

Catalytic reduction of nitric oxide by methane over CaO catalyst

Wei Xu[†], Huiling Tong, Changhe Chen and Xuchang Xu

Key Laboratory for Thermal Science and Power Engineering of Ministry of Education,
Department of Thermal Engineering, Tsinghua University, Beijing, 100084, China

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Abstract—The selective catalytic reduction of nitric oxide by methane was studied over CaO catalyst in a bubbling fluidized bed in the temperature range of 800-900 °C, in which NO cannot be reduced by CH₄ without CaO catalyst. The nitric oxide conversion was found to depend on oxygen and CH₄ feed concentration, and also on temperature. In addition, the presence of water vapors in the flue gas enhanced the NO reduction admirably well in the absence of O₂. But water vapor has an inhibiting effect on the reaction while O₂ is present in the flue gas. The addition of CO₂ poisoned the CaO catalyst and exhibited a detrimental effect on NO conversion at the working temperature range, 800-900 °C. However, with a temperature rise to 900 °C the CO₂ poisoning effect on NO reduction was weakened. The mechanism was studied and discussed according to the references in the paper.

Key words: CaO, Fluidized Bed Reactor, NO Reduction, Methane, Carbon Dioxide

INTRODUCTION

The catalytic reduction of nitric oxide with hydrocarbons in place of ammonia has received increased attention from both academic and industrial points of view. Since natural gas is rich in reserves and used widely as fuel, it will be perspective if methane is effective on NO_x reduction. Furthermore, it can overcome the problems of ammonia as reductant, such as leakage, storage, transportation, high cost, and equipment corrosion. Since many scientific researchers [1,2] have found that CaO is a good sorbent for SO₂ capture in the flue gas in the range of 750-950 °C, it is therefore necessary to study its catalytic ability to reduce NO_x in the flue gas and explore the feasibility of removing the SO₂ and NO_x simultaneously in this temperature range by hydrocarbons.

Research has been using methane as a reducing agent to reduce NO_x since 1984 [3]. CH₄ is regarded as a non-selective reductant which can be activated only at high temperature because of the very strong C-H bond. Conducting research on the fixed bed reactor Tsujimura et al. [5] found that CaO was capable of catalyzing the NO reduction by CO and the effectiveness depended on its catalytic activity and surface [5,6]. Also, based on study in a fixed bed reactor, Fliatoura [7] found that CaO could catalyze NO reduction by CH₄ in the range of 550-850 °C, conversion of NO to N₂ was increased with temperature rise, and 100% conversion was achieved at 850 °C. But it retained 50% at 650 °C and decreased to 20% at 770 °C while the O₂ fraction was changed from 1% to 10%. It can be seen that the rise of O₂ fraction in the gas would inhibit NO reduction. But Li and Armor [8] thought that the NO conversion rate would fall with temperature rise, because of CH₄ oxidation.

Bertrand et al. [9] reported that the CO₂ component could weaken the ability of CO to reduce NO_x markedly but they did not provide

a detailed discussion. Comparing the experimental results with CO₂ absent and 2.5% CO₂ present in the gas, Fliatoura et al. [7] found that CO₂ species could inhibit NO reduction by CH₄ in the range of 550-850 °C, and the inhibition in the reduction during temperature range 550-650 °C was larger than that observed during 700-850 °C. But only 10% NO conversion dropped at 800 °C when 2.5% vol. CO₂ was added to the reactor system. However, Dam-Johansen et al. [10,11], who studied NO reduction by CO over CaO catalyst in a fixed bed at 800-950 °C, found that the conversion of NO to N₂ was close to 85% constantly with 4% CO present and in the absence of O₂ and CO₂, but it would drop continuously from 80% in the beginning to 20% in the presence of 10%vol. CO₂ in the gas. Whereas, when the supply of CO₂ was turned off the catalytic activity of CaO would recover right away. It indicated that the decrease of the reducing activity was not due to the pore sintering of the catalyst. Furthermore, Dam-Johansen [11,13] found that CO could be oxidized rapidly at 850 °C in the presence of water vapor and O₂ in the gas and no lime in the reactor, while the oxidation rate for CO was slow in the absence of water vapors in the gas.

