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Simultaneous absorption of NO and SO_2 into hexamminecobalt(II)/iodide solution

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Abstract

An innovative catalyst system has been developed to simultaneously remove NO and SO_2 from combustion flue gas. Such catalyst system may be introduced to the scrubbing solution using ammonia solution to accomplish sequential absorption and catalytic oxidation of both NO and SO_2 in the same reactor. When the catalyst system is utilized for removing NO and SO_2 from the flue gas, $Co(NH_3)_6^{2+}$ ions act as the catalyst and I^- as the co-catalyst. Dissolved oxygen, in equilibrium with the residual oxygen in the flue gas, is the oxidant. The overall removal process is further enhanced by UV irradiation at 365 nm. More than 95% of NO is removed at a feed concentration of 250–900 ppm, and nearly 100% of SO_2 is removed at a feed concentration of 800–2500 ppm. The sulfur dioxide co-existing in the flue gas is beneficial to NO absorption into hexamminecobalt(II)/iodide solution. NO and SO_2 can be converted to ammonium sulfate and ammonium nitrate that can be used as fertilizer materials. The process described here demonstrates the feasibility of removing SO_2 and NO simultaneously only by retrofitting the existing wet ammonia flue-gas-desulfurization (FGD) scrubbers.

Keywords: Absorption; Nitric oxide; Sulfur dioxide; Iodide; Oxidation; Ammonia solution

1. Introduction

Combustion of fossil fuels generates NO_x pollutants that cause acid rain and urban smog. The removal of NO_x from combustion flue gas streams is often necessary to meet stringent effluent discharge limits. Among the existing treatment processes for removing NO_x from flue streams, selective catalytic reduction (SCR) by NH_3 at 300–500 °C is considered the best available NO_x control technology. However, the application of SCR is limited because of its high capital and operating costs. There is still an urgent need for a more costly effective method for controlling NO_x emission.

Absorption techniques (chemical scrubbing) have the advantage of eliminating NO_x and SO_2 simultaneously. Modification of the existing scrubber operation to accomplish removal of both SO_2 and NO_x is more cost effective relative to a separate NO_x control system. However, this approach has not been successfully practiced due to the low water solubility of NO, which accounts

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for 90–95% of the NO_x in a typical flue gas stream. Effective removal of NO from the flue gas may be achieved if the former is oxidized first to the more soluble NO_2. A suitable catalyst is necessary for gas phase oxidation of NO since it is not reactive at a low concentration. Although much work has been performed on catalytic oxidation of nitric oxide in the gas phase since 1920 s, a viable process has yet to be developed because the solid catalyst is easily poisoned by SO_2 existing in the flue gas. The treatment cost using a strong oxidant, such as OCl_2^- (Sada and Kumazawa, 1977; Yang and Shaw, 1998) and H_2O_2 (Thomas and Vanderschuren, 1996, 1997, 1998; Paiva and Kachan, 1998), has been too high to make it a practical NO_x control process. Other approaches to treating NO in aqueous scrubbers have included the addition of heavy metal chelators to sequester nitric oxide for the subsequent removal (Pham and Chang, 1994; Shi et al., 1996) and even the addition of yellow phosphorous emulsions and O_2 to oxidize nitric oxide to a combination of nitrite and nitrate salts (Chang and Liu, 1990; Liu et al., 1991).

Flue gases are sometimes scrubbed with aqueous ammonia to reduce their sulfur dioxide. The byproduct ammonium sulfate can be used as a usable fertilizer. The AMASOX desulfurization process was put into application to a 500 MW Power plant in Kenosha in the US 10 years ago. The $Co(NH_3)_6^{2+}/I^-$ system may be introduced to the existing wet desulfurization process using ammonia solution to accomplish sequential absorption and catalytic oxidation of both NO and SO_2. NO can be absorbed and converted to nitrite and nitrate in a single reactor. SO_2 can also be absorbed and oxidized to sulfate at the same time.

