

Experimental study of the influence of sodium salts as additive to NO_xOUT process

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(Received 26 May 2009 • accepted 19 November 2009)

Abstract—An experimental study of the SNCR process with urea as reducing agent and sodium salts as additive has been carried out, and detailed analysis of the reaction mechanism has been given here. In the temperature range of 800–975 °C, NO concentration decreases at first and then increases while the concentration of N₂O increases at first and then decreases with the increasing of temperature, and the turning point is 900 °C. With increasing of normalized stoichiometric ratio of reduction nitrogen to NO_x (NSR), NO removal efficiency increases, while the concentration of N₂O also increases, which decreases overall NO_x removal efficiency. With sodium salts as additive, the concentration of N₂O decreases with increasing of sodium salts addition at all temperatures, while the concentration of NO decreases at first and then increases at low-temperature side of the temperature window and increases at high-temperature side with additional increasing, whose changing extent is smaller than N₂O. Since sodium salts as additive can remove N₂O effectively and have no large influence on the removal of NO, the effect of sodium salts as additive is the combined effect of the production of active radicals and the removal of HNCO produced by the decomposition of urea through neutralization reactions, which is more important. To achieve the same effect under each condition, the needed addition of NaOH and CH₃COONa is less than that of Na₂CO₃ counting as Na atom. For the decomposition of CH₃COONa can produce CH₃COO, its addition can promote the reduction of NO more obviously at the lower temperature than Na₂CO₃ or NaOH. Overall NO_x removal efficiency at 900 °C with NSR=1.5 had been improved from about 30% to 70.45% through the addition of sodium salts. Sodium salts as additive caused the flue gas to become alkaline gas, but it was not serious for sodium salts existing as NaNCO.

Key words: NO_x OUT, Sodium Salts, N₂O Removal, Overall NO_x Removal Efficiency, Flue Gas Alkaline

INTRODUCTION

Nitrogen oxide (NO_x) pollution is an environmental problem worldwide. It can cause the greenhouse effect, acid rain and destruction of the ozone layer. NO_x produced from combustion is made of NO mainly, and a little part of which would be NO translated into NO₂ when combustion gases are mixed with air and cooled quickly.

At present, several NO_x removal processes have been developed, such as selective catalytic reduction (SCR) [1], selective non-catalytic reduction (SNCR), reburning [2], etc. Among them, selective non-catalytic reduction (SNCR) denitrification process is a well-known commercial process for NO_x control. Besides low cost and ease of combining with other processes, it also takes up small space and has simple facilities, especially suitable for the existing power plants which will carry out renovation [3,4].

There are three most widely used reduction agents: ammonia [5, 6], urea [7,8] as well as ammonium bicarbonate [9]. Because urea exists as stable solid, it has advantages in transportation and storage. Though the main composition of NO_x in flue gas achieved from combustion of industrial boilers is NO, the amount of N₂O produced is large in the SNCR process with urea as reduction agent (NO_x-OUT process). Zhou et al. have performed special research on the generation and emission of N₂O [10]. So far, many researches have been done on urea as reduction agent [11-13], but N₂O has not been

taken into consideration or given enough attention. Using additives to improve reaction characteristics of SCNR process has been studied by many scholars; the additives are usually hydrocarbons to De NO_x process [14,15] and sodium salts to NO_xOUT process [16-19]. Most studies on the NO_xOUT process with additives did not consider the detailed effects on N₂O for its low concentration or explained the effect just from the aspect of active radicals' effect. To reduce N₂O emissions and enhance NO_x removal efficiency, the effect of sodium salts (Na₂CO₃, NaOH, and CH₃COONa) as additive to the NO_xOUT process has been studied in this article. One N₂O molecule contains two nitrogen atoms, which has a certain influence on the reflection of the total nitrogen content of NO_x and the utilization rate of reduction agent. To reflect the amount of NO_x more correctly, besides the concentrations of NO, NO, N₂O, the concentrations of NO_{x1} (NO+NO₂+N₂O) and NO_{x2} (NO+NO₂+2N₂O) that have outstanding importance of N₂O have been brought into analysis.

EXPERIMENTAL EQUIPMENT AND TECHNOLOGICAL PRINCIPLES

1. Experimental Equipment

Experiments were conducted in a pilot reactor, as shown in Fig. 1. The reactor is Ø610 mm flue lined with a 300 mm×25 mm corundum tube, which is covered by an aluminum silicate fiber-insulating layer (150 mm thick) and a steel protective layer (5 mm thick) as the outermost layer. The 6 m long reactor is vertically upward for 3 m, and then bends 90° presenting a horizontal trend. The simu-

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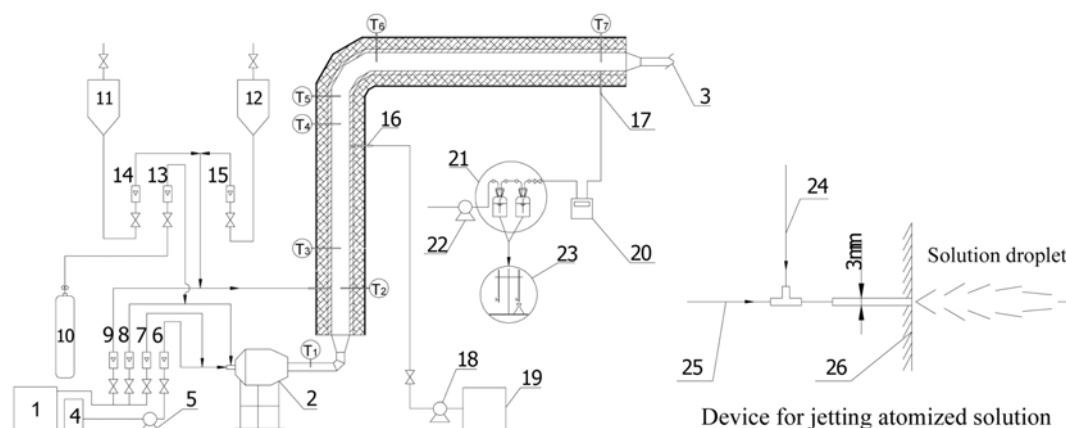


Fig. 1. Structure diagram of experimental table.

