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A New Method for Treating Waste Gases Containing NO_x with Low Concentration Based on Rare Earth Metal Complex

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A novel method for removing exhaust gas of NO_x with low concentration based on rare earth metal complex was proposed in this paper. The absorptivities of NO_x by different solvents and complexes between yttrium and substituted salicylate under different conditions were investigated. The results showed that the esters *e.g.*, ethyl acetate and butyl acetate have higher absorptivity than that of ketone, water or alcohol and the better volume ratio of solvents to NO_x is 1 to 0.9. When added yttrium perchlorate and methyl salicylate to butyl acetate, the absorptivity increases because of coordinated catalytic absorption. The better molar ratio of yttrium perchlorate to methyl salicylate is 1 to 1 and the better amount ratio of yttrium perchlorate to NO_x is over 3 to 1. When the absorption liquid of NO_x with butyl acetate added yttrium perchlorate and methyl salicylate extracted by water, methyl salicylate is in organic phase can be used to absorb NO_x again and yttrium perchlorate with NO_x is in aqueous phase can be used as nitrating agent. The method is economic and effective because not only almost 100 % NO_x are removed, but also nitration products are formed. A technological process for the absorption recovery of NO_x with low concentration from waste gas is proposed.

Keywords: Waste gases, NO_x, Rare earth.

INTRODUCTION

Nitrogen oxides (NO_x) released from the burning of fossil fuel, especially from coal-fired power plants, cause considerable environmental and health problems [1]. With the rapid development of economy and increase of energy consumption, the emissions of NO_x increase quickly which is far from emissions targets. So, the treatment of NO_x is extremely urgent [2]. Although the starting of treating NO_x is late in china, the technology develops rapidly by introducing absorption and research [3-12]. The main technologies are combustion, adsorption, selective catalytic reduction, selective non-catalytic reduction and liquid absorption. The absorbent efficiency of chemical absorption is the best [13-15]. Nitric oxide (NO) is the main composition of NO_x with concentration of 90-95 % which is sparingly soluble in water and cannot be separated easily. By liquid absorption, NO need to be oxidized to NO_2 which absorbed easily by different absorbents. The common oxidants are HNO_3, MnO_4^-, ClO_2^-, H_2O_2, $Na_2S_2O_8$, *etc*. [16-19]. These oxiziding methods have many defects, for example, slow rate, low efficiency, no recycle and high cost. So, new catalytic oxidation must be developed to increase absorbent rate and efficiency. It is reported NO can be activated and absorbed highly by chelates of metal ion [20-22]. For example, the complex of Fe-EDTA can absorb NO with high efficiency, mild condition and simple device, but the complex results in secondary pollution because of difficult treatment. In the coordinated system of cobaltammine or ethylenediamine, NO can be catalytic oxidated with O_2 in the air and absorbed by complex, but the mechanism is not clear. Because of the high price of cobalt and district wastewater discharge for system of ammine, the method is restricted for use. Therefore, alternative cost-effective and environmentally friendlier processes are of ardent interest.

We found a characteristic colour reaction occurred when nitric oxide (NO) reacted with the mixture of yttrium perchlorate and methyl salicylate at a given temperature, forming a comparative, stable blue-green product. A simple and fast mean to detect NO was proposed [23]. The reaction is characteristic blue reaction of coordinated rare earth and salicylates with NO and only rare earth not others metal can catalyze this reaction [24,25]. The blue product is possible to be N_2O_3 formed by catalytic oxidation of NO to NO_2 with coordination of rare earths perchlorate and salicylates. Based on the results and actual demand for treating waste gases in oxalic acid production, a method for treating waste gases containing NO_x based on coordination by rare earth and salicylate was studied. The absorbent efficiency of NO_x by different solvents, complexes

between rare earth and salicylate under different conditions and the recycle of absorption liquid will be investigated. The completion of this project not only can provide a novel technology for the treatment of waste gas containing NO_x with low concentration and the comprehensive utilization of absorbed NO_x, but can also find new application field for the surplus yttrium, which has very important theoretical and practical significance for both rare earth industry and environmental protection.