As mentioned above, we can find that most studies of NO reduction over CaO catalyst are focused on CO and H₂ as reductants. Although Fliatoura used CH₄ to reduce NO on a fixed bed [7], there is no report on such issue in a fluidizing bed reactor so far. Furthermore, Fliatoura's experimental results differ considerably with other researchers', such as the effect of coexisting O₂ and H₂O on NO reduction. Fliatoura [7] considered that the coexistence of O₂ and H₂O had a few promoting effects on NO reduction by CH₄ at 700-850 °C, while Dam-Johansen [11,13] thought it could promote oxidation of CO and then make NO conversion decrease at 850 °C. Besides, the poisoning of CaO by CO₂ was not consistent with results from other researchers.

In recent years, considerable attention has been focused on the simultaneous removal of SO₂ and NO_x in a single reactor to economize the capital investment, operating cost, and the space for equipment [14,15]. CaO is cheap and widely used as sorbent for SO₂ removal in the temperature range of 750-1100 °C [1,2]. The objec-

[†]To whom correspondence should be addressed.

E-mail: w-xu04@mails.tsinghua.edu.cn

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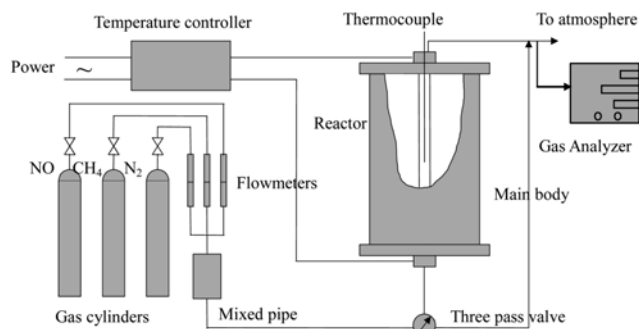


Fig. 1. Schematic diagram of experimental apparatus.

tive of this research is to study the effect of temperature and feed gas composition on NO reduction by CH_4 over CaO catalyst, and to explore the feasibility of simultaneous denitration in the desulfurization process at 800–900 °C.

EXPERIMENTAL

1. Apparatus

Fig. 1 shows a schematic diagram of the experimental apparatus, including a bubbling fluidized bed reactor. The experimental apparatus consisted of a gas assembly, reactor, gas analyzer and a temperature controller. A reactor made of quartz having inner diameter of 0.03 m and a height of 0.4 m was placed inside of a furnace. A gas distributor made of sintered quartz was mounted at the lower part of the reactor, which was located 0.28 m from the reactor outlet, so that incoming gas could be heated up 0.12 m below the distributor. The gas components were provided by high pressure cylinders of nitrogen ($\text{N}_2 \geq 99.5\%$), methane ($\text{CH}_4 \geq 99.9\%$), oxygen ($\text{O}_2 \geq 99.5\%$), carbon dioxide ($\text{CO}_2 \geq 99.5\%$), and standard NO gas prepared in advance (4,680 ppm NO, N_2 balance). The gas flow of every component gas was controlled precisely by mass flow meters. Water vapors were added into the gas by carry-over of the N_2 flow into water bath with temperature controlled at 70 °C. The water vapor fraction in the gas was regulated by controlling the N_2 flow into the water bath. The outlet NO and CO components were monitored continuously by the gas analyzer model GA-40, Madur Electronics, U.S.A. To ensure accuracy and precision, the gas analyzer was calibrated before each test. During the experiments a solid catalyst was put on the distributor for complete interaction of NO and CH_4 with the fluidized solid catalyst. In order to observe the effect of gas components on NO reduction by CH_4 , the composition of the gas was changed in a certain range. While the composition of CH_4 or O_2 in the gas flow was changed, it is difficult to regulate nitrogen flow precisely to keep the total gas flow constant. Here, some fluctuation was expected in the total gas flow. For example, the flow data indication for CH_4 was changed from 32 ml/min to 64 ml/min and the total gas flow arrived at 3.046 L/min from 3.023 L/min. However, the difference was less than 1%. The gas flow value in the experiment indicated atmospheric data.

