Catalysis Letters 69 (2000) 165–168

Steady-state N_2O decomposition on Pt and Rh surfaces using a free-jet molecular-beam excited by nozzle heating

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Received 3 April 2000; accepted 24 August 2000

Steady-state N_2O decomposition reaction on polycrystalline Pt and Rh surfaces has been studied using a supersonic free-jet molecular beam (2.1×10^{18} molecules/cm^2 s). The energy of the incident N_2O beam was controlled by a nozzle heating technique in conjunction with a seeding technique. The decomposition rate shows both translational and vibrational energy dependence on the Pt surface. However, there is also the surface temperature dependence of the decomposition rate even varying the incident beam energy, indicating precursor-mediated dissociation of N_2O on the Pt surface. On the other hand, no energy dependence was observed on the Rh surface, suggesting that the decomposition dynamics are different between Pt and Rh surfaces.

Keywords: N_2O decomposition, molecular beam, nozzle heating, Pt, Rh, translational energy, vibrational energy

1. Introduction

Dynamical studies of activated decomposition using a supersonic molecular beam have been widely performed to elucidate the effects of translational and vibrational energies of incident molecules. Especially, decomposition of alkanes such as CH_4 and C_2H_6 on transition metal surfaces has been studied in relation to catalytic reactions [1–6]. However, almost all studies pointed to the adsorption (trapping)–desorption dynamics, and they did not perform catalytic reactions. So far as the authors know, dynamical studies are rarely carried out for catalytic reactions such as N_2O decomposition ($N_2O \rightarrow N_2 + \frac{1}{2}O_2$).

N_2O is one of the simple molecules, and the unimolecular decomposition always proceeds via NN–O bond scission to form N_2 gas and oxygen adsorbate followed by O_2 desorption. The elementary steps of N_2O decomposition are described as follows [7]:

$$N_2O \rightleftharpoons N_2O_{ad} \tag{1}$$

$$N_2O_{ad} \rightarrow N_2 + O_{ad} \tag{2}$$

$$2O_{ad} \rightleftharpoons O_2 \tag{3}$$

Therefore, the decomposition of N_2O is suitable for the study of the dynamics of catalytic reaction. Furthermore, the catalytic decomposition of N_2O, a strong greenhouse effect gas, has been attracting much attention from the environmental point of view [7]. Rh catalysts such as Rh/ZSM-5 [8], Rh/ZnO [9] and Rh/USY [10,11] are found to have high activities at low reaction temperatures. On the other hand, on Pt surfaces, the decomposition of N_2O occurs at higher pressures (0.01–0.5 Torr) and temperatures (700–1500 K) [12]. In general, N_2O has less reactivity on Pt and only a few studies were reported at ultrahigh vacuum (UHV) conditions. Only molecularly adsorbed N_2O was observed by thermal desorption spectroscopy (TDS) above 78 K on Pt(111) under a UHV condition [13].

In this study, translational and vibrational energy dependence of steady-state N_2O decomposition on polycrystalline Pt and Rh surfaces using a free-jet molecular beam has been investigated. In the range of energies studied, catalytic N_2O decomposition proceeded. It was found that the incident energy affected the catalytic decomposition rate on Pt, but not on Rh.

2. Experimental

A molecular-beam reaction apparatus consists of a single chamber equipped with a free-jet nozzle and a differentially-pumped quadrupole mass spectrometer (QMS) [14]. A reaction gas was exposed to polycrystalline Pt or Rh foil (15 × 20 mm) from the nozzle. The nozzle assembly [15] consists of a ceramic nozzle (0.24 mm diameter orifice) and a thin graphite heater surrounding the ceramic. Surface temperature (T_S) and nozzle temperature (T_N) were measured by a chromel–alumel thermocouple, which was calibrated by a pyrometer. The thermocouples were spotwelded to the backside of the metal films and put into the small space between the nozzle and surrounding ceramic heater, respectively. T_N can be raised up to 1700 K. However, the ceramic nozzle was used below 1200 K, at which the amount of thermally dissociated N_2O was negligible. Excitation of vibrational states of incident molecules can be controlled by the T_N. In addition, the translational energy of molecules increases with increasing the T_N. Two reaction gases (100% N_2O: 99.9% minimum purity and 10.2% N_2O in He: 99.99% minimum purity) were used

