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Thermodynamic Studies on Simultaneous Desulfurization and Denitrification by Chlorine-based Composite

Yunyang Wang
North China Electric Power University, Baoding, China

ABSTRACT: This paper studied the reaction mechanism and got the overall reaction equation based on the experimental study and the analysis results of desulfurization and denitrification by chlorine-based composite. And studied the chemical and thermodynamic properties of simultaneous desulfurization and denitrification by chlorine-based composite on the basic of chemical and thermodynamic principle. The desulfurization and denitrification by chlorine-based compositeis method is feasible seen from the point of view of thermodynamics. The rise of temperature is not conducive to the chemical reaction.

KEYWORD: Sodium chlorite, sodium chlorate, desulfurization and denitrification, reaction mechanism, thermodynamics

1 INTRODUCTION

A large number of sulfur dioxide(SO_2) and nitrogen oxides (NO_X) emissions from fossil fuel combustion is the main cause of air pollution[1]. After years of efforts, the gaseous emissions of large coal-fired power station has reached the effective control[2]. But due to the large quantity, wide distribution and low affordability, as the second largest source of atmospheric pollution, small and medium sized coal-fired industrial boilersits' pollution control is still in its infancy[3]. Thus it has important theoretical significance and application value to develop an efficient, economical, and safe application of coal-fired industrial boilers' desulfurization and denitrification technology for air pollution control.

Sodium chlorate ($NaClO_3$) is a strong oxidizing solid. It is affordable and can be storaged and transported conveniently. Besides, the operating conditions of $NaClO_2$/$NaClO_3$ system matches the limestone slurry better.It can achieve efficient removal of NO_X without changing the existing condition of the body structure and desulfurization system operating conditions. Thus greatly reducing the investment and operating cost of the system for denitrification. In our previous study, we studied the simultaneous desulfurization and denitrification reaction in the bubbling reactor using low concentrations of $NaClO_2$ and $NaClO_3$ mixed solution and accessed a higher efficiency of simultaneous desulfurization and denitrification. The removal products are mainly sulfate ions, nitrate ions and chloride ions. Based on the preliminary findings, we speculated $NaClO_2$/$NaClO_3$ simultaneous desulfurization and denitration reaction mechanism and obtain the overall reaction equation; studied the chemical thermodynamic properties of $NaClO_2$/$NaClO_3$ simultaneous desulfurization and denitration reaction. Thus made the accurt judgments of the direction and degree of chemical reactions, providing a theoretical basis for $NaClO_2$/$NaClO_3$ simultaneous desulfurization and denitration technology's optimization and development.

2 REACTION MECHANISM

2.1 *Redox trend analysis*

Standard electrode potential of SO_2, NO, $NaClO_2$, $NaClO_3$ and other species may existed during the reaction are shown in Table 1.

Table 1 Related Redox Electrode Potential [4,5]

Redox	NO_3^-/NO_2	NO_3^-/NO	NO_2/NO	SO_4^{2-}/SO_3^{2-}	ClO_2^-/Cl^- (acidity)	ClO_2/Cl^- (acidity)	ClO_3^-/Cl^- (acidity)
Electrode potential Φ_A(eV)	0.94	0.96	1.07	0.93	1.570	1.511	1.45

As Table 1 shows, the electric potential of ClO_2^-/Cl^- (Acidity), ClO_2^-/ClO^- (Acidity) and ClO_3^-/Cl^- (Acidity) electrode pairs is significantly higher than SO_4^{2-}/SO_3^{2-}, NO_2/NO, NO_3^-/NO, NO_3^-/NO_2^- and other redox electrode pairs. Meanwhile, $NaClO_2$ and $NaClO_3$ is easy to decompose into chlorine dioxide (ClO_2) in the acidic environment. And ClO_2 has strong oxidation than ClO_2^- and ClO_3^- in the acidic environment. Therefore, SO_2 and NO can be oxidized to their highest valence state when passing the $NaClO_2/NaClO_3$ solution.

2.2 *Reaction Process*

It can be confirmed that it indeed carried out the reaction of NO and SO_2 removal in the bubbling reactor combined with the removal efficiency experiments and the analysis results of reaction product, the main products of desulfurization and denitrification were SO_4^{2-} and NO_3^-. ClO_2^- and ClO_3^- were changed into Cl^- after the reaction.

$NaClO_3$ and $NaClO_2$ have low concentration in this experiment, and the pH of the solution is higher than 4. Thus almost no ClO_2 and Cl_2 diffuse from liquid phase to gas phase, namely that redox reactions in the gas phase can be negligible. Therefore, this paper focuses on the reaction mechanism in the liquid phase.

