Articles

Study on Oxidation Mechanism of Nitrogen Monoxide in Indoor Environment

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With the aid of wind-tunnel experimental setup, the possibilities that nitrogen monoxide (NO) is oxidized to nitrogen dioxide (NO_2) in various environments were stucied, which include indoor, outdoor and darkroom conditions. By comparing their effects, a conclusion can be drawn that NO can be oxidized to NO_2 in indoor environment with a low rate, and micro amount of ozone, propylene and methane can accelerate the reaction: $2NO + O_2 \rightarrow NO_2$. The initial concentration of NO has effect on the oxidation rate. When the initial concentration of NO ranges between 500 and 900 μg/L, natural logarithm of initial rate and natural logarithm of initial concentration have a good linear relation, so do ln(1/[NO]) and the time (t). Besides that, the possible oxidation mechanism of indoor NO has also been studied.

Keywords nitrogen oxidation, oxidation rate, influence factor, dynamics, wind-tunnel setup

Introduction

In recent years, the study on the effect of indoor light-concentration gaseous pollution to human health is deeply concerned. The main reason is that, with the perfecting of the indoor gas tightness and heat-shielding performance, the appearance of new architectural and decorative material, the usage of modern office and other electrical equipment, the air pollution problem in indoor environment becomes more and more serious. Among those indoor pollutants, nitrogen oxide (NO_x: $NO + NO_2$) is a mostly pollutant.

The measuring of NO_x indoors began in 1970s. The report of Miyazaki shows that, the concentration of NO_x will increase by a big margin when gas heater is used in winter.[1] Yamanaka studied the decay rate of NO_x indoors and also pointed out that the concentration of NO will increase greatly (even more than 1.0 mg/L) when gas heater is used.[2] Studying on the NO_x in waste gas, Shingo[3] pointed out that when the temperature is above 773 K and the concentration of methane is ten times than that of NO, they will have a notable effect on the oxidation rate of NO. Based on the theoretically detailed analysis of the possible reaction in indoor environment, Charles[4] pointed out that many reactions indoors depend directly or indirectly on the existence of ozone and hydrocarbon, and the reaction between NO and O_3 is the main path to oxidize NO to NO_2 when there is no sunlight.

From the aspect of chemical reaction, the indoor environment can be regarded as a big reactor in which various reactions occur among all kinds of the chemical substances indoors, so both the factors which affecting the oxidation rate of NO and the oxidation mechanism are complicated. Otherwise, the various pollutants are very small in quantity, thus it is difficult to measure its amount or analyze its mechanism. Looking through the correlative literature, few reports on the oxidation mechanism of NO indoors can be found, but this article has just studied the problem in detail.

Experimental

Instruments, devices and standard gases

Wind-tunnel setup, as shown in Fig. 1, constituted

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of tow cylinders. Fan was fixed at the end of one side of the less cylinder. During the experiment, two kinds of wind-tunnel setups were used, one was made of polypropylene resin (128 L), the other was made of polyvinyl chloride resin (72 L). Polypropylene resin could absorb ultraviolet ray because it contained ultraviolet absorbent, while polyvinyl chloride resin was transparent and could be permeated through by the ultraviolet ray.

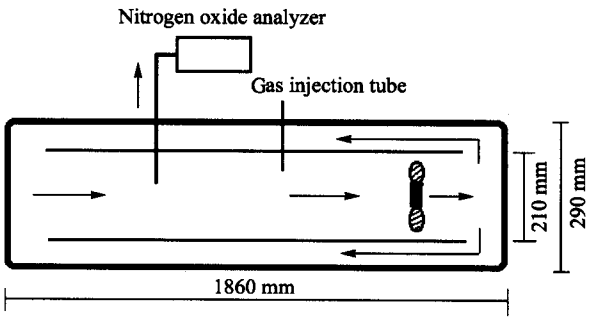

Fig. 1 Diagrammatic drawing of wind-tunnel setup.