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in this experiment. An acceleration of N_2O can also be accomplished with the mixture gas (10.2% N_2O in He) in conjunction with a supersonic expansion, which is termed a seeding technique [1]. A rotational energy of the beam is always low enough because of cooling during the initial part of the free-jet expansion [16]. The flux of N_2O was controlled by a mass flow controller (MFC) and constant at 2.1×10^{18} molecules/cm^2 s. The molecular-beam N_2O decomposition reaction was performed under the steady-state condition. An angle of the incident beam was fixed at surface normal. The Pt or Rh surface was pretreated at 1400 K by flowing O_2 in order to remove surface contaminants [14]. The amounts of both reactant (N_2O) and products (O_2 and N_2) were analyzed by QMS. It was confirmed that steady-state N_2O decomposition (i.e., the product N_2/O_2 ratio was 2/1) occurred on both Pt and Rh surfaces at higher surface temperatures.

In this study, we use the free-jet beam for the N_2O decomposition reaction, therefore, distance between the nozzle and the foil should be carefully taken. The sample was placed inside an isentropic region of a free-jet beam termed a zone of silence, which is surrounded by Mach disk and barrel shock. The Mach disk location (x_M) is given by following equation [16]:

$$x_M = 0.67d(P_0/P_b)^{1/2}, \tag{4}$$

where d is the diameter of nozzle orifice, P_0 is the pressure behind a nozzle and P_b is the pressure in a chamber, respectively. In this study, P_b was below 5×10^{-3} Torr, and the pressure behind the nozzle (P_0) was 100–300 Torr. So, the distance between the nozzle and the sample was determined to be 15 mm. If the distance is too short, the temperatures of the nozzle and the sample were considerably affected by each emission. In our experimental conditions, T_N was increased up to 730 K at the surface temperature (T_S) = 1500 K, and T_S = 550 K at T_N = 1200 K. The translational and vibrational energies were changed in the range of 8–35 and 1–5 kcal/mol, respectively.

3. Results and discussion

3.1. Decomposition dynamics on polycrystalline Pt surface

The N_2O decomposition rate on the Pt foil was first order with respect to the partial pressure of N_2O and increased with increasing T_S. This behavior is in good agreement with a previous study of N_2O decomposition on a polycrystalline Pt wire at a pressure range of 0.01–0.50 Torr [12]. Figure 1 shows the N_2O decomposition rate on the Pt foil as a function of surface temperature (T_S). The term T_N = r.t. in figure 1 means that the nozzle was not heated resistively but was heated by emission from the foil, as stated in section 2. The decomposition reaction started at the T_S of around 850 K. In the case of 100% N_2O (figure 1), the decomposition rate was increased with increasing T_N (above 1000 K). Typically, the N_2O conversion was about 1% at T_S = 1500 K and T_N = 1200 K. The similar trend was observed using the 10.2% N_2O/He mixture gas (not shown). These results show that the translational and/or vibrational energy of the incident beam affects the catalytic decomposition of N_2O on the polycrystalline Pt surface. The translational energy (E_{trans}) [17] and the vibrational energy (E_{vib}) [18] of the incident molecules were estimated from the following equations:

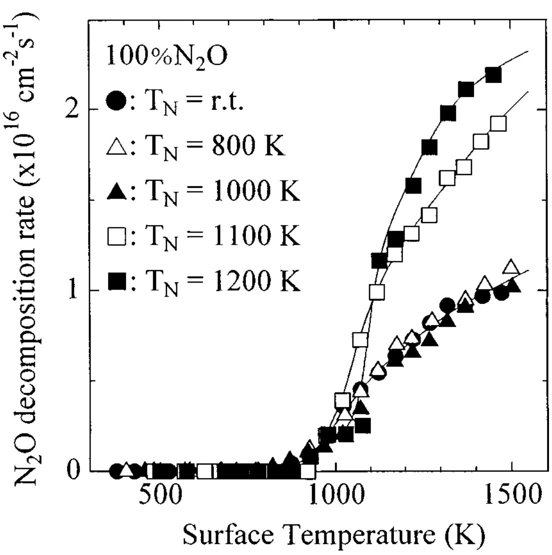
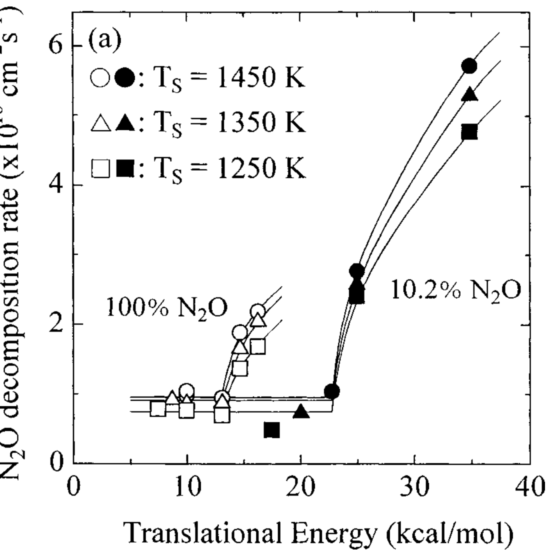


