

Thermodynamics Analysis of Integrated Process for Simultaneous Desulfurization and Denitrification with manganese dioxide

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Abstract: The direction and limitation of desulfurization and denitrification reaction were analyzed by calculating thermodynamic functions, and the reaction mechanism of desulfurization and denitration was proposed. The pollutant removal efficiencies were deduced by the equilibrium partial pressure of SO₂ and NO at different reaction temperatures. Results showed that the integrated process for simultaneous desulfurization and denitrification with manganese dioxide was thermodynamically feasible, and the reaction depth was greater. The Gibbs function were -207.47, -188.52 KJ.mol⁻¹, respectively. The equilibrium partial pressure of SO₂ and NO was extremely small, indicating that the removal of SO₂ and NO could be almost completely removed in the flue gas. The paper provides a theoretical basis for further research and practical application of the technology.

Introduction

With the rapid development of China's economy, the resulting environmental problems are increasingly prominent and serious. As the main components of air pollutants, Sulfur Dioxide (SO₂) and Nitrogen Oxides (NO_x) discharged from the flue gas have been received much attention from the government and the public. It is known that the emission of SO₂ and NO_x are primary contributors to acid rain, which is associated with acidification of lakes and streams, corrosion of buildings and monuments. Moreover, they can affect human health by irritating lungs and lowering resistance to respiratory infection (such as influenza) [1]. As the world's largest producer and consumer of coal, China has paid great attention on the emission of SO₂ and NO_x [2], which reduce emissions on the one hand, open up new ideas for resource utilization of SO₂ and NO_x on the other using cost-effective way [3-4]. Recently, many literatures have been published about the research on simultaneous removal of SO₂ and NO_x, the methods contained catalysis [5], photocatalysis [6], electron beam [7], nonthermal plasma [8], and wet method [9-13]. Among them, wet scrubbing process has gained much more concern due to the SO₂ is easily soluble in water and could be removed completely after scrubbing by absorbent. Nevertheless, NO is insoluble as the majority of NO_x in the flue gas (about 95%), so wet method is difficult for denitrification [14]. Up to date, lots of technologies about wet method have been developed for simultaneous removal of SO₂ and NO_x. Among them, many oxidations have been tested for SO₂ and NO_x removal, such as KMnO₄, Ca(ClO)₂, NaClO, NaClO₂, and H₂O₂ [1, 9-12, 15]. However, the oxidants were difficult to be widely applied in industry due to their high cost, and the utilization of by-products is difficult, easy to form secondary pollution. Up to date, manganese oxides (MnO_x) have received special emphasis

as a quite effective absorbent for sulfur dioxide recovery [16, 17]. Besides, lots of literatures have been published about the research on simultaneous removal of SO₂ and NO_x with pyrolusite [18, 19, 20], which main ingredient is Manganese dioxide (MnO₂). Manganese dioxide can not only emerge in the flue gas SO₂ and NO_x under acidic conditions, but also economically valuable byproducts manganese sulfate and manganese nitrate [18]. In the work, desulfurization and denitrification reaction direction and limits were analyzed, according to enthalpy, entropy, Gibbs function change and other thermodynamic functions, which established theoretical foundation for the research of simultaneous removal of SO₂ and NO_x. Manganese dioxide suspension about corrosivity is very small, less demanding on the equipment material, and it can be regenerated by electrolytic, after manganese dioxide is reduced into divalent manganese ions. So it is suitable as absorbent of desulfurization and denitrification reaction.

In this paper, the reaction enthalpy, entropy, Gibbs function and other thermodynamic functions of desulfurization and denitrification were calculated, and the equilibrium partial pressure of nitric oxide and sulfur dioxide, based on ideal gas as the research object. Then the feasibility of the method, spontaneity, and reaction limits were studied thermodynamically, and compared with the method described in the literature, indicating the removal efficiency and superiority of pollutants, which provide a theoretical basis for further research and practical application of the technology.

Reaction Mechanism

The absorption process involved in gas-liquid-solid three mass transfers, chemical reaction in liquid phase, and manganese dioxide solid surface chemical reactions. So for better understanding the process of simultaneous removal of SO₂ and NO_x with manganese dioxide, the reaction mechanism of simultaneous desulfurization and denitration was considered in step by step pattern. Then, the absorption process could be written as follows: (1) the diffusion of SO₂ and NO_x in gas phase; (2) SO₂ and NO_x transfer from gas to the liquid phase; (3) the diffusion of SO₂ and NO_x in liquid phase; (4) the oxidation reaction of SO₂ and NO_x with manganese dioxide.

