Ag(I)/Ag(II) 산화환원 이온쌍을 이용한 전기화학적 매개산화 공정에서 NOx, SOx 제거

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Removal of NOx and SOx in mediated electrochemical oxidation using Ag(I)/Ag(II) redox system

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Introduction

Development of an indirect process for electrochemical removal NO_x, SO_x and other odor gases by using the redox mediators like Ag(I)/Ag(II) in aqueous nitric acid medium. A high degree of destruction could be achieved by using redox mediators for the indirect destruction of waste gases in combination with an electrochemically generated oxidizing agent [1-3]. The inherent advantage of a mediated electrochemical process for the destruction of waste gases containing NO_x and SO_x is the use of the electron as a "clean reagent" instead of chemicals which in mostof the conventional techniques have to be added in large amounts. Mediated Electrochemical processes are further attractive due to their versatility, energy efficiency and amenability to automation and scale up. The principle of electrochemical gas purification has been takes place by the absorption of the pollutant species from the gas phase into a liquid electrolyte where the electrochemical oxidation or reduction takes place either directly at the electrode of an electrochemical cell or indirectly via a redox mediator.

The present investigation is aimed to study the removal of NOx (NO and NO_2) and SO_2 from simulated NO or SO_2-Air gas mixture by Ag(II) redox mediatorsgenerated by mediated electrochemical oxidation in aqueous nitric acid medium and optimization of process parameters. So that this knowledge can be utilized to make rational use of resources like sustainable MEO process, enhance the useof redox mediators for waste gas removal from industrial gas pollutants.

Experiment

Removal of NO, NO_2 and SO_2 gases were carried out with Ag(I)/Ag(II) redox mediators in nitric acid medium by wet scrubbing method. The experimental system is divided into two parts, i.e., Ag(II) redox mediator generation by electrochemical process and NOx gas treatment by wet scrubbing method. All the processes were conducted at room temperature and atmospheric pressure conditions. A schematic diagram of the experimental system is shown in Fig. 1 and the experimental conditions were given in Table 1

The removal of NOx and SOx system is composed of NO, SO_2 and Air gas units, scrubbers, data logging system and gas analyzer. The scrubber is (ID= 5cm; height =120 cm)

a glass vessel filled with different type of packing materials. The simulated NO-air and SO_2-air gas mixture was obtained by controlled mixing of air with NO and SO_2 using mass flow controllers (MFC). Gas mixture were introduced at the bottom of the scrubber at constant initial NO and SO_2 concentration and the scrubbing liquid Ag(II) solution introduced at the top of the scrubber in counter current flow pattern.

The NO, NO_2 and SO_2 analysis were carried by the Gas analyzer instrument (Teledyne Model No.9560). The inlet and outlet concentration of NO, NO_2 and SO_2 were analyzed with respect to time of reaction. From the analysis, the conversion and removal efficiencies for NO, NO_x and SO_2 were calculated based on the inlet and outlet concentration of gas feeds.

Results and Discussion

In the scrubber, the charged NO is completely converted to NO_2 with Ag(II) ions. The equal moles of NO charged was oxidized to NO_2 and further the produced NO_2 will give HNO_2 and HNO_3 with water at 80% conversion rate.

During the scrubbing it is found out, the following reaction mechanism is happened and the product of HNO_3 and small amount of NO_2 are released from the scrubber [4, 5].

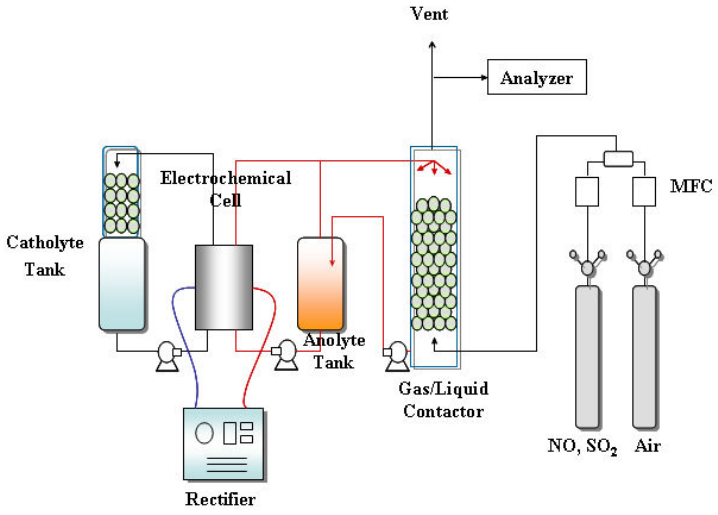

Fig. 1. Schematic diagram of for the electrochemical removal of NOx and SO_2.

Table 1 Experimental condition for NO_x removal process

Parameters	Ranges
Feed NO & SO_2 concentration	100 - 400 ppm
Gas flow rate	5 - 20 L/min
Gas superficial velocity	0.07 - 0.26 m/sec
Concentration of Ag(I)	0.01 - 0.1 M
Concentration of HNO_3	3 - 8 M
Liquid flow rate [Ag(II)]	0.05 - 4 L/min
Packing materials	Raschig rings (Ø : 1, 2 cm) Tri-pack (Ø : 2.5 cm)
Temperature	15 - 45 ℃

$$2\ NO + 5\ Ag(II) + 3\ H_2O \rightarrow HNO_3 + NO_2 + 5\ Ag(I) + 5\ H^+ \quad \text{---------- (1)}$$

$$NO_2 + Ag(II) + H_2O \rightarrow HNO_3 + Ag(I) + H^+ \quad \text{---------- (2)}$$

$$NO_2(g) \xrightarrow{H_2O\ (l),\ HNO_3(l)} NO_2(dissolve) \quad \text{---------- (3)}$$

$$SO_2 + 2\ Ag(II) + 2\ H_2O \rightarrow H_2SO_4 + 2\ Ag(I) + 2\ H^+ \quad \text{---------- (4)}$$