Figure 1. N_2O decomposition rate at several nozzle temperatures (T_N) on Pt foil as a function of surface temperature (T_S) using 100% N_2O.

$$E_{\mathrm{trans}} = \frac{m_h}{m_m}\int_0^{T_g} c_{pm}\,\mathrm{d}T, \tag{5}$$

$$E_{\mathrm{vib}} = hcN_0\sum_i \frac{g_i\omega_i \exp(-\omega_i hc/kT_g)}{1 - g_i\omega_i \exp(-\omega_i hc/kT_g)}, \tag{6}$$

where m is the molecular mass, c_p is the molecular specific heat at constant pressure, T_g is the gas temperature (= nozzle temperature, T_N), the subscript m indicates the mean value for the mixture (N_2O + He), h indicates the heavy species (i.e., N_2O in this study), N_0 is Avogadro's number, h is Planck's constant, c is speed of light, g_i is the degeneracy of mode i, ω_i is the frequency of mode i in cm^{-1} and k is Boltzmann's constant. Note that E_{trans} is determined by both T_g (i.e., T_N) and m_h/m_m (i.e., 100 or 10.2% N_2O), while E_{vib} is determined only by T_N. Figure 2 (a) and (b) shows the translational energy dependence and the nozzle temperature (T_N) dependence of the N_2O decomposition rate on the Pt foil, respectively. The data points in figure 2 (a) and (b) were obtained from the reaction rate measurements such as in figure 1. As shown in figure 2(a), the effect of the translational energy is obviously elucidated using 10.2% N_2O. The barrier height for the catalytic N_2O decomposition by E_{trans} is estimated to be about 23 kcal/mol from figure 2(a). On the other hand, the increase of the rate for 100% N_2O at E_{trans} = 15 kcal/mol in figure 2(a) is due to the effect of E_{vib}, which can be seen in figure 2(b). The increase in the activity for 100% N_2O was observed above T_N = 1000 K (figure 2(b)). From



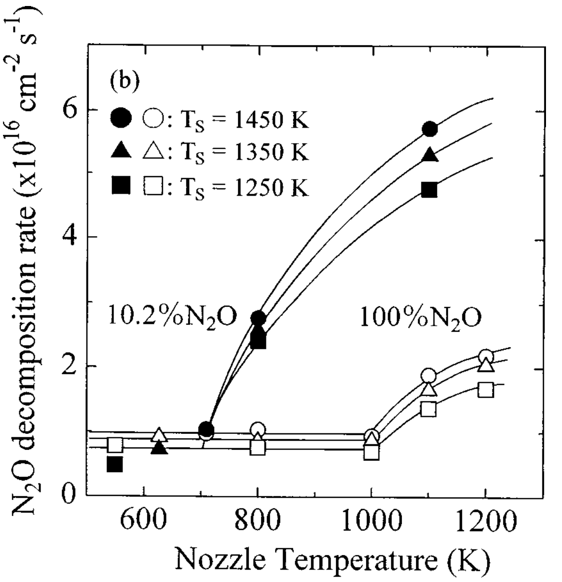


Figure 2. Incident energy dependence of N_2O decomposition rate on Pt foil at the region of higher surface temperatures (T_S): (a) translational energy dependence and (b) nozzle temperature (vibrational energy) dependence. The translational energy of the incident molecules was calculated from equation (5).

equation (6), the vibrational energy is estimated to be about 3.5 kcal/mol at $T_N = 1000$ K. In figure 2(b), comparing the activity between the 100 and 10.2% N_2O at the same T_N the difference again shows the net effect of E_{trans}.