Desulfurization Reaction Mechanism. The main existence forms of sulfur were S (IV) and S (VI) species, with the reaction took place in liquid phase. The possible existence forms of sulfur species were H₂SO₃, HSO₃⁻, SO₃²⁻, HSO₄⁻ and SO₄²⁻ in aqueous solution, respectively. The S (IV) species could be oxidized into S (VI) species by O₂ and MnO₂, therefore, SO₄²⁻ was the main existence form of sulfur in the solution [18]. The reaction of SO₂ absorption in the solution could be written as:

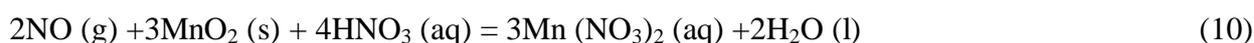


Denitration Reaction Mechanism. The absorption process of NO_x with MnO₂ was more complex than that of SO₂, and numerous chemical reactions were involved in the process. The main nitrogen oxides species in liquid and gas phases were considered as NO, NO₂, N₂O₃, N₂O₄, HNO₂, and HNO₃ [20]. It is known that the solubility of NO is very low as the main component in gas phase. Therefore, the oxidation of NO to NO₂ was a limiting step for the manufacture of HNO₃. Other reactions such as NO and NO₂ to N₂O₃ and NO to N₂O₄ were quick. In addition, in the liquid phase, high soluble compounds of N₂O₃ and N₂O₄ dissolved and reacted rapidly with water, then nitrous and nitric acids were produced [21]. The main reactions of NO_x absorption in the solution could be

written as:



It is known from the potential diagram of Mn-SO₂-NO_x-H₂O system that the oxidation potential of MnO₂ and O₂ is stronger than SO₂, NO₂, and HNO₂, which can be oxidized to SO₄²⁻ and NO₃⁻ respectively [18]. Therefore, there are two oxidants of simultaneous removal of SO₂ and NO_x with manganese oxide, namely MnO₂ and O₂, and the reaction products were manganese sulfate, manganese nitrate and sulfate, nitrate. Thus, the overall reaction of simultaneous removal of SO₂ and NO_x with MnO₂ could be written as:



Thermodynamic calculation

The reaction enthalpy and entropy with the reaction temperature becomes negligible, under the condition of the reaction temperature changed little, so the standard state reaction enthalpy, entropy and standard formation Gibbs function were calculated, representatively. To estimate reaction depth of the two chemical reactions (Eqs. 9 and 10), thermodynamic calculations of the two equations were performed according to the reactions (Eqs. 11-13). Thermodynamics parameters including, standard formation enthalpy ($\Delta_f H_m^\theta$), standard entropy ($\Delta_f S_m^\theta$), and standard formation Gibbs function ($\Delta_f G_m^\theta$) of substances were given in Table 1 [22]. Enthalpy change, entropy change, and Gibbs function of the reactions (Eqs. 9 and 10) adjusted at 298.15 K were obtained by Eqs. 11-13, respectively [9, 23, 24]:

$$\Delta_r H_m^\theta = \sum \gamma \Delta_f H_m^\theta (\text{products}) - \sum \gamma \Delta_f H_m^\theta (\text{reactants}) \quad (11)$$

$$\Delta_r S_m^\theta = \sum \gamma \Delta_f S_m^\theta (\text{products}) - \sum \gamma \Delta_f S_m^\theta (\text{reactants}) \quad (12)$$

$$\Delta_r G_m^\theta = \sum \gamma \Delta_f G_m^\theta (\text{products}) - \sum \gamma \Delta_f G_m^\theta (\text{reactants}) \quad (13)$$

According to the thermodynamics dates in Table 1, thermodynamic calculation results were shown in Table 2. The results stated that $\Delta_r H_m^\theta$ values of the two chemical reactions are negative, which was conformed to the exothermic nature of the process [25, 26]. Therefore, increasing the reaction

temperature was unfavorable for the two reactions from the thermodynamic point of view. $\Delta_r S_m^\theta < 0$ $\text{J} \cdot (\text{mol} \cdot \text{K})^{-1}$ indicated that entropy of the reaction was reducing in the process, which implied that the amount of gas molecule continuously decreased during the reaction [27]. The negative values of $\Delta_r G_m^\theta$ indicated that two reactions happened spontaneously, and the reaction depth was greater [23], which implied that the simultaneous removal of SO_2 and NO_x with MnO_2 is thermodynamically feasible. According to the literature [28], KMnO_4 as the oxidant, Gibbs function of simultaneous desulfurization and denitration were -396.53 , -95.88 $\text{KJ} \cdot \text{mol}^{-1}$, respectively. It is known that flue gas desulfurization by MnO_2 is feasible, and has a high enough removing efficiency [29]. About denitration, the values of $\Delta_r G_m^\theta$ is -188.52 , indicated the reaction depth was greater, which implied that the better removal efficiency and superiority of pollutants, compared with KMnO_4 (the values is -95.88).

Table 1. Standard formation enthalpy, standard entropy, and standard formation Gibbs function.

Substance	$\Delta_f H_m^\theta / (\text{KJ} \cdot \text{mol}^{-1})$	$\Delta_f S_m^\theta / \text{J} \cdot (\text{mol} \cdot \text{K})^{-1}$	$\Delta_f G_m^\theta / (\text{KJ} \cdot \text{mol}^{-1})$
$\text{SO}_2(\text{g})$	-296.81	248.22	-300.13
$\text{MnO}_2(\text{s})$	-520.1	53.1	-465.2
$\text{MnSO}_4(\text{aq})$	-1130.1	-53.6	-972.8
$\text{NO}(\text{g})$	91.29	210.76	87.60
$\text{HNO}_3(\text{aq})$	-207.36	146.40	-111.34
$\text{Mn}(\text{NO}_3)_2(\text{aq})$	-635.6	218	-451.0
$\text{H}_2\text{O}(\text{l})$	-285.83	69.95	-237.14

Table 2. Enthalpy change, entropy change, Gibbs function, and equilibrium constant of reactions.

