

Novel homogeneous catalyst system for the oxidation of concentrated ammonium sulfite

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Abstract

A homogeneous catalyst system made up of $[\text{Co}(\text{NH}_3)_6]^{2+}/\text{I}^-$ has been put forward to catalyze the oxidation of concentrated ammonium sulfite. The experiments were performed in a packed column with sulfite concentrations above 2.5 mol l^{-1} , temperature range $20\text{--}65^\circ\text{C}$, and oxygen partial pressure $0.052\text{--}0.21 \text{ atm}$. The experimental results indicate that the $\text{Co}(\text{NH}_3)_6^{2+}/\text{I}^-$ homogeneous catalyst system can obviously accelerate the concentrated ammonium sulfite oxidation rate. After 2 h reaction, the sulfite conversion is only 12.5% with no catalysts while 72.1% sulfite conversion can be obtained with $0.02 \text{ mol l}^{-1} \text{ Co}(\text{NH}_3)_6^{2+}$ and $0.005 \text{ mol l}^{-1} \text{ I}^-$ in the ammonium sulfite solution. The sulfite oxidation rate increases 284% as $\text{Co}(\text{NH}_3)_6^{2+}$ concentration increases from 0.01 to 0.02 mol l^{-1} . But there is little use increasing the $\text{Co}(\text{NH}_3)_6^{2+}$ concentration above 0.04 mol l^{-1} . The sulfite oxidation rate may increase 229% as the temperature increases from 20 to 65°C . Sulfite oxidation rate is independent of the initial sulfite concentration. Increasing the oxygen partial pressure can increase the sulfite conversion. The reaction order with respect to oxygen is 1.2 and sulfite is zero. The apparent activation energy determined is 23.5 kJ mol^{-1} .

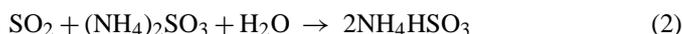
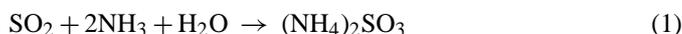
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Keywords: Ammonium sulfite; Catalysis; Kinetics; Oxidation; Cobalt

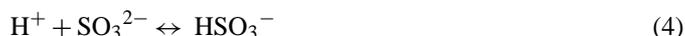
1. Introduction

Flue gases are sometimes scrubbed with aqueous ammonia to reduce their sulfur dioxide content. Ammonium sulfite thus formed can be oxidized to ammonium sulfate that is used as a fertilizer. Though ammonium sulfite may be used directly as a product, it may decompose into SO_2 again if it is used as a fertilizer or wasted water will discharge if used as a raw material for papermaking. Therefore, it is crucial to turn ammonium sulfite into ammonium sulfate efficiently and economically to enhance the commercial competitive power for ammonia desulfurization technique.

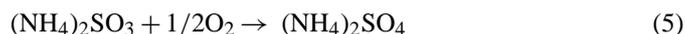
The following reactions may take place in ammonia desulfurization process:



The ionization equilibrium between sulfite and bisulfite is



Sulfite and bisulfite will be oxidized by oxygen as follows:



The oxidation rate is affected by sulfite concentration, oxygen partial pressure, sulfate concentration and pH values. The temperature and catalysts are also important factors determining the reaction rate.

Many scholars have studied both the homogeneous and heterogeneous liquid phase oxidation of sulfite because it is an ideal process to produce ammonium sulfate from ammonium sulfite directly.

The researches made in low sulfite ranges ($2 \times 10^{-3} \sim 0.092 \text{ mol l}^{-1}$) under homogeneous conditions showed [1,2] that the order for the oxidation of ammonium sulfite in sulfite was 1.5 and in oxygen was zero.

