Kinetics and Reaction Mechanism of Catalytic Oxidation of Ammonium Sulfite

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The effects of five catalysts on the oxidation rate of ammonium sulfite were compared by intrinsic experiments using self-designed bath reactor. Fe^{2+} was turned out to be a good catalyst for oxidation of ammonium sulfite. Using stirred bubbling reactor, the kinetics of catalytic oxidation of sulfite in the ammonium-based wet flue gas desulfurization process were investigated by varying concentrations of $(NH_4)_2SO_4$, $(NH_4)_2SO_3$ and Fe^{2+}, pH, air flow rate and temperature. The reaction was found to be first order with respect to ammonium sulfite, 0.4 order with respect to Fe^{2+} and the oxidation could reach the maximum rate when pH value was close to 6. The mechanism of the oxidation was discussed and concluded that the oxidation is controlled by diffusion of oxygen.

Keywords: Kinetics, Mechanism, Catalyst, Ammonium sulfite, Ammonia-based flue gas desulphurization.

INTRODUCTION

Ammonia-based flue gas desulfurization process is a well-known technique with high efficient removal of SO_2 and the ammonium sulfite is obtained as a byproduct consequently. If ammonium sulfite is used directly as a product, it may decompose into SO_2 again which will produce new environmental pollution[1,2]. Compared with ammonium sulfite, ammonium sulfate-the oxidation product of ammonium sulfite, is much more valuable and stable when it is used as a fertilizer in agriculture. However, due to the low oxidation rate, most of the injected air is wasted during the forced oxidation process of flue gas desulfurization, resulting in excess investment and energy[3]. Therefore, it is crucial to turn ammonium sulfite into ammonium sulfate efficiently and economically to realize large-scale application of ammonia-based flue gas desulfurization.

Many scholars have studied the problem of the oxidation of aqueous ammonium sulfite. Gurkan *et al.*[4] made a research on the kinetics of the heterogeneous oxidation of ammonium sulfite with oxygen transferring from the gas phase and proposed that the reaction mechanism and consequently the order of the intrinsic rate of reaction were dependent on the oxygen to sulfite ratio. Zhou *et al.*[5] conducted experiments of the heterogeneous oxidation of concentrated ammonium sulfite and found the reaction to be 0.2 order with respect to sulfite above a critical sulfite concentration and first order with respect

to oxygen. Long *et al.*[6] studied a homogeneous catalyst system for the oxidation of concentrated ammonium sulfite. The sulfite oxidation rate was found to be independent of the initial sulfite concentration, the reaction order with respect to oxygen was 1.2. Jia *et al.*[7] investigated the kinetics of oxidation of total sulfite using bubbling apparatus, the reaction was found to be -0.5 order with respect to sulfite in the temperature range of 303.15-333.15 K.

Except for ammonium sulfite, the catalytic oxidation reactions of other kinds of byproducts in wet flue gas desulfurization have received much attention during the last 40 years[8]. Zhao *et al.*[9] studied the reaction rate of sodium sulfite oxidation with cobalt ion catalyst, the reaction was found to be first order with respect to sulfite when the reaction rate was controlled by reaction kinetics and zero order with respect to sulfite when the reaction rate was controlled by the gas-liquid rate of mass transfer characteristics. Lancia *et al.*[10] conducted a study of catalytic oxidation of calcium bisulfite with manganese. The reaction was found to be first order with respect to bisulfite and 0.5 order with respect to partial pressure of oxygen and manganese ion concentration. Karatza *et al.*[11] found the reaction of calcium bisulfite catalytic oxidation to be 1.5 order with respect to bisulfite and first order with respect to ferrous ion concentration. Karatza *et al.*[11] continued to finish a research on reaction rate of sulfite oxidation catalyzed by cuprous ions, the reaction was found to be 1.5 order with respect to bisulfite, zero order with respect to dissolved oxygen and 0.3 order with

respect to ferrous ion concentration. They also draw a conclusion that cooper is less effective than iron as a catalyst[12].

