

Kinetics of gas–liquid reaction between NO and $\text{Co}(\text{NH}_3)_6^{2+}$

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Abstract

Wet ammonia desulphurization process can be retrofitted for combined removal of SO_2 and NO from the flue gas by adding soluble cobalt(II) salts into the aqueous ammonia solutions. The $\text{Co}(\text{NH}_3)_6^{2+}$ formed by ammonia binding with Co^{2+} is the active constituent of scrubbing NO from the flue gas streams. A stirred vessel with a plane gas–liquid interface was used to measure the chemical absorption rates of nitric oxide into the $\text{Co}(\text{NH}_3)_6^{2+}$ solution under anaerobic and aerobic conditions separately. The experiments manifest that the nitric oxide absorption reaction can be regarded as instantaneous when nitric oxide concentration levels are parts per million ranges. The gas–liquid reaction becomes gas film controlling as $\text{Co}(\text{NH}_3)_6^{2+}$ concentration exceeds 0.02 mol/l. The NO absorption rate is proportional to the nitric oxide inlet concentration. Oxygen in the gas phase is favorable to the absorption of nitric oxide. But it is of little significance to increase the oxygen concentration above 5.2%. The NO absorption rate decreases with temperature. The kinetic equation of NO absorption into the $\text{Co}(\text{NH}_3)_6^{2+}$ solution under aerobic condition can be written as

$$N_{\text{NO}} = \frac{K_{\text{NO,G}} k_4 K_1 \left(p_{\text{NO}} + \gamma C_{\text{Co}(\text{NH}_3)_6^{2+},\text{L}} \right) C_{\text{Co}(\text{NH}_3)_6^{2+},\text{L}}^2 p_{\text{O}_2}}{k_{-3} + k_4 K_1 C_{\text{Co}(\text{NH}_3)_6^{2+},\text{L}}^2 p_{\text{O}_2}}$$

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1. Introduction

The role of NO_x and SO_2 pollutants in acid-rain formation and the destruction of lakes and forest ecosystems have been established. The removal of these contaminants to comply with environmental emission standard is of imperative necessity. The wet processes have certain economical advantages in combined NO_x/SO_2 elimination. The development of efficient processes for simultaneous SO_2 and NO_x removal from power-plant flue gases is particularly important because fossil–fuel–fired steam boilers represent a major source of sulphur and nitrogen oxide emissions. Nitric oxide is 90–95% of the NO_x present in typical flue

gas streams [1]. But existing wet flue gas desulphurization (FGD) scrubbers in power plants are incapable of eliminating NO from the flue gas because of its low solubility in water. Several methods have been developed to enhance NO absorption, including the use of oxidants to oxidize NO to the more soluble NO_2 [2–4] and the addition of various iron(II) chelates to bind and activate NO [5–7]. So far, none of these methods have been put into commercial application.

The process using an ammonia scrubber to recover sulfur dioxide from the flue gas has been developed and put into commercial application. The authors put forward a novel technique for the simultaneous elimination of NO and SO_2 from the flue gas by adding soluble cobalt(II) salts into the aqueous ammonia solution [8–10]. The hexamminecobalt(II) formed by cobalt(II) binding with ammonia

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Nomenclature

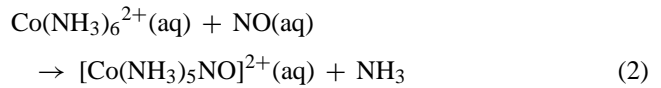
C_{NO}	NO concentration in gas phase (mol/m ³)
$C_{\text{Co(NH}_3)_6^{2+},\text{L}}$	$\text{Co(NH}_3)_6^{2+}$ concentration in bulk liquid (mol/l)
$C_{\text{Co(NH}_3)_6^{2+},\text{C}}$	critical concentration of $\text{Co(NH}_3)_6^{2+}$ (mol/l)
$C_{[\text{Co(NH}_3)_5\text{NO}]^{2+}}$	$[\text{Co(NH}_3)_5\text{NO}]^{2+}$ concentration (mol/l)
C_{O_2}	oxygen concentration (mol%)
C_{D}	$[(\text{NH}_3)_5\text{Co-O-O-Co(NH}_3)_5]^{4+}$ concentration (mol/l)
D	$[(\text{NH}_3)_5\text{Co-O-O-Co(NH}_3)_5]^{4+}$
$D_{\text{Co(NH}_3)_6^{2+},\text{L}}$	diffusivity of $\text{Co(NH}_3)_6^{2+}$ in liquid (m ² /s)
$D_{\text{NO,L}}$	diffusivity of NO in liquid (m ² /s)
H_{NO}	Henry law constant of NO in water (Pa m ³ /kmol)
$k_{\text{NO,G}}$	mass-transfer coefficient for NO in gas phase (mol/(m ² s Pa))
$K_{\text{NO,G}}$	overall mass-transfer coefficient for NO in gas phase (mol/(m ² s Pa))
k_{-3}	rate constant for reverse reaction (3) (s ⁻¹)
K_1	equilibrium constant for reaction (3) (mol l ⁻¹ Pa ⁻¹)
k_4	rate constant for reaction (4) (s ⁻¹ l mol ⁻¹)
$k_{\text{NO,L}}$	mass-transfer coefficient for NO in liquid phase (mol/(m ² s))
n_{NO}	NO molar number
N_{D}	rate of $[(\text{NH}_3)_5\text{Co-O-O-Co(NH}_3)_5]^{4+}$ reaction (mol/(m ² s))
N_{NO}	rate of NO absorption (mol/(m ² s))
P	total pressure (Pa)
p_1	partial pressure of inerts (Pa)
p_{NO}	NO partial pressure (Pa)
p_{O_2}	oxygen partial pressure (Pa)
R	gas constant (8.314 kJ/(kmol K))
S	interfacial area (m ²)
T	absolute temperature (K)
v_{G}	gas volume rate (m ³ /s)