Mishra [3], Neelakantan [4] and Ahmad [5] have studied this reaction under heterogeneous conditions. Mishra found that the

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reaction was zero order with respect to sulfite and 1.5 order with respect to oxygen. Ahmad reported that the reaction was zero order with respect to sulfite above a critical sulfite concentration, second order below a critical sulfite concentration, and first order in oxygen. Gurkan [6] found that the reaction mechanism and consequently the order of the intrinsic rate of reaction were dependent on oxygen to sulfite ratio. All of their experimental results were obtained in low sulfite ranges (0.04–0.7 mol l⁻¹).

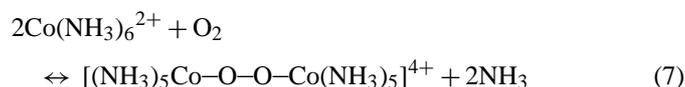
Mishra [3], Neelakantan [4] and Ahmad [5] have studied the catalysis of cobalt on the oxidation of ammonium sulfite. Bub [7,8] has systematically studied the oxidation of sodium sulfite catalyzed by cobalt, analyzed its catalytic mechanism and obtained its kinetic equation. Mishra found that in the ammonium sulfite solution, under aerobic condition, the stable species will be Co(NH₃)₆³⁺ ions. In the absence of ammonia, the species present should be some hydrated oxide of Co³⁺. This hydrated species of Co³⁺ may be more active as a catalyst as compared to Co(NH₃)₆³⁺ ions. With the result, in the presence of ammonia, the concentration of the active species is reduced and thereby lowering the rate of the oxidation of ammonium sulfite.

Zhuo [9] and Li [10] have studied the oxidation of concentrated ammonium sulfite under heterogeneous conditions. They reported that the oxidation rate of ammonium sulfite decreased as the sulfite concentration increased when the sulfite concentration was above 0.5 mol l⁻¹. The oxidation reaction should be carried out under low total salt concentration (sulfite and sulfate <1 mol l⁻¹). The catalysis of cobalt disappeared if the ammonium concentration was high enough to produce hexamminecobalt ions.

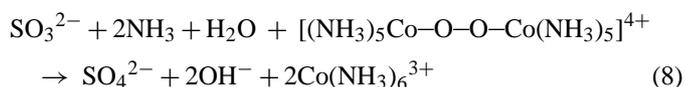
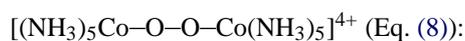
The authors [11] put forward a novel homogeneous catalyst system made up of [Co(NH₃)₆]²⁺ and iodide to achieve catalytic oxidation of sulfite in aqueous ammonia solution. Co(NH₃)₆²⁺ ions act as the catalyst and I⁻ ions act as the co-catalyst. UV irradiation enhances regeneration of Co(NH₃)₆²⁺ ions. Oxygen in the gas phase is the source of oxygen for dissolved oxygen that serves as oxidant. In this paper we report the study of such homogeneous catalysts on the oxidation of concentrated ammonium sulfite.

2. Theoretical

The hexamminecobalt(II) ion, Co(NH₃)₆²⁺, is oxygenated in aqueous ammonia, the dioxygen displacing one of the ammonia ligands. A brown binuclear complex, with bridging dioxygen, is formed; decrease of the oxygen pressure or increase of the ammonia concentration deoxygenates the complex [12,13]:

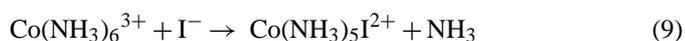


The bridging O–O group is considered a peroxide ion. The oxidizability of [Co(NH₃)₅Co–O–O–Co(NH₃)₅]⁴⁺ can be assumed to be equal to that of H₂O₂. Such process is called the activation of oxygen molecule which makes some processes not possible with free gaseous dioxygen carry out. Therefore, sulfite can be oxidized quickly to sulfate in aqueous solution by

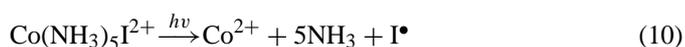


However, hexamminecobalt(II) may also be oxidized to hexamminecobalt(III) by oxygen. The hexamminecobalt(III) ion, Co(NH₃)₆³⁺, cannot be oxygenated in aqueous ammonia to form dioxygen complex. In other words, the hexamminecobalt(III) ion is unable to activate oxygen molecules. The oxidizing ability of the hexamminecobalt solution will diminish as the reaction proceeds.