Though the oxidation of ammonium sulfite has been studied by several researchers and has resulted in different conclusions, it should be noted that most of these previous investigations dealt with oxygen absorption into ammonium sulfite solutions without catalyst or just with cobalt ions. They did not taken other transition metal ions into consideration which was quite different from the catalytic oxidation of calcium sulfite. In addition, these previous investigations were conducted under conditions significantly different from those encountered in ammonia-based flue gas desulfurization plants. Therefore, it can be concluded that more data and a closer study on the mechanism is necessary. The present work was undertaken to make a systematic study of the catalytic oxidation of ammonium sulfite, under conditions relevant to ammonia based wet flue gas desulfurization plants.

EXPERIMENTAL

All the chemicals used were of analytical grade in order to reduce the influence of impurities. The software Origin 8.5 was used for regressive analysis of the experimental data.

The oxidation of ammonium sulfite was carried out in a stirred bubbling reactor which was installed in a magnetic stirring constant-temperature bath (Fig. 1). The stirred bubbling reactor was a glass cylindrical vessel, 11.2 cm in internal diameter and 15.5 cm in height. After adding 1000 mL solution consist of certain amount of ammonium sulfite and ammonium sulfate prepared by high purity water without oxygen and a set amount of catalyst into the reactor, the stirrer started at a predetermined speed of 120 rpm. The time was noted and the air was injected into the solution in a steady manner. HCl and NaOH were used to adjust the pH. The reaction ceased at the scheduled time and the concentration of sulfate was then measured by means of ion chromatography (ICS-2500, Dionex, USA) which was determined according to the standard curve of sulfate. The observed oxidation rate was calculated using the following formula:
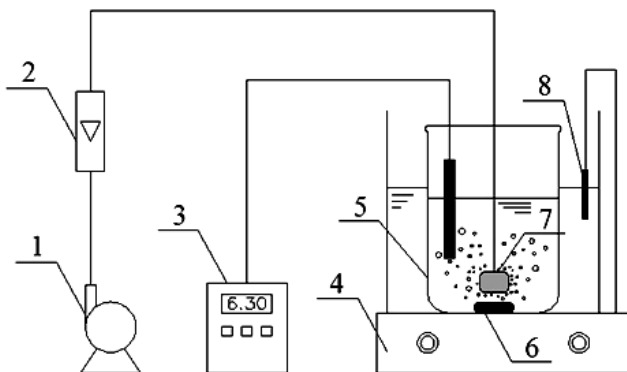
$$r = dC_{SO_4^{2-}} / dt \tag{1}$$

Fig. 1.   Experimental apparatus of ammonium sulfite oxidation (1- air compressor; 2- air flow meter; 3- pH meter; 4- magnetic stirring constant-temperature water bath; 5- stirred bubbling reactor; 6- magnetic stirrer; 7- aeration header; 8- thermocouple)

The intrinsic reaction of sulfite oxidation was carried in an intermittent reactor (Fig. 2). Firstly, a known quantity of high purity water was added into the intermittent reactor which was installed in a magnetic stirring constant-temperature bath. The stirrer started at a predetermined speed and a dissolved oxygen probe was fixed in the solution. A certain quantity of ammonium sulfite solution was then added into the reactor to a total volume of 1 L and the reaction started at the same time. The time was noted and the concentration of dissolved oxygen was recorded during the reaction process. The concentration of sulfate could be calculated using the following formula:

$$SO_3^{2-} + 0.5O_2 \rightarrow SO_4^{2-} \tag{2}$$
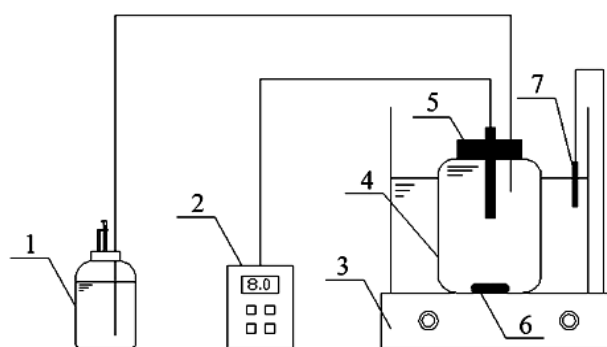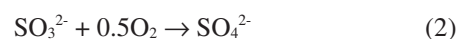

Fig. 2.   Experimental apparatus of intrinsic reaction (1- quantitative liquid filling injector; 2- dissolved oxygen meter; 3- magnetic stirring constant-temperature water bath; 4- intermittent reactor; 5- rubber stopper; 6- magnetic stirrer; 7- thermocouple)