Subscripts

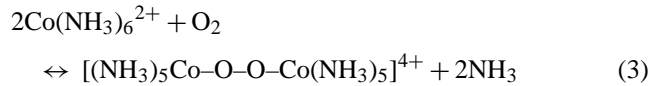
in	inlet of the gas stream
out	outlet of the gas stream

can not only coordinate nitric oxide but also activate oxygen molecules in aqueous ammonia solution. The oxidant is the oxygen coexisting in the flue gas. Therefore, NO can be absorbed and oxidized simultaneously in the hexaminecobalt(II) solution. The mechanism of NO absorption into the hexaminecobalt(II) solution can be expressed as follows:

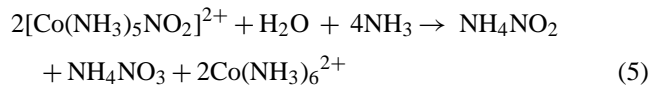
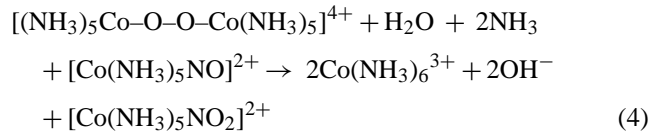
Nitric oxide dissolves into aqueous solution by reacting with $\text{Co(NH}_3)_6^{2+}$:



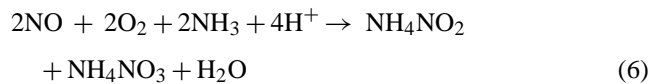
The activation of oxygen in $\text{Co(NH}_3)_6^{2+}$ solution [11,12]:



Nitric oxide is turned into NO_2^- and NO_3^- :



The net reaction can be written as follow:



According to the discussion above, the oxidation and absorption of NO can be realized simultaneously in the $\text{Co(NH}_3)_6^{2+}$ solution.

The reaction between NO and $\text{Co(NH}_3)_6^{2+}$ is a heterogeneous reaction. The relation between the reactions and mass transfer is very complicated. It is imperative to investigate such relation for the scale-up of this technique and the design of industrial equipment. A study on the kinetics of NO absorption into $\text{Co(NH}_3)_6^{2+}$ solution is reported in this paper.

2. Experimental section

The experiments were conducted in a stirred cell (as shown in Fig. 1) that has a water jacket through which water was circulated from a thermostat to maintain the desired temperature. Three turbine impellers are mounted on the same stirring rod. The upper and the bottom one provide, respectively, the mixing in the gas phase and the stirring in the liquid phase, while the middle one is used to sweep the interface between gas phase and liquid phase. The middle stirred baffle was floating on the solution. The experiments were performed at a stirred speed of 260 rpm to minimize the resistance of mass transfer in the liquid. The gas-liquid interfacial areas were changed by using a stirred cell with cross-section area of 38 cm² to substitute a stirred cell with cross-section area of 28 cm². The absorption was carried out at atmospheric pressure. The gas phase consisted of NO in nitrogen. Two percent

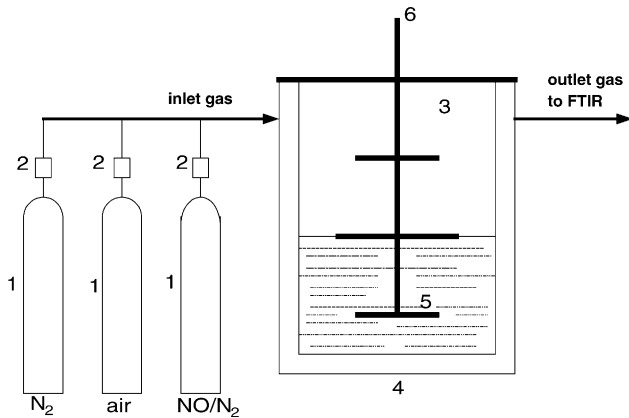


Fig. 1. Stirred cell reactor used for absorption experiments. 1: Cylinder; 2: massmeter; 3: stirred cell; 4: water jacket; 5: stirred baffle; 6: stirrer rod.