- | | | | |
|--------------------------|-----------------------------------|--|---------------------------|
| 1. Air compressor | 8. Burning air | 15. Additives solution | 22. Vacuum pump 2 |
| 2. Burner | 9. Carrier air for reducing agent | 16. Sampling point 1 | 23. Titration device |
| 3. Outlet of the reactor | 10. Ammonia tank | 17. Sampling point 2 | 24. Solution |
| 4. Oil tank | 11. Liquid storage tank 1 | 18. Vacuum pump 1 | 25. Carrier air |
| 5. Oil pump | 12. Liquid storage tank 2 | 19. Gas analyzer | 26. Reactor inner surface |
| 6. Oil | 13. Ammonia gas | 20. Gas meter | |
| 7. Atomizing air | 14. Urea solution | 21. Alkaline matters collection device | |

lated flue gas was generated by an oil burner in front of the reactor with 0# diesel oil as fuel. The temperature of flue gas was controlled by regulating the amount of fuel and burning air, and measured by seven S type thermocouples arranged along the reactor. For the low nitrogen content of 0# diesel oil, NO_x concentration of the flue gas achieved from the burning of the oil was much lower than that in conventional utility boilers. To increase the concentration of NO_x in flue gas, NH_3 had been mixed into the burning air to generate NO_x , whose production was regulated by the flow rate of NH_3 .

In the experiments, the concentration of urea solution was 2.1 mol/L, the concentration of sodium salts solution was 2.5 mol/L, and the flow rate of flue gas through the reactor was maintained at 280 m^3/h . It has been known that the effect of the process is greatly influenced by the mixing effect of the reduction agent and the main flue gas stream [20-22]. To achieve a better mixing effect, the aqueous solutions of urea and sodium salts were atomized by compressed air before being injected from the nozzle into the flue gas; the atomization effect was good when the amount of atomized air was 4.5 m^3/h with the inner diameter of nozzle $\varnothing 3 \text{ mm}$. The flow rates of solutions and compressed air were controlled by flow meters. The concentrations of NO_x and flue gas composition were measured by NGA200 type multi-component gas analyzer (Rosemount Company) on-line at sample site 1. The distance between sample site 1 and the nozzle is 2 m (gas's residence time=0.25 s). The alkaline matter in the gas was dissolved by the water in the washing bottle and measured through chemical titration with HCl as neutralization reagent; the gas sample was extracted from sample site 2, which is located 5 m away behind the nozzle.

2. Technological Principles of Reactions

Rota et al. [23] had put forward the detailed reaction principles of NO_x OUT process, in which the decomposition reactions of urea are as follows:



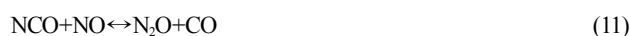
NH_3 and NH_2 produced from the decomposition of urea reduce NO through reactions:



NH_3 will be oxidized to NO at higher temperatures:



HNCO will be converted into N_2O through the following reactions:



The decomposition reactions of N_2O at higher temperatures are:



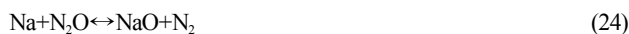
From the two reactions above, it can be found that the removal of N_2O mainly depends on the decomposition under higher temperature and the existence of enough active radicals.

NCO can also be oxidized to NO through the following reactions:





The technological principles with Na₂CO₃ as additive have been explained by some scholars [16] as following reactions:



From the reactions above, they considered that the main effect of Na₂CO₃ is to raise the concentrations of atoms and radicals, such as O, H, OH etc., which promote NO_x reduction on the low-temperature side of the optimum temperature.

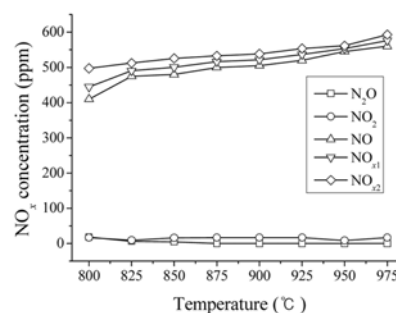
The mechanism and effect of hydrocarbons as additive to the process has a generally accepted conclusion: it extends the temperature window and shifts it towards lower temperature through promoting the production rate of active radicals, but decreases the maximum NO_x removal efficiency [15].

RESULTS AND DISCUSSION

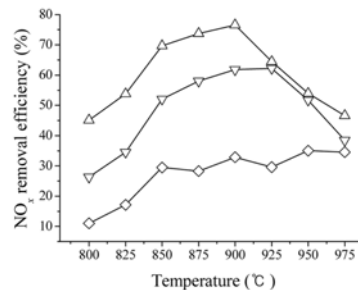
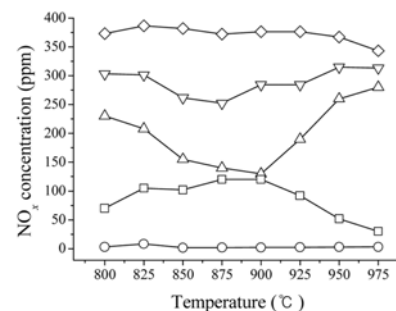
For the heat dissipation of the reactor, the temperature of the reactor declined along the reactor. So the reaction temperature was not a fixed temperature but a temperature section. Since the temperature was controlled by the flow rate of oil, the compositions of flue gas had some difference at different temperatures. The concentrations of main compositions of flue gas under different temperatures are shown in Table 1.