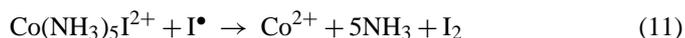
In order to maintain the capability of activating oxygen molecule, hexamminecobalt(III) ions must be deoxidized to hexamminecobalt(II) ions once again. One measure can be considered to take is adding iodide anions into the solution. Iodide may displace one ammonia molecule from the hexamminecobalt(III) ions (Eq. (9)):



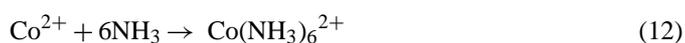
Ultraviolet light irradiating the Co(NH₃)₅I²⁺ aqueous solution may lead to photo oxidation–reduction decomposition with conversion of Co(III) to Co(II) (Eq. (10)) [14]:



The iodine radicals generated in reaction (10) may react with Co(NH₃)₅I²⁺ as follows:



The regeneration of cobalt(II) is completed by reactions (10) and (11). Thus, hexamminecobalt(II) ions are regenerated by the coordination of Co²⁺ with ammonia in aqueous solution (Eq. (12)):



Iodine generated in reaction (11) ought to be reduced to iodide once again so as to keep the continual regeneration of cobalt(II). By chance, sulfite in the aqueous solution can reduce iodine to iodide (Eq. (13)):



The net reaction can be written as



According to the discussion above, homogeneous catalytic oxidation of ammonium sulfite may be achieved by adding cobalt(II) salt and iodide salt into aqueous ammonium sulfite solution and irradiating the solution with ultraviolet beam to regenerate cobalt(II) cations during the reaction. The process consists of the recycles of cobalt(II) and iodide. The oxidant in the process may be the oxygen coexisting in the flue gas. The hexamminecobalt and iodide that are not consumed in the net reaction can be considered as homogeneous catalysts. The ammonia desulfurization method can be improved by such

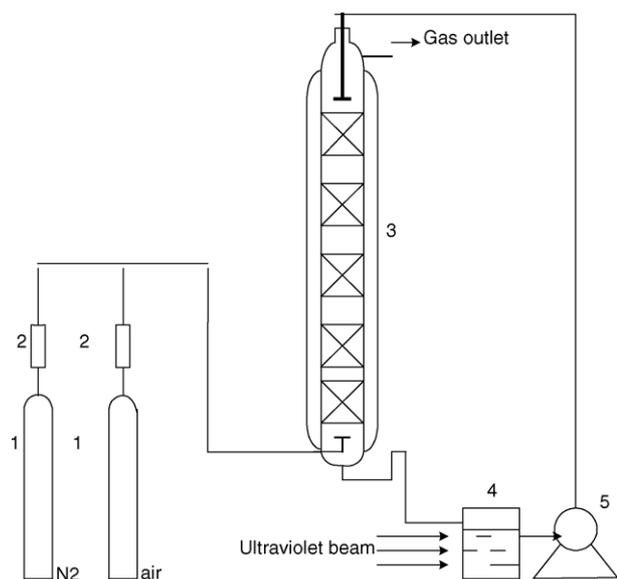


Fig. 1. Flowchart of experiments performed in a packed column: (1) cylinder, (2) massmeter, (3) packed tower, (4) circulation tanker, (5) pump.

method to leave out the oxidizing section, simplify the technique, reduce its energy consumption and enhance its economic competitiveness.

