The Chemical Interaction between Plasma-excited Nitrogen and the Surface of Oxide Catalysts

S. Kameoka, M. Kuroda, T. Kuriyama, S. Ito and K. Kunimori

Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305, Japan

Abstract

The chemical interaction between plasma-excited nitrogen and the surface of oxide catalysts (Al_2O_3, TiO_2, HY, SiO_2 and MgO) was studied by temperature-programmed desorption (TPD), infrared (IR) spectroscopy and X-ray photoelectron spectroscopy (XPS). After the plasma-excited nitrogen was exposed to the oxide catalysts at room temperature, products (NH_3, N_2 etc.) were desorbed from the samples (after heating up to 500°C). These results suggested that the plasma-excited nitrogen reacted with the surface hydroxyl groups on the oxides. The chemical reactivities of the surface hydroxyl groups with the plasma-excited nitrogen were different among the oxide catalysts.

Introduction

It is well known that the chemical reactivity of N_2 is very low and that N_2 does not chemisorb on oxides such as Al_2O_3 and TiO_2 at and above room temperature. However, we have recently found that N_2 chemisorption occurs on Al_2O_3 surfaces if the gas is excited by plasma discharge [1]. During the course of the study, it has been suggested that the plasma-excited nitrogen may react with surface OH groups on oxide catalysts to form NH_3 [1,2]. Miyahara reported that hydrazine as well as ammonia was produced directly by the reaction of the plasma N_2 with surface OH groups on various oxides such as MgO [3]. However, no detailed information on the chemical interaction between the plasma-excited nitrogen and oxide surfaces has been obtained so far [2]. In this work, the plasma-induced chemisorption of N_2 and its chemical reactivity on various oxide catalysts with high surface areas (Al_2O_3, TiO_2, HY, SiO_2 and MgO) have been studied by using temperature-programmed desorption (TPD), infrared spectroscopy (IR) and X-ray photoelectron spectroscopy (XPS).

Experimental

A sample of TiO_2 (P-25) was obtained from Degussa Co. Ltd.. Al_2O_3 and SiO_2 (JRC-ALO-4, JRC-SIO-3) samples were provided by the Catalysis Society of Japan. HY was prepared by treating NaY-type zeolite (SK-40, Linde Co.) with 1N NH_3 solution at ca. 70°C, followed by calcination at 400°C. MgO and $Mg(OH)_2$ were obtained from Wako chemicals. Plasma-excited nitrogen was generated at room temperature by using a rf (radio frequency) power source (13.56MHz) [4]. TPD and IR measurements were performed by using the same experimental procedures as in the previous papers [1,2,4]. Closed reactor system was used to analyze the plasma-reaction products, which have also been reported previously [2]. A plasma reaction chamber was attached to a UHV chamber (base pressure <2×10^{-10} Torr), which was equipped with XPS spectrometer [5]. The sample after the N_2 plasma reaction could be quickly carried into the UHV chamber via a gate valve system [5]. XPS measurements were taken with AlK_α radiation and the electron energy analyzer was set at 44 eV pass energy. The N1s binding energies were measured relative to the $Ti2p_{3/2}$ peak at 459.0 eV [6] for TiO_2 sample and the Al2p (at 74.6 eV) and O1s (at 532.6 eV) peaks [7] for HY sample.

Results and Discussion

1. TPD study of plasma-induced nitrogen chemisorption on the oxide catalysts

Fig. 1 shows the TPD spectra of chemisorbed nitrogen on the Al_2O_3 and HY after the N_2 plasma treatment. It should be noted that no chemisorption of nitrogen was observed after the N_2 flow at room temperature (without plasma excitation) for all the samples (Al_2O_3, TiO_2, HY and SiO_2). It was confirmed by both QMS signal (m/e=14, 28) and TCD response that N_2 was desorbed from the catalyst during the TPD in the He flow. A desorption peak of N_2 was observed at around 300°C from Al_2O_3 and at 455-480°C from HY (Fig. 1), respectively. However, no significant N_2 desorption peak was observed from TiO_2 (not shown; very broad peak), and no N_2 desorption peak observed from SiO_2. These results

