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Rapid Oxidation of NO to NO_2 at ppm Concentration Level in a Heterogeneous Photocatalytic Reaction on Metal Oxide Powders

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Photocatalytic reactions of NO at ppm level with O_2 were studied in the presence of TiO_2 (anatase), PbO, and ZnO using a chemical luminescence NOX analyzer and a second derivative spectrometer. The rate of oxidation of NO was very high, e.g. 1930% cm^{-2} h^{-1} in a photocatalytic reaction on TiO_2 (anatase). Photoadsorption of NO_x also took place on these metal oxides.

Conversion of NO in low concentration to NO_2 in air is an important subject in the atmospheric chemistry in connection with the decay process of NO_x and the acid precipitation. NO can be oxidized by oxygen, but the rate is extremely low at the atmospheric concentration level. Photochemical oxidations of NO in the presence of hydrocarbons have been studied, and discussed in terms of intervention of intermediate organic radical species.

Airborne particulate substances contain various metal oxides, and some of them are active in heterogeneous photocatalytic reactions.[1,2] For example, the airborne particles obtained from some urban areas contain 1 to 4% of ZnO, PbO, TiO_2, and Fe_2O_3.[3] A few authors reported heterogeneous photocatalytic reactions of air pollutants. Courbon and Pichat studied photochemical processes of $N^{18}O$ on TiO_2 (anatase).[4] They reported photoadsorption of NO, isotopic exchange of O atom between $N^{18}O$ and TiO_2, and photodecomposition of NO. However, they did not mention oxidation of NO. This communication preliminarily reports rapid photocatalytic oxidation of NO at ppm level on metal oxides. This experimental fact appears remarkable from the point of view of the atmospheric chemistry.

A Pyrex tube (20 mm i.d., 320 mm length) was placed horizontally in which metal oxide powders (0.2 to 0.4 g) were spread approximately in the region of 10 x 160 mm. Metal oxide powders employed were purchased from Furuuchi Kagaku Co. Ltd.; TiO_2 (anatase, 99.99%), PbO (99.999%), and ZnO (99.99%). A low pressure mercury lamp (13 W), apart 2 cm from the reactor set in parallel, irradiated the reactor. Gas mixtures containing NO were passed through the reactor at the flow rate of ca. 200 ml min^{-1} at 1 atm at the ambient temperature. The flow gases, N_2 containing 1000 ppm NO, N_2, and O_2, were purified with silica-gel columns before being mixed. The concentration of NO was adjusted by regulating the flow rates of these gases. A part of the flow gas was divided for analysis before the reactor. The effluent gas from the reactor was introduced to a chemical luminescence NOX analyzer (Bendix, Model 8101-B). The NOX analyzer gives the analytical value for

NO and NO_x. The value of NO_x is given as the sum of NO, NO_2, and other higher oxides. Then, a second derivative spectrometer (LSI Spectrometrics, Model III d^2 Laboratory Analyzer) was employed to analyse NO_2 in the effluent gas.

A gas mixture of NO (ca. 2 ppm), N_2 (0.2%), and O_2 (99.8%) was passed into the reactor which did not contain catalyst powder. The concentration of NO at the outlet of the reactor did not change from that at the inlet, regardless of the irradiation. Figure 1 illustrates the concentration of NO_x and NO_x - NO for an NO (1.7 ppm), N_2 (0.2%), and O_2 (99.8%) system in the presence of TiO_2 (anatase) powder. NO_x - NO represents the difference of the analytical values obtained for NO_x and NO by the NOX analyzer. NO_x markedly dropped when the reactor was irradiated, and then gradually increased. When the lamp was turned off, the NO_x concentration jumped up, exceeding that of the inlet NO, and then decreased gradually. NO_x - NO appeared at the time of illumination, and diminished after the illumination stopped. These features were greatly magnified by replacing the Pyrex reactor with a fused quartz one.