Table 1. Concentrations of different compositions in the flue gas

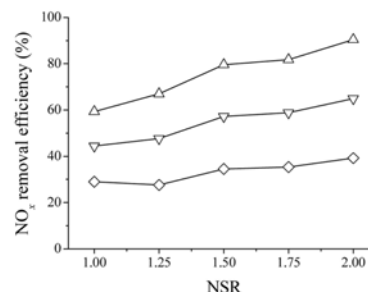
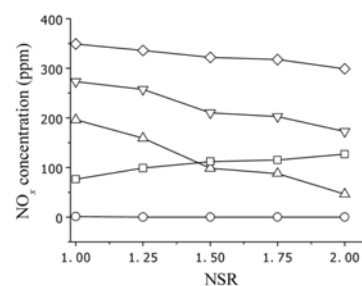
| T/°C | Compositions of the flue gas/Volume percentage | | | |
|---------|--|-----------------|------------------|----------------|
| | O ₂ | CO ₂ | H ₂ O | N ₂ |
| 800-648 | 11.40 | 5.13 | 6.66 | 76.81 |
| 825-675 | 10.65 | 5.63 | 7.42 | 76.30 |
| 850-690 | 9.96 | 6.09 | 7.92 | 76.06 |
| 875-707 | 9.22 | 6.59 | 8.65 | 75.54 |
| 900-720 | 8.72 | 6.92 | 9.07 | 75.29 |
| 925-733 | 8.25 | 7.23 | 9.10 | 75.42 |
| 950-744 | 7.83 | 7.51 | 9.29 | 75.37 |
| 975-765 | 7.43 | 7.78 | 9.45 | 75.34 |



(a) Initial NO_x concentrations of the flue gas



(b) NO_x concentrations and removal efficiencies at different temperature with NSR=1.5



(c) NO_x concentrations and removal efficiencies with different NSR at 900 °C

Fig. 2. Initial NO_x concentrations of the flue gas with 230 L/h NH₃ mixed into burning air and process performance with NSR =1.5 and no additives. □ for N₂O, ○ for NO₂, △ for NO, ▽ for NO_{x1}, and ◇ for NO_{x2}.

1. Without Additive

NH_3 can be oxidized to NO_x in combustion [24]. Fig. 2(a) shows the initial NO_x concentrations in the flue gas at different temperatures with 230 L/h NH_3 mixed into the burning air.

As shown in the figure, the amount of NO_2 and N_2O produced from the oxidation of NH_3 is low, and the main component of NO_x is NO. NO_2 concentrations were around 16 ppm at different temperatures, and N_2O concentration was 18 ppm at 800 °C, and then decreased to zero when temperature above 850 °C. For the production of thermal NO_x increases with the temperature, the concentration of NO_x increases with temperature, but the extent is not significant due to the fuel NO_x being the major contributor to NO_x . After the flue gas gets out of the burner, it passes through a stainless steel tube, in which there is a mixer made of stainless steel in the tube. NH_3 will decompose due to the catalytic effect of steel, so no NH_3 was detected in the initial flue gas and the gas was tested weak acidic through a neutralization titration, which was caused by HNCO produced from the decomposition of urea.

Fig. 2(b) presents the concentrations and NO_x removal efficiency at different temperatures with steady normalized stoichiometric ratio of reduction nitrogen to NO_x (NSR) 1.5. At the temperature range of 800–975 °C, the amount of NO_2 is low at all temperatures, and NO concentration decreases at first and then increases as temperature is increasing, while N_2O concentration increases at first and then decreases, and the turning point is 900 °C. At 875 °C and 900 °C, N_2O concentration was high to 120 ppm, which is much higher than the other scholars' research results [8,17,23]. The generation amount of N_2O is greatly affected by oxygen content, humidity and reaction temperature. There are two reasons for the high N_2O concentration: the high oxygen content of the flue gas and the high humidity in the pipe before reduction agent sprayed out. Urea had decomposed to certain extent in the pipe before being injected into the flue gas, which was caused by the high ambient temperature near the reactor, and the same problem also exists in industrial utilities. NO_{x1} concentration also shows the similar tendency as NO, while NO_{x2} concentration does not change much for the inverse changing tendency of NO and N_2O . At a temperature above 900 °C, NO concentration increases quickly for the effect of the reaction path that the reduction agent oxidized to NO_x became large.

In the temperature range of 825–950 °C, NO removal efficiencies are above 50%, and the highest is 76.56% at 900 °C with NSR=1.5. As the existence of N_2O , NO_{x1} removal efficiencies are among 50–60% and the highest NO_{x2} removal efficiency is just about 30%. Compared with experimental results with flue gas mixed with some pure gases [17,19,23], the optimum temperature is lower; while compared with experimental results with flue gas generated from combustion [8,12], the reaction temperature is basically consistent. The experimental results of the process with NH_3 as reduction agent also exist the problem that the optimum temperature with flue gas achieved from combustion is lower than that with flue gas mixed by a kind of pure gas [6,25,26]. Besides the main compositions of gases (O_2 , CO_2 , H_2O , N_2), there are some trace compositions (hydrocarbon, CO, SO_2 etc.) in the flue gas resulting from combustion. Just these trace compositions enhance the reaction activity and decrease the reaction temperature. That is, flue gas compositions have relatively large influence on the temperature window of process, so it is necessary to find the particular temperature window and optimal tem-

perature of the special flue gas in the industrial application of the process. N_2O concentrations are lower than 50 ppm when the reaction temperature is above 950 °C, which is also one reason for the higher N_2O concentrations than the other experimental results (whose optimum reaction temperature is higher than 950 °C).

