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Low-pressure chemical and photochemical reactions of oxides of nitrogen on alumina taken as a model substance for mineral dust in relation to air pollution

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Abstract

The interaction of γ-Al_2O_3, taken as a model substance of tropospheric mineral dust, with N_2O, NO and NO_2 has been studied using kinetic and temperature-programmed desorption (TPD) mass-spectrometry in presence and absence of UV irradiation. At low surface coverages (<0.001 ML), adsorption of N_2O and NO_2 is accompanied by dissociation and chemiluminescence, whereas adsorption of NO does not lead to appreciable dissociation. Upon UV irradiation of Al_2O_3 in a flow of N_2O, photoinduced decomposition and desorption of N_2O take place, whereas in a flow of NO, only photoinduced desorption is observed. Dark dissociative adsorption of N_2O and NO and photoinduced N_2O dissociation apparently occur by a mechanism involving electron capture from surface F- and F^+-centers. Photoinduced desorption of N_2O and NO may be associated with decomposition of complexes of these molecules with Lewis acid sites, V-centers or OH-groups. TPD of N_2O and NO proceeds predominantly without decomposition, while NO_2 partially decomposes to NO and O_2.

Keywords: Air pollution; Mineral dust; Alumina; Nitrogen oxide; UV irradiation; Adsorption; Dissociation

1. Introduction

Heterogeneous processes involving oxides of nitrogen (N_2O, NO and NO_2) and mineral dust aerosols play an important role in tropospheric chemistry [1–4]. Mineral dust has complex chemical and mineralogical compositions, in which aluminum is one of the major elements. Mineral dust is approximately 60% SiO_2 and 10–15% Al_2O_3, whereas other oxides, such as Fe_2O_3, MgO and CaO are less abundant [4]. The interaction of nitrogen oxides at room temperature with powder aluminas has been studied using FT-IR, DRIFTS and Knudsen cell measurements [5–9]. The emphasis was made on NO_2, probably because NO_2 is closely linked to tropospheric ozone formation. Uptake coefficients for NO_2 were measured, surface species formed upon adsorption were identified, and reaction mechanism for the NO_2–Al_2O_3 system was proposed [3,5,6]. Less is known about adsorption and reactions of NO and especially N_2O on alumina [7–9]. A variety of N-containing surface species was detected by FT-IR, but possible formation of gaseous products was not monitored. The effect of UV irradiation on adsorption and reactions of nitrogen oxides with Al_2O_3 was not reported so far.

In the present work, γ-Al_2O_3 was taken as a model substance for mineral dust and its interaction with N_2O, NO and NO_2 was studied using kinetic and temperature-programmed desorption (TPD) mass spectrometry in presence or absence of UV-irradiation. NO and NO_2 are involved in the same atmospheric chemical cycle, whereas N_2O is a greenhouse gas influencing the environment. The advantage of mass spectrometry is its high sensitivity enabling to quantify the composition of the gas phase at very low pressure and surface coverage and thus to study the kinetics and mechanisms of thermal and photon-induced adsorption and desorption processes on γ-Al_2O_3 under conditions modeling the environment. Average concentrations of N_2O, NO and NO_2 in the troposphere are within 0.1–0.3 ppb [1]. However, in polluted environment and in air photochemical

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smog, the concentrations of NO and NO_2 can reach 200–300 ppb [1,6]. These concentrations are far above the sensitivity limit of the mass spectrometric technique which is capable of analyzing gaseous mixtures containing $\geq 10^9$ molec cm^{-3} ($\geq$0.04 ppb) of nitrogen oxides.