The total amount of NO charged into the scrubber is completely oxidized by the Ag(II) ions in the scrubber at fixed gas and liquid velocities. The NO is oxidized to HNO_3 very rapidly by Ag(II) ions which is shown of reaction steps in equations 1 to 3. Fig. 2 shows the NO concentration profiles based on the NO measured at the inlet and outlet of the scrubber. It is clear that the efficiency for NO removal attained 100% in a short span of 40 to 60 seconds and there after it is sustained for a large time as long as 120 minutes. The total removal efficiency for NO and NO_X is 100 % and 80 % for the scrubber.

The charged SO_2 is rapidly oxidized to H_2SO_4 by Ag(II) ions (Eq. 4). In all experimental condition, the removal efficiency for SO_2 is 100 %. Table 2 shows the results for NO, NOx and SO_2 removal efficiency in all experimental conditions.

Conclusions

Studies were carried out on the development of a environmental friendly sustainable process or method for complete removal and treatment of waste industrial exhaust gases like NOx and SOx by electrochemically generated Ag(I)/Ag(II) redox mediator system in aqueous nitric acid medium. The conversion and removal efficiency for NO, NOx and SO_2 is high with Ag(II) redox mediator. NO conversion was investigated as a function of parameters such as NO and SO_2 concentration, gas and liquid superficial velocities, Ag(I) concentration and HNO_3 concentration. NO and SO_2 were rapidly oxidized by Ag(II) ions and absorbed into nitric acid. Optimization studies were also carried for the above parameters with maximum conversion of NO and SO_2.

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Reference

[1] M. Aurousseau, F. Lapicque, A. Storck, Simulation of NOx scrubbing by ceric solutions: Oxidation of Nitrous acid by Ce(IV) species in acidic solutions, Ind. Eng. Chem. Res. 33, 191-196 (1994).

[2] E. JuzeliGnasf, K. Jiittner, K.H. Kleifges, Electrochemical study of direct and indirect NO reduction with complexing agents and redox mediator, Electrochimica Acta 42, 2947-2953 (1997).

[3] J. M. Nzikou, M. Aurousseau, F. Lapicque, Electrochemical investigations of the Ce(III)/Ce(IV) related to a Ce(IV) assisted process for SO_2/NO_x abatement, J. Appl. Electrochem. 25, 967-972 (1995).

[4] J. Bringmann, K. Ebert, U. Galla, H. Schmieder, Oxidative separations of nitrogen oxides form off-gases by electrochemical mediators, J. Appl. Electro. Chem. 27, 870-872 (1997).

[5] P. Hoffmann, C. Roizard, L. Lapicque, S. Venot, A. Maire, A Process for the simultaneous removal of SO_2 and NOx using Ce(IV) redox catalysis, Institution of chemical Engineers, Trans IchemE, 75(B), 43-53 (1997).

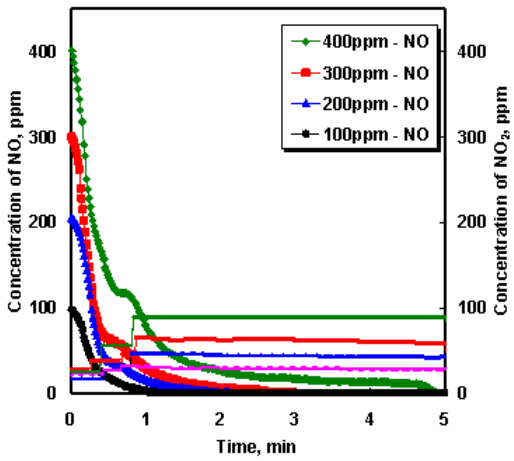

Fig. 2. NO outlet concentration profiles and NO removal efficiences as a function of time.

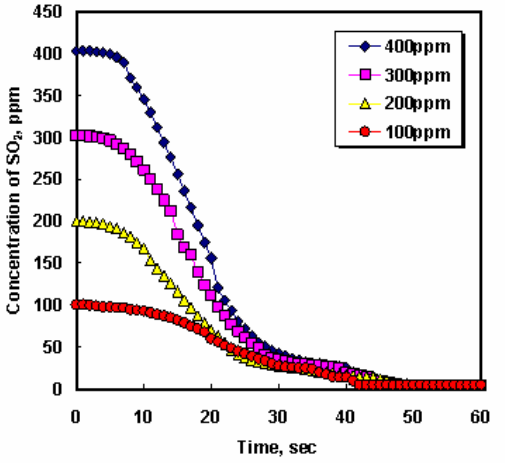

Fig. 3. SO_2 outlet concentration profiles and SO_2 removal efficiencies as a function of time.

Table 2. Removal efficiency of NO, NOx & SO_2 by Ag(I)/Ag(II) MEO process at various experimental conditions

Parameters		Removal Efficiency, %		
		NO	NOx	SO_2
Packing Material	Rasching Ring (Glass, 1cm)	100	82	100
	Rasching Ring (PTFE, 2cm)	100	77	100
	Tri-Packs® (Teflon, 1")	100	75	100
Superficial Gas Velocity, m/sec	0.07	100	82	100
	0.13	100	82	100
	0.19	98	80	100
	0.25	97	80	100
Concentration of Ag(I), M	0.01	91	76	100
	0.025	97	78	100
	0.05	99	80	100
	0.1	100	82	100