NO in nitrogen was supplied from a cylinder and was further diluted with N₂ to the desired concentrations before being fed to the stirred cell. The feed concentration of NO ranged from 150 ppm to 900 ppm. The continuous gas flow was maintained at about 0.2–0.4 L/min. The solution was prepared by adding Co(C₂H₅O₂)₂·4H₂O into the aqueous ammonia solution. The chemicals of analytical reagent grade were used throughout the study.

The quantitative analysis of gas compositions was achieved by an on-line Fourier transform infrared spectrometer (Nicolet E.S.P. 460 FT-IR) equipped with a gas cell and a quantitative package, named Quant Pad. The inlet and outlet gases were directly introduced into the gas cell of the FTIR, with pipes insulated through the regulated electric coils to obtain the transient N₂O, NO, NO₂, and H₂O concentrations in both the inlet and outlet gases, as well as the transient NO conversion. This set-up is conveniently operated to monitor the nitric oxide removal efficiency.

The absorption rate can be calculated as follow [13]:

$$-N_{\text{NO}} = \frac{v_{\text{G}} P}{R T S} \left[\left(\frac{p_{\text{NO}}}{p_{\text{I}}} \right)_{\text{in}} - \left(\frac{p_{\text{NO}}}{p_{\text{I}}} \right)_{\text{out}} \right] \quad (7)$$

2.1. Effect of liquid volume on NO absorption rate

The experiments are performed at 50 °C. The inlet NO concentration is 400 ppm. The gas–liquid interfacial area is 28 cm². Co(NH₃)₆²⁺ concentration is 0.04 mol/l. The reaction rates vary from 0.823 × 10⁻⁵ mol/(m² s) to 0.853 × 10⁻⁵ mol/(m² s) as liquid volumes in the stirred cell increase from 160 ml to 265 ml, which indicates that the nitric oxide absorption rate is almost independent of the liquid volume.

The experiments are also carried out at the same conditions as above, but with 5.2% oxygen present in the gas phase. The reaction rates vary from 1.462 × 10⁻⁵ mol/(m² s) to 1.513 × 10⁻⁵ mol/(m² s) as liquid volumes in the stirred cell increase from 160 ml to 265 ml. It can also be concluded that the nitric oxide absorption rate is independent of the liquid volume under aerobic condition.

2.1.1. Effect of gas–liquid interfacial area on NO absorption rate

The experiments are performed at 50 °C. The inlet NO concentration is 430 ppm. The liquid in the stirred cell is 265 ml, 0.04 mol/l Co(NH₃)₆²⁺ solution. The reaction rates vary from 8.530 × 10⁻⁶ mol/(m³ s) to 11.91 × 10⁻⁶ mol/(m³ s) as the gas–liquid interfacial areas increase from 28 cm² to 38 cm². A conclusion can be drawn that the absorption rate is proportional to the gas–liquid interfacial area.

The experiments were also done under the same conditions as above, but with 5.2% oxygen present in the gas phase. The reaction rates vary from 1.513 × 10⁻⁴ mol/(m³ s) to 2.050 × 10⁻⁴ mol/(m³ s) as the gas–liquid interfacial areas increase from 28 cm² to 38 cm², which manifests that the absorption rate is proportional to the gas–liquid interfacial area under aerobic condition.

According to the principle proposed by Levenspiel and Godfrey [13], the gas–liquid reaction can be regarded as an irreversible instantaneous reaction if its absorption rate is proportional to the gas–liquid interfacial area and independent of the liquid volume. A conclusion can be drawn from the experimental results that the NO absorption into Co(NH₃)₆²⁺ solution can be regarded as irreversible instantaneous reaction when the NO inlet concentration is ppm ranges and the Co(NH₃)₆²⁺ concentration is about 0.04 mol/l. The reaction may be finished within the liquid film.

3. Theoretical

3.1. Nitric oxide reacts with Co(NH₃)₆²⁺ under anaerobic condition

Under anaerobic condition, the reactions between nitric oxide and Co(NH₃)₆²⁺ are reaction (1) followed with reaction (2). As discussed above, the reaction between nitric oxide and Co(NH₃)₆²⁺ is instantaneous, the corresponding kinetic equation is independent of reaction rate and can be given by

$$N_{\text{NO}} = -\frac{1}{S} \frac{dn_{\text{NO}}}{dt} = K_{\text{NO,G}} (p_{\text{NO}} + \gamma C_{\text{Co(NH}_3)_6^{2+},\text{L}}) \quad (8)$$

with

$$\gamma = \frac{1}{H_{\text{NO}}} \frac{D_{\text{Co(NH}_3)_6^{2+},\text{L}}}{D_{\text{NO,L}}} \quad (9)$$

$$K_{\text{NO,G}} = \frac{1}{\left(\frac{1}{H_{\text{NO}} k_{\text{NO,L}}} + \frac{1}{k_{\text{NO,G}}} \right)} \quad (10)$$