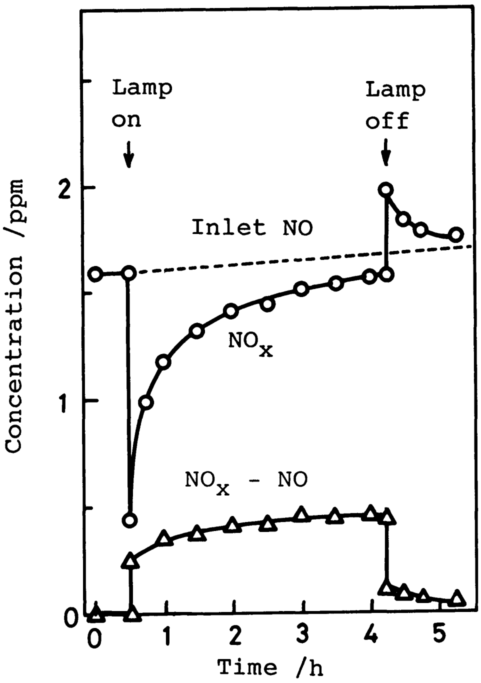

Fig. 1. Concentration of NO_x and NO_x - NO in the effluent gas in the photocatalytic reaction of NO with O_2 in the presence of TiO_2.

The effluent gas from the NO and O_2 systems in the presence of illuminated TiO_2 was analysed for NO_2 concentration by using the second derivative spectrometer. The results for various NO concentrations are presented in Table 1, along with NO_x - NO obtained from the NOX analyzer. The concentrations of NO_2 fairly agree with those of NO_x - NO. Hence, NO_x - NO comprises mostly NO_2. NO was evidently converted to NO_2 on TiO_2 (anatase) in a photocatalytic oxidation. Table 2 shows the amounts of NO_2 formation during the reactions.

The difference in the concentration between the inlet NO and the outlet NO_x indicates that photoadsorption takes place. We thus integrated this difference during the illumination. The integrated values for TiO_2 (anatase), PbO, and ZnO are tabulated as the adsorbed NO_x in Table 2. The desorption was measured under N_2 gas flow in the dark initially at the ambient temperature, and then at higher temperatures raised up to 400 °C. The amounts of adsorbed NO_x are in good agreement with the sum of NO_x desorbed at the ambient temperature and up to 400 °C. Courbon and Pichat[4] previous

Table 1. NO_2 concetration obtained from the second derivative spectrometer as compared with NO_x - NO determined by the NOX analyzer

Inlet /ppm	Outlet /ppm			NO_2 /ppm
NO	NO_x	NO	NO_x - NO	
1.36	1.24	0.76	0.48	0.31
3.85	3.65	3.00	0.65	0.55
4.00	3.70	3.13	0.57	0.52

The data were obtained from the photochemical reaction with TiO_2 after standing for more than 30 min under nearly steady state conditions.

Table 2. Formation of NO_2 and adsorption of NO_x on various metal oxide powders

Metal oxides	Inlet NO	Total NO supplied	Resulting NO_2	Adsorbed NO_x	Desorbed amount/ 10^{-6}mol			
					Ambient temp		up to 400 °C	
	ppm	10^{-6}mol	10^{-6}mol	10^{-6}mol	NO	NO_x	NO	NO_x
TiO_2	1.80	3.32	0.49	0.58	0.04	0.10	0.15	0.42
ZnO	1.98	1.47	0.02	0.10	0.00	0.00	0.07	0.08
PbO	2.00	1.50	0.07	0.03	0.00	0.00	0.01	0.02

ly reported the photoadsorption of NO on irradiated TiO_2 (anatase).

In addition to the metal oxides shown in Table 2, the similar measurements were conducted with some other compounds. Bi_2O_3 showed some activity in photochemical NO_2 formation; TiO_2 (rutile), V_2O_5, Al_2O_3, and Fe_2O_3 were inert. TiO_2 (rutile), Bi_2O_3, and Fe_2O_3 appreciably adsorbed NO under illumination.