EXPERIMENTAL

Content of NO_2^- in water detected by Griess reagent: Standard solution of sodium nitrite (1 μmol/mL) was configurated by $NaNO_2$ (0.069 g) dissolved in water and diluted with water to 1000 mL. Solution of *p*-aminobenzene sulfonic acid was configurated by *p*-aminobenzene sulfonic acid (0.4 g) dissolved in 100 mL hydrochloric acid (20 %). Solution of naphthalene ethylenediamine hydrochloride was configurated by naphthalene ethylenediamine hydrochloride dissolved in 100 mL water. Sodium nitrite ($NaNO_2$) (0.1, 0.25, 0.4, 0.6, 0.8, 1.0, 1.5 mL) was added to colorimetric tubes respectively. 2 mL solution of *p*-aminobenzene sulfonic acid and 1 mL solution of naphthalene ethylenediamine hydrochloride were added to colorimetric tubes and standard tube. The absorbance at 540 nm of reaction solutions in colorimetric tubes and standard tube was tested and standard curve was drawn in Fig. 1. The equation is obtained as follow: A = 42.7c + 0.064, which can be used to calculate the content of NO_2^-.

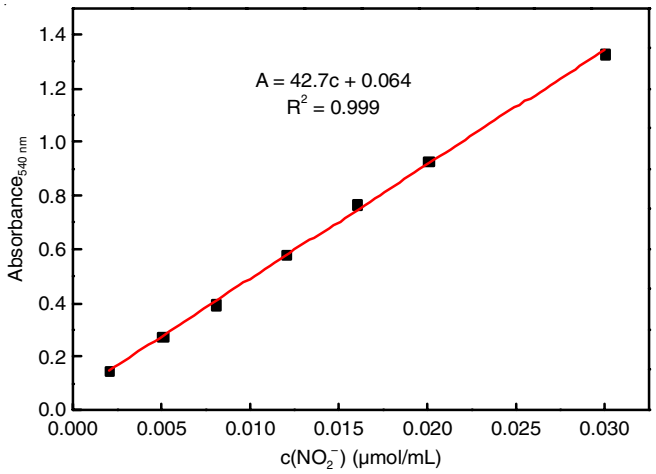


Fig. 1. Standard curve for content of NO_2^- by Griess reagent

Fig. 2 shows the experimental apparatus set-up. Nitric oxide was produced by $NaNO_2$, $FeSO_4$, H_2SO_4 pumped into N_2. Firstly, NO was inletted to organic solvents or the mixture of yttrium perchlorate and methyl salicylate which can absorb NO. The unabsorpted NO was inletted to potassium permanganate solution which can oxidize NO to NO_2 and can be changed to NO_2^- when absorbed by water. The content of NO_2^- can be calculated by Griess reagent according to Fig. 1.

RESULTS AND DISCUSSION

Absorbent efficiency of NO by different solvents: Table-1 showed absorbent efficiency of NO by different solvents. Nitric oxide was inletted to different organic solvents. Then the absorption liquid (1 mL) was added to yttrium perchlorate (1 mmol) and methyl salicylate (1 mmol), which was reacted at 100 °C. The UV-visible absorption of reaction solution is at 550-750 nm with the maximum absorption at 640 nm. The unabsorpted NO was oxided by potassium to NO_2^- which can be tested by Griess reagent with the maximum absorption at 540 nm. Table-1 showed that when the amount of NO is 2 mmol, the absorptivity of butyl acetate is the best with little unabsorbent NO. When the amount of NO is increased to 4 mmol, the amount of unabsorbent NO increased little. But when increased to 6 mmol, the amount of unabsorbent NO increased remarkably. Obviously, the saturation capacity of butyl acetate for absorbing NO is 4 mmol/100 mL. The efficiency of ethyl acetate is better than that of butyl acetate, but the low boiling point and good water solubility of ethyl acetate lead to inconvenience. So butyl

TABLE-1
ABSORBENT EFFICIENCY OF NO BY DIFFERENT SOLVENTS

Solvent	Amount of NO (mmol)	$Abs_{640\ nm}$	$Abs_{540\ nm}$	Amount of unabsorbent NO (μmol)
Acetone	2	0.059	0.375 (8)	12.59
Alcohol	2	0.122	0.048	0.20
Butyl acetate	2	0.253	0.005	0.02
Butyl acetate	4	0.247	0.009	0.04
Butyl acetate	6	0.250	0.485 (6)	4.73
Ethyl acetate	6	0.136	0.287 (3)	1.23
BA-MS-Y	6	0.310	0.297 (6)	3.61