RESULTS AND DISCUSSION

In this section, effects of five catalysts, including Co^{2+}, Mn^{2+}, Zn^{2+}, Fe^{2+} and Fe^{3+} are compared by intrinsic experiment sat fixed concentration of ammonium sulfite and temperature (Fig. 3). It is obvious that Fe^{2+} has much better catalytic effectthan other catalyst when the catalysts are in the same concentrations. The similar conclusions were drawn by Karatza and Lancia, when they studied the catalytic oxidation of calcium bisulfite[10,13]. Therefore, Fe^{2+} is an effective catalyst which is suitable for applying in wet flue gas desulfurization system.
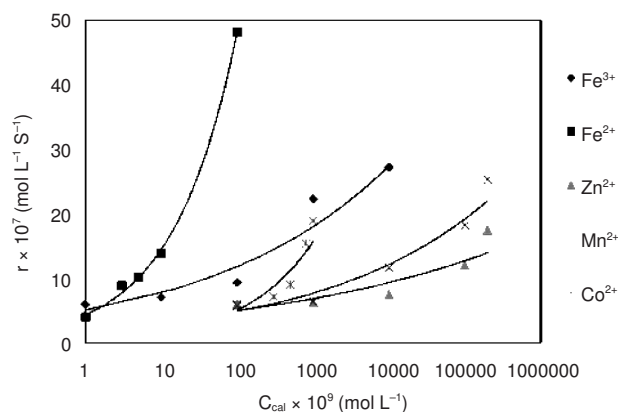

Fig. 3.   Effect of different catalysts on the oxidation rate [$C(NH_4)_2SO_3$ = 1.5 mmol/L; T = 298.15 K]

Results of oxidation of ammonium sulfite

Effect of SO_4^{2-} concentration: The relation of sulfite oxidation rate and ammonium sulfate concentration in this work is shown in Fig. 4. It can be seen that the oxidation rate decreases as the ammonium sulfate concentration increases. While the ammonium sulfate concentration was raised to 4 mol/L, the oxidation rate of sulfite was reduced by about 16 % compared to the zero magnesium sulfate concentration. The result certificated that too high concentration of sulfate will inhibit the oxidation of sulfite. The similar tendency has been reported by Zhou *et al.*[5]. One reason that sulfate ion hampers the oxidation may be due to the decrease of the solubility of oxygen in solution and the diffusion coefficient changes[14,15].
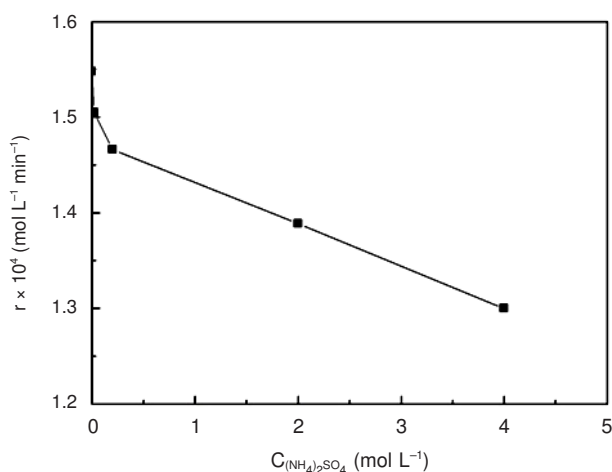

Fig. 4. Effect of sulfate concentration on the oxidation rate [$C(NH_4)_2SO_3$ = 20 mmol/L; $C(Fe^{2+})$ = 1 × 10^{-7} mol/L; pH = 5.5; Q = 120 L/h; T = 298.15 K]

Effect of concentration of SO_3^{2-}: Fig. 5 shows that the oxidation rate of sulfite increases as the ammonium sulfite concentration increases. The oxidation rate of sulfite is found to be first order with respect to ammonium sulfite. As reported by Zhao *et al.*[9], the reaction with Co^{2+} was first order with respect to the sodium sulfite when controlled by the intrinsic reaction, which is similar to our results. However, Wang *et al.*[19] found that the un-catalyzed oxidation of saturated magnesium sulfite is zero order with respect to sulfite. Jia *et al.*[16] found the reaction without catalyst to be -0.5 order with respect to ammonium sulfite[7]. Different kinds of sulfite have different characters and reaction conditions, such as ionic strength, catalysts or inhibitors, range of sulfite concentration, pH and solubility, which may strongly affect the experimental results.

