Fuel 89 (2010) 3431–3435

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Absorption of NO into $NaClO_3$/NaOH solutions in a stirred tank reactor

Rui-tang Guo [a,*], Xiang Gao [b], Wei-guo Pan [a], Jian-xing Ren [a], Jiang Wu [a], Xiao-bo Zhang [a]

[a] School of Energy Source and Environmental Engineering, Shanghai University of Electric Power, Shanghai, PR China
[b] State Key Laboratory of Clean Energy Utilization, Zhejiang University, Hangzhou, PR China

ARTICLE INFO

Article history:
Received 15 December 2009
Received in revised form 9 March 2010
Accepted 10 March 2010
Available online 20 March 2010

Keywords:
Absorption
NO
$NaClO_3$
Kinetics
Stirred tank reactor

ABSTRACT

The absorption kinetics of NO into aqueous solutions of $NaClO_3$/NaOH was investigated under different experimental conditions in a stirred tank reactor. It is proven that the absorption process is a fast pseudo-*m*th reaction. The reaction was found to be second-order with respect to NO and first-order with respect to $NaClO_3$. The frequency factor and average activation energy of this reaction were 2.696×10^6 m^3/(mol s) and 13.88 kJ/mol, respectively. The addition of NaOH to solutions of $NaClO_3$ decreased the absorption rate of NO. And the absorption rate of NO increased with increasing reaction temperature. In this study, the flue gas flow rate almost had little effect on the absorption of NO.

1. Introduction

SO_2 and NO, which can cause acid rain, are the major pollutants from coal-fired power plants. Conventionally, they are removed by different control devices at high cost and large space requirements. So the combined SO_2/NO control technologies come into being. Among these technologies, Yang et al. [1] indicated that wet processes remain the most economically competition and have the advantage of controlling other acid gases and particulates at the same time. Because of the low solubility of NO in water, it is difficult for NO to be absorbed by aqueous solutions. Therefore, in order to effectively remove NO from flue gas by wet scrubbing method, it is desirable to oxidize NO to soluble NO_2. Many reagents are found to be effective to remove NO. Wei et al. [2] used a stirred tank reactor to study the performance of NO absorption by $NaClO_2$/Na_2CO_3 solutions and found that $NaClO_2$ was an excellent absorbent of NO. Brorgren et al. [3] studied the absorption of NO in an alkaline solution of $KMnO_4$ on a packed column. The results showed that the reaction could be expressed as first order with respect to NO and $KMnO_4$. Deshwal et al. [4] used aqueous ClO_2 solution to clean up NO from simulated flue gas in a bubbling reactor. It was shown that the mechanism of NO_x removal changed when medium of solution changed from acidic to alkaline. Chen et al. [5] studied the oxidation and absorption mechanism of NO in a packed tower with NaClO solution and found the pH value of absorption solution had great impact on the performance of NO removal. Myers and Overcamp [6] used H_2O_2/NaOH solutions as the absorbent for NO absorption, their results showed that the NO:NO_2 ratio in the flue gas had a major influence on overall removal efficiency.

Although $NaClO_3$ is a widely used strong oxidant capable of oxidizing NO to soluble NO_2, yet till now, the removal of NO from flue gas using $NaClO_3$ as the oxidant has not been reported in the literatures. Therefore, the absorption mechanism of NO into $NaClO_3$/NaOH solution is the major objective of the present study.

2. Experimental

All experiments were done in a stirred reactor as shown in Fig. 1. The system can be divided into three parts: a simulated gas system, a stirred tank reactor and a flue gas sampling and analyzing system. The simulated flue gas was prepared by pure N_2 and 5000 ppm NO (balanced with N_2) purchased from New Century Gas Co., Hangzhou. Their flow rates were controlled by two mass flow controllers (MFC, QixingHuachuang Co., China) to the required concentration, and then the simulated flue gas was mixed adequately in the mixing box before fed into the reactor. The flow rate of the simulated flue gas was kept at a desired value. The liquid temperature was controlled to the desired temperature within ±0.2 °C through a water bath. At the start of the experiment, a solution containing $NaClO_3$/NaOH purchased from Hangzhou Guohua Chemical Engineering Limited Company was freshly prepared and fed into the reactor. A continuous flue gas analyzer (Rosemount Analytical NGA2000, Emerson Process Management Co. Ltd.) was used to analyze the concentration of NO_x in the outlet flue gas stream.

* Corresponding author.
E-mail address: grta@zju.edu.cn (R.-t. Guo).

