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Absorption of NO from simulated flue gas by using $NaClO_2/(NH_4)_2CO_3$ solutions in a stirred tank reactor

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Abstract-Experiments were performed in a stirred tank reactor to study the absorption kinetics of NO into aqueous solutions of $NaClO_2/(NH_4)_2CO_3$ solutions. The absorption process is a fast pseudo-reaction, and the reaction was found to be second-order with respect to NO and first-order with respect to $NaClO_2$, respectively. The frequency factor and the average activation energy of this reaction were 4.56×10^{11} $m^6/(mol^2\ s)$ and 33.01 kJ/mol respectively. The absorption rate of NO increased with increasing reaction temperature, but decreased with increasing $(NH_4)_2CO_3$ solution.

Key words: NO, $(NH_4)_2CO_3$, Absorption, Kinetics

INTRODUCTION

SO_2 and NO are the main harmful byproducts of the combustion process in coal-fired power plants which have caused a variety of environmental problems such as acid rain and photochemical smog. Up to now, limestone-based wet flue gas desulfurization technology has been the most effective and widely used method for SO_2 control [1]. To control NO pollution, many technologies such as low NOx burners, reburning, selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR) have been applied. Among these, SCR has been regarded as the most effective. The complicated air pollution devices for each pollutant result in high cost and space requirements. If NO is oxidized into more soluble NO_2, then it can be removed with SO_2 by wet flue gas desulfurization scrubber. Makansi [2] indicated that a wet scrubbing combined SO_2/NO removal system was one of the advanced air pollution control technologies and had a promising future.

Many oxidants were used to oxidize NO into NO_2, such as $NaClO_2$ [3-6], $KMnO_4$ [7,8], ClO_2 [9,10], $NaClO_3$ [11], Fenton reagent [12]. $NaClO_2$ seems to be a perfect choice due to its high absorption rate and easily-handled waste water [4]. Deshwal [5] found that $NaClO_2$ was a better oxidant for NO absorption at a pH less than 4. Yang [6] showed that SO_2 increased the reaction rate of NO to NO_2 in acid solution but decreased the rate in alkaline solution. After NO is converted into NO_2, the absorption rate of NO_2 into the absorption solution in existing scrubbers for desulfurization has great impact on NO removal efficiency of combined SO_2/NO removal system. Shen [13] pointed out that with typical conditions for limestone-based wet flue gas desulfurization scrubber, the O_2 in flue gas would oxidize sulfite in the solution and cause the depletion of sulfite in the liquid boundary; as a result, the estimated NO_2 removal efficiency was less than 50%. Ammonia has been successfully used for control hazardous pollutants from flue gases [14]. Zhou [15] found that NH_4^+ could inhibit the dissolution rate of O_2 into water; thus an ammonia-based flue gas desulfurization system may be a suitable choice for NO_2 absorption. Considering that $(NH_4)_2CO_3$ has good solubility, the current study investigated the absorption kinetics of NO into $NaClO_2$/ $(NH_4)_2CO_3$ solutions in a stirred tank reactor. The effect of various operating parameters on the absorption kinetics was also tested and discussed.

EXPERIMENTAL

All experiments were performed in a stirred tank reactor, as shown in Fig. 1, which was also used in our previous work [11,16]. The reactor was a cylindrical vessel of 100 mm inner diameter and 160 mm height; four baffles of 10 mm width were equipped in the inner wall. The simulated flue gas was prepared by mixing pure N_2 and 5,000 ppm NO (balanced with N_2). The flow rate of simulated flue gas was kept at 2 L/min and the volume of absorption liquid was keep at 700 mL. A continuous flue gas analyzer (ThermoFisher 60i) was used to analyze the concentration of NOx in the outlet flue gas stream.