The devices are as follows: nitrogen oxide analysis meter (CLAD-100, Simaza, Japan), illumination meter (LX-300, Costom Company, Japan), intensity meter of ultraviolet ray (UVR-2, UD-25, Topcon Company, Japan), ozone analyzer (UVAD-1000, Simaza, Japan), ozone producer (Animal Medicine Company, Japan).

Standard gases are as follows: NO (206 mg/L, Oxidation Company, Japan), NO_2 (168 mg/L, Oxidation Company, Japan), high pure N_2 (99.99%, Oxygen Industry Company, Tokushima, Japan), propylene (99.5%, Oxygen Industry Company, Tokushima, Japan), methane (99.7%, Oxygen Industry Company, Tokushima, Japan).

Experimental method

Before the experiment, the electric supply of the nitrogen oxide analysis meter and the fan in the wind-tunnel setup were turned on. When it stabilized, 2 L of NO (standard gas) was drawn from NO steel cylinder into a gas bag, a fixed quantity of NO was injected by syringe needle into the wind-tunnel setup and the concentration of NO_x ($NO + NO_2$) at different time was monitored with the nitrogen oxide analysis meter (time interval was 10 min, the total experiment time was 3 h). Simultaneously, the physical influencing factors such as temperature, humidity, illumination and intensity of the ultraviolet ray were measured.

When the influence of the NO oxidation by propylene and methane was measured, the essential experiment operation was the same as show nabove. The initial concentration of the NO in wind-tunnel setup was kept at 550 μg/L. After 5 min, 99.5% propylene or 99.7% methane was injected into the wind-tunnel setup and the data were registered (time interval was 10 min, the total experiment time was 70 min). When the influence of NO oxidation by O_3 was measured, the initial concentration of the NO in wind-tunnel setup was kept at 550 μg/L. After 5 min, the pipe of ozone producer was inserted into the gas injection tube. The concentration of O_3 in wind-tunnel was measured by ozone analyzer. When the concentration of O_3 reached 17 μg/L, ozone producer was shut off at once, then, the concentration of NO_x ($NO + NO_2$) at different time was monitored (initial time interval was 1 min, then time interval was 4 min after 10 min, the total experiment time was 42 min).

When measured the main influencing factors of the NO oxidation, the reaction temperature was adjusted by electrical furnaces, the humidity was adjusted by putting a medical glass with water in the wind-tunnel setup, and illumination and the intensity of ultraviolet ray were adjusted by fluorescent lamp or sunlight.

Besides, the nitrogen oxide analysis meter was rectified and performed zero adjustment by infiltration meter (PD-1B) and high pure N_2 timely.

Results and discussion

Oxidation rate of NO *in different environments*

In the condition of identical initial concentration of NO, temperature and humidity, the wind-tunnel setup was put in darkroom, indoor and outdoor environments respectively. The results show that the concentration of NO_2 and NO alter with time (shown in Figs. 2 and 3).

Figs. 2 and 3 show that, the production rate of NO_2 is somewhat slow at the early stage of the reaction in the outdoor environment with sunlight, for the reason that there is about ten minutes' induction period. NO is oxidized to NO_2 rapidly and the concentration of NO_2 reaches a peak value at special time and then decreases. The phenomenon above indicates that the oxidation of NO accords with the chain reaction mechanism of photochemistry.

However, in indoor environment without sunlight, the oxidation rate of NO is very slow. In darkroom, the rate is too slow to detect the production of NO_2.

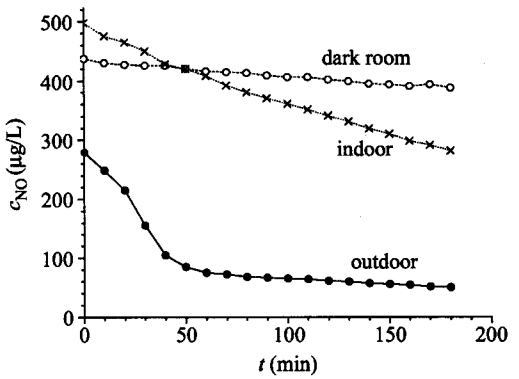

Fig. 2 Change in NO concentration. Dark room: illuminance, 0 Lux; temperature, 290 K; humidity, 30%. Indoor: illuminance, 0 Lux; temperature, 290 K; humidity, 30%;. Outdoor: illuminance, 20000 Lux; temperature, 298 K; humidity, 40%.