RESULTS AND DISCUSSIONS

1. Effect of Temperature on NO Reduction by CH_4 with Blank

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Table 1. Gas composition (volume fraction, %) with blank reactor in the test (3.056 L/min total gas flow)

N_2	O_2	CH_4	NO	CO_2	H_2
98.34–99.23%	0 or 0.4	0.767 or 1.53	829/ppm	0	0

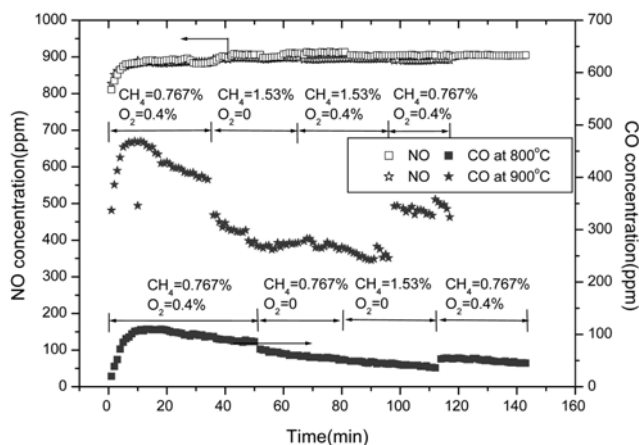


Fig. 2. Results with blank reactor at 800 °C and 900 °C.

Reactor

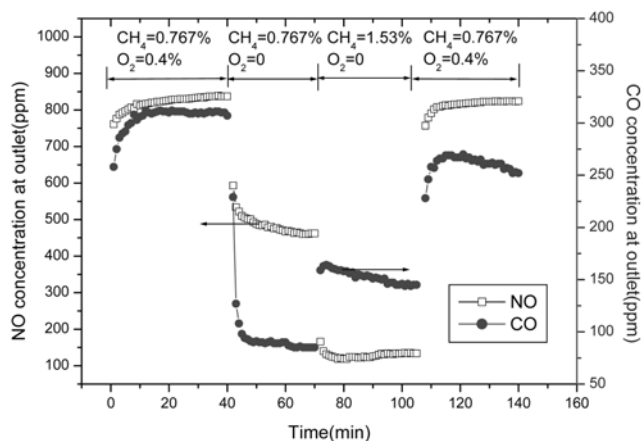
The blank reactor with air only was heated to 800 °C, the gas at a flow rate of ~ 3 L/min with composition mentioned in Table 1 was fed, and NO and CO concentrations from the outlet of the reactor were recorded by the gas analyzer. The results are shown in Fig. 2. It was observed that the NO concentration remained almost constant while oxygen flow was decreased to zero and the flow of CH_4 was increased from 32 to 64. It meant that the quartz, which was made up of the reactor, had no catalytic effect on the reaction of NO reduction by CH_4 . It is the same as Tsujimura's [5] findings of quartz sand having no catalytic effect on NO reduction by CO. However, the CO trend appeared to show that a small part of CH_4 was oxidized into CO at 800 °C, even though there should be no O_2 species in the gas flow, while O_2 flow meter indication was 0. Since, gas composition in the cylinders was not very pure, such as $\text{N}_2 \geq 99.5$ vol% and $\text{O}_2 \leq 500$ ppm in the N_2 cylinder. Besides, NO concentration calculated theoretically should be ~ 830 ppm. However, the measured data was located in the range of 890–905 ppm, which means that there was less than 7% error in the process of gas preparation. All the following data were based on the experimental results. Also, we heated the quartz reactor to 900 °C and did a similar experiment as above. The gas flow condition was similar to that in Table 1 except there was some different change with CH_4 and O_2 flow shown in Fig. 2. It was found that CH_4 could not reduce NO with CaO absent in the reactor at 900 °C either, no matter whether O_2 present or absent in the gas. In addition, that CO produced at 900 °C was much more than that at 800 °C, from which we could infer that CH_4 oxidation was enhanced with temperature rise. This conclusion was consistent with that by Fliatoura [7] and Li [8].