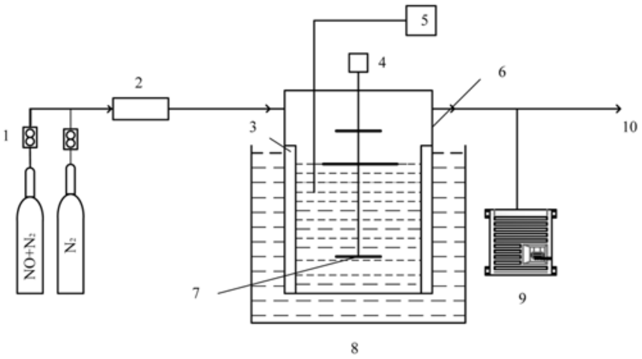

Fig. 1. Schematic of the experimental apparatus.

1. Mass flow controller	6. Stirred tank reactor
2. Mixing box	7. Stirring impeller
3. Baffle	8. Water bath
4. Stirrer rod	9. Flue gas analyzer
5. pH meter	10. Vent

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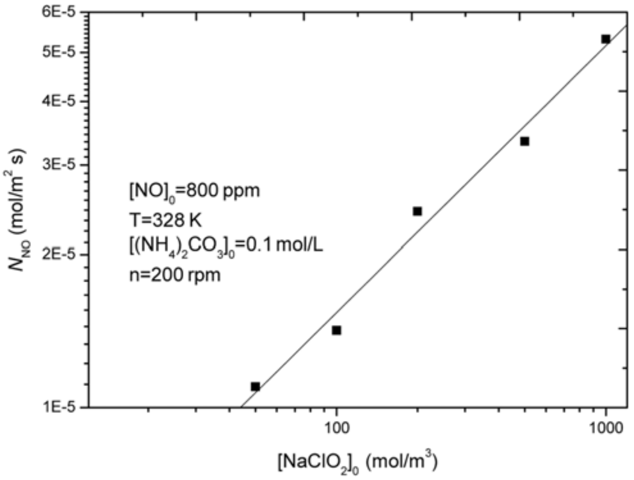

Fig. 2. Effect of $NaClO_2$ concentration on NO absorption rate.

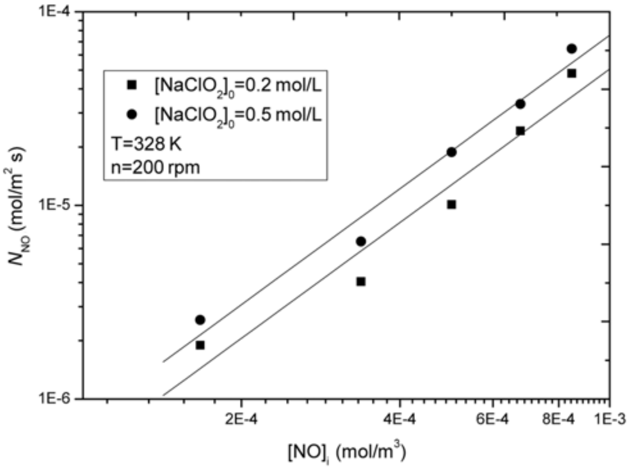

Fig. 3. Effect of gas-liquid interfacial NO concentration on its absorption rate.

Reaction temperature was controlled to the desired temperature within ±0.2 °C by using a water bath. Under the experimental conditions, the gas and the liquid phase flow in the reaction tank are mixed completely. When the absorption rate of the system remained stable, the inlet and outlet concentration of NOx was measured, and the absorption rate could be calculated by [11]:

$$-N_{NO} = \frac{v_G p}{RTS}\left[\left(\frac{p_{NO}}{p_I}\right)_{in} - \left(\frac{p_{No}}{p_I}\right)_{out}\right] \tag{1}$$

RESULTS AND DISCUSSION

1. Effect of $NaClO_2$ Concentration on NO Absorption Rate

The effect of $NaClO_2$ concentration on NO absorption rate is shown in Fig. 2; there is a linear relation between log N_{NO} and log $[NaClO_2]_0$. It is obvious that NO absorption rate increases with increasing $NaClO_2$ concentration. In alkaline solutions of $NaClO_2$, NO can be oxidized into NO_3^- [17]:

$$4NO+3ClO_2^-+4OH^-=4NO_3^-+3Cl^-+2H_2O \tag{2}$$

Because the solubility of NO in water is very low, the oxidation step is of great impact on the absorption process of NO; thus the NO absorption rate increases with increasing $NaClO_2$ concentration.