Zamansky et al. [17] studied the variation of N_2O concentration with Na_2CO_3 as additive, but the detailed law was not given out for their high temperature window and low N_2O content. At the optimum temperature, a detailed analysis on NO_x concentrations with different NSR was carried out. At 900 °C, the concentrations of NO, NO_2 , N_2O , NO_{x1} , NO_{x2} in initial flue gas are 482, 9.2, 0, 491.6, and 491.6 ppm respectively. In Fig. 2(c), it shows the concentrations and removal efficiencies of NO_x at 900 °C with different NSR.

As NSR increases from 1.0 to 2.0, the removal efficiency of NO increases from 59.27% to 90.46%, while that of NO_{x1} and NO_{x2} increase from 44.43% to 64.91% and from 28.97% to 39.18% respectively. Compared with the results of Gao [11], NO and NO_2 removal efficiencies are higher with the same NSR. It can be explained by the atomizing of the solution before being injected into the main flue gas leading to a better mixing. 900 °C is the optimal temperature of the process, and it also the temperature that has the largest generation amount of N_2O , which diminishes NO_x reduction performance.

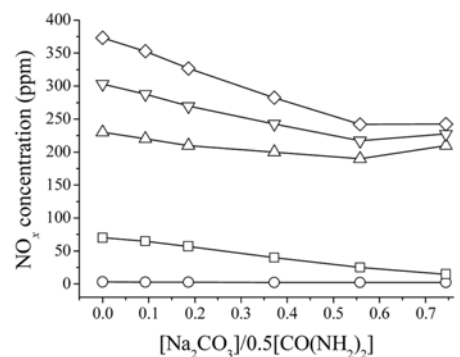
2. With Sodium Salts as Additive

Na_2CO_3 , NaOH, and CH_3COONa were used in the experiments to investigate the influence of sodium salts to the process. The additions of the sodium salts solution were fixed at 2.5 ml/min, 5 ml/min, 10 ml/min, 15 ml/min and 20 ml/min, which are 1.34×10^{-3} , 2.68×10^{-3} , 5.36×10^{-3} , 8.04×10^{-3} , 1.07×10^{-2} respectively, when counted as (mol/ Nm^3 flue gas) for the total flue gas quantity was maintained at 280 Nm^3/h . In the analysis of the experimental results, the additions of sodium salts adopt different expression ways to outstanding different analysis emphases.

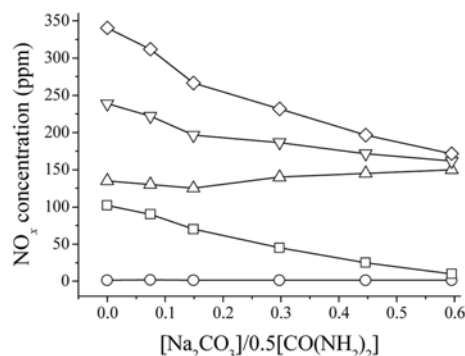
2-1. Influence on NO_x Concentrations

Fig. 3 shows the concentrations of NO_x at four typical temperatures with different Na_2CO_3 additions and NSR=1.5. The proportional relationship of Na_2CO_3 and urea, Na_2CO_3 addition is counted as molar ratio of Na_2CO_3 to reduction nitrogen, which is $[\text{Na}_2\text{CO}_3]/0.5[\text{CO}(\text{NH}_2)_2]$. Because NO_x concentration at various temperatures is different as Fig. 2(a) shows, $[\text{Na}_2\text{CO}_3]/0.5[\text{CO}(\text{NH}_2)_2]$ with same Na_2CO_3 addition at different temperatures have a little difference.

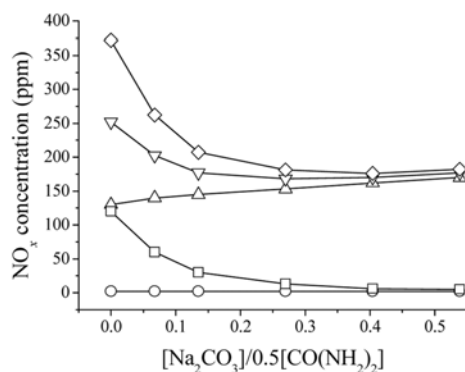
As shown in Fig. 3(a) and Fig. 3(b), NO concentration decreases at first and then increases with the increasing of Na_2CO_3 addition at 800 °C and 850 °C, the turning point of addition becomes less with the increasing of temperature. While at 900 °C and 950 °C as Fig. 3(c) and Fig. 3(d) show, NO concentrations increase with the increasing of Na_2CO_3 addition, which means Na_2CO_3 only reduces N_2O and the active radicals produced from its decomposition reactions go against the removal of NO on the high-temperature side of the optimum temperature. Because 800 °C and 850 °C are lower than the optimum NO reduction temperature (900 °C) and the active radicals under which are not enough, Na_2CO_3 as additive can promote NO reduction through increasing the active radicals' concentration before reaching the turning point. If the addition exceeds the turning point, the active radicals' concentration will be larger than NO reduction needed, which is harm to NO removal. The experimental results shown from Fig. 3 also indicate that the optimum