2. Experimental Results of NO Reduction by CH_4 over CaO Catalyst at 800 °C

The composition of CaO is listed in Table 2. The CaO particles of 0.45–1.0 mm were activated by 15% vol water steam in a fluidizing bed reactor at 150 °C for 45 min, N_2 as balance gas. The con-

Table 2. Composition of CaO used in the experiment

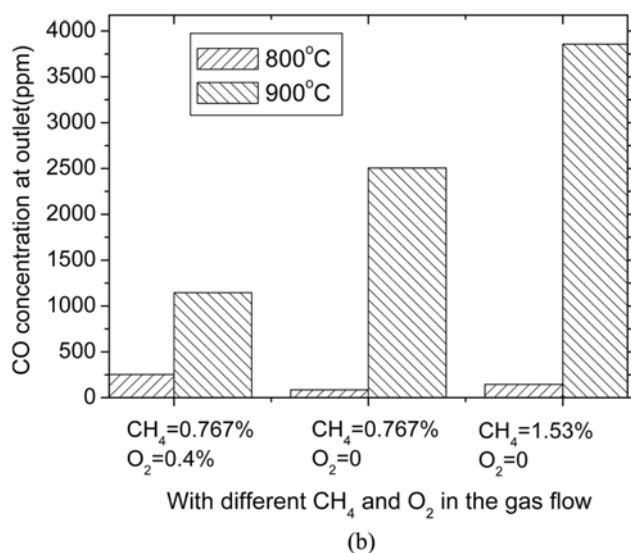
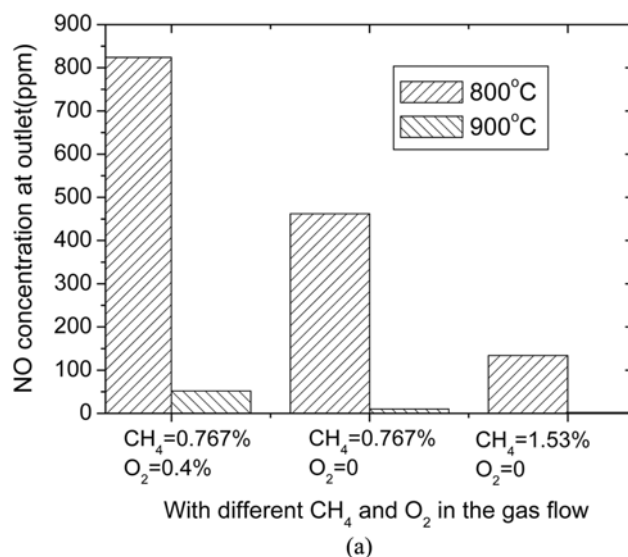
Weight percent / %					
SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O
3.64	0.34	0.44	86.45	3.51	1.01
Na ₂ O	MnO	P ₂ O ₅	TiO ₂	Weight loss	
0.048	0.01	0.11	0.013	4.43	

**Fig. 3. Experimental results of NO reduction by CH₄ over CaO catalyst at 800 °C.**

version of CaO to Ca(OH)₂ was found to be 28% by weight. Then 7.5 g activated CaO was mixed with 22.6 g quartz sand (0.28–0.45 mm), which was put in a quartz reactor heated to 800 °C to calcine for 10 min, the calcined sorbents with surface area of 7.968 m²/g and pore volume of 0.02466 cm³/g by BET analysis. Then the gas, same as mentioned in Table 1, was turned on and the NO and CO concentration at the reactor outlet was recorded. The experimental result is listed in Fig. 3. To compare the result in Fig. 3 with that in Fig. 2, we could find that NO concentration was decreased from 905 ppm with CaO absent to 837 ppm with CaO present in the reactor while O₂ was 0.4% at 800 °C, which means that a small but limited part of NO was reduced by CH₄ over CaO catalyst. However, CO concentration arrived at ~300 ppm, which was higher than that with CaO absent. It indicated that CaO promoted the oxidation of CH₄ under this condition. Furthermore, NO concentration was decreased from 837 ppm to 460 ppm when O₂ was changed from 0.4% to 0, and NO concentration was decreased further to 134 ppm while CH₄ was doubled. All the results above indicated that CaO could catalyze NO reduction by CH₄ while O₂ was little or absent. However, till now there has been no reasonable explanation on CO increase from 90 ppm to 160 ppm while CH₄ flow indication was doubled and O₂ flow was switched off. Since there was little O₂ in the gas, oxygen of CO could come from the impurity of the gas cylinders, or from NO and CaO. In a word, the CaO's catalytic activity towards NO reduction by CH₄ could have been weakened when O₂ concentration increased (e.g., to 0.4% vol).