2. Experimental

A powder γ-Al_2O_3 manufactured at Donetsk chemical plant ($S = 200$ m^2 g^{-1}) was used. The major impurities were MgO ($\sim 10^{-3}$ wt.%), Si ($<10^{-2}$ wt.%) and Fe ($<10^{-4}$ wt.%). Finely ground alumina was deposited on the walls of a tubular quartz reactor ($d = 35$ mm, $h = 10$ mm) from a suspension in bidistilled water. The reactor suitable for *in situ* UV irradiation was connected to a high-vacuum pumping system supplied with gas-storage bulbs. The alumina sample was pretreated in an oxygen flow at 950 K for 20 h and then in vacuum at 1000 K for 1 h. ^{15}NO (94.9 at.% of ^{15}N), N_2O and NO_2 produced at the St.-Petersburg Institute of Applied Chemistry were used after low-temperature fractional distillation. The purity of the gases was higher than 99.5 at.%.

The gas-phase composition above the alumina sample was measured with a MI-1201 mass spectrometer ($m/\Delta m > 600$); the sensitivity to the nitrogen oxides studied was better than 10^9 molec cm^{-3}. The use of ^{15}NO enabled us to easily discriminate background peaks ^{12}CO ($m/e = 28$) and $^{12}CO_2$ ($m/e = 44$) and those of the reaction products $^{15}N_2$ ($m/e = 30$) and $^{15}N_2O$ ($m/e = 46$) in mass spectra.

UV irradiation was carried out using a high-aperture (1:1.6) monochromator supplied with Xe-lamp as a light source (Fig. 1). In chemiluminescence experiments, the light emitted upon N_2O or NO_2 adsorption was focused with an ellipsoidal mirror and a quartz lens (not shown in Fig. 1) onto a FEU-39A photomultiplier with a quartz entrance window. Either full emission in the 200–600 nm range or certain spectral interval selected by narrow band color filters were measured. The registration system was calibrated using a tungsten SI-80-20u (MELZ) band lamp as reference light source and a thermopile (St.-Petersburg Electrotechnical Institute) or photocells F-7, F-13 (MELZ) as light detectors.

Static and flow experiments were performed in this study. In the latter case, the input gas flow was adjusted in such a way that the equilibrium pressure above the sample was in the interval of 10^{-5} to 10^{-6} Torr. Under such conditions, the deviation of output signal of the mass-spectrometer from its equilibrium value caused by UV irradiation was directly proportional to $d\Theta/dt$, where Θ is surface coverage.

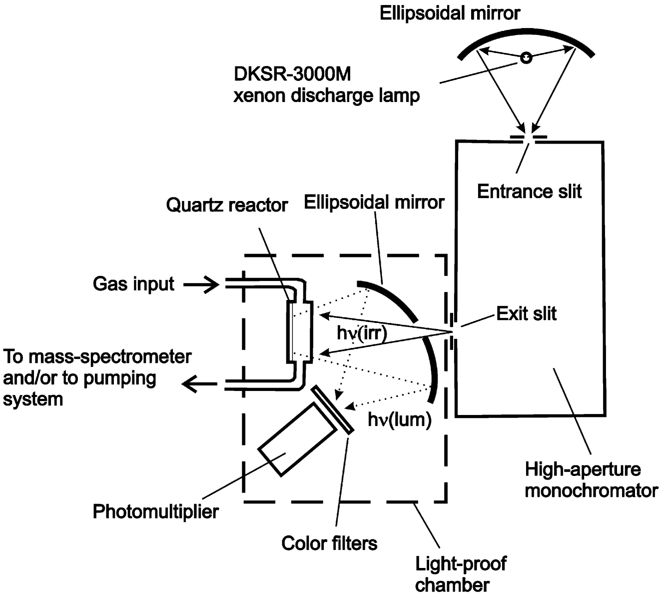

Fig. 1. Schematic drawing of the experimental setup.

The number of photons absorbed by the alumina sample was calculated as IK_{abs}, where I is the photon flux incident upon the sample surface, and K_{abs} is absorption coefficient. The flux I in photon s^{-1} at a given wavelength and at a spectral slit width 2 nm was measured using a calibrated FEU-99 photomultiplier. Absorption coefficient K_{abs} was determined from diffuse reflectance spectra of alumina recorded with a Beckman UV-5270 instrument supplied with an integrating sphere using $BaSO_4$ as reference.

