents and additives in the selective non-catalytic reduction (SNCR) process. *Chemosphere* **2006**, *65*, 170–175. [[CrossRef](#)]
23. Javed, M.T.; Nimmo, W.; Gibbs, B.M. Experimental and modeling study of the effect of CO and H<sub>2</sub> on the urea DeNO(x) process in a 150kW laboratory reactor. *Chemosphere* **2008**, *70*, 1059–1067. [[CrossRef](#)] [[PubMed](#)]
24. Alzueta, M.U.; Rojel, H.; Kristensen, P.G.; Glarborg, P.; Dam-Johansen, K. Laboratory study of the CO/NH<sub>3</sub>/NO/O<sub>2</sub> system: Implications for hybrid reburn/SNCR strategies. *Energy Fuels* **1997**, *11*, 716–723. [[CrossRef](#)]