2. Theoretical

$Co(NH_3)_6^{2+}$ ion, which is formed after dissolving cobalt nitrate in dilute ammonia solution, may react with dissolved NO according to the following equations:

$$NO(g) \leftrightarrow NO(aq) \tag{1}$$

$$Co(NH_3)_6^{2+}(aq) + NO(aq) \rightarrow [Co(NH_3)_5NO]^{2+}(aq) + NH_3(aq) \tag{2}$$

The co-ordination reaction between nitric oxide and hexamminecobalt ion in the liquid phase enhances absorption of nitric oxide in the ammonia solution.

$Co(NH_3)_6^{2+}$ ion may also react with dissolved oxygen to form a brown binuclear complex with bridging dioxygen (Mori et al., 1968; Simplicio and Wilkins, 1969):

$$2Co(NH_3)_6^{2+} + O_2(aq) \leftrightarrow [(NH_3)_3Co{-}O{-}O{-}Co(NH_3)_3]^{4+} + 2NH_3(aq) \tag{3}$$

The bridging O—O group has an O—O bond length nearly equal to that of H_2O_2, making $[(NH_3)_5Co{-}O{-}O{-}Co(NH_3)_5]^{4+}$ a strong oxidation agent. Reaction (3) may be considered activation of molecular oxygen to form a reactive dioxygen complex. Such properties of $[Co(NH_3)_6]^{2+}$ are the key to the successful development of the $Co(NH_3)_6^{2+}/I^-$ in ammonia catalyst system for removing NO from the flue gas.

The catalytic process involves oxidation of nitric oxide in the dilute ammonia solution, regeneration of $[Co(NH_3)_6]^{2+}$ cations, and regeneration of I^- ions. The oxidation of NO in the complex ion to form nitrite and nitrate can be described as

$$[(NH_3)_5Co{-}O{-}O{-}Co(NH_3)_5]^{4+} + H_2O + 2NH_3 + [Co(NH_3)_5NO]^{2+} \rightarrow 2Co(NH_3)_6^{3+} + 2OH^- + [Co(NH_3)_5NO_2]^{2+} \tag{4}$$

$$2[Co(NH_3)_5NO_2]^{2+} + H_2O + 2NH_3 \rightarrow NH_4NO_2 + NH_4NO_3 + 2Co(NH_3)_6^{2+} \tag{5}$$

The hexamminecobalt(III) ion, $[Co(NH_3)_6]^{3+}$, is unable to activate dissolved oxygen molecules to form the reactive dioxygen complex. The NO removal rate decreases with decreasing concentration of hexamminecobalt(II) ion as the reaction proceeds.

One measure can be taken is to add iodide anions into the solution. Iodide may displace one ammonia molecule from the hexamminecobalt(III) ions (reaction (6)).

$$Co(NH_3)_6^{3+} + I^- \rightarrow Co(NH_3)_5I^{2+} + NH_3 \tag{6}$$

UV irradiating the $Co(NH_3)_5I^{2+}$ aqueous solution may lead to photo oxidation–reduction decomposition with conversion of Co(III) to Co(II) (reaction (7)) (Haim and Taube, 1963).

$$Co(NH_3)_5I^{2+} \xrightarrow{h\nu} Co^{2+} + 5NH_3 + I^{\bullet} \tag{7}$$

The iodine atoms generated in reaction (7) can react with $Co(NH_3)_5I^{2+}$ as follows:

$$Co(NH_3)_5I^{2+} + I^{\bullet} \rightarrow Co^{2+} + 5NH_3 + I_2 \tag{8}$$

The regeneration of cobalt(II) is completed by reaction (7) and reaction (8). Furthermore, hexamminecobalt(II) ion are also regenerated by the co-ordination of Co^{2+} with ammonia in aqueous solution (reaction (9)).

$$Co^{2+} + 6NH_3 \rightarrow Co(NH_3)_6^{2+} \tag{9}$$

Iodide is regenerated by sulfur dioxide existing in the flue gas as the following equation:

$$2H_2O + I_2 + SO_2 \rightarrow 2I^- + SO_4^{2-} + 4H^+ \tag{10}$$

The overall reaction for NO removal by sequential absorption and oxidation is expressed as