Effect of Fe^{2+} concentration: The effect of Fe^{2+} concentration on the oxidation date was investigated using Fe^{2+} concentration from 1 × 10^{-7} to 1 × 10^{-4} mol/L. The result is shown in Fig. 6. As the Fe^{2+} catalyst, the oxidation rate can be significantly increased by solely increasing the Fe^{2+} concentration, but the rate of increase was not constant. A similar tendency was described by Zhao *et al.*[9,17] when they studied the forced oxidation of calcium sulfite with catalysts of Co^{2+} and Mn^{2+}. However, the most significant difference with previous literatures is that the oxidation rate kept increasing with the increasing concentration of Fe^{2+}, the phase reaction rate keeps steady had not been found. The reason may be that
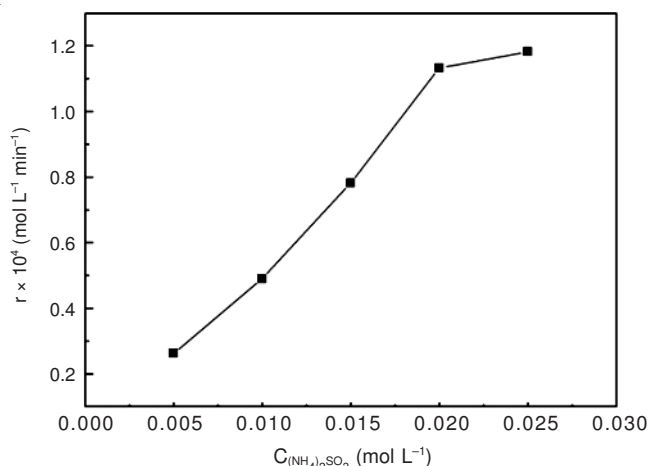

Fig. 5. Effect of sulfite concentration on the oxidation rate [$C(NH_4)_2SO_4$ = 20 mmol/L; $C(Fe^{2+})$ = 1×10^{-7} mol/L; pH = 5.5; Q = 120 L/h; T = 298.15 K]
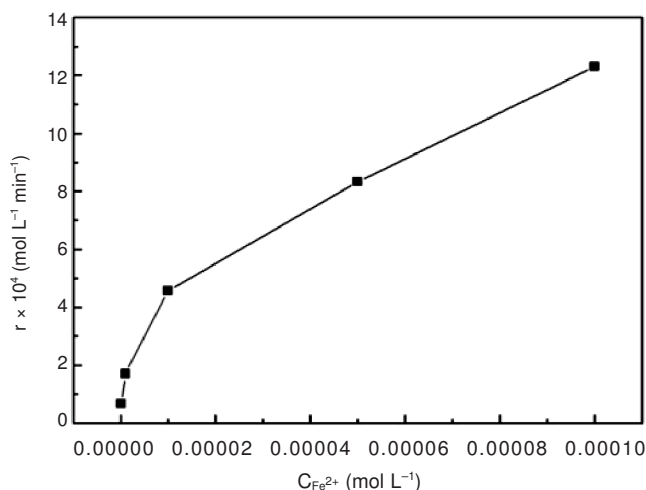

Fig. 6. Effect of Fe^{2+} concentration on the oxidation rate [$C(NH_4)_2SO_3$ = 20 mmol/L; $C(NH_4)_2SO_4$ = 20 mmol/L; pH = 5.5; Q = 120 L/h; T = 298.15 K]

the sulfite oxidation rate was always determined by the reaction kinetics with lower pH controlling. The oxidation rate was found to be 0.4 order with respect to the concentration of Fe^{2+}.