The critical concentration is expressed as follow

$$C_{\text{Co(NH}_3)_6^{2+},\text{C}} = \frac{D_{\text{NO,L}}}{D_{\text{Co(NH}_3)_6^{2+},\text{L}}} \frac{k_{\text{NO,G}}}{k_{\text{NO,L}}} p_{\text{NO}} \quad (11)$$

when $C_{\text{Co(NH}_3)_6^{2+},\text{L}} \geq C_{\text{Co(NH}_3)_6^{2+},\text{C}}$

$$N_{\text{NO}} = k_{\text{NO,G}} p_{\text{NO}}. \quad (12)$$

It can be concluded that the NO absorption rate may be increased by increasing Co(NH₃)₆²⁺ concentration when

$\text{Co}(\text{NH}_3)_6^{2+}$ concentration is very low. But, it is unnecessary to increase $\text{Co}(\text{NH}_3)_6^{2+}$ concentration further above its critical concentration because NO absorption has become gas film controlling. The absorption rate can not be increased further with $\text{Co}(\text{NH}_3)_6^{2+}$ concentration.

3.2. Nitric oxide reacts with $\text{Co}(\text{NH}_3)_6^{2+}$ under aerobic condition

When there is oxygen in the flue gas, reactions (2)–(4) take place successively. The reaction (3) can be assumed to reach equilibrium quickly. Because NH_3 is much excessive and its concentration is nearly constant, Eq. (13) can be obtained

$$C_D = K_1 C_{\text{Co}(\text{NH}_3)_6^{2+},L}^2 P_{\text{O}_2} \quad (13)$$

where D stands for $[(\text{NH}_3)_5\text{Co}-\text{O}-\text{O}-\text{Co}(\text{NH}_3)_5]^{4+}$ and K_1 stands for the equilibrium constant of reaction (3).

According to the steady state assumption, the concentration of $[\text{Co}(\text{NH}_3)_5\text{NO}]^{2+}$ is unchangeable, Eq. (14) can be obtained from reactions (2) and (3)

$$\begin{aligned} N_D = K_{\text{NO,G}} (p_{\text{NO}} + \gamma C_{\text{Co}(\text{NH}_3)_6^{2+},L}) \\ - k_{-3} C_{[\text{Co}(\text{NH}_3)_5\text{NO}]^{2+}} - k_4 C_D C_{[\text{Co}(\text{NH}_3)_5\text{NO}]^{2+}} = 0 \end{aligned} \quad (14)$$

Eq. (15) can be obtained from Eq. (14):

$$\begin{aligned} C_{[\text{Co}(\text{NH}_3)_5\text{NO}]^{2+}} &= \frac{K_{\text{NO,G}} (p_{\text{NO}} + \gamma C_{\text{Co}(\text{NH}_3)_6^{2+},L})}{k_{-3} + k_4 C_D} \\ &= \frac{K_{\text{NO,G}} (p_{\text{NO}} + \gamma C_{\text{Co}(\text{NH}_3)_6^{2+},L})}{k_{-3} + k_4 K_1 C_{\text{Co}(\text{NH}_3)_6^{2+},L}^2 P_{\text{O}_2}} \end{aligned} \quad (15)$$

According to reaction (2), NO absorption rate can be expressed as Eq. (16)

$$N_{\text{NO}} = K_{\text{NO,G}} (p_{\text{NO}} + \gamma C_{\text{Co}(\text{NH}_3)_6^{2+},L}) - k_{-3} C_{[\text{Co}(\text{NH}_3)_5\text{NO}]^{2+}} = \frac{K_{\text{NO,G}} k_4 K_1 (p_{\text{NO}} + \gamma C_{\text{Co}(\text{NH}_3)_6^{2+},L}) C_{\text{Co}(\text{NH}_3)_6^{2+},L}^2 P_{\text{O}_2}}{k_{-3} + k_4 K_1 C_{\text{Co}(\text{NH}_3)_6^{2+},L}^2 P_{\text{O}_2}} \quad (16)$$

In terms of Eq. (16), if $k_{-3} \ll k_4 K_1 C_{\text{Co}(\text{NH}_3)_6^{2+},L}^2 P_{\text{O}_2}$, NO absorption rate is independent of oxygen partial pressure. If $k_{-3} \gg k_4 K_1 C_{\text{Co}(\text{NH}_3)_6^{2+},L}^2 P_{\text{O}_2}$, NO absorption rate is proportional to oxygen partial pressure.