3. Effect of Temperature on NO Reduction by CH₄ over CaO

To use the mixture of CaO and quartz sand the same as before and heat it to 900 °C in advance for 10 min calcination, we then switched on the gas flow same as that in Table 1. The experimental results

**Fig. 4. (a) NO comparison at outlet of the reactor over CaO catalyst between 800 °C and 900 °C. (b) CO comparison at outlet of the reactor over CaO catalyst between 800 °C and 900 °C.**

are shown in Fig. 4(a) and Fig. 4(b).

It was found that NO concentration at 900 °C was much lower than that at 800 °C under the same conditions. Even if there was 0.4% vol O₂ in the flue gas, the NO reduction conversion was close to 95% at 900 °C and only 9% at 800 °C. It can be seen that the temperature rise improved the CaO catalytic activity on NO reduction by CH₄. The interesting thing is that CO in the flue gas would increase at ten times in the process. With O₂ drop or CH₄ rise in the gas there was a clear CO increasing trend. Comparing the NO and CO concentration value in Fig. 4(a) and Fig. 4(b) it could be found that the scale of CO changed was much more than that of NO changed. It could be deduced that more CH₄ was oxidized with temperature rise. Since the amount of oxygen was not enough, the main product was CO rather than CO₂. Furthermore, it is possible that oxygen of CO came not only from NO but also from CaO, besides the impurity in the gas cylinders. Of course, the issue needs further study.

4. Effect of Water Vapor on NO Reduction by CH₄

Table 3. Gas composition/% (Total gas flow ~3.2 L/min)

	N ₂	O ₂	CH ₄	NO	CO ₂	H ₂ O
Gas species fraction	99.23-93.83	0 or 0.37	0.72 or 1.44	829 or 790/ppm	0	0 or 4.66

Table 4. Effect of water vapor on NO reduction by CH₄ with blank reactor

Gas species concentration	CH ₄ =32, O ₂ =12		CH ₄ =32, O ₂ =0		CH ₄ =64, O ₂ =0	
	C _{H2O} =4.66%	C _{H2O} =0	C _{H2O} =4.66%	C _{H2O} =0	C _{H2O} =4.66%	C _{H2O} =0
NO (ppm)	980	906	991	913	991	906
CO (ppm)	409	86	335	51	318	36

These experiments were conducted at 800 °C. The gas composition is listed in Table 3. The nitrogen flow was divided into two parts, one of which was kept as the original and the other was passed through a water bath at 70 °C. The latter flow was controlled as 0.33 L/min; the water vapor fraction in the gas is listed in Table 3. After water was carried through, the gas pipe was heated to 120 °C to prevent the vapor from condensing.

The work has been divided into three parts.

4-1. CaO absent in the reactor

The experimental results listed in Table 4 show that water vapor in the gas could promote oxidation characteristics in the absence of CaO. The CH₄ and N₂ were oxidized into CO and NO, respectively. Dam-Johansen [11,13] also found that H₂O fraction could activate CO to be oxidized into CO₂. We therefore concluded that water vapors in the reactor gas could inhibit NO reduction by CH₄ in the absence of CaO catalyst.

4-2. Effect of water vapor on NO reduction by CH₄ over CaO catalyst with O₂ absent in the gas

The experiments were conducted at 800 °C too. With the same mixture of CaO and quartz sand as before, gas composition was listed in Table 3. The results were listed in Fig. 5. It was shown that there were more NO being reduced by CH₄ with H₂O vapor present than absent, and CO in the gas was increased correspondingly in the meantime. It can be concluded that water vapor in the gas can

promote NO reduction and CH₄ oxidation with CaO present in the reactor while O₂ is absent. Because of the very strong C-H bond of CH₄ maybe more CH₄ was activated with H₂O present in the gas over CaO catalyst. The activated species could not be consumed without enough oxygen in the gas and could easily take part in the NO reduction reaction.

4-3. Effect of water vapor on NO reduction by CH₄ over CaO catalyst with O₂ present in the gas

The parameters of temperature (800 °C) and gas composition (listed in Table 3) were the same as before. By adjusting the N₂ flow into the water bath, the water vapor fraction in the gas could be controlled precisely. Experimental results are listed in Fig. 6. We found that the addition of water vapors in the reactor system had no effect on NO reduction by CH₄ in the presence of oxygen. Compared with the results in Fig. 5, it can be found that the reducing ability of CH₄ was largely weakened in the presence of water vapors in the gas. This is because the CO concentration at the outlet of the reactor increased by increasing water vapors in the gas. Though H₂O vapor could promote the activation of CH₄, the O₂ in the gas would react with the activated species more easily. So the NO reduction was inhibited. The results are in accordance with Dam-Johansen [11,13] but differ with Fliatoura [7].