The results in figure 2 (a) and (b) indicate that the N_2O decomposition rate on the Pt foil is affected by both E_{vib} and E_{trans}. N_2O has three fundamental vibrational modes, which are symmetric stretch (ω_1), bending (ω_2) and antisymmetric stretch (ω_3), respectively. Considering the energy spacing of each mode, bending is the most excited one by the nozzle heating. For example, the populations of all upper excited states (p) of the three vibrational modes at the $T_N = 1100$ K are $p_1 = 0.186$, $p_2 = 0.463$ and $p_3 = 0.054$, respectively. At this stage, however, it is difficult to determine which mode is important to increase the reaction probability. For the effect of E_{trans}, a distortion at collision of N_2O with the surface may be important. Likewise, Ceyer et al. reported that the CH_4 deformation during collision to the surface activated the dissociation since the carbon atom can get sufficiently close to the surface [1].

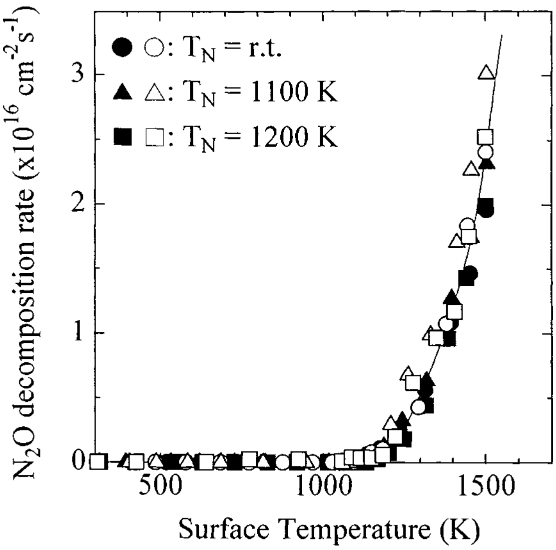


Figure 3. N_2O decomposition rate at several nozzle temperatures (T_N) on Rh foil as a function of surface temperature (T_S). The filled and open symbols are the data using 100 and 10.2% N_2O, respectively.

3.2. Difference in the dynamics between Pt and Rh

The behavior of the molecular-beam N_2O decomposition on the Rh foil was different from that on the Pt foil. Figure 3 shows the N_2O decomposition rate on the Rh foil as a function of surface temperature (T_S) using 100% N_2O (filled symbols) and 10.2% N_2O (open symbols). The reaction started at ~1150 K, which is much higher than the starting temperature on the Pt foil, and coincides with the temperature region of the second-order desorption of oxygen from a Rh(111) surface [19]. No activation of the decomposition rate was observed on the Rh foil with increasing T_N up to 1200 K for both the 100% N_2O and the seeded beams (figure 3). This result suggests that the dynamics of N_2O decomposition reaction are different between the Pt and Rh surfaces.

On the Rh surface, the dissociative adsorption of N_2O (steps (1) and (2)) easily occurs even at low temperatures [20], and the desorption of O_2 (step (3)) is rate determining. So, the overall decomposition rate may not be affected by the energy of the incident N_2O molecules. The surface oxygen coverage may be close to unity at the lower surface temperatures (below 1150 K), and the higher surface temperatures are needed for the catalytic N_2O decomposition (figure 3). On the polycrystalline Pt surface, the recombinative desorption of oxygen occurs below 800 K [21], and therefore, the surface oxygen coverage may be close to zero at which the steady-state N_2O decomposition proceeds. Therefore, the dissociative adsorption of N_2O is rate determining on the Pt surface, and may be affected by both translational and vibrational energies. It should be noted that there is also the positive T_S dependence on the decomposition rate at the constant incident energy (figure 1), and the precursor-mediated dissociation [22–24] of N_2O (i.e., step (2)) may also play an important role in the catalysis on the Pt surface. A negative dependence on dissociative chemisorption of alkanes with surface temperature at constant incident translational energy has been reported [3,25]. Madix et al. [26] reported a positive dependence on C_2H_6 dissociation with surface temperature (above 1000 K) of Pt(110). However, this behavior was interpreted as the result of surface phase transition [26]. The positive or negative dependence with the surface temperature at a constant incident translational energy depends on the relative barrier heights to dissociative chemisorption and desorption from the precursor state [24]. Harris et al. [27] proposed "thermally assisted tunneling" in order to explain a strong positive dependence on the surface temperature in the system of CH_4 dissociation on Pt(111). More detailed investigations of the dissociation dynamics should be required to more fully understand these phenomena.

Acknowledgement

We would like to thank Dr. Kazuhiro Karahashi, Fujitsu Laboratories Ltd., for his help in the preparation of the nozzle assembly.

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