The well-known third order rate equation holds for the gaseous oxidation of NO with O_2 without any catalysts;[5, 6] $2NO + O_2 \longrightarrow 2NO_2$. The rate equation is $dx/dt = k(a - x)^2(b - x/2)$, where a and b denote the initial concentration of NO and O_2, and x the concentration of produced NO_2. The half-life period of NO $t_{1/2}$ is approximated under the condition of b>>a; $t_{1/2} = 1/(2kab)$. The rate constant k is $1.45 \times 10^4\ l^2\ mol^{-2}\ s^{-1}$ according to Stedman and Niki.[6] The values of $t_{1/2}$ are estimated for NO 100 ppm and 1 ppm, with O_2 1 atm and 0.2 atm from the above approximation, and are presented in Table 3.

Sakamaki et al. reported[7] photochemical reaction of an NO (1.5 ppm)- C_3H_6 (3 ppm)- dry air system under the light intensity equivalent to the natural solar radiation. $t_{1/2}$ obtained from their report is presented in Table 3 along with a similar data from another source.[8] Ogita et al. reported[9] photocatalytic oxidation of NO (93 ppm) in air in the presence of TiO_2 (Merck, anatase). They studied the reaction in a static quartz reactor with illumination of a low pressure mercury lamp (4 W). The half life period obtained by them is very large (Table 3) as compared with the present results, being even much greater than that obtained from the third order rate equation mentioned above for NO 100 ppm. The reason may stem from photolysis of NO_2 back to NO as suggested previously by Stedman and Niki.[6] There is a discrepancy in the

Table 3. Comparison of the rates and the half life periods of oxidation of NO in various processes

Metal oxide powders	NO	O_2	rate	$t_{1/2}$	Ref.
	ppm	atm	% $cm^{-2}h^{-1}$	min	
Third order reaction					
-	100	0.2	174	17.2	calcd
-	2	1.0	17.4	172	calcd
-	1	1.0	8.7	344	calcd
-	1	0.2	1.7	1718	calcd
Photochemical reaction NO- C_3H_6(2-3 ppm)- air					
-	1.5	0.2		100	7
-	1.0	0.2		40	8
Photocatalytic reaction by Ogita et al.					
TiO_2	93	0.2		40	9
Present work					
TiO_2	1.80	1.0	1930	2.2	
PbO	1.98	1.0	1050	4.0	
ZnO	2.00	1.0	323	12.8	

photocatalytic activity of TiO_2 (anatase) between the present study and Ogita et al.'s. The reason is unknown, but Ogita et al. showed that the activity of TiO_2 (anatase) was much enhanced with KOH impregnation.

Table 3 presents the average rates of oxidation per unit illuminated catalyst area evaluated from the data in Table 2. The reaction time was taken as the contact time of the flow gas under an assumption of a piston flow over the catalyst powders. Apparent half life periods of NO were calculated with an assumption of the first order reaction under the present experimental conditions.

The light intensity was measured for the present system by using a chemical actinometer of iron (III) oxalate. The photon intensity was approximately 1.5×10^{14} cm^{-2} s^{-1} at the inside of the Pyrex reactor for the wave length 300 to 525 nm.10) The band gap energy of TiO_2 (anatase) equals photon energy of the wave length ca. 400 nm. Thus the effective wave length for the reaction on TiO_2 (anatase) is between 300 and 400 nm in the Pyrex reactor. The fraction of photon intensity for 300 to 400 nm is estimated to be roughly 40% of that for 300 to 525 nm by considering the spectral distribution of a low pressure mercury lamp,11) giving 6×10^{13} cm^{-2} s^{-1} for the effective photon intensity in the present experimental conditions. By assuming that two electrons are involved in the reaction, the quantum efficiency of 4% is derived for TiO_2 (anatase). The identical procedure gives the quantum efficiency of 0.5% for ZnO and 0.7% for PbO. The solar radiation gives the photon intensity ca. 2.0×10^{16} cm^{-2} s^{-1} for the wave length 300 to 400 nm outside the troposphere.12) The present experimental irradiation is thus roughly 1/300 of the natural solar radiation.

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