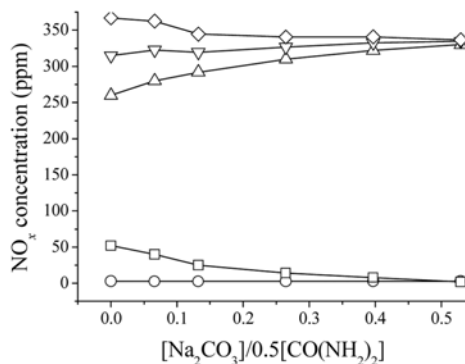
(a) 800 °C



(b) 850 °C



(c) 900 °C

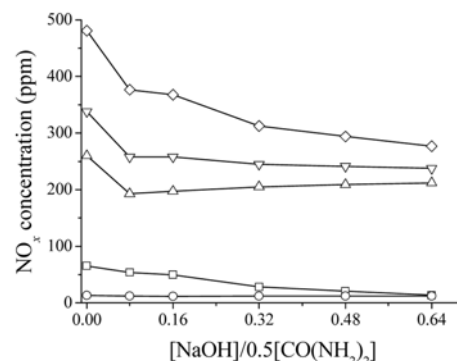


(d) 950 °C

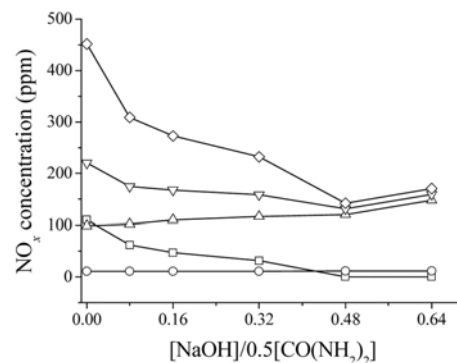
Fig. 3. Variation of NO_x concentrations with different Na_2CO_3 additions at four typical temperatures with $\text{NSR}=1.5$. Na_2CO_3 addition is counted as molar ratio of Na_2CO_3 to reduction nitrogen, \square for N_2O , \circ for NO_2 , \triangle for NO , ∇ for NO_{x1} , and \diamond for NO_{x2} .

temperature for NO reduction is about 900 °C, under which the active radicals to initiate and maintain NO reduction reactions are just enough with no additions.

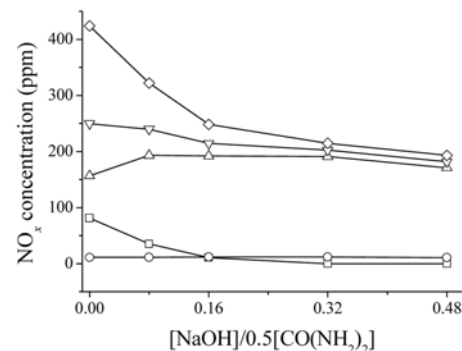
N_2O concentration decreases as Na_2CO_3 addition increases and can be decreased to zero if the addition of Na_2CO_3 is large enough at all temperatures. If we just explain the phenomenon from the production of active radicals, the changing extent of NO is much smaller than that of N_2O especially under the temperature 850 °C and 900 °C. If the amount of active radicals can cause the decomposition of large amount of N_2O , it will also affect NO reduction significantly inevitably. So alkaline material, Na_2CO_3 and radicals produced from its decomposition have taken place neutralization reactions with HNCO



(a) 820 °C



(b) 900 °C



(c) 960 °C

Fig. 4. Variation of NO_x concentrations with different NaOH additions at three typical temperatures with $\text{NSR}=1.5$. NaOH addition is counted as molar ratio of NaOH to reduction nitrogen, \square for N_2O , \circ for NO_2 , \triangle for NO , ∇ for NO_{x1} , and \diamond for NO_{x2} .

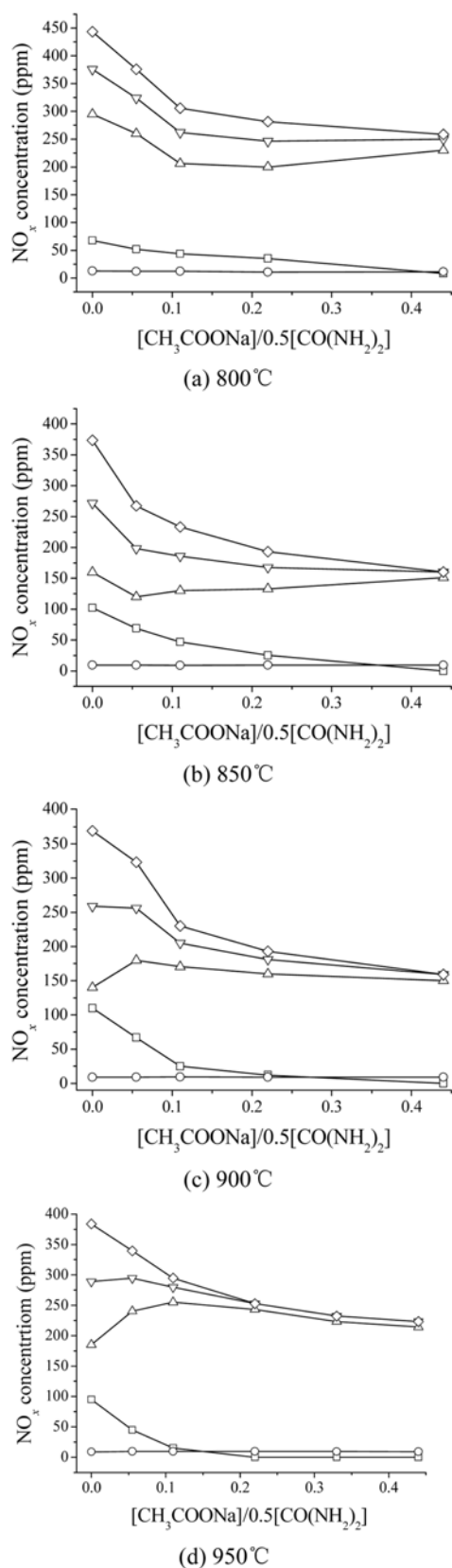


Fig. 5. Variation of NO_x concentrations with different CH_3COONa additions at four typical temperatures with $\text{NSR}=1.5$. CH_3COONa addition is counted as molar ratio of CH_3COONa to reduction nitrogen, \square for N_2O , \circ for NO_2 , \triangle for NO , ∇ for NO_{x1} , and \diamond for NO_{x2} .

produced from decomposition of urea as reaction Eq. (30) to Eq. (32) show, which avoids the generation of N_2O .