Effect of pH: The experimental results indicating the dependence of pH on the oxidation rate of ammonium sulfite are shown in Fig. 7. The oxidation rate of sulfite increased slowly with pH from 4.5 to 5.5 and increased quickly with pH from 5.5 to 6.0, while the oxidation rate began to decrease rapidly with pH above 6.5. This tendency is similar to that reported by Zhang and Milleroon[18] for presence of sulfite in seawater. However, Jia *et al.*[7] reached an discrepant conclusion with a theory that the sulfite oxidation mechanism depends on the bisulfite concentration and the ratio of bisulfite concentration to sulfite concentration decreases with the pH increases. It's difficult to explain the phenomenon on a specific theory. Linek and Vacek[8] found that the oxidation effect of oxygen significantly reduced under low pH. Therefore, the changes of the reaction rate with different pH can be considered due to the interaction of different impact factors. Under lower pH, the bisulfite concentration maintained at a high level while the effect of oxygen was greatly reduced, resulting in a lower
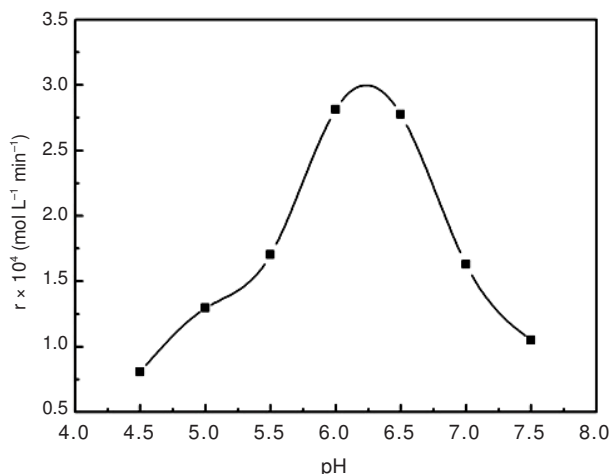
Fig.7.   Effect of pH on the oxidation rate [$C_{(NH_4)SO_3}$ = 20 mmol/L; $C_{(NH_4)SO_4}$ = 20 mmol/L; $C_{Fe^{2+}}$ = 1 × 10^{-7} mol/L; Q = 120 L/h; T = 298.15 K]

oxidation rate. When pH value raised, the effect of oxygen increase while the bisulfite concentration declined rapidly, causing the corresponding reduction of the oxidation rate.

Effect of air flow rate: Fig. 8 showed that the oxidation rate of sulfite increased quickly with the air flow up to150 L/h, above which it increased slowly. This tendency is similar to that reported by Shen *et al.*[19]. The reason may be that when the air flow was below 150 L/h, the bubbled air dispersed uniformly, resulting in a quiet bubbling area and had little stirring effect on the reaction solution, the gas-liquid contact area increased as the air flow increased. When the air flow increased up to 150 L/h, some air froth collided and agglome-rated, resulting in a turbulent bubbling area and a little change of gas-liquid contact area thus mass transfer rate of oxygen increased slowly.
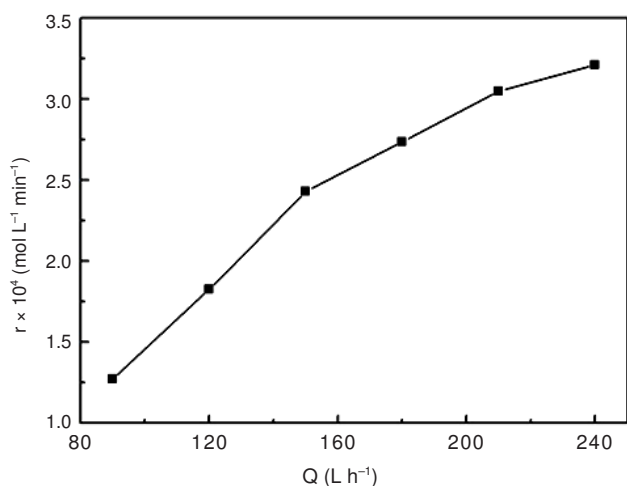

Fig. 8.   Effect of air flow rate on the oxidation rate [$C_{(NH_4)_2SO_3}$ = 20 mmol/L; $C_{(NH_4)_2SO_4}$ = 20 mmol/L; $C_{Fe^{2+}}$ = 1 × 10^{-7}mol/L; pH = 5.5; T = 298.15 K]

Effect of temperature: Fig. 9 showed that the oxidation rate of sulfite increases as the temperature increases.