( ) = diluted multiples

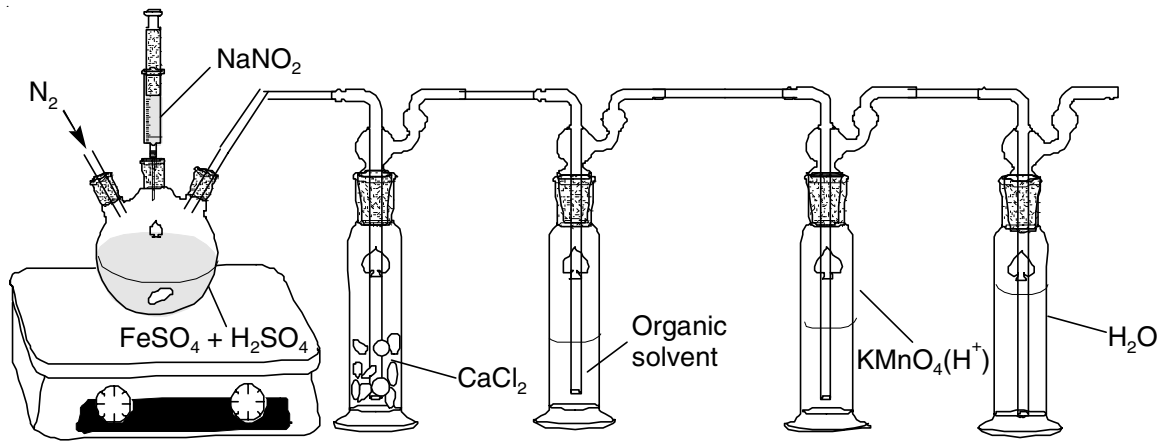


Fig. 2. Experimental apparatus for production,absorption oxidation, detection of NO

acetate is selected to absorb NO with molar ratio of NO to butyl acetate being 0.5 to 100. When added perchlorate and methyl salicylate to butyl acetate (BA-MS-Y), the absorbent efficiency of NO is better than that of butyl acetate because of coordination catalytic oxidation.

Absorbent efficiency of NO-NO_2 by water, sodium hydroxide and BA-MS-Y: NO-NO_2 was formed by 2 mmol $NaNO_2$, $FeSO_4$, H_2SO_4 under air atmosphere which firstly inletted to 100 mL water or sodium hydroxide or BA-MS-Y. The absorbent solution of water and sodium hydroxide can be tested by Griess reagent with the maximum absorption at 540 nm and the absorbent solution of BA-MS-Y can be tested at 640 nm.The unabsorbent NO-NO_2 was inletted to BA-MS-Y which has absorption at 640 nm. Table-2 shows absorbent efficiency of NO-NO_2 by water, sodium hydroxide and BA-MS-Y. From the results it is suggested that the NO-NO_2 is absorbed completely by BA-MS-Y. The absorbent efficiency of BA-MS-Y is better than that of butyl acetate, water and sodium hydroxide. So BA-MS-Y is more suitable for absorption of NO-NO_2.

TABLE-2
ABSORBENT EFFICIENCY OF NO-NO_2 BY WATER, SODIUM HYDROXIDE AND BA-MS-Y

Absorbent solvent	Absorbance of absorbent solution	Absorbance of unabsorbent NO-NO_2 in solution of BA-MS-Y	Amount of absorbent NO-NO_2 (mmol)
H_2O	0.292 (540 nm)	1.441 (640 nm)	0.70
NaOH	1.576 (540 nm)	0.859 (640 nm)	1.22
BA-MS-Y	2.214 (640 nm)	0 (640 nm)	2.00

Treatment and recycle of NO_x based on coordination of rare earth and salicylate

Better amount of rare earth and salicylate: Yttrium perchlorate (0.64 mmol) and methyl salicylate (0.64 mmol) were reacted with 0.08, 0.16, 0.24, 0.32, 0.40, 0.48 mmol NO for 20 min in 5 mL butyl acetate at 100 °C, respectively. The UV-visible absorption of reaction solution at 640 nm showed in Fig. 3. The results show that there is good linear relation when the amount of NO is below 0.16 mmol. But the absorbance decreases when the amount of NO exceeds 0.16 mmol because of side reaction. So the better molar ratio of yttrium perchlorate or methyl salicylate to NO is over 3 to 1.