5. Effect of CO₂ on NO Reduction by CH₄

The experiments were conducted at 800 °C and 900 °C. Gas composition was similar to that in Table 1, except that 0-13% vol CO₂

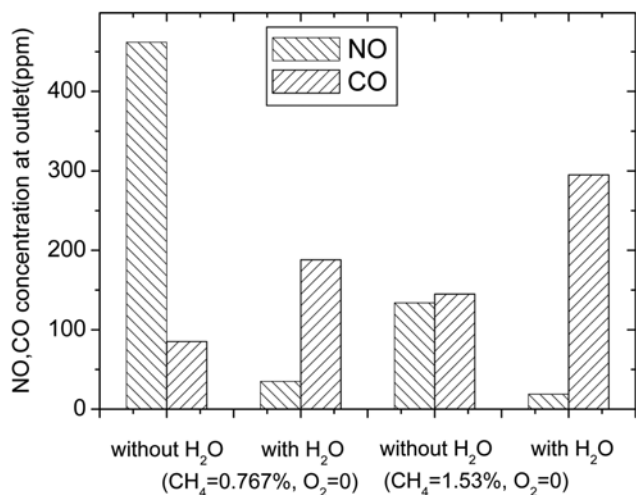


Fig. 5. Comparison of NO reduction by CH₄ over CaO catalyst with water vapor present or absent (CH₄=0.767%, O₂=0 and CH₄=1.53%, O₂=0).

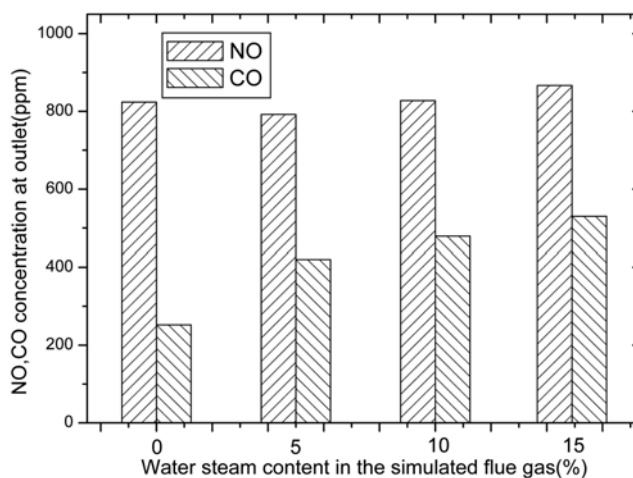


Fig. 6. Effect of water vapor fraction on NO reduction by CH₄ over CaO catalyst with 0.37%vol O₂ in the gas.