According to the Arrhenius formula:

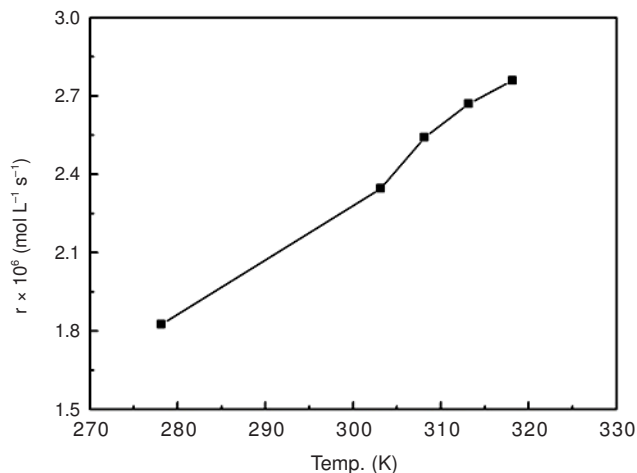$$\ln k = \ln k_0 - \frac{E_a}{R} \cdot \frac{1}{T} \qquad (3)$$

Fig. 9.   Effect of air flow rate on the oxidation rate [$C_{(NH_4)_2SO_3}$ = 20 mmol/L; $C_{(NH_4)_2SO_4}$ = 20 mmol/L; $C_{Fe^{2+}}$ = 1 × 10^{-7} mol/L; pH = 5.5; Q = 120 L/h]

It can be seen that a plot of ln k *versus* 1/T is a straight line, the activation energy E_a can be calculated according to the slope of the line. The reaction rate constant k which quan-tifies the speed of a chemical reaction increases with a rise in temperature. This is why the oxidation rate increases as the temperature increase. The apparent activation energy for the oxidation was calculated to be 7.73 kJ/mol,which is much lower than the previously reported activation energy for the oxidation of ammonium sulfite[5-7].

Mechanism of oxidation of ammonium sulfite: The ammonium sulfite oxidation may include two steps: an intrin-sic reaction of sulfite in the solution and diffusion of oxygen from air bubbles into the solution on the basis of the oxidation processes of calcium sulfite[3,6].

Intrinsic reaction: The intrinsic experiments of ammo-nium sulfite oxidation were conducted by varying concen-tration of $(NH_4)_2SO_3$, Fe^{2+} and temperature. The results of intrinsic reaction were shown in Figs. 10-12. Fig. 10 shows that the reaction rate was accelerated by increasing concen-tration of Fe^{2+} and it's found to be 0.5 order with respect to Fe^{2+} concentration. Fig. 11 illustrated that the reaction rate increases as the ammonium sulfite concentration increases. The reaction is found to be second order with respect to ammo-nium sulfite. Furthermore, the dissolved oxygen concentration decreased linearly with reaction time under excess of sodium sulfite, indicating that the reaction was zero order with respect to dissolved oxygen concentration.

Based on the experimental results above, the intrinsic reaction rate can be expressed as:

$$r_i = kC^2_{(NH_4)_2SO_3}C^{0.5}_{Fe^{2+}} \qquad (4)$$

The effect of temperature on the intrinsic reaction rate is shown in Fig. 12. The apparent activation energy was calcu-lated to be 76.49 kJ/mol with a frequency factor of 2.7 × 10^{16} L/(mol s).

If intrinsic reaction were the controlling step, the reaction rate calculated by eqn. 10 should be 8.14 × 10^{-3} mol/(L min) when the concentration of dissolved sulfite is 20 mmol/L at 298.15 K. Fig. 4 shows that the oxidation rate is only 1.54
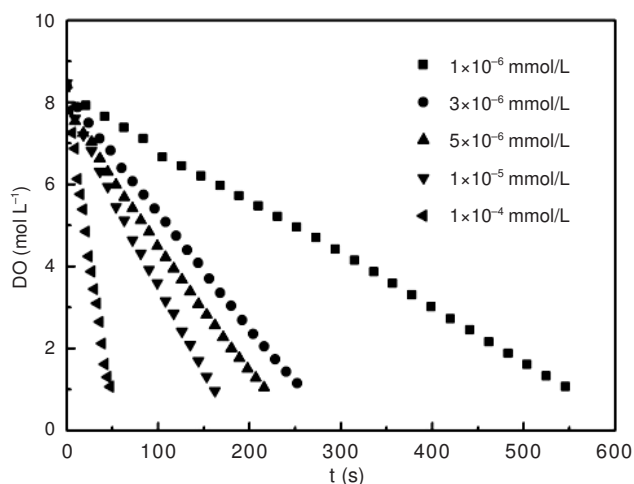
Fig. 10. Effect of Fe^{2+} concentration on the intrinsic oxidation rate [$C_{(NH_4)_2SO_3}$ = 1.5 mmol/L; T = 298.15 K]