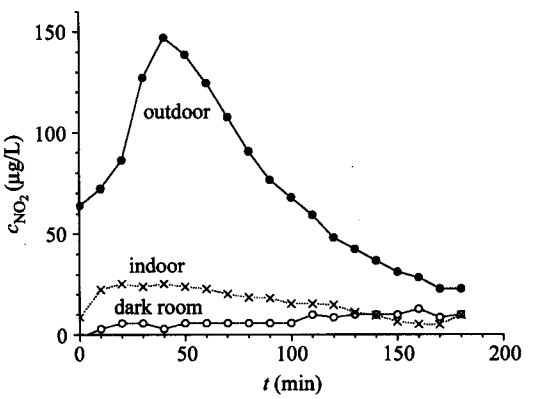

Fig. 3 Change in NO_2 concentration. Dark room: illuminance, 0 Lux; temperature, 290 K; humidity, 30%. Indoor: illuminance, 0 Lux; temperature, 290 K; humidity, 30%. Outdoor: illuminance, 20000 Lux; temperature, 298 K; humidity, 40%.

To sum up, NO can be oxidized to NO_2 in indoor environment, but its oxidation rate is far slower than that in outdoor environment with sunlight. It is mainly because that intensity of ultraviolet ray is very weak indoors, and the initial procedure of chain reaction is so slow that it is difficult to produce free radical.

Effect of the initial concentration of NO

Supposing that the initial concentration of NO ranges between 500 and 900 μg/L, and the oxidation rate of NO ($-d[NO]_0/dt$) is only related to four factors following: the intensity of light indoors (I), the initial concentration of NO ($[NO]_0$), coexistent hydrocarbon ($[HC]_0$) and ozone ($[O_3]_0$), then

$$-\frac{d[NO]_0}{dt} = k \cdot I \cdot [NO]_0^{\alpha} \cdot [HC]_0^{\beta} \cdot [O_3]_0^{\gamma} \qquad (1)$$

where k is the rate constant of the reaction, and α, β *and* γ are reaction orders of NO, HC, O_3, respectively. If we only change the initial concentration of NO, while I, $[HC]_0$ and $[O_3]_0$ are fixed, the following formula will be obtained

$$-\frac{d[NO]_0}{dt} = k_{obs} \cdot [NO]_0^{\alpha} \qquad (2)$$

where $k_{obs} = k \cdot I \cdot [HC]_0^{\beta} \cdot [O_3]_0^{\gamma}$. So we will get

$$\ln\left(-\frac{d[NO]_0}{dt}\right) = \ln k_{obs} + \alpha \cdot \ln[NO]_0 \qquad (3)$$

Based on the experimental findings that different initial concentrations of NO have different effects on the oxidation rate of NO, a straight line is obtained by curve fitting $\ln(-d[NO]_0/dt)$ with $\ln[NO]_0$ (shown in Fig. 4).

$$\ln(-d[NO]_0/dt) = -5.9998 + 1.0455\ln[NO]_0$$
$$R = 0.9934$$

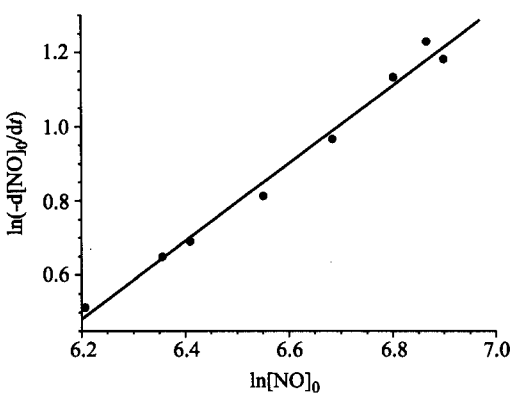

Fig. 4 Relationship between $\ln(-d[NO]_0/dt)$ and $\ln[NO]_0$. Illuminance, 46—58 Lux; temperature, 283 K; humidity, 29%; ultraviolet ray strength, 0.2 μW/cm^2.