0016-2361/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.fuel.2010.03.020

Nomenclature

A	frequency factor, $m^3/(mol\ s)$
$c_{NO,i}$	interfacial concentration of NO at the gas–$NaClO_3$/NaOH solution interface, mol/m^3
$c_{NO,iw}$	interfacial concentration of NO at the gas–water interface, mol/m^3
D_{NO}	diffusion coefficient of NO, m^2/s
E_i	enhancement factor
Ea	average activation energy, kJ/mol
E^0_{NO/NO_2^-}	electrochemical half-cell reduction potentials of NO/NO_2^-, V
H_{NO}	Henry's constant of NO, $Pa\ m^3/mol$
I	ionic strength, mol/L
K	salting-out parameter
k_g	gas phase mass transfer coefficient, m/s
k_{mn}	rate constant of (m, n)-order reaction, $m^3/(mol\ s)$
M	non-dimensional criterion number of absorption
m	the reaction order of NO
N_{NO}	NO absorption rate, $mol/(m^2\ s)$
N	the reaction order of $NaClO_3$
P	total pressure, Pa
p_I	partial pressure of inerts, Pa
p_{NO}	NO partial pressure, Pa
$p_{NO,i}$	NO partial pressure at the gas–$NaClO_3$/NaOH solution interface, Pa
R	gas constant, J/(mol K)
S	interfacial area, m^2
T	absolute temperature, K
X_a, X_c, X_g	contribution to K of anions, cations and the gas, respectively, mol/L
μ	dynamic viscosity of the solution, kg/(m s)
v_G	gas volume rate, m^3/s
v_i	stoichiometry of reactant i or product i
Subscripts	
b	bulk
i	gas–liquid interface
in	inlet of the gas stream
out	outlet of the gas stream
0	initial value
w	water
θ	standard

Under these experimental conditions, the gas and the liquid phase flow in the reaction tank can be mixed completely. It was found that the absorption rate of the system remained stable after 5–6 min, thus the inlet and outlet gas samples were analyzed at 8 min for all experimental runs. The absorption of NO can be calculated by Ref. [7]:

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

Liquid samples from the reactor were analyzed by a Metrohm ion chromatograph at regular intervals. The solution pH was continuously monitored with a Mettler Delta 320 pH electrode inserted into the liquid.

3. Results and discussion

3.1. Reaction mechanism between NO and $NaClO_3$

The reaction between NO and chlorate ion in an alkaline solution is considered to be:

$$3NO + ClO_3^- \rightarrow 3NO_2 + Cl^- \quad (2)$$

$$3NO_2 + ClO_3^- + OH^- \rightarrow 3NO_3^- + Cl^- + H_2O \quad (3)$$

The overall reaction for NO absorption may be written as:

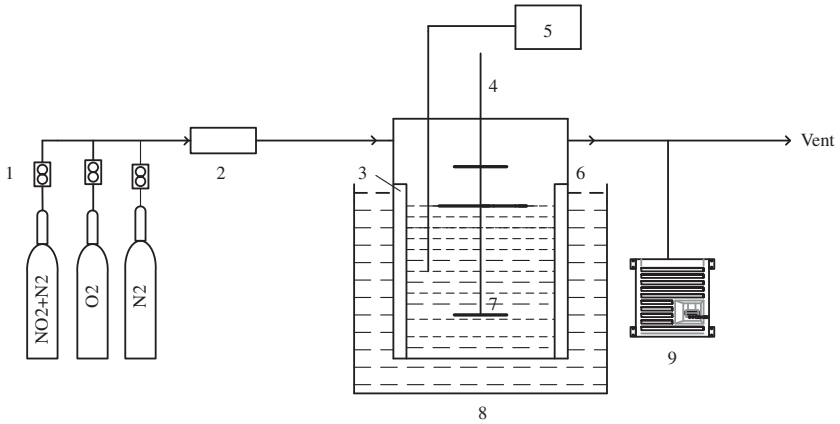
$$2NO + ClO_3^- + 2OH^- \rightarrow 2NO_3^- + Cl^- + H_2O \quad (4)$$

Formation of nitrate and chloride as suggested in the above mechanism was confirmed by analyzing the sample from the reactor using Metrohm ion chromatograph. And the formation of NO_2 was proven by the Rosemount flue gas analyzer. Compared with Cl^-, the concentrations of the other chlorine acid radicals such as ClO_2^- and ClO^- were very low. The measured concentrations of Cl^-, ClO_2^- and ClO^- after an experimental run are shown in Table 1. It is obvious that Cl^- is the main reduction product of ClO_3^-.

3.2. Data analysis

According to two-film theory, the absorption rate of NO in the stirred tank can also be expressed by:

$$N_{NO} = \frac{k_g}{RT}(p_{NO,b} - p_{NO,i}) \quad (5)$$



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

Fig. 1. Schematic of the experimental apparatus.