3. Experimental

The experiments were carried out in a column (18 mm i.d., 1000 mm long) packed with 2 mm glass ring packing. The schematic diagram of the experiments is shown in Fig. 1. The column used had a water jacket through which water from a thermostatic bath was circulated to maintain the desired temperature. The experiments were carried out at atmospheric pressure. A 360 nm ultraviolet beam irradiated the circulation glass tank to catalyze the regeneration of cobalt(II). Before performing an experiment, the system was flushed with the O₂–N₂ mixture of desired composition. A 500 ml of the reactant solution was admitted into the circulation glass tank. The packed column was operated with a continuous feed of influent gas, at 0.3 l min⁻¹, at the bottom and a continuous feed of ammonium sulfite solution, at a superficial flow rate of 5 m³ m⁻² h⁻¹ (25 ml min⁻¹), over the top. Samples were withdrawn periodically to analyze the change of sulfite concentration. The samples were diluted with oxygen free distilled water (purged with nitrogen). The sulfite conversion and oxidation rate was determined from the change of sulfite concentration in the duration of the experimental run.

It is known that even minute quantity of impurity, especially metal ions, affects the oxidation rate of sulfite solution. Thus, special precautions were taken to prevent the presence of impurities. All the chemicals used were of analytical grade. Ammonium sulfite solutions were newly prepared by passing SO₂ gas through aqueous ammonia and diluted to a specific concentration. CoSO₄ and KI were directly put into the ammonium sulfite solutions to act as homogeneous catalysts.

A Dionex DX 500 ion chromatography system was used to determine sulfite concentration. The IC system was equipped

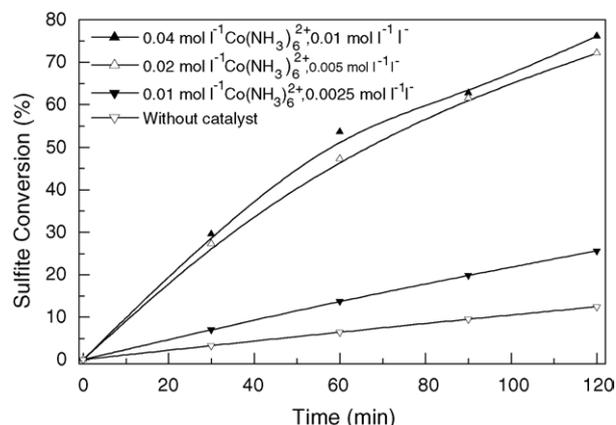


Fig. 2. Effect of catalysts on sulfite conversion in a packed column (sulfite = 2.5 mol l⁻¹, 21% O₂, 50 °C).

with a GP40 gradient pump and an AD20 Absorbance detector. A Dionex IonPac AS4A-SC column (4 mm × 50 mm) was used to separate ions which were detected by the AD20 Absorbance detector. Sodium carbonate/bicarbonate (0.0018/0.0017 mol l⁻¹) eluant with an isocratic flow rate of 2.0 ml min⁻¹ was used. The sulfite calibration curve was obtained using standard sodium sulfite solutions ranged from 4.310 × 10⁻⁵ to 1.902 × 10⁻³ mol l⁻¹. Least-squares fits to the data yield Eq. (15) with a correlation coefficient (*r*²) 0.9998. An eight-sample relative standard deviation of sulfite measurement was determined to be 0.9%:

$$H = 0.9576 \times 10^3 + 0.5434 \times 10^8 C \quad (15)$$

where *H* stands for peak height and *C* stands for sulfite concentration.

4. Results and discussion

4.1. Effect of catalysts on sulfite oxidation

Fig. 2 shows the effect of Co(NH₃)₆²⁺/I⁻ catalysts on the conversion of sulfite. It can be concluded that Co(NH₃)₆²⁺/I⁻ ions enhance the conversion of sulfite remarkably. After 2 h, the sulfite conversion is only 12.5% with no catalysts while 25.6% with 0.01 mol l⁻¹ Co(NH₃)₆²⁺ and 0.0025 mol l⁻¹ I⁻, 72.1% with 0.02 mol l⁻¹ Co(NH₃)₆²⁺ and 0.005 mol l⁻¹ I⁻ in the ammonium sulfite solution separately. The conversion of sulfite increases as the Co(NH₃)₆²⁺/I⁻ concentration increases.