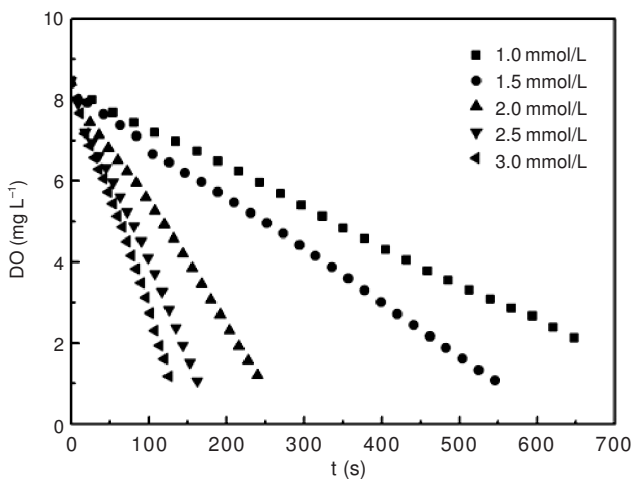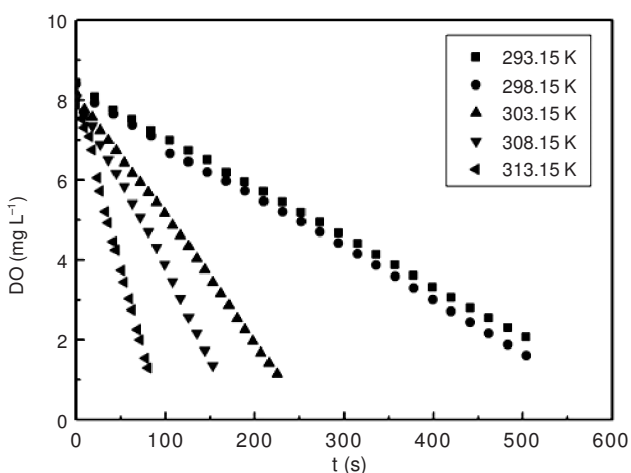Fig. 11. Effect of sulfite concentration on the intrinsic oxidation rate [$C_{Fe^{2+}}$ = 1×10⁻⁶ mmol/L; T = 298.15 K]

Fig. 12. Effect of temperature on the intrinsic oxidation rate [$C_{(NH_4)_2SO_3}$ = 1.5 mmol/L; $C_{Fe^{2+}}$ = 1 × 10⁻⁶ mmol/L]

× 10⁻⁴ mol/(L min), which is much lower than the calculated intrinsic reaction rate. Therefore, it is confirmed that the intrinsic reaction is not the controlling step.

Diffusion of oxygen: In the quiet bubbling area (Q ≤ 150 L/h), it was assumed: (1) the air forth bubbles were equal in size and showed little agglomeration during three rise process; (2) the oxygen concentration in the single air forth remained constant; (3) the pressure of the air forth remained constant during the rise process, since the height of reactor was relatively low, the pressure of the air forth was equal to the atmospheric pressure. The assumption mentioned above lead to:

$$Q = M\pi r_g^3 \tag{5}$$

$$r = Mr_M = \frac{Q}{\pi r_g^3} r_M \tag{6}$$

The mass transfer rate of oxygen is controlled by the liquid film mass transfer process and the diffusion rate of oxygen is obtained according to the double film theory:

$$r_M = K_L'(C_{O_2}^* - C_{O_2}) \tag{7}$$

Further, as the chemical reaction was rapid:

$$K_L' = \left[\frac{2}{m+1} D_{O_2} k (C_{O_2}^*)^{m-1} (C_{SO_3^{2-}})^n\right]^{1/2} \tag{8}$$