TPD spectra were measured in the 300–1000 K interval at a heating rate 0.4 K s^{-1} after evacuation of the sample at 293 K.

3. Results and discussion

Room-temperature admission of N_2O, NO and NO_2 ($P_0 = 0.1$–0.001 Torr) onto pretreated alumina is accompanied by an initial "fast" pressure drop ($\sim$1 s) followed by a much slower gas uptake (500–1000 s). Table 1 gives the concentrations of nitrogen oxides in the gas phase and on the surface for some equilibrium pressures. The surface concentration was calculated from the pressure drop in a calibrated volume upon adsorption. Assuming that the surface area occupied by one adsorbed NO_x molecule is about 20 Å^2, one can calculate that a monolayer coverage ($\Theta = 1$) corresponds to $\sim 5 \times 10^{14}$ molec cm^{-2}. At low coverages Θ falling in the range 4×10^{-3} to

Table 1
Equilibrium concentration of N_2O, NO and NO_2 in gas phase and on alumina

Molecule	Equilibrium concentration in gas phase		Surface coverage		b (Torr^{-1})[a]
	molec cm^{-3}	Torr	molec cm^{-2}	Θ	
N_2O	7×10^{12}	2×10^{-4}	2×10^{12}	4×10^{-3}	20
NO	1.5×10^{13}	4.3×10^{-4}	3.2×10^{12}	6.4×10^{-3}	15
NO_2	2×10^{11}	5.7×10^{-6}	1×10^{13}	2×10^{-2}	3600

[a] Estimated from Langmuir adsorption isotherm equation $\Theta = bP/(1 + bP)$.

2×10^{-2} (Table 1), the adsorbed molecules, rather strongly bound to the surface, cannot be removed by evacuation at room temperature. According to the TPD data, the energy of desorption of N_2O and NO is in the range of 120–140 and 90–135 kJ mol^{-1}, respectively. The adsorption–desorption equilibrium constants (b) derived from Langmuir adsorption isotherm equation $\Theta = bP/(1 + bP)$ are similar for N_2O and NO, whereas the much higher b value for NO_2 suggests that the adsorption equilibrium is strongly shifted toward the adsorbed species.

Upon adsorption on alumina, N_2O partially decomposes into N_2 and O_2, the latter being strongly held on the surface, so that the N_2/O_2 ratio in the gas phase considerably exceeds the stoichiometric value of two. The extent of N_2O dissociation decreases with increasing initial pressure, most likely, because of a limited number of surface sites able to dissociate N_2O. The concentration of these sites was estimated in Ref. [10] as 10^9 to 10^{10} cm^{-2}. The N_2O adsorption is accompanied by chemiluminescence with maximum emission at 420 nm with a halfwidth $\Delta\lambda_{1/2} \sim 100$ nm. Fig. 2 illustrates the relation between the emission intensity and N_2O pressure upon N_2O admission onto Al_2O_3 at 375 K. The emission intensity increases with pressure, but at constant pressure its intensity decreases exponentially with a characteristic time 7.68 ± 0.43 s (solid line 3 in Fig. 2). The emission completely disappears after sample evacuation. Upon repeated N_2O admission, the emission reappears with much lower intensity suggesting a limited number of emission centers is involved.

The dissociative adsorption of N_2O and associated chemiluminescence can be explained assuming that N_2O adsorbs mainly on F- and F$^+$-centers (i.e., oxygen vacancies filled with two or one electron(s), respectively) and then dissociates after electron capture:

$$\mathrm{F} + \mathrm{N_2O} \rightarrow \mathrm{N_2}\uparrow + \mathrm{O_{ads}}^{2-} + h\nu \qquad (1)$$

$$\mathrm{F}^+ + \mathrm{N_2O} \rightarrow \mathrm{N_2}\uparrow + \mathrm{O_{ads}}^{-} + h\nu \qquad (2)$$

The $O_{ads}{}^-$ species can further convert to a lattice $O_{lat}{}^{2-}$ by capturing an electron from F- or F$^+$-centers. The filling of an oxygen vacancy implies the elimination of the F-center: the electron is transferred from the level of the F-center located inside the bandgap to the $O_{lat}{}^{2-}$ level in the valence band or to the $O_{ads}{}^-$ level located near the top of valence band. The energy of rearrangement of such center is evolved as a light quantum (chemiluminescence).