Fig. 3 manifests that increasing the complex catalysts' concentrations may speed up the sulfite oxidation rate, especially when their concentrations are low. For example, the sulfite oxidation rate increases 284% (from 0.00594 to 0.0228 mol l⁻¹ min⁻¹) as Co(NH₃)₆²⁺ concentration increases from 0.01 to 0.02 mol l⁻¹. But the sulfite oxidation rate increases only 8.1% as the Co(NH₃)₆²⁺ concentration increases from 0.02 to 0.04 mol l⁻¹.

As discussed previously, the homogeneous Co(NH₃)₆²⁺/I⁻ catalysts can accelerate the concentrated sulfite oxidation rate because Co(NH₃)₆²⁺ is able to activate oxygen molecule. Due to the different catalytic mechanism, contrary to the sit-

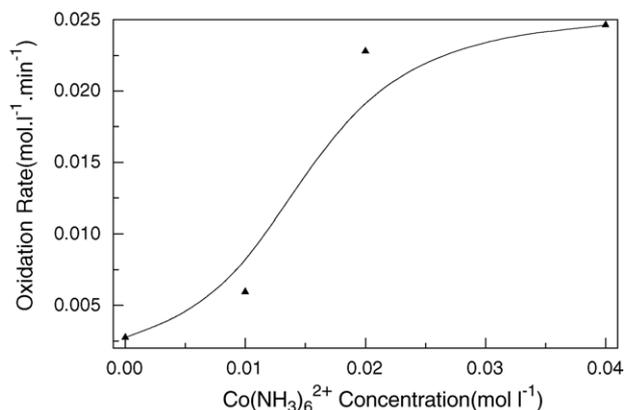


Fig. 3. Effect of catalysts on sulfite oxidation rate in a packed column (sulfite = 2.5 mol l^{-1} , 21% O_2 , 50°C).

uation catalyzed by cobalt ions, ammonia is indispensable to the $\text{Co}(\text{NH}_3)_6^{2+}/\text{I}^-$ catalytic system so as to stabilize the $\text{Co}(\text{NH}_3)_6^{2+}$ ions. Increasing the $\text{Co}(\text{NH}_3)_6^{2+}/\text{I}^-$ concentration may speed up the sulfite oxidation if the $\text{Co}(\text{NH}_3)_6^{2+}/\text{I}^-$ concentration is below a critical value. According to the experimental results, it is insignificant to increase the $\text{Co}(\text{NH}_3)_6^{2+}$ concentration further above 0.04 mol l^{-1} under the experimental conditions. The reason is that $\text{Co}(\text{NH}_3)_6^{2+}$ ions only activate oxygen molecules which makes some processes not possible with free gaseous dioxygen carry out but do not enhance oxygen solubility in aqueous solution. Increasing the $\text{Co}(\text{NH}_3)_6^{2+}$ concentration further above 0.04 mol l^{-1} may not increase the $[(\text{NH}_3)_5\text{Co}-\text{O}-\text{O}-\text{Co}(\text{NH}_3)_5]^{4+}$ concentration in the aqueous solution further because of the small Henry's constant for O_2 . As a result, the sulfite oxidation rate can not increase further.

4.2. Effect of temperature on the sulfite oxidation

Experiments are performed at four different temperatures in the range of $20\text{--}65^\circ\text{C}$ for a fixed sulfite concentration of 2.5 mol l^{-1} . The experimental results are depicted in Figs. 4 and 5.