From the slope of the line, it can be seen that the reaction order of NO: $\alpha = 1.0455 \approx 1$. That is to say, the oxidation rate of NO increases linearly with the increase of its initial concentration within the given range.

Additionally, $\ln(1/[NO])$ also has a good linear relationship with the time t (shown in Fig. 5),

$$\ln \frac{1}{[NO]} = 6.462 + 0.00278t \quad R = 0.9991 \qquad (4)$$

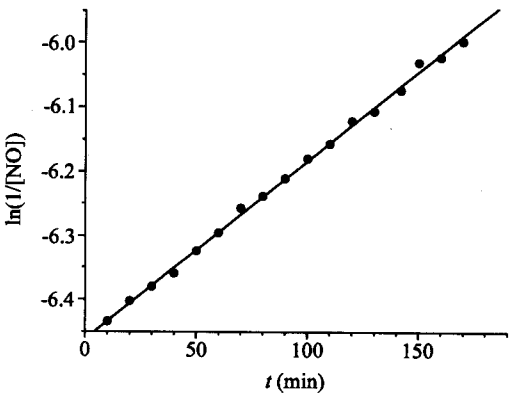

Fig. 5 Relationship between $\ln(1/[NO])$ and time (t). Illuminanc, 46—58 Lux; temperature, 283 K; humidity, 29%; ultraviolet ray strength, 0.2 $\mu W/cm^2$.

This is the characteristic of the first-order reaction. The two results above got from different dynamics methods are identical, thus it can be determined that the reaction order of NO is first-order while its initial concentration ranges between 500 and 900 $\mu g/L$.

Effect of coexistent ozone

In indoor environment, the oxidation rate of NO is relevant to ozone directly or indirectly. Fig. 6 shows the experimental results when NO coexists with ozone, from which it can be seen that the oxidation rate will be greatly accelerated when there is micro O_3 coexistent. This is mainly because the reaction

$$O_3 + NO \underset{k_{-2},\ h\nu}{\overset{k_2}{\rightleftharpoons}} NO_2 + O_2 \qquad (5)$$

is an opposing reaction of 2-2 order. When the sunlight irradiates the reaction system, the intensity of ultraviolet ray is strong, and so that the rate of the reverse reaction increases. While there is no sunlight or the intensity of

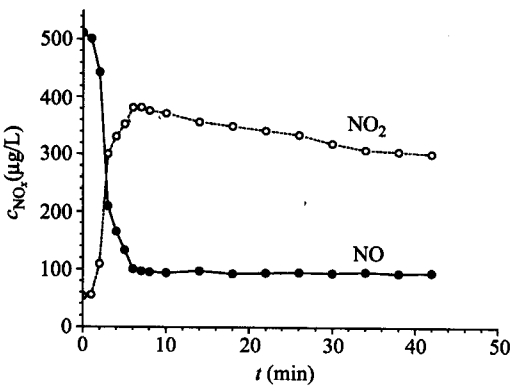

Fig. 6 Change in the concentration of NO_x when micro O_3 (17 $\mu g/L$) coexisting. Illuminance, 46—58 Lux; temperature, 283 K; humidity, 29%; ultraviolet ray strength, 0.2 $\mu W/cm^2$.