Assuming that the rate of F-center decay, dC_F/dt is a linear function of N_2O pressure, $P(N_2O)$, one can write:

$$-\frac{dC_F}{dt} = kP(N_2O)C_F,$$

where k is a coefficient of proportionality. At a constant N_2O pressure, the rate of F-center decay and, correspondingly, the emission intensity decay, I_L are described by an exponential function:

$$I_L = \alpha\left(-\frac{dC_F}{dt}\right) = \alpha k_1 C_F = k_1 C_F^0 \exp(-k_1 t)$$

where α is probability of light emission, $k_1 = kP(N_2O)$ and C_F^0 is F-center concentration at the moment of reaching a constant pressure. The exponential character of the luminescence decay is well proved by curve 3 in Fig. 2.

At the initial "fast" adsorption stage at room temperature, NO_2 interacts with alumina yielding NO, whereas NO_2 and O_2 are not found by mass spectrometry in the gas phase. The NO_2 adsorption is accompanied by chemiluminescence whose spectral characteristics are identical to those observed upon N_2O adsorption. The NO_2 dissociation likely occurs on F- and F$^+$-centers and is described by the overall reaction:

$$\mathrm{F(2F^+)} + \mathrm{NO_2} \rightarrow \mathrm{NO} + \mathrm{O_{ads}}^{2-} + h\nu \qquad (3)$$

Unlike those of N_2O and NO_2, NO adsorption on Al_2O_3 at 225–375 K is not followed by a noticeable change of the gas phase composition. However, the possibility of NO

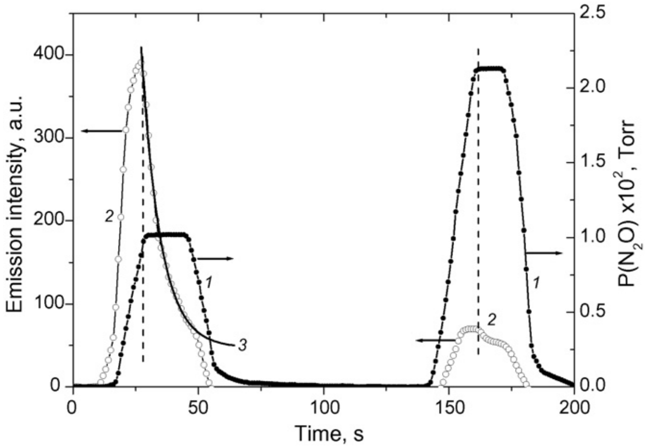

Fig. 2. Kinetics of chemiluminescence upon N_2O admission onto Al_2O_3 sample at 375 K. (1) N_2O pressure; (2) emission intensity; (3) calculated exponential curve of the emission decay at constant N_2O pressure. The onset of the pressure plateau is marked by the vertical dash lines.