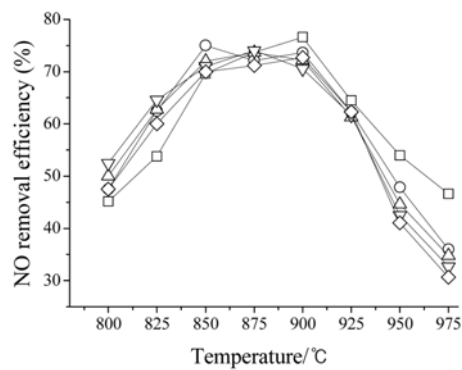
The reaction above is the main path for N_2O removal. According to the reactions as Eq. (11) and Eq. (12) show, the avoiding of one molecular N_2O 's generation will cause one molecular NO can't be removed. So the variation of NO concentration is the combined effect of active radicals and the removal of HNCO through neutralization reactions, which caused the little change of NO concentration under 850°C and 900°C . It also can explain that NO concentration increases when the addition of Na_2CO_3 is too large, which is caused by the removal of large amount of HNCO at 800°C and 850°C . At 950°C , the increasing extent of NO is larger than the decreasing extent of N_2O , so the function of the active radicals is larger enough to have an adverse effect on NO reduction. As shown from the concentration of NO_{x1} and NO_{x2} at 800°C and 900°C , the optimal additions of Na_2CO_3 are, respectively, 0.55 and 0.40, while it doesn't reach the optimal additions at 850°C and 950°C .

Fig. 4 shows the concentrations of NO_x at three typical temperatures with different NaOH additions and $\text{NSR}=1.5$. The effect of NaOH is similar to Na_2CO_3 , and the addition counted as Na atom was much fewer with the same effect. According to the mechanism introduced above, NaOH has participated in the reactions as Na_2CO_3 except Eq. (18). In contrast to Na_2CO_3 , the participation of NaOH in the reaction system is more direct and does not have the problem of decomposition equilibrium, so its needed addition counted as Na atoms is fewer to get the same effect.

Fig. 5 shows the concentrations' variation of NO_x at four typical temperatures with different CH_3COONa additions and $\text{NSR}=1.5$. Besides smaller addition than Na_2CO_3 , there is a significant difference from the two other sodium salts that the enhancement to NO reduction at lower temperature was more obvious (especially at 800°C). The decomposition of CH_3COONa at high temperature will produce CH_3COO , which also has participated in the reactions as a hydrocarbon. Hydrocarbon as additive can produce active radicals to improve NO reduction on the low-temperature side of the optimum temperature, but it does not influence the removal of N_2O significantly, which verifies the point that N_2O was not mainly removed through its decomposition but the removal of HNCO .

2-2. Influence on NO_x Removal Efficiency

Fig. 6 shows NO_x removal efficiency at different temperatures with different Na_2CO_3 additions and $\text{NSR}=1.5$. Na_2CO_3 addition is counted as mole value Na_2CO_3 per Nm^3 flue gas. From Fig. 6(a), it can be found that Na_2CO_3 as additive increases NO removal efficiency at lower temperature and decreases it at higher temperature, but the effect is not very obvious and the variation of Na_2CO_3 addition also has little influence. As shown in Fig. 6(b), adding Na_2CO_3 can enhance the removal of NO_{x1} obviously, and NO_{x1} removal efficiency increases as Na_2CO_3 addition is increased. As shown in Fig. 6(c), adding Na_2CO_3 raises NO_{x2} removal efficiency significantly and NO_{x2} removal efficiency increases obviously with the increasing of Na_2CO_3 addition. In all, the main function of Na_2CO_3 as additive is that of reducing N_2O emission and having a little effect on NO re-



(a) NO

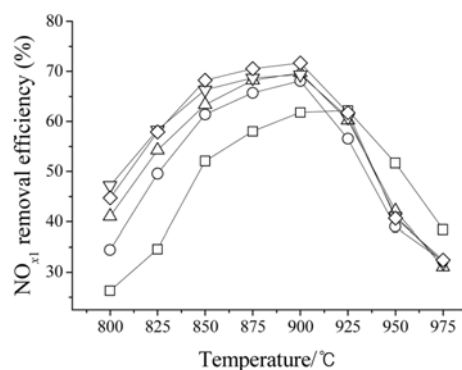
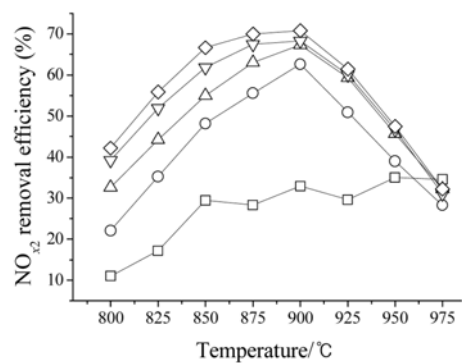
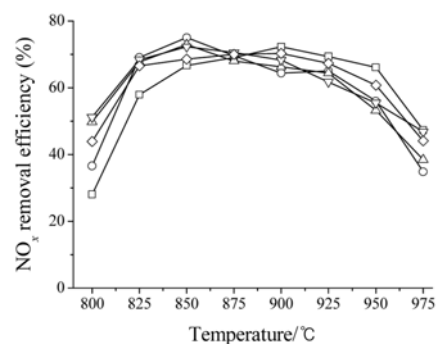
(b) NO_{x1}(c) NO_{x2}