Reaction	$\Delta_r H_m^\theta (\text{KJ} \cdot \text{mol}^{-1})$	$\Delta_r S_m^\theta \text{J} \cdot (\text{mol} \cdot \text{K})^{-1}$	$\Delta_r G_m^\theta (\text{KJ} \cdot \text{mol}^{-1})$	$K^\theta (298.5 \text{ K})$
Equation 9	-313.19	-354.92	-207.47	$e^{83.70}$
Equation 10	-271.3	-372.52	-188.52	$e^{76.05}$

The chemical reaction equilibrium constants (K^θ) of Equation 9 and 10 in different reaction temperatures were given as follows [23]:

$$\Delta_r G_m^\theta = -RT \ln K^\theta \quad (14)$$

The values of K at different reaction temperatures were shown in Table 3, which were $> 10^5$, so the reactions carried out in the positive direction, and the reaction depth was greater, proved that the simultaneous removal of SO_2 and NO_x with MnO_2 was thermodynamically feasible.

When the reaction reaches equilibrium, the Gibbs free energy of the chemical reaction becomes zero, that is $\Delta_r G_m^\theta = -RT \ln(I_p)$, $I_p = \frac{P_C^c}{P_A^a}$, where P_C^c , P_A^a are the partial pressure of the reactants and

reaction products. Then the equilibrium partial pressure of SO₂ and NO in different reaction temperatures could be calculated by equation 15.

$$\ln P_{\text{SO}_2} = -\frac{24954.30}{T} \quad \ln P_{\text{NO}} = -\frac{11337.50}{T} \quad (15)$$

The equilibrium partial pressure at different reaction temperatures was calculated through Equation 15, the results were listed in Table 4. The values indicated that the partial pressure is gradually increasing with the increase of temperature, further indicated that increasing the reaction temperature is not conducive to the removal of SO₂ and NO. But, even if the reaction temperature reached 390 K, the equilibrium partial pressure of SO₂ and NO are also extremely small, indicating that the removal of SO₂ and NO with the acidic solution of manganese dioxide is almost completely removed in the flue gas.

Table 3. The chemical reaction equilibrium constants in different reaction temperatures

Reaction temperature (K)	290	310	330	350	370	390
Equation 9	e ^{86.05}	e ^{80.50}	e ^{75.62}	e ^{71.30}	e ^{67.44}	e ^{63.40}
Equation 10	e ^{78.19}	e ^{73.15}	e ^{68.71}	e ^{64.79}	e ^{61.28}	e ^{58.14}

Table 4. Equilibrium partial pressure of SO₂ and NO in different reaction temperatures

Reaction temperature (K)	290	310	330	350	370	390
P _{SO₂} (Mpa)	4.26×10 ⁻³⁸	1.10×10 ⁻³⁵	1.44×10 ⁻³³	1.09×10 ⁻³¹	5.12×10 ⁻³⁰	1.63×10 ⁻²⁸
P _{NO} (Mpa)	1.05×10 ⁻¹⁷	1.31×10 ⁻¹⁶	1.20×10 ⁻¹⁵	8.55×10 ⁻¹⁵	4.92×10 ⁻¹⁴	2.37×10 ⁻¹³

Conclusion

In this work, the reaction mechanism and total chemical reaction equations were investigated. Enthalpy change, entropy change, Gibbs function and reaction equilibrium constants were calculated respectively. Gibbs function $\Delta_r G_m^\theta < -40 \text{ KJ.mol}^{-1}$, and reaction equilibrium constants $K^\theta > 10^5$ of each reaction, which indicated that the simultaneous removal of SO₂ and NO_x with manganese dioxide is thermodynamically feasible, two reactions happened spontaneously, and the reaction depth was greater. $\Delta_r H_m^\theta$, the two chemical reactions are negative, which was conformed to the exothermic nature of the process, indicating increasing the reaction temperature was unfavorable for the two reactions. In the same time, the equilibrium partial pressure of SO₂, NO were tested gradually increasing trend with increasing temperature, which shows that the reaction temperature is not conducive to SO₂, NO removal from thermodynamics analysis. Even if the

reaction temperature reached 390K, the equilibrium partial pressure of SO₂ and NO are also extremely small, indicating that the removal of SO₂ and NO with the acidic solution of manganese dioxide is almost completely removed in the flue gas, and compared with the method KMnO₄ described in the literature, has the better removal efficiency and superiority of denitration.

In a word, the simultaneous removal of SO₂ and NO_x with manganese dioxide was thermodynamically feasible, and it can be almost 100% removal. It has broad application prospects, but its practical application process and its complexity, unpredictability, should go further experimental study.

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