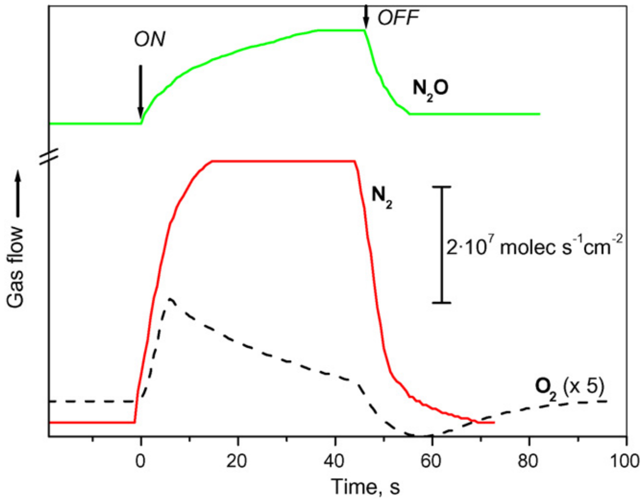

Fig. 3. Kinetics of photoinduced N_2O decomposition and desorption over Al_2O_3 in a flow-through mode. Initial flow rate of N_2O is 1×10^{13} molec s^{-1} cm^{-2}.

Table 2
Summary of TPD data

Molecule	Coverage (molec cm^{-2})	Product distribution and temperature of peak maximum									
		N_2O (%)	T_{max} (K)	NO (%)	T_{max} (K)	NO_2 (%)	T_{max} (K)	N_2 (%)	T_{max} (K)	O_2 (%)	T_{max} (K)
N_2O	8×10^{10}	81.1	520					18.7	400	0.2	400
N_2O	2.5×10^{12}	95.3	507					4.4	465 (sh 370)	0.2	~420
NO	2×10^{12}	0.6	520	99.4	415						
NO	8×10^{12}	4.8	512	95.0	335					0.2	810
NO_2	3×10^{13}	1.5	675	74.6	585, 780	10.3	655–730			13.6	765

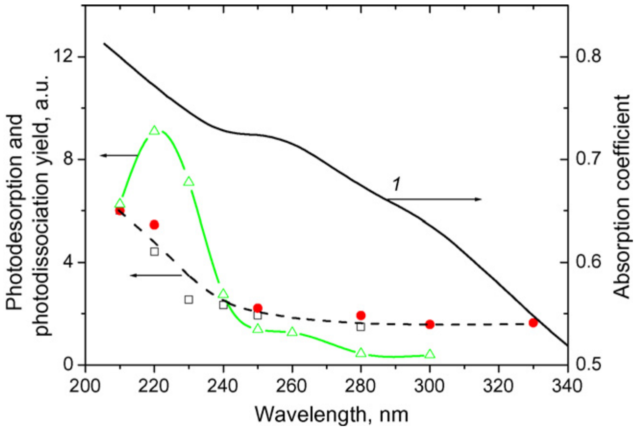

Fig. 4. Relative efficiency of photoinduced decomposition and desorption of N_2O and NO vs. UV-irradiation wavelength: (△) N_2O decomposition; (□) N_2O desorption; (●) NO desorption. (1) Absorption spectrum of Al_2O_3.

disproportionation into N_2O and O_2 which both remain on the surface cannot be completely ruled out.

The effect of light irradiation on adsorption and reactions of nitrogen oxides has been studied in a flow regime at an equilibrium pressure of 10^{-5} to 10^{-6} Torr. UV-irradiation (λ = 220–330 nm) of Al_2O_3 in presence of N_2O leads to dissociation and desorption of these molecules (Fig. 3). Small amounts of gaseous O_2 are also detected under UV irradiation. Photodissociation is the major process, since the N_2 pressure increase is ~3 times that of N_2O. Upon UV-irradiation of Al_2O_3 in a NO flow under similar conditions, there is no evidence of decomposition and only photon-induced desorption is observed.

Spectral dependences for the photon-induced dissociation of N_2O and desorption of N_2O and NO are shown in Fig. 4. The yields in Fig. 4 are normalized to the number of light quanta adsorbed by alumina at a specific wavelength. The spectral dependence of absorption coefficient for pretreated Al_2O_3 is also presented in Fig. 4 for comparison purpose (curve 1). The photodissociation curve displays a distinct maximum at ~220 nm and a shoulder at ~260 nm, whereas the photodesorption yield decreases monotonically with increasing wavelength.