Fig. 6. NO_x removal efficiencies with different Na₂CO₃ addition at different temperatures and with NSR=1.5. Na₂CO₃ addition is counted as mole per Nm³ flue gas, □ for 0, for ○ for 2.68×10^{-3} , △ for 5.36×10^{-3} , ▽ for 8.04×10^{-3} , and ◇ for 1.07×10^{-2} .

duction, but it greatly promotes the overall NO_x removal.

Fig. 7 shows NO_x removal efficiency at different temperatures with different CH₃COONa addition and NSR=1.5. In contrast to Na₂CO₃ as additives, the improvement to NO removal efficiency at lower temperatures is much larger as Fig. 7(a) shows. With enough, NO_{x2} removal efficiencies are maintained above 60% under the temperature of 825 °C-950 °C with CH₃COONa addition 1.07×10^{-2} mol/Nm³. It can be concluded that the effect of hydrocarbon is larger than sodium salts on the aspect of producing active radicals, while sodium salts can enhance overall NO_x removal efficiency significantly through the removal of N₂O.



(a) NO

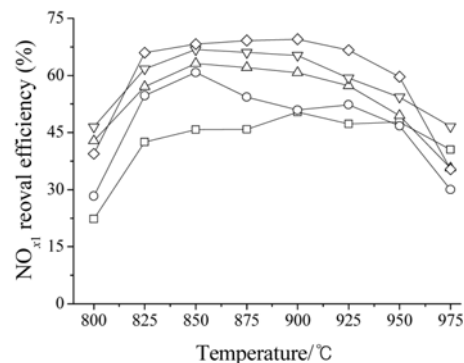
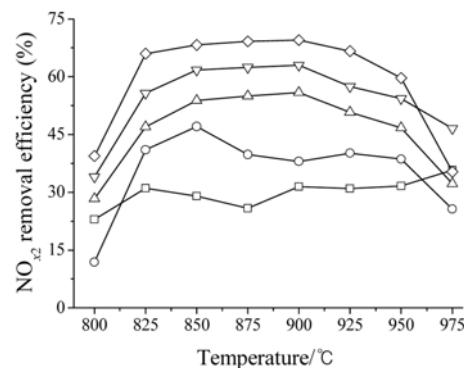
(b) NO_{x1}(c) NO_{x2}

Fig. 7. NO_x removal efficiencies with different CH₃COONa addition at different temperatures and with NSR=1.5. CH₃COONa addition is counted as mole value per Nm³ flue gas, □ for 0, ○ for 2.68×10^{-3} , △ for 5.36×10^{-3} , ▽ for 8.04×10^{-3} , and ◇ for 1.07×10^{-2} .

2-3. Influence on Acidity and Alkalinity of Flue Gas

Although adding sodium salts can reduce N₂O concentration to a great extent, adding alkaline material will also make the flue gas alkaline. Flue gas alkaline is caused by leaked NH₃ [27] and sodium salts contained. To survey the alkaline matters, 20 L flue gas was extracted from sample site 2 and washed by the subsequent washing bottle to dissolve the alkaline matters under different experimental conditions. Then the washing liquid was neutralized with 0.001 mol/L hydrochloride, whose consumption (C_T) was used to reflect the content of the alkaline matter in 20 L flue gas. It is known by calculation that the theoretical consumptions (C_{T0}) of hydrochloride to convert the sodium salts contained in 20 L flue gas into NaCl