ultraviolet ray is very weak, the rate of the reverse reaction will be very slow (may be ignored). Thus, in indoor environment, the forward reaction can be considered as

$$\underset{(A)}{O_3} + \underset{(B)}{NO} \xrightarrow{k_2} \underset{(C)}{NO_2} + \underset{(D)}{O_2} \qquad (6)$$

where $k_2 = 4.43 \times 10^{-4} (\mu g/L)^{-1} \cdot s^{-1}$.[5] If $[B]_0 = 20$ $\mu g/L$ fixed and only $[A]_0$ changed, the following results are got when $[A]_0 = 2$ $\mu g/L$ and $[A]_0 = 20$ $\mu g/L$,

	A +	B	$\xrightarrow{k_2}$ C +	D	(a)
$t = 0$	2	20	0	0	
$t = t$	$20 - x_1$	$20 - x_1$	x_1	x_1	

	A +	B	$\xrightarrow{k_2}$ C +	D	(b)
$t = 0$	20	20	0	0	
$t = t$	$20 - x_2$	$20 - x_2$	x_2	x_2	

According to dynamics equation of second-order reaction, the results are got as

$$\frac{1}{[A]_0 - [B]_0} \ln \frac{[B]_0(2 - x_1)}{[A]_0(20 - x_2)} = k_2 t$$

$$\frac{1}{20 - x_2} = \frac{1}{[A]_0} + k_2 t$$

from which $x_1 = 0.018$ $\mu g/L$, $x_2 = 0.18$ $\mu g/L$. So when $[O_3]$ increases ten times, $[NO_2]$ also increases ten

times. Ozone indoors mostly comes from the outdoor environment. Generally, in the room with good air exchange (such as office, meeting-room), the concentration of O_3 is only 20—30% of outdoors. In this experiment, $[O_3]$ in the given laboratory is 15—52 $\mu g/L$, measured by a ozone analysis meter. But various electrical equipments such as duplicator and printer discharge electric arc and create O_3 concomitantly. Leovic[6] has reported that a duplicator can create 1.3—7.9 mg of O_3 an hour in different humidity conditions. All above show that, as the sunlight indoor and the intensity of ultraviolet ray are weak, the reaction of NO with O_3 is an important factor to increase the concentration of NO_2 indoors. Fig. 6 also shows that, the concentration of product NO_2 will sharply increase within 8 min, then it will decline slowly. There are possible reasons as follows. In this experiment, $[O_3] = 17$ $\mu g/L$, $[NO]_0 = 2$ $\mu g/L$, so O_3 can also react with the product NO_2 at the same time. The reaction is

$$O_3 + NO_2 \underset{h\nu}{\overset{k_2'}{\rightleftharpoons}} NO_3\cdot + O_2 \qquad (7)$$

At the beginning of the reaction of Eq. (5), $[NO_2]$ is very small, so the main reaction is the forward reaction. With the increase of $[NO_2]$, the rate of the reaction of Eq. (7) also increases, which makes $[NO_2]$ decline with time. The free radical $NO_3\cdot$ is decomposed owing to the sunlight shining, so $[NO_3\cdot]$ outdoors is very small in the daytime but it will get to 0.430 $\mu g/L$ at night. With micro O_3 coexistent, there is other aspect of the reason that $[NO_2]$ declines. For example, NO_2 can be photo-decomposed under the light of fluorescent lamp.

$$NO_2 + O_2 \xrightarrow{h\nu} O_3 + NO$$

Also NO_2 can react with other free radicals indoors such as $HO\cdot$ and $RC(O)O_2\cdot$,

$$HO\cdot + NO_2 \longrightarrow HNO_3$$

$$RC(O)O_2\cdot + NO_2 \longrightarrow RC(O)O_2NO_4$$

and these reactions can reduce the concentration of NO_2.