The positions of maxima on the N_2O dissociation curve are close to those of F^+-center absorption bands [11,12]. It is therefore assumed that photodecomposition occurs with the participation of F^+-centers:

$$F^+ + h\nu \rightarrow [F^+]* \rightarrow F^{++} + e \quad (4)$$

$$e + N_2O \rightarrow N_2\uparrow + O_{ads}{}^- \quad (5)$$

Photoinduced desorption of N_2O and NO can be rationalized assuming photon-stimulated decomposition of complexes formed from these molecules with surface centers such as Lewis acid sites, OH-groups or V-centers. The energy of a light quantum absorbed upon charge transfer in an Al^{3+}–O^{2-} pair can be transferred to the complexes causing their decomposition. The efficiency of the process correlates with the alumina absorption spectrum.

The data of TPD experiments obtained after adsorption of nitrogen oxides on alumina at 300 K are summarized in Table 2. Thermodesorption of adsorbed N_2O and NO occurs predominantly without decomposition, while in the case of NO_2, the major desorption product is found to be NO. The temperature of the desorption peaks depends on the initial coverage suggesting that the adsorption sites are not homogeneous.

4. Conclusion

The use of highly sensitive mass spectrometry as an analytical tool made it possible to disclose some new features concerning adsorption and reaction of nitrogen oxides on γ-Al_2O_3 taken as a model substance for mineral dust, which may have some implications for atmospheric chemistry. These features could be revealed only at very low surface coverages and partial pressures (see Table 1) modeling real atmospheric conditions. Probably, this is why they were overlooked in earlier FT-IR studies performed with much higher initial NO_2 concentrations ((1.2–85) × 10^{13} molec cm^{-3} [5] or (1.7–120) × 10^{14} molec cm^{-3} [6]).

Strong bonding of the adsorbed molecules with alumina at low coverages found in this work prevents desorption of these molecules during night time into the atmosphere. However, desorption of N_2O and NO as well as dissociation of adsorbed N_2O do occur under UV-irradiation. The relative quantum efficiencies measured in this study for photodesorption and photodissociation point on the feasibility of these processes in the troposphere during day time. Finally, it should be noted that the gaseous products resulting from interaction of N_2O and NO with alumina were not studied. Only appearance of NO in the gas phase upon admission of NO_2 onto Al_2O_3 was reported [6].

In the present work complete dissociation of NO_2 into NO and O_2 and partial dissociation of N_2O into N_2 and O_2 upon dark adsorption on alumina are reported for the first time.

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References

[1] K.I. Zamaraev, M.I. Khramov, V.N. Parmon, Catal. Rev. 36 (1994) 617.
[2] A.R. Ravishankara, C.A. Longfellow, Phys. Chem. Chem. Phys. 1 (1999) 5433.
[3] V.H. Grassian, J. Phys. Chem. A 106 (2002) 860.
[4] C.R. Usher, A.E. Michel, V.H. Grassian, Chem. Rev. 103 (2003) 4883.
[5] C. Börensen, U. Kirchner, V. Scheer, R. Vogt, R. Zellner, J. Phys. Chem. A 104 (2000) 5036.
[6] G.M. Underwood, T.M. Miller, V.H. Grassian, J. Phys. Chem. A 103 (1999) 6184.
[7] C. Morterra, F. Bocuzzi, S. Coluccia, G. Ghiotti, J. Catal. 65 (1980) 231.
[8] D.V. Pozdnyakov, V.N. Filimonov, Kinet. Catal. 14 (1973) 760.
[9] T. Venkov, K. Hadjiivanov, D. Klissurski, Phys. Chem. Chem. Phys. 4 (2002) 2443.
[10] A.O. Klimovskii, T.K. Krutitskaya, A.A. Lisachenko, I.M. Pridnikov, Phys. Low-Dimens. Struct. 3–4 (1998) 167.
[11] L. Oster, D. Weiss, N. Kristianpoller, J. Phys. D 27 (1994) 1732.
[12] B.D. Evans, J. Lumin. 60–61 (1994) 620.