The absorption rate of NO into $NaClO_2$ solution can be seen as being the m-th order relative to NO [5,18], which can be given by the following equation according to the gas-liquid mass transfer theory proposed by Danckwerts [19]:

$$N_{NO} = \sqrt{\frac{2}{m+1} k_{mn} D_{NO} c_{NO,i}^{m+1} c_{NaClO_2}^{n}} \tag{3}$$

The value of reaction order of $NaClO_2$ can be obtained from the slope of the straight line in Fig. 2. The slope of this line is about 0.5, that is, n/2=0.5, thus n=1. So the reaction was first-order dependent on $NaClO_2$.

2. Effect of Gas-liquid Interfacial NO Concentration on Its Absorption Rate

Fig. 3 shows the effect of gas-liquid interfacial NO concentration on its absorption rate. The value of $c_{NO,i}$ and D_{NO} can be calculated by using the same method reported in our previous work [11]. As can be seen from Fig. 3, the observed absorption rate of NO increases with the increasing gas-liquid interfacial NO concentration. It is clear that there is a linear relationship between log N_{NO} and log $[NO]_i$. The average slope of the lines in Fig. 3 is about 1.5, i.e., (m+1)/2=1.5, so the value of m is 2. This suggests the reaction is second-order with respect to NO. Chu [20] reported a similar result with $NaClO_2$/NaOH solutions. After determining the value of m and n, the reaction rate constant can be obtained from Eq. (3).

3. Effect of $(NH_4)_2CO_3$ Concentration on NO Absorption Rate

Fig. 4 shows the effect of $(NH_4)_2CO_3$ concentration on NO absorption rate. It seems that NO absorption rate decreases with increasing $(NH_4)_2CO_3$ concentration. A similar phenomenon was also found by Chu et al. [20] during the absorption process of NO into $NaClO_2$/NaOH solutions. On one hand, the concentration of H^+ decreases with increasing $(NH_4)_2CO_3$ concentration, which would inhibit the formation of ClO_2; another strong oxidant can also oxidize NO into NO_2 [3]. On the other hand, the pH value of absorption solutions increases with increasing $(NH_4)_2CO_3$ concentration, but NO oxidation rate decreases with pH value [11]. Therefore, higher $(NH_4)_2CO_3$ concentration is unfavorable for NO absorption.

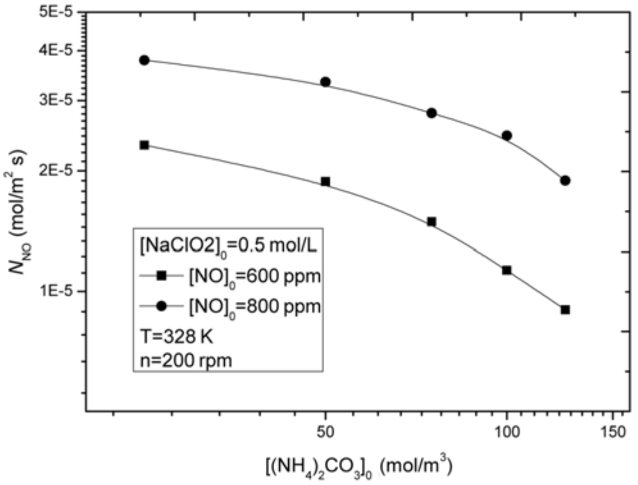

Fig. 4. Effect of $(NH_4)_2CO_3$ concentration on NO absorption rate.

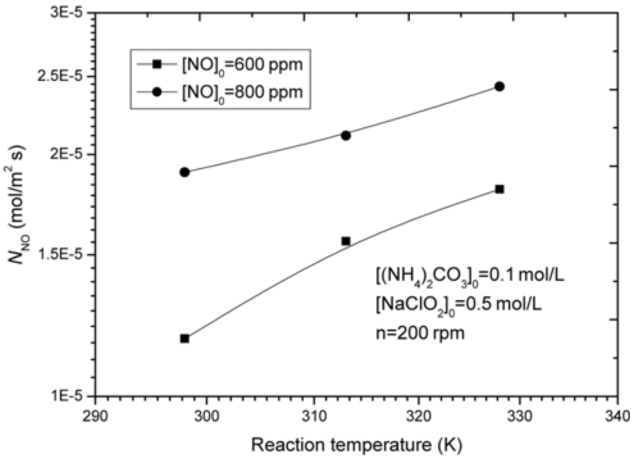

Fig. 5. Effect of reaction temperature on NO absorption.