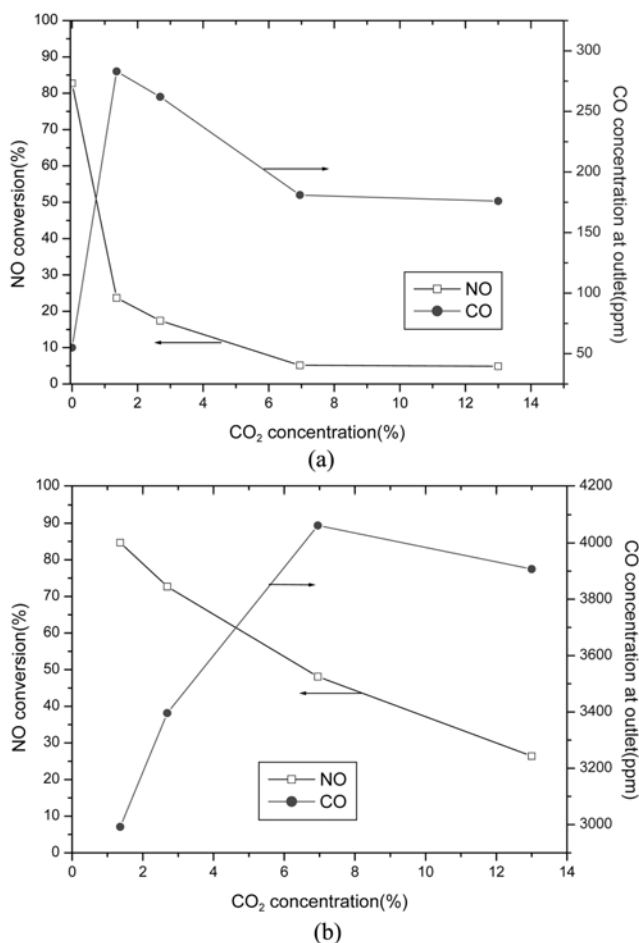


Fig. 7. (a) Effect of CO₂ on NO reduction by CH₄ over CaO catalyst at 800 °C. (b) Effect of CO₂ on NO reduction by CH₄ over CaO catalyst at 900 °C.

was added into the flue gas and the nitrogen flow was decreased correspondingly to keep the total gas flow constant. The results with a blank reactor showed that NO cannot be reduced by CH₄ in the presence of CO₂. In the second step the mixture of CaO and quartz sand (same as before) was put into the reactor which was heated to 800 °C or 900 °C and calcined for 10 min. Then the total gas flow of ~3 L/min was turned on and we could observe the gas composition change at the outlet of the reactor. The experimental results of CO₂ fraction on NO reduction by CH₄ over CaO are listed in Fig. 7(a) and Fig. 7(b). It was shown that NO conversion to N₂ was decreased with a rise in CO₂ concentration, which means that there was a clear inhibiting effect from CO₂ on NO reduction. But, the inhibiting effect was weakened with temperature increasing from 800 °C to 900 °C, however, in which CO species increased sharply just as that in Fig. 4(b). It meant that CaO could promote CH₄ oxidation at high temperature. Till now there has been no reasonable explanation on the strange trend of CO with CO₂. Fliatoura [7] and Korf [16] thought that the inhibiting effect of CO₂ was attributed to its competition with NO on absorption sites, and CO₂ absorption increased with temperature dropping so that the inhibiting effect became prominent. The deduction can explain the experimental results here too.

The fraction of CH₄ was changed continuously from 0.76% vol

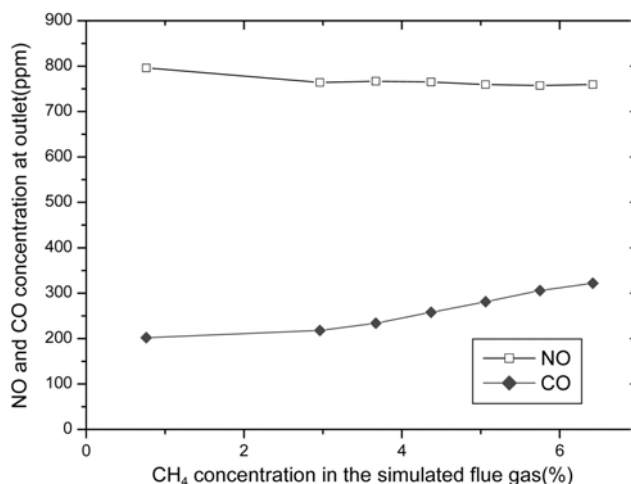


Fig. 8. Effect of CH₄ fraction on NO reduction.

to 6.4% vol to see its effect on NO reduction in the presence of 13.1-12.3% vol CO₂. The calculated NO concentration lies between 785 ppm and 829 ppm. The experimental results are listed in Fig. 8. Considering the gas species change into the reactor, NO concentration was less decreased and CO was less increased with CH₄ rise. It can be concluded that high CO₂ fraction in the practical gas will severely inhibit NO reduction by CH₄ over CaO catalyst, and the situation cannot be improved even if there is high CH₄ supply.

CONCLUSIONS

The paper studied the relevant factors on NO reduction by CH₄ over CaO catalyst in a bubbling fluidized bed and made a preliminary exploration of its mechanism. The main conclusions were listed in the following:

1. In the range of 800-900 °C, NO in the gas can be reduced by CH₄ over CaO catalyst with O₂ absent.
2. At 800 °C water vapor can promote NO reduction by CH₄ over CaO with O₂ absent and severely inhibit the reaction with O₂ present.
3. CO₂ species in the gas can decrease the catalytic activity of CaO towards NO reduction by CH₄, and the effect will be slowed down with temperature rise.
4. In the process, CO products are undesired in the industry, and this aspect needs further study.

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