Effect of coexistent propylene and methane

There are unsaturated hydrocarbon (C_3H_6) and ozone in indoor air environment, and the reaction of O_3 with the unsaturated hydrocarbon is a main source of free radical $HO\cdot$ indoors.[7] The experiment result shows that micro coexistent propylene has great effect on the oxidation rate of NO (Fig. 7). When $[C_3H_6]$ ranges in 16—80 $\mu g/L$ and $[NO]_0$ is constant, the oxidation rate of NO increases with the increase of $[C_3H_6]$. According to the analysis of the references and the experiment results, the effect of C_3H_6 on the oxidation rate may be carried out according to such mechanism of chain reaction.[6]

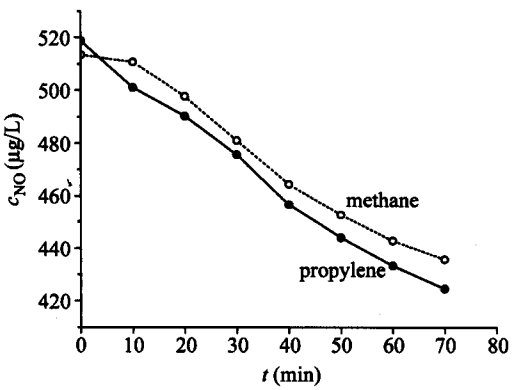

Fig. 7 Change in the concentration of NO when propylene (39 $\mu g/L$) or methane (390 $\mu g/L$) coexisting. Illuminance, 45—57 Lux; temperature, 284 K; humidity, 52%, ultraviolet ray strength 0.2 $\mu W/cm^2$.

The chain initiation:

$$O_3 + C_3H_6 \rightarrow \underset{\diagdown O \diagup}{\overset{O}{H_2C\text{-}CHCH_2}} \rightarrow HCHO + CH_3CHOO\cdot \qquad (8)$$

$$CH_3CHOO\cdot + O_2 \rightarrow \cdot OH + CH_3\overset{O}{\overset{\|}{C}}OO \qquad (9)$$

The chain transfer:

$$C_3H_6 + \cdot OH \longrightarrow CH_3\dot{C}HCH_2OH \qquad (10)$$

$$CH_3\dot{C}HCH_2OH + O_2 \longrightarrow CH_3\dot{C}H(O_2)CH_2OH \qquad (11)$$

$$CH_3\dot{C}H(O_2)CH_2OH + NO \longrightarrow CH_3\dot{C}H(O)CH_2OH + NO_2 \qquad (12)$$

$$CH_3\dot{C}H(O)CH_2OH \longrightarrow CH_3CHO + \cdot CH_2OH \qquad (13)$$

$$\cdot CH_2OH + O_2 \longrightarrow HCHO + HO_2\cdot \qquad (14)$$

$$HO_2\cdot + NO \longrightarrow NO_2 + \cdot OH \quad (15)$$

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The chain termination:

$$\cdot OH + NO + M \longrightarrow HONO \quad (16)$$

$$\cdot OH + NO_2 + M \longrightarrow HONO_2 \quad (17)$$

In Eqs. (8) and (9), O_3 existing in the air indoors originally reacts with coexistent propylene and thus produces ring ozonide, and it is decomposed into $CH_3CHOO\cdot$ radical subsequently. Then $CH_3CHOO\cdot$ reacts with oxygen to produce the radical $\cdot OH$. The free radical $\cdot OH$ created in Eq. (9) will be the chain reaction initiator of NO in Eqs. (10)—(15). The chain transfer process in the Eqs. (10)—(15) is also the main process that NO is oxidized to NO_2. Eqs. (16) and (17) are the chain termination process, and M refers to reactor walls or other inert molecules which are only used to transfer energy.

Using gas cooking stoves or other gas heaters indoors, it can discharge unburned methane, and the effect of methane coexistent on the oxidation rate of NO (Fig. 7). has been studied The results show that methane coexistent has weaker effect on the oxidation rate of NO than propylene coexistent.

Conclusions

According to literature and the results of this research, when the initial concentration of NO is less than 500 μg/L, the oxidation rate of NO is very slow in the indoor environment. But with micro ozone and unsaturated hydrocarbon coexistent, the rate accelerates obviously. Though illumination and the intensity of ultraviolet ray have some effect on the rate, they are very weak in indoor environment, thus the two factors are not the main influence factor to promote the oxidation of NO.

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