Fig. 4 shows the effect of temperature on the sulfite conversion. It can be concluded that the sulfite conversion increases

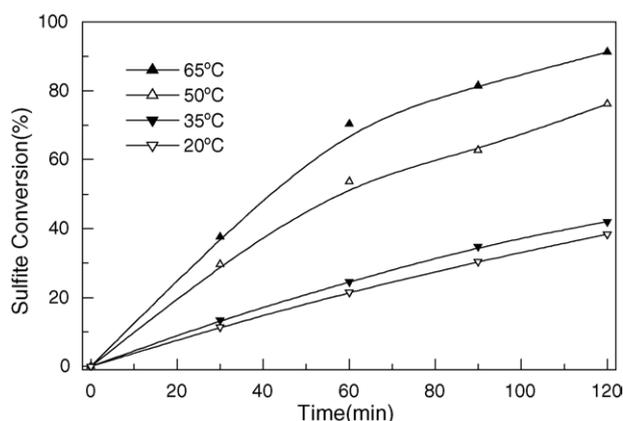


Fig. 4. Effect of temperature on sulfite conversion in a packed column (sulfite = 2.5 mol l^{-1} , $\text{Co}(\text{NH}_3)_6^{2+} = 0.04 \text{ mol l}^{-1}$, $\text{I}^- = 0.01 \text{ mol l}^{-1}$, 21% O_2).

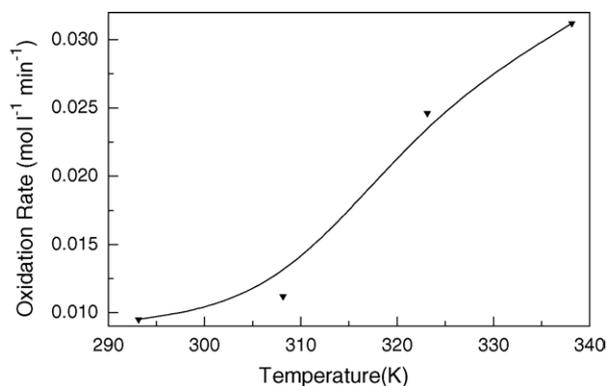


Fig. 5. Effect of temperature on sulfite oxidation rate in a packed column (sulfite = 2.5 mol l^{-1} , $\text{Co}(\text{NH}_3)_6^{2+} = 0.04 \text{ mol l}^{-1}$, $\text{I}^- = 0.01 \text{ mol l}^{-1}$, 21% O_2).

as the temperature increases. The sulfite conversion increases from 38.4% to 91.2% when the temperature increases from 20 to 65°C after the reaction has proceeded two hours. Fig. 5 demonstrates that increasing the temperature can speed up the reaction rate greatly. The sulfite oxidation rate may increase 229% (from 0.00949 to $0.0312 \text{ mol l}^{-1} \text{ min}^{-1}$) as the temperature increases from 20 to 65°C . It can be concluded that a high temperature is of benefit to the sulfite oxidation in this catalytic system.

4.3. Effect of oxygen partial pressure on the sulfite oxidation

The experiments are carried out at 50°C with different oxygen partial pressure in the gas phase for a fixed sulfite concentration of 2.5 mol l^{-1} . The experimental results are depicted in Figs. 6 and 7.

It can be seen from Fig. 6 that increasing the oxygen partial pressure can increase the sulfite conversion. After 2 h, the sulfite conversions are 20.2% with 5.2% oxygen, 39.4% with 10.4% oxygen, 70.7% with 15.6% oxygen and 76.1% with 21% oxygen in the gas phase, respectively. Fig. 7 indicates that the sulfite oxidation rate varies almost linearly with oxygen partial pressure. The sulfite oxidation rate increases 440% (from 4.57×10^{-3} to $2.46 \times 10^{-2} \text{ mol l}^{-1} \text{ min}^{-1}$) when the oxygen partial pressure increases from 5.2% to 21%. Increasing the partial pressure of