The concentration of dissolved oxygen in the solution was close to zero and the intrinsic reaction order of oxygen, m = zero and that of sulfite, n = 2. Therefore, the diffusion rate of oxygen can be written as:

$$r_M \left[\frac{2}{m+1} D_{O_2} k (C_{O_2}^*)^{m-1} \left(C_{SO_3^{2-}}\right)^n\right]^{1/2} \cdot \left(2D_{O_2} k C_{O_2}^* C_{SO_3^{2-}}^2\right)^{1/2} \tag{9}$$

$$r = \frac{Q}{\pi r_g^3} \left(2D_{O_2} K C_{O_2}^* C_{SO_3^{2-}}^2\right)^{1/2} \tag{10}$$

The catalytic effect of Fe^{2+} was regarded as magnification of the reaction coefficient k and was simplified as follows:

$$r = \frac{Q}{\pi r_g^3} \cdot \left(2D_{O_2} K C_{O_2}^* C_{SO_3^{2-}}^2 C_{Fe^{2+}}\right)^{1/2} \tag{11}$$

According to eqn. 11, it was concluded that the diffusion rate of oxygen was proportional to the air flow rate, the oxidation rate was first order with respect to sulfite and 0.5 order with respect to Fe^{2+} concentration. The reaction in this work was found to be first order with respect to ammonium sulfite and 0.4 order with respect to Fe^{2+}. The experimental results were generally consistent with eqn. 11.

Based on the discussions above, it can be considered that the diffusion of oxygen is the controlling step of the oxidation of ammonium sulfite.

Conclusion

Though the ammonia-based wet flue gas desulfurization process has been increasingly used on the industrial boiler in recent years, the catalytic oxidation of ammonium sulfite only gained very little attention. In this paper, the catalytic oxidation of ammonium sulfite with ferrous iron relevant to ammonia-based wet flue gas desulfurization plants, including the kinetics of sulfite oxidationunder related operating parameters and the mechanism of the oxidation, has been systematically studied.

Effects of five catalysts, including Co^{2+}, Mn^{2+}, Zn^{2+}, Fe^{2+} and Fe^{3+} are compared by intrinsic experiments at fixed concentration of ammonium sulfite and temperature. The results showed that Fe^{2+} is the most suitable one for flue gas desulfurization systems. Using stirred bubbling reactor, the kinetics of ammonium sulfite oxidation was studied by varying $(NH_4)_2SO_4$ concentration, $(NH_4)_2SO_3$ concentration, Fe^{2+} concentration, pH, air flow rate and temperature. The reaction was found to be first order with respect to sulfite, 0.4 order with respect to Fe^{2+} and the apparent activation energy for the oxidation was calculated to be 7.73 kJ/mol. The oxidation rate can be speeded up by increasing the ammonium sulfite concentration and Fe^{2+} concentration, raising the air flow and maintaining the pH value at 6, while the sulfate concentration and the temperature can also affect the oxidation rate.

The mechanism of the oxidation of ammonium sulfite was discussed, it was concluded that the oxidation was controlled by diffusion of oxygen. This finding will be beneficial for designing or optimizing the oxidation process in the ammonium-based flue gas desulfurization process.

Notation

$C_{Fe^{2+}}$ = Concentration of ferrous iron (mol/L)
$C_{(NH_4)_2SO_3}$ = Concentration of ammonium sulfite (mol/L)
$C_{(NH_4)_2SO_4}$ = Concentration of ammonium sulfate (mol/L)
C_{O_2} = Concentration of oxygen in the solution (mol/L)
$C^*_{O_2}$ = Equilibrium concentration of oxygen at the interface (mol/L)
$C_{SO_3^{2-}}$ = Concentration of sulfite (mol/L)
D_{O_2} = Diffusion coefficient of oxygen in the solution (m^2/s)
E_a = Apparent activation energy (kJ/mol)
k = The reaction rate constant
k_0 = Frequency factor
K_L' = Concentration of ferrous iron, m/s
M = Amount of forth in unit time
m = Reaction order of oxygen
n = Reaction order of sulfite
Q = Air flow (L/h)
R = Gas contant, 8.3145 J/(mol K)

r = The reaction rate, mol/(L min)
r_g = Radius of balls (m)
r_i = Intrinsic reaction rate, mol/(L s)
r_M = Diffusion rate of oxygen in single forth, mol/(L s)
T = Temperature (K)
t = Reaction time (s)

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