4. Results and discussion

4.1. Effect of $\text{Co}(\text{NH}_3)_6^{2+}$ concentration on NO absorption rate

Fig. 2 shows the effect of $\text{Co}(\text{NH}_3)_6^{2+}$ concentration on NO absorption under anaerobic condition. It can be

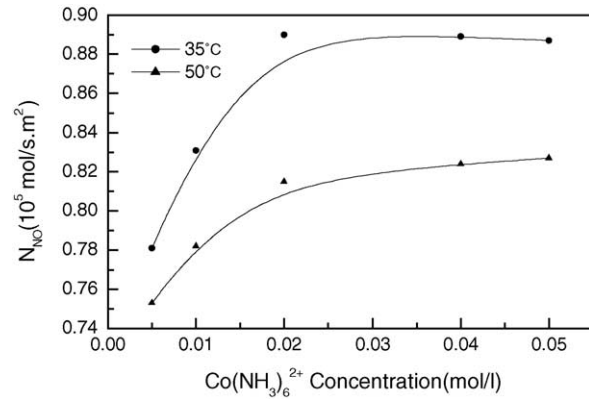


Fig. 2. Effect of $\text{Co}(\text{NH}_3)_6^{2+}$ concentration on reaction rate (without oxygen). Gas-liquid interfacial area = 28 cm^2 , NO inlet concentration = 400 ppm.

seen from Fig. 2 that NO absorption rate is proportional to $\text{Co}(\text{NH}_3)_6^{2+}$ concentration as $\text{Co}(\text{NH}_3)_6^{2+}$ concentration increases from 0.005 mol/l to 0.02 mol/l. For example, at 35 °C the nitric oxide absorption rate increases 6.4% (from $0.781 \times 10^{-5} \text{ mol}/(\text{s m}^2)$ to $0.831 \times 10^{-5} \text{ mol}/(\text{s m}^2)$) as $\text{Co}(\text{NH}_3)_6^{2+}$ concentrations increase from 0.005 mol/l to 0.01 mol/l. But the nitric oxide absorption rates increase little as $\text{Co}(\text{NH}_3)_6^{2+}$ concentrations increase further above 0.02 mol/l. For instance, at 50 °C, the nitric oxide absorption rate increases only 1.1% (from $0.815 \times 10^{-5} \text{ mol}/(\text{s m}^2)$ to $0.824 \times 10^{-5} \text{ mol}/(\text{s m}^2)$) when $\text{Co}(\text{NH}_3)_6^{2+}$ concentration increases from 0.02 mol/l to 0.04 mol/l. It can be concluded that the nitric oxide absorption into $\text{Co}(\text{NH}_3)_6^{2+}$ solution changes from two film controlling to gas film controlling when $\text{Co}(\text{NH}_3)_6^{2+}$ concentration exceeds 0.02 mol/l. NO absorption rate is independent of $\text{Co}(\text{NH}_3)_6^{2+}$ concentration when $\text{Co}(\text{NH}_3)_6^{2+}$ concentration is over 0.02 mol/l.

4.2. Effect of NO concentration on its absorption rate

Fig. 3 shows the effect of NO inlet concentration on its absorption rate into $\text{Co}(\text{NH}_3)_6^{2+}$ solution. It can be seen from Fig. 3 that NO absorption rate is proportional to the nitric oxide inlet concentration. For instance, at 50 °C, NO absorption rate into 0.05 mol/l $\text{Co}(\text{NH}_3)_6^{2+}$ solution increases 63.2% (from $7.784 \times 10^{-6} \text{ mol}/(\text{s m}^2)$ to $12.7 \times 10^{-6} \text{ mol}/(\text{s m}^2)$) as nitric oxide inlet concentration increases from 312 ppm to 923 ppm. It can be explained by the fact that NO absorption into $\text{Co}(\text{NH}_3)_6^{2+}$ solution is gas film controlling when $\text{Co}(\text{NH}_3)_6^{2+}$ concentration is over 0.02 mol/l.

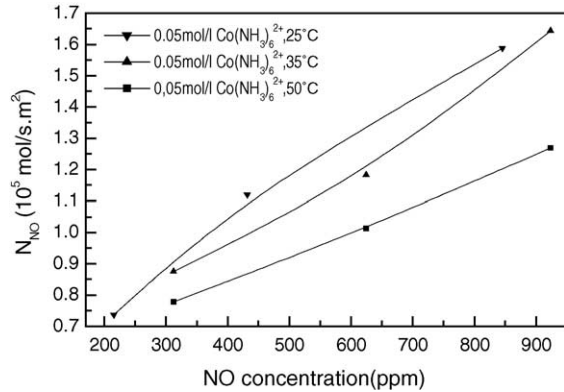


Fig. 3. Effect of NO concentration on absorption rate (without oxygen). Gas–liquid interfacial area = 28 cm².