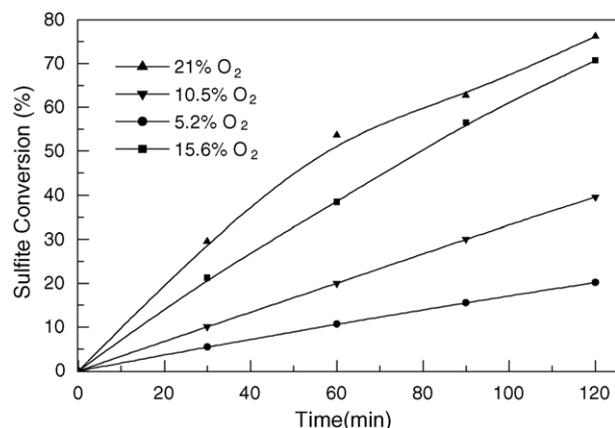


Fig. 6. Effect of oxygen partial pressure on sulfite conversion in a packed column (sulfite = 2.5 mol l^{-1} , $\text{Co}(\text{NH}_3)_6^{2+} = 0.04 \text{ mol l}^{-1}$, $\text{I}^- = 0.01 \text{ mol l}^{-1}$, 50°C).

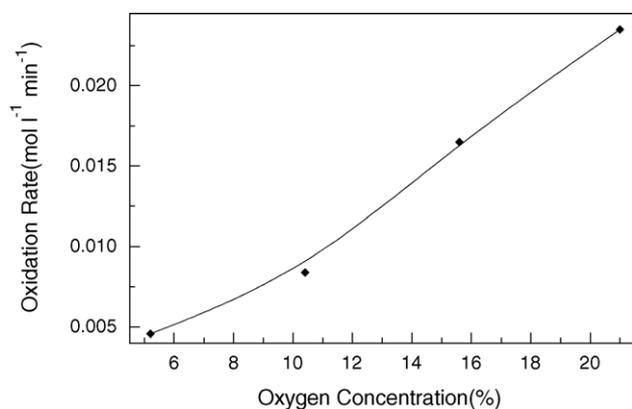


Fig. 7. Effect of oxygen partial pressure on sulfite oxidation rate in a packed column (sulfite = 2.5 mol l^{-1} , $\text{Co}(\text{NH}_3)_6^{2+} = 0.04 \text{ mol l}^{-1}$, $\text{I}^- = 0.01 \text{ mol l}^{-1}$, 50°C).

oxygen in the gas phase, according to the Henry law, the oxygen dissolved in the aqueous solution will increase. As a result, the sulfite oxidation may be speeded up.

4.4. Effect of sulfite concentration

The sulfite conversions with different initial sulfite concentrations at 50°C are shown in Fig. 8. As reported by Zhou et al. [9], the sulfite oxidation rate decreases with the increase of sulfite concentration when the concentration is above its critical concentration about 0.5 mol l^{-1} . However, our experimental results indicate that the sulfite conversion with an initial sulfite concentration 2.5 mol l^{-1} is almost equal to those with initial sulfite concentrations of 3.2 and 1.9 mol l^{-1} . Thus, it can be concluded that the sulfite oxidation rate is independent of the initial sulfite concentration in this homogeneous catalytic process.

4.5. Kinetic equation

According to the experimental results described above, an apparent kinetic equation can be given as follow:

$$R = kp_{\text{O}_2}^b \quad (16)$$

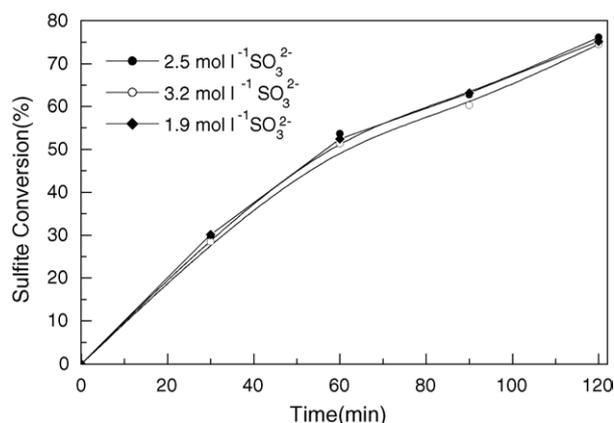


Fig. 8. Effect of sulfite concentration on sulfite conversion in a packed column (oxygen = 21%, $\text{Co}(\text{NH}_3)_6^{2+} = 0.04 \text{ mol l}^{-1}$, $\text{I}^- = 0.01 \text{ mol l}^{-1}$, 50°C).