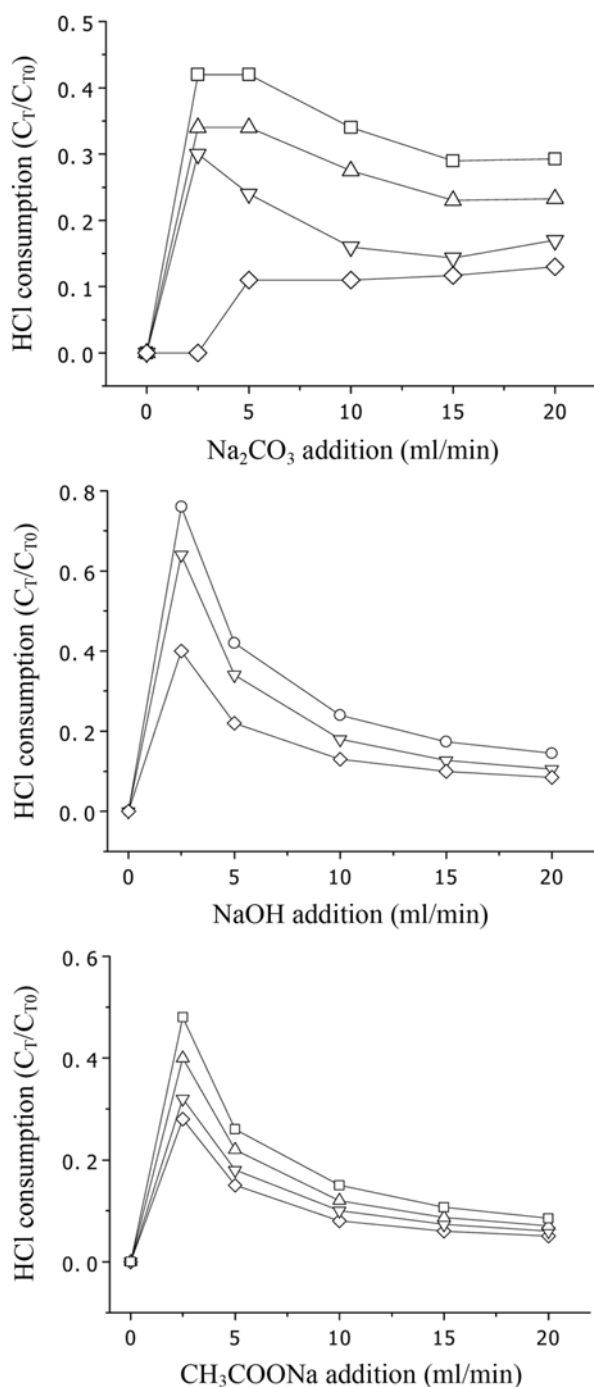


Fig. 8. The ratio of HCl consumption at typical temperatures with different sodium salts additions to the theoretical HCl consumption of sodium salts fed to the flue gas. C_T : the consumption of HCl to neutralize alkaline matter contained in 20 L flue gas under certain reaction conditions; C_{T0} : the theoretical consumption of HCl to convert the sodium salts contained in 20 L flue gas into NaCl completely under certain reaction conditions. The concentration of hydrochloric acid solution is 0.001 mol/L; NSR=1.5; and \square for 800 °C; \circ for 820 °C; \triangle for 850 °C; ∇ for 900 °C; \diamond for 950 °C.

completely are two times of Na_2CO_3 addition and equal to NaOH and CH_3COONa addition in values when their addition is counted

as ml/min. So the addition of the sodium salts is counted as ml/min in the analysis of the consumption of HCl. Fig. 8 shows the ratio of C_T to C_{T0} at certain temperatures with different sodium additions.

As shown above, the consumptions of HCl are all lower than the calculated value, which suggests that part of sodium salts exists as NaNCO in the treated flue gas. This is because one molecule of Na_2CO_3 contains two molecule Na atoms, whose C_T/C_{T0} value is much less than the two others under the same conditions. The reason for the much larger consumption of HCl for Na_2CO_3 as additive than the two others is that it has low decomposition rate at high temperatures. Since hydrocarbon as additive can significantly decrease NH_3 slips, the C_T/C_{T0} value with CH_3COONa as additive is less than that with NaOH as additive obviously, though they all have one Na atom per molecule.

Except that Na_2CO_3 ' addition is larger than 15 ml/min or under reaction temperature 950 °C, the C_T/C_{T0} values decrease with the increasing of all the sodium salts additions under the same temperature. When the additive's concentration is increased with other conditions unchanged, the amount participating in the reaction system increases while the ratio participating in the reaction system decreases, which caused the main changing trend of C_T/C_{T0} with additives' addition. When Na_2CO_3 ' addition is larger than 15 ml/min or under reaction temperature 950, the amount of new added Na_2CO_3 reacts with NCO or HNCO to produce stable NaNCO becoming less for NCO and HNCO that has been absorbed basically already or their production becoming less for too high temperature.

With same sodium salts' addition, the consumption of HCl and the value of C_T/C_{T0} decreases with increasing of the temperature, which is caused by more full reactions between the reactants for the higher reaction rate under higher temperature.

CONCLUSION

Through the experimental study of SNCR process with urea as reduction agent and sodium salts as additive on a pilot experimental rig, some characteristics of the process and its theoretical explanations have been given.

At the temperature range of 800-975 °C without additives, NO concentration decreases first and then increases, while N_2O concentration increases at first and then decreases as temperature increases with the same NSR; the turning point is 900 °C. With the increasing of NSR, NO removal efficiency increases, and the amount of N_2O produced also increases at a certain temperature. Without additive, NO removal efficiency is high to 90.46% with NSR=2.0 at the optimum reaction temperature of 900 °C, but overall NO_x removal efficiencies are much lower for the production of large amount of N_2O . Because the flue gas used in the experiments results from the combustion of 0# diesel oil instead of a mixer of some pure gases, the results are close to industrial application.

With sodium salts as additive, NO concentrations decrease at first and then increase at low-temperature side of the temperature window, and increase all the time at high-temperature side of the temperature window with increasing of salts' addition. N_2O concentrations keep decreasing with increasing of salts' addition in the temperature window. Counted as Na atoms, the addition of NaOH and CH_3COONa needed to get the same effect on the removal of N_2O is much fewer than Na_2CO_3 . In contrast to Na_2CO_3 and NaOH, CH_3

COONa can extend the temperatures through improving NO_x removal efficiency at lower temperature obviously, which is caused by CH₃COO it contains. Totally, addition of sodium salts has much larger effect on the removal of N₂O than NO. So besides the increasing of the active radicals' production rate, the neutralization reaction between sodium salts and HNCO produced from the decomposition of urea has an important effect on the removal of N₂O. Through the addition of sodium salts, overall NO_x removal efficiencies achieved in the temperature range of 825 °C to 950 °C are above 50% and the highest at optimum temperature is above 70%.

Sodium salts as additive increased the alkalinity of flue gas, but it's not serious for sodium salts existing as NaNCO.

ACKNOWLEDGEMENTS

Project Supported by The National High Technology Research and Development of China (863 Program) (2008AA05Z303); Project Supported by National Natural Science Foundation of China (NSFC) (50776019); Project Supported by The program for New Century Excellent Talents in Universities of China (NCET-05-0496).

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