4.3. Effect of oxygen partial pressure on NO absorption rate

Fig. 4 shows the effect of oxygen partial pressure on NO absorption rate. It can be concluded that oxygen can promote NO absorption into $\text{Co}(\text{NH}_3)_6^{2+}$ solution. For example, at 50 °C the NO absorption rate into 0.04 mol/l $\text{Co}(\text{NH}_3)_6^{2+}$ solution increases 64.6% (from 8.24×10^{-6} mol/(s m²) to 13.53×10^{-6} mol/(s m²)) as oxygen concentration increases from 0% to 5.2%. But the rate increases only 10.1% (from 13.53×10^{-6} mol/(s m²) to 15.29×10^{-6} mol/(s m²)) as oxygen concentration increases from 5.2% to 10.4%. Under aerobic condition, the dissolved oxygen, in equilibrium with oxygen in the feed gas, activated by $\text{Co}(\text{NH}_3)_6^{2+}$ in aqueous ammonia solution, oxidizes nitric oxide to soluble nitric dioxide quickly. The nitric oxide oxidation rate may increase with oxygen partial pressure. Therefore, higher oxygen partial pressure in gas stream may be favorable to the formation of soluble nitrogen dioxide and enhance nitric oxide absorption into the $\text{Co}(\text{NH}_3)_6^{2+}$ solution. On the other hand, the formation of binuclear complex with bridging dioxygen, $[(\text{NH}_3)_5\text{Co}-\text{O}-\text{O}-\text{Co}(\text{NH}_3)_5]^{4+}$, is connected with $\text{Co}(\text{NH}_3)_6^{2+}$ concentration. In other words, the activa-

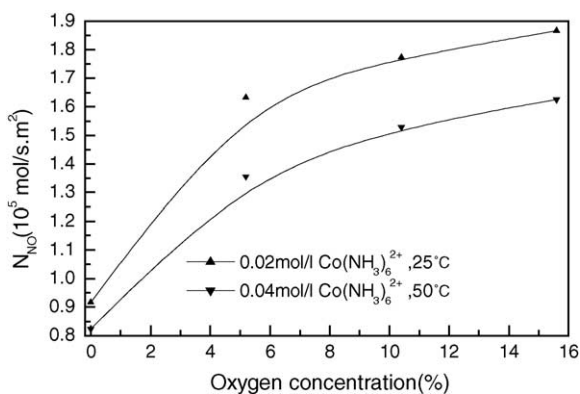


Fig. 4. Effect of oxygen concentration on absorption rate. Gas–liquid interfacial area = 28 cm², NO inlet concentration = 400 ppm.

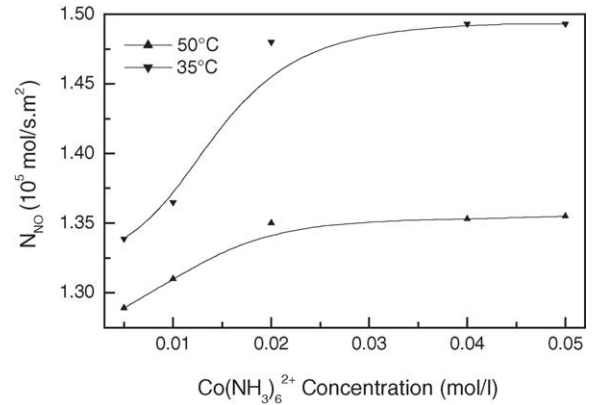


Fig. 5. Effect of $\text{Co}(\text{NH}_3)_6^{2+}$ concentration on reaction rate (5.2% oxygen). Gas–liquid interfacial area = 28 cm², NO inlet concentration = 400 ppm.

tion of oxygen molecule may also be decided by $\text{Co}(\text{NH}_3)_6^{2+}$ concentration. Therefore, at a certain $\text{Co}(\text{NH}_3)_6^{2+}$ concentration, it is of little significance to increase the oxygen concentration above 5.2%.

4.4. Effect of $\text{Co}(\text{NH}_3)_6^{2+}$ concentration on NO absorption rate under aerobic condition

Fig. 5 shows the effect of $\text{Co}(\text{NH}_3)_6^{2+}$ concentration on NO absorption rate when there is 5.2% oxygen in the flue gas. It can be seen from Fig. 5 that the NO absorption rate is proportional to $\text{Co}(\text{NH}_3)_6^{2+}$ concentration as $\text{Co}(\text{NH}_3)_6^{2+}$ concentration increases from 0.005 mol/l to 0.02 mol/l. For example, at 50 °C the nitric oxide absorption rate increases 4.7% (from 1.289×10^{-5} mol/(s m²) to 1.350×10^{-5} mol/(s m²)) as $\text{Co}(\text{NH}_3)_6^{2+}$ concentration increases from 0.005 mol/l to 0.02 mol/l. But the nitric oxide absorption rate increases little as $\text{Co}(\text{NH}_3)_6^{2+}$ concentrations increase further above 0.02 mol/l. For instance, at 50 °C, the nitric oxide absorption rate increases only 0.2% (from 1.350×10^{-5} mol/(s m²) to 1.353×10^{-5} mol/(s m²)) when $\text{Co}(\text{NH}_3)_6^{2+}$ concentration increases from 0.02 mol/l to 0.04 mol/l. It can be concluded that the nitric oxide absorption into the $\text{Co}(\text{NH}_3)_6^{2+}$ solution changes from two film controlling to gas film controlling when $\text{Co}(\text{NH}_3)_6^{2+}$ concentration exceeds 0.02 mol/l. The NO absorption rate is independent of $\text{Co}(\text{NH}_3)_6^{2+}$ concentration.