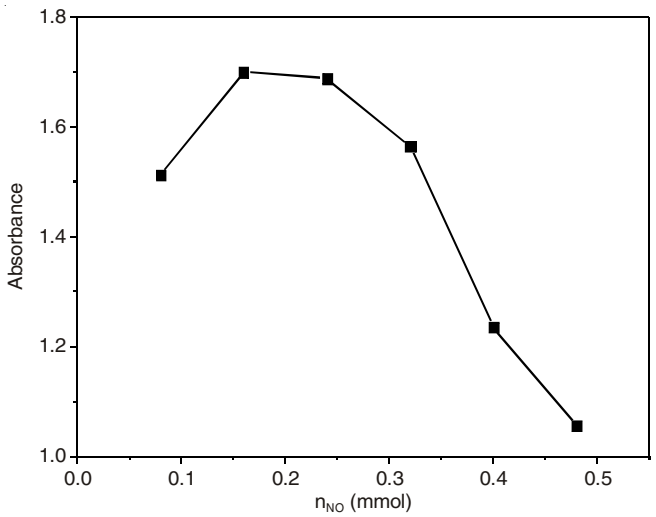


Fig. 3. UV-visible absorption of solution between different amount of NO with quantitative amount of yttrium perchlorate and methyl salicylate

Recycle of reacted solution: The absorbent solution in BA-MS-Y obtained above was extracted by water. The yellow phase in the upper layer is butyl acetate including methyl salicylate and the blue phase in the below layer is water including yttrium perchlorate and NO_x. The volume of yellow phase is 92 mL which used to absorb NO and then added yttrium perchlorate and methyl salicylate. The absorbance showed in Fig. 4-III which is less than that of pure butyl acetate (Fig. 4-I) because of the presence of little water. When added yttrium perchlorate and methyl salicylate to yellow phase, there is little absorbance at 640 nm (Fig. 4-II). The water phase can be used as nitration reagent (Table-3). The results indicate that the butyl acetate can be recycled to absorb NO_x and the solution including yttrium perchlorate and NO_x can be used as nitration agent with rare earth being deposited. For example, when hydrochloric acid was added to water phase and extracted by butyl acetate, 3-nitro methyl salicylate (3-MNS) and 5-nitro methyl salicylate (5-MNS) were synthesized by recrystallization. The ^{1}H NMR of 3-MNS and 5-MNS are given in Table-3.

Flow chart for treatment of NO_x: The flow chart for treatment of NO_x showed in Fig. 5. Tail gas is absorbed by organic solvent, then added rare earth perchlorate and methyl salicylate to form blue solution. The blue solution is extracted by water.

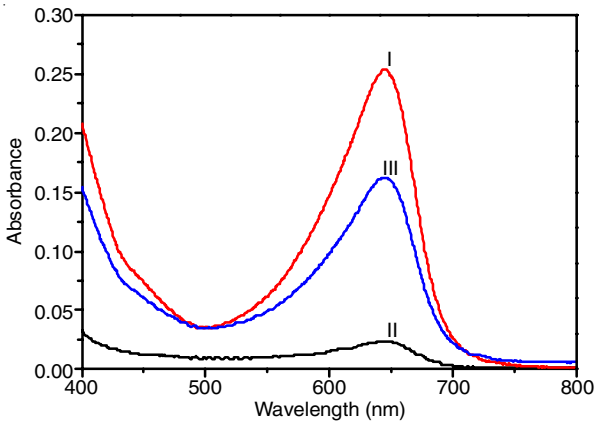
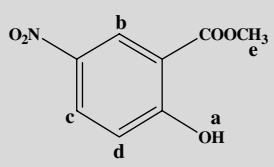
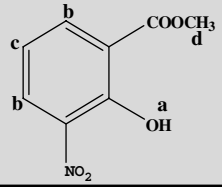


Fig. 4. (I) UV-visible absorption of the blue solution reacted by yttrium perchlorate and methyl salicylate absorbing NO; (II) UV-visible absorption of the yellow phase added yttrium perchlorate and methyl salicylate; (III) UV-visible absorption of water phase added yttrium perchlorate, methyl salicylate and NO