$NaClO_2$ and $NaClO_3$ have strong oxidizing power in the acidic environment. They can produce strong oxidizing intermediate species through a series of reactions like ClO_2. The main reaction mechanisms are presumed as follows:

$$NaClO_3 + 2HCl \rightarrow ClO_2\uparrow + 1/2Cl_2\uparrow + NaCl + H_2O \quad (1)$$

$$11NaClO_2 + 8HCl \rightarrow 4ClO_2 + 4HClO_3 + 11NaCl + 2H_2O \quad (2)$$

$$2NaClO_2 + Cl_2 \rightarrow 2NaCl + 2ClO_2 \quad (3)$$

Based on the reaction mechanism presumed above, the possible substances existed in acidic $NaClO_2/NaClO_3$ solution include ClO_2^-, ClO_3^-, ClO_2, Cl_2 and perchlorate ($HClO_3$), etc. ClO_2^- and ClO_3^- in acidic environment can produce ClO_2 or Cl_2 through a series of reactions. Since the intermediates ClO_2 and Cl_2 both have strong oxidizing power, the removal rate of simultaneous desulfurization and denitrification process improved significantly.

SO_2 is a relatively soluble gas, and its reaction with ClO_2^-, ClO_3^- and ClO_2 belongs to extremely fast irreversible reaction. It is rapidly oxidized when entering the film, resulting in a concentration gradient increases. Thereby increased the gas-liquid mass transfer rate. Based on the above conditions, the overall reaction equations of desulfurization by $NaClO_3/NaClO_2$ are considered as follows:

$$2\,NaClO_3 + SO_2 \rightarrow 2\,ClO_2 + Na_2SO_4 \quad (4)$$

$$5SO_2 + 2ClO_2 + 6H_2O \rightarrow 5H_2SO_4 + 2HCl \quad (5)$$

$$2SO_2(g) + NaClO_2(aq) + 2H_2O(l) \rightarrow 2H_2SO_4(aq) + NaCl(aq) \quad (6)$$

NO is a difficult material to be absorbed by water or lye. But it can obtain a high NO removal rate in a short time. Thus there may be a process that NO is rapidly oxidized to water-soluble substances (such as NO_2, etc.) first, and then being absorbed by the absorbent.

Based on the previous findings[6], the overall reaction equations of denitration by $NaClO_3/NaClO_2$ are considered as follows:

$$2NO + 2ClO_2^- + H_2O \rightarrow 2HNO_3 + Cl^- + ClO^- \quad (7)$$

$$2NO + 3ClO^- + H_2O \rightarrow 2HNO_3 + 3Cl^- \quad (8)$$

$$5NO + 3ClO_2 + 4H_2O \rightarrow 5HNO_3 + HCl \quad (9)$$

Based on the reaction mechanism presumed above, the overall reaction equations of simultaneous desulfurization and denitration by $NaClO_3/NaClO_2$ acid solution are considered as follows:

$$5SO_2(g) + NaClO_2(l) + NaClO_3(l) + 5H_2O(l) \rightarrow 5H_2SO_4(l) + 2NaCl(l) \quad (10)$$

$$10NO(g) + 3NaClO_2(l) + 3NaClO_3(l) + 5H_2O(l) \rightarrow 10HNO_3(l) + 6NaCl(l) \quad (11)$$

3 THERMODYNAMIC ANALYSIS AND CALCULATION

3.1 *Chemical reaction enthalpy*

The standard molar reaction enthalpy $\Delta_r H_m^\Theta$ of constant pressure and variable temperature chemical reaction and the enthalpy $\Delta_r H_m(T)$ at certain temperature can be determined by the following formula. The Standard enthalpy and the isobaric heat capacity of various substances participating in the reaction are shown in Table 2. Given that there is no isobaric heat capacity value about $NaClO_3$ and $NaClO_2$, we use the isobaric heat capacity value of a similar material, $NaClO_4$.

$$\Delta_r H_m^\Theta(T) = \Delta_r H_m^\Theta + \Delta_r C_{p,m}\Delta T \quad (12)$$

$$\Delta_r H_m^\ominus = \sum v_B \Delta_f H_m^\ominus(B,T) \qquad (13)$$

$$\Delta_r C_{p,m} = \sum v_B C_{p,m}(B) \qquad (14)$$

Table 2 The standard formation enthalpy, standard molar Gibbs function, standard molar entropy and heat capacity of substances [7]

substances	$\Delta_f H_m^\ominus$(kJ/mol)	$\Delta_f G_m^\ominus$(kJ/mol)	$S_m^\ominus$(J/(K•mol))	$C_{p,m}^\ominus$(J/(K•mol))
NaCl(aq)	-407.27	-393.17	115.5	-90.0
SO_2(g)	-296.81	-300.13	248.223	39.88
H_2SO_4(aq)	-909.27	-744.63	20.1	293
$NaClO_2$(aq)	-306.7	-244.8	160.3	--
$NaClO_3$(aq)	-344.09	-269.91	221.3	--
NO(g)	91.29	87.60	210.76	29.85
H_2O(l)	-285.830	-273.14	69.95	75.35
$NaClO_4$(cr)	-383.3	-254.9	142.3	111.3
HNO_3(aq)	-207.36	-111.34	146.4	-86.6

We can get the following conclusions for the reaction (10):

$\Delta_r C_{p,m}^\ominus$=486.25J/(K•mol), $\Delta_f H_m^\ominus$=-1796.9kJ/mol

When it is at the optimum reaction temperature of desulfurization and denitration, namely 323.15K, we can get the following conclusions:

$\Delta_r H_m^\ominus$(323.15K)=-1784.74kJ/mol

Similarly, for reaction (11), the values of $\Delta_r C_{p,m}$, $\Delta_r H_m^\ominus$ and $\Delta_r H_m^\ominus$(323.15K) are -2749.05 J/(K•mol), -2048.6kJ/mol and -2117.33kJ/mol.