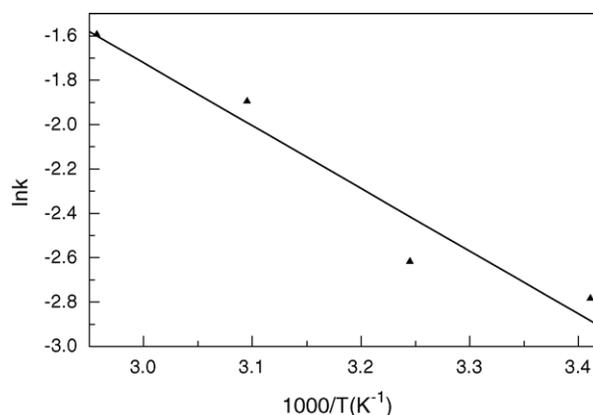


Fig. 9. Plot of $\ln k$ vs. $1/T$.

b is obtained as 1.2 by linear fitting the experimental data shown in Fig. 7 and the sulfite oxidation rate constant k is $0.144 \text{ l}^{-1} \text{ min}^{-1} \text{ atm}^{-1.2}$ at 50°C (correlation coefficient = 0.988). In other words, in this homogeneous catalytic oxidation process, the reaction order is 1.2 order with respect to oxygen.

According to Eq. (16), k at other temperatures can also be calculated from the data in Fig. 5 as: $0.0617 \text{ mol l}^{-1} \text{ min}^{-1} \text{ atm}^{-1.2}$ at 20°C , $0.0729 \text{ mol l}^{-1} \text{ min}^{-1} \text{ atm}^{-1.2}$ at 35°C , $0.203 \text{ mol l}^{-1} \text{ min}^{-1} \text{ atm}^{-1.2}$ at 65°C .

The logarithm of sulfite oxidation rate constants is plotted with the increase of absolute temperature at temperatures of 20, 35, 50 and 65°C (Fig. 9). The apparent activation energy for the overall sulfite oxidation is calculated to be 23.5 kJ mol^{-1} with a preexponential factor of $8.61 \times 10^2 \text{ mol l}^{-1} \text{ min}^{-1} \text{ atm}^{-1.2}$. This value is lower than the previously reported activation energy for sulfite heterogeneous oxidation. The reason could be that the $\text{Co}(\text{NH}_3)_6^{2+}/\text{I}^-$ homogeneous catalysts reduce the apparent activation energy greatly.

5. Conclusion

An innovative catalyst system made up of $\text{Co}(\text{NH}_3)_6^{2+}/\text{I}^-$ has been developed to catalyze the concentrated ammonium sulfite oxidation. $\text{Co}(\text{NH}_3)_6^{2+}$ ions act as the catalyst and I^- ions act as the co-catalyst. UV irradiation enhances regeneration of $\text{Co}(\text{NH}_3)_6^{2+}$ ions. Oxygen in the gas phase is the source of oxygen for dissolved oxygen that serves as oxidant.

The experiments show that the $\text{Co}(\text{NH}_3)_6^{2+}/\text{I}^-$ homogeneous catalyst system can obviously accelerate the concentrated ammonium sulfite oxidation. Increasing the $\text{Co}(\text{NH}_3)_6^{2+}$ concentration can increase the sulfite oxidation rate. But there is little use increasing the $\text{Co}(\text{NH}_3)_6^{2+}$ concentration further above 0.04 mol l^{-1} under the experimental condition.

The sulfite oxidation rate can be speeded up by increasing the oxygen concentration in gas and (or) raising the reaction temperature. The sulfite oxidation rate is independent of sulfite concentration.

Though the study on the homogeneous catalytic oxidation of ammonium sulfite under the condition of industrial importance has been performed systematically and some useful results have

been obtained, it is imperative to make further studies into such process.

Acknowledgements

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