TABLE-3
^{1}H NMR OF 3-MNS AND 5-MNS

5-MNS (A): δ Assignment	3-MNS (A): δ Assignment
11.41 1H/a	11.81 1H/a
8.72 2H/b	8.19 1H/b
8.43 1H/c	7.17 1H/c
7.20 3H/d	4.04 1H/d
4.06 3H/e	
	

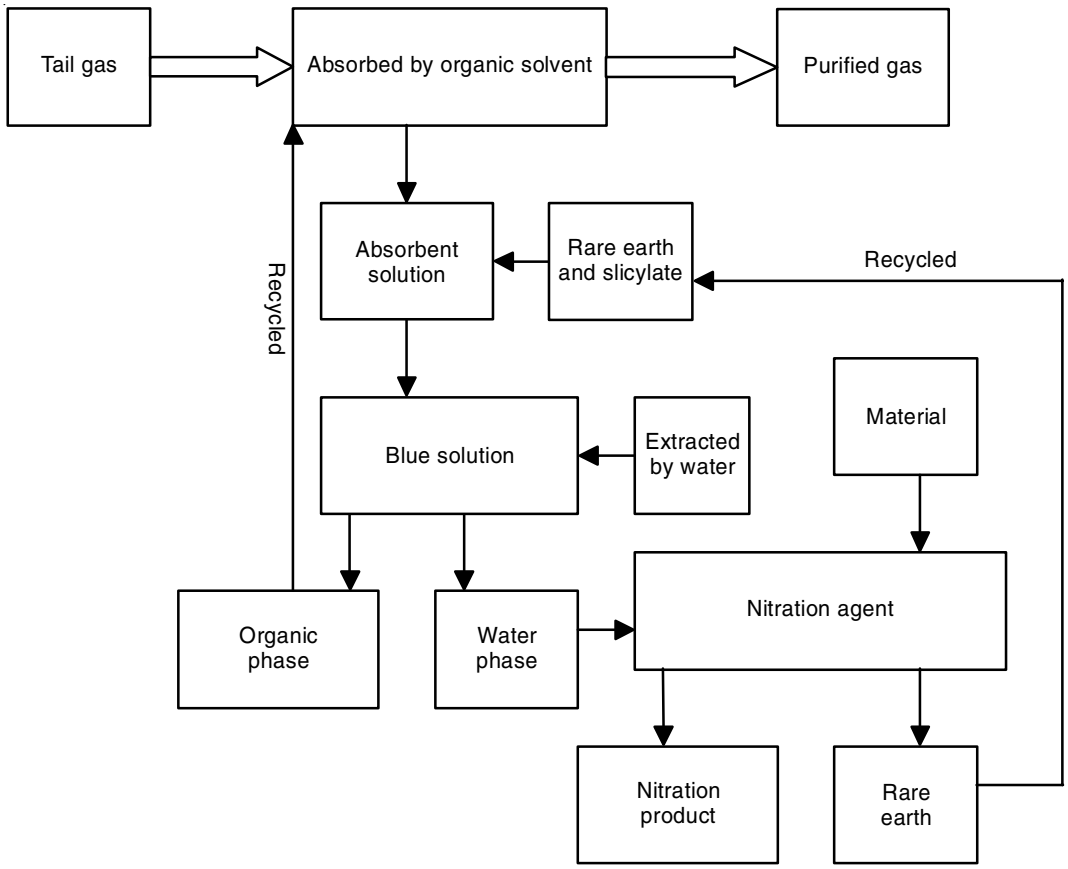


Fig. 5. Flow chart for treatment of NO_x

The water phase is used as nitration agent to get nitration product with rare earth being deposited which can be used again to absorb NO_x. The organic phase can also be recycled to absorb NO_x. The flow chart is only suitable for absorbing NO_x with low concentration.

Conclusion

The organic solvent ethyl acetate or butyl acetate can absorb NO_x with high efficiency. The better volume ratio of solvents to NO_x is 1 to 0.9.When added yttrium perchlorate and methyl salicylate to butyl acetate, the efficiency increases. The better molar ratio of yttrium perchlorate to methyl salicylate is 1 to 1 and the better amount ratio of yttrium perchlorate to NO_x is over 3 to 1. When the blue solution is extracted by water, two phases are obtained. The water phase can be used as nitrating agent with rare earth being deposited which can be used again to absorb NO_x. The organic phase can also be recycled to absorb NO_x. A technological process for absorbing NO_x with low concentration from waste gas is proposed.

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