It can be judged that they are exothermic reactions because of the values of $\Delta_r H_m^\ominus$ and $\Delta_r H_m^\ominus$(323.15K) of each reaction is less than 0. Raising the temperature is not conducive to the reaction purely from the viewpoint of thermodynamics, and the experimental phenomena also explains the results.

3.2 *Gibbs function of the chemical reaction*

The standard Gibbs function of molar reaction $\Delta_r G_m^\ominus$ and $\Delta_r G_m^\ominus$(T) can be calculated by the following equation:

$$\Delta_r G_m^\ominus = \sum_B v_B \Delta_f G_m^\ominus(B) \qquad (15)$$

$$\Delta_r G_m^\ominus(T) = \Delta_r H_m^\ominus(T) - T\Delta_r S_m^\ominus(T) \qquad (16)$$

$$\Delta_r S_m^\ominus = \sum_B v_B S_m^\ominus(B) \qquad (17)$$

$$\Delta_r S_m^\ominus(T) = \Delta_r S_m^\ominus + \Delta_r C_{p,m} \ln\frac{T}{298.15} \qquad (18)$$

Values of standard Gibbs function and standard entropy of each substance participating in the reaction are shown in Table 2.

We can get the following conclusions for reaction (10):

$\Delta_r G_m^\ominus$=-1128.43kJ/mol,

$\Delta_r S_m^\ominus$=-1640.965J/(K•mol)

When it is at the optimum reaction temperature of desulfurization and denitration, namely 323.15K, we can get the following conclusions:

$\Delta_r S_m^\ominus$(323.15K)=-1.602kJ/(K•mol),

$\Delta_r G_m^\ominus$(323.15K)=-1267.05kJ/mol

Similarly, for reaction (11), the values of $\Delta_r G_m^\ominus$, $\Delta_r S_m^\ominus$, $\Delta_r S_m^\ominus$(323.15K) and $\Delta_r G_m^\ominus$(323.15K) are -1438.59kJ/mol, -1.445kJ/(K•mol), -1.666kJ/(K•mol) and -1578.96kJ/mol.

It can be known by the above calculation results that the values of $\Delta_r G_m^\ominus$ and $\Delta_r G_m^\ominus$(323.15K) are much smaller than -40kJ/mol in the $NaClO_2/NaClO_3$ solution of simultaneous desulfurization and denitrification reaction [8], so the reaction (10) and (11) can be carried out and the limits is deep.

3.3 *Calculation of chemical reaction equilibrium constant*

The standard chemical reaction equilibrium constant can be calculated by the standard molar Gibbs function:

$$K^\ominus = \exp[-\frac{\Delta_r G_m^\ominus}{RT}] \qquad (19)$$

$$\Delta_r G_m^\ominus = -RT\ln K^\ominus \qquad (20)$$

We can get the following conclusion according to the formula (19):

$$\ln K^\ominus = -\frac{\Delta_r G_m^\ominus}{RT} \qquad (21)$$

We can get the following conclusions for reaction (10):

$\ln K^\ominus = -(-1128.43 \times 1000)/(8.314 \times 298.15) = 455.23$,

$K^\ominus = e^{455.23}$.

When

T=323.15K,

$\ln K = -(-1267.05 \times 1000)/(8.314 \times 323.15) = 471.61$,

$K^{\Theta}=e^{471.61}$.

Similarly, for the reaction (11), the values of K^{Θ} and K(323.15K) are $e^{580.35}$ and $e^{587.7}$.

We can know that every value of the equilibrium constant is big by the results calculated. Therefore, the reaction can be carried forward and be carried out more completely.

4 SUMMARY

This paper calculated and analyzed the chemical reaction enthalpy change, Gibbs function of chemical reactions and chemical reaction equilibrium constants and other thermodynamic parameters based on the $NaClO_2/NaClO_3$ solution of simultaneous desulfurization and denitrification reaction and the thermodynamic principles. The chemical reaction enthalpy results show that $NaClO_2/NaClO_3$ solution of simultaneous desulfurization and denitrification reaction is an exothermic reaction. Simply raising the temperature of the reaction is adversely. The chemical Gibbs function results show that the simultaneous desulfurization and denitration reaction can be carried out in the standard state and the optimum reaction temperature (323.15K). And the limit is deep. The equilibrium constant values of $NaClO_2/NaClO_3$ solution of simultaneous desulfurization and denitration reaction are very large, from which we can get that the reaction can be carried forward, and the reaction was more complete. Therefore, $NaClO_2/NaClO_3$ solution of simultaneous desulfurization and denitrification reaction is feasible from the point of thermodynamic view.

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