4. Effect of Reaction Temperature on NO Absorption Rate

The effect of reaction temperate on NO absorption rate is illustrated in Fig. 5. As can be seen from Fig. 5 the NO absorption rate increases with increasing reaction temperature. Increasing reaction temperature can enhance the diffusion of NO in absorption solution; furthermore, the reaction rate constant would increase too. Because the solubility of NO in water is very low, compared with the dissolution of NO, the oxidation of NO plays a more important role during the absorption process; as a result, increasing reaction temperature can promote the absorption of NO.

The reaction rate constant varies with temperature, which can be calculated from Eq. (3). According to the Arrhenius equation:

$$k_{mn} = A\exp\left(-\frac{Ea}{RT}\right) \tag{4}$$

The value of the frequency factor and the activation energy can be obtained from the Arrhenius plot shown in Fig. 6. They are 4.56× 10^{11} m^6/(mol^2 s) and 33.01 kJ/mol, respectively.

CONCLUSIONS

The absorption characteristic of NO into $NaClO_2/(NH_4)_2CO_3$ solutions was studied by using a stirred tank reactor. The operating parameters included 200-1,000 ppm NO, 0.05-1 mol/L $NaClO_2$, 0.025-0.125 mol/L $(NH_4)_2CO_3$, 298-328 K. The reaction was found to be second-order with respect to NO and first-order with respect to $NaClO_2$. The frequency factor and the average activation energy of this reaction were 4.56×10^{11} m^6/(mol^2 s) and 33.01 kJ/mol, respectively. The addition of $(NH_4)_2CO_3$ into the solution of $NaClO_2$ would decrease the reaction rate.

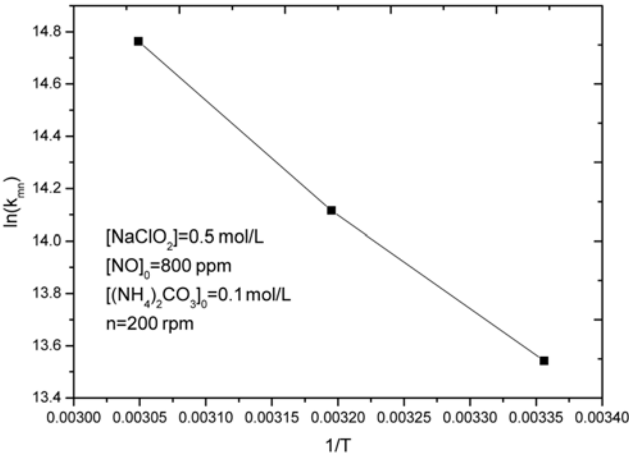

Fig. 6. Arrhenius plot of lnk_{mn} vs. 1/T.

NOMENCLATURE

[ ] : concentration in liquid phase [mol/m^3]
A : frequency factor [m^6/(mol^2 s)]
c : concentration [mol/m^3]
D_{NO} : diffusion coefficient of NO [m^2/s]
Ea : average activation energy [kJ/mol]
k_{mn} : rate constant of (m,n)-order reaction [m^6/(mol^2 s)]
m : the reaction order of NO
N_{NO} : NO absorption rate [mol/(m^2 s)]
n : the reaction order of $NaClO_2$
P : total pressure [Pa]
p_I : partial pressure of inerts [Pa]
p_{NO} : NO partial pressure [Pa]
R : gas constant [J/(mol k)]
T : absolute temperature [K]
v_G : gas volume rate [m^3/s]

Subscripts

i : interface
in : inlet of the gas stream
out : outlet of the gas stream
0 : initial value

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