4.5. Effect of NO concentration on its absorption rate under aerobic condition

Fig. 6 shows the effect of nitric oxide inlet concentration on its absorption rate with 5.2% oxygen present in the gas stream. It can be concluded that, similar to the condition without oxygen, the absorption rate is also proportional to the nitric oxide inlet concentration. The reason is that NO absorption rate is gas film controlling and the reaction rate is mainly determined by NO partial pressure when $\text{Co}(\text{NH}_3)_6^{2+}$ concentration is 0.05 mol/l.

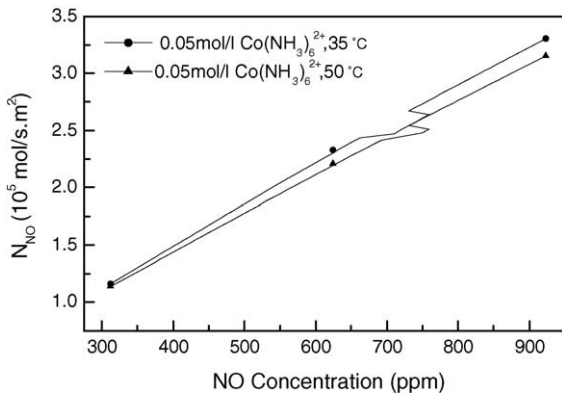


Fig. 6. Effect of NO concentration on absorption rate (5.2% oxygen, gas-liquid interfacial area = 28 cm²).

4.6. Effect of temperature on NO absorption rate

Fig. 7 shows the experimental results obtained at different temperature under anaerobic and aerobic conditions separately. It can be concluded from Fig. 7 that the nitric oxide absorption rate into Co(NH₃)₆²⁺ solution decreases with temperature. The nitric oxide absorption rate decreases 10.4% (from 14.93 × 10⁻⁶ mol/(s m²) to 13.53 × 10⁻⁶ mol/(s m²)) as temperature increases from 35 °C to 50 °C with 5.2% oxygen present in the flue gas. The nitric oxide absorption rate decreases 23.8% (from 9.85 × 10⁻⁶ mol/(s m²) to 7.51 × 10⁻⁶ mol/(s m²)) as temperature increases from 21 °C to 65 °C under anaerobic condition.

It is reported that at high temperature the balance of Eq. (17) [14] lies to the left. High temperature is disadvantageous to the stability of Co(NH₃)₆²⁺ and the coordination of nitric oxide with Co(NH₃)₆²⁺. In other words, high temperature is harmful to NO absorption into Co(NH₃)₆²⁺ solution. On the other hand, the solubility of oxygen in aqueous solution decreases with temperature, which is also disadvantageous to the oxidation and absorption of NO

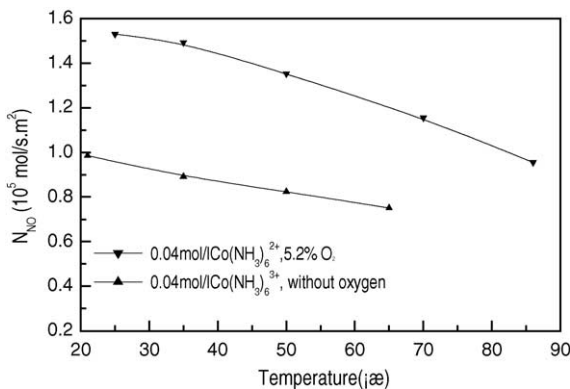


Fig. 7. Effect of temperature on reaction rate (gas-liquid interfacial area = 28 cm²).

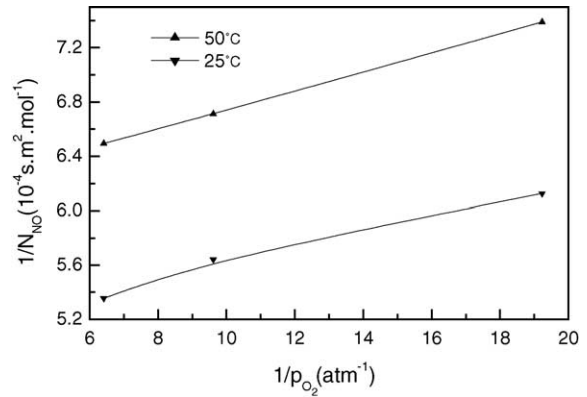


Fig. 8. Plots of 1/N_{NO} vs. 1/p_{O₂}.

4.7. Kinetic equation for NO catalytic oxidation in Co(NH₃)₆²⁺ solution

The kinetic Eq. (16) can be rewritten as follow:

$$\frac{1}{N_{\text{NO}}} = \frac{k_{-3}}{K_{\text{NO,G}} k_4 K_1 (p_{\text{NO}} + \gamma C_{\text{Co(NH}_3)_6^{2+},\text{L}}) C_{\text{Co(NH}_3)_6^{2+},\text{L}}^2 p_{\text{O}_2}} + \frac{1}{K_{\text{NO,G}} (p_{\text{NO}} + \gamma C_{\text{Co(NH}_3)_6^{2+},\text{L}})} \quad (18)$$

A linear curve can be given by plotting 1/N_{NO} against 1/p_{O₂} (Fig. 8). The slope is $\frac{k_{-3}}{K_{\text{NO,G}} (p_{\text{NO}} + \gamma C_{\text{Co(NH}_3)_6^{2+},\text{L}}) k_4 K_1 C_{\text{Co(NH}_3)_6^{2+},\text{L}}^2}$ and the intercept is $\frac{1}{K_{\text{NO,G}} (p_{\text{NO}} + \gamma C_{\text{Co(NH}_3)_6^{2+},\text{L}})}$.

In terms of the curves in Fig. 8, considering the fact that the absorption is gas film controlling when Co(NH₃)₆²⁺ concentration is above 0.04 mol/l, the kinetic equation of NO absorption into Co(NH₃)₆²⁺ solution at 50 °C can be given as follow (correlation coefficient 0.980). The comparison be-

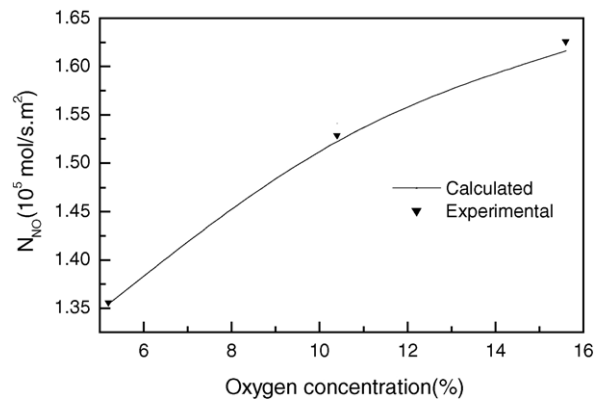


Fig. 9. Comparison between the calculated and experimental values. Gas-liquid interfacial area = 28 cm²; NO inlet concentration = 400 ppm; 50 °C, Co(NH₃)₆²⁺ = 0.04 mol/l.

tween the calculated and experimental NO absorption rate values can be seen in Fig. 9. It can be seen from Fig. 9 that the calculated values are accordant with the experimental values.

$$N_{\text{NO}} = \frac{k_{\text{NO,G}} p_{\text{NO}} p_{\text{O}_2} C_{\text{Co}(\text{NH}_3)_6^{2+},\text{L}}^2}{2.664 \times 10^{-5} + p_{\text{O}_2} C_{\text{Co}(\text{NH}_3)_6^{2+},\text{L}}^2}. \quad (19)$$

5. Conclusion

The experimental results in the stirred cell demonstrate that the nitric oxide absorption into $\text{Co}(\text{NH}_3)_6^{2+}$ solution can be regarded as an instantaneous reaction when nitric oxide levels are ppm ranges. The gas–liquid reaction becomes gas film controlling as $\text{Co}(\text{NH}_3)_6^{2+}$ concentration exceeds 0.02 mol/l. The rate of nitric oxide absorption into $\text{Co}(\text{NH}_3)_6^{2+}$ solution is independent of $\text{Co}(\text{NH}_3)_6^{2+}$ concentration when $\text{Co}(\text{NH}_3)_6^{2+}$ concentration is above 0.02 mol/l. The NO absorption rate is proportional to the nitric oxide inlet concentration.

Oxygen in the gas phase can promote nitric oxide absorption into $\text{Co}(\text{NH}_3)_6^{2+}$ solution. But there is little significance to increase oxygen concentration further above 5.2%. The NO absorption rate into $\text{Co}(\text{NH}_3)_6^{2+}$ solution decreases with temperature. The kinetic equation of NO absorption into the $\text{Co}(\text{NH}_3)_6^{2+}$ solution under aerobic condition can be written as:

$$N_{\text{NO}} = \frac{K_{\text{NO,G}} k_4 K_1 \left(p_{\text{NO}} + \gamma C_{\text{Co}(\text{NH}_3)_6^{2+},\text{L}} \right) \times C_{\text{Co}(\text{NH}_3)_6^{2+},\text{L}}^2 p_{\text{O}_2}}{k_{-3} + k_4 K_1 C_{\text{Co}(\text{NH}_3)_6^{2+},\text{L}}^2 p_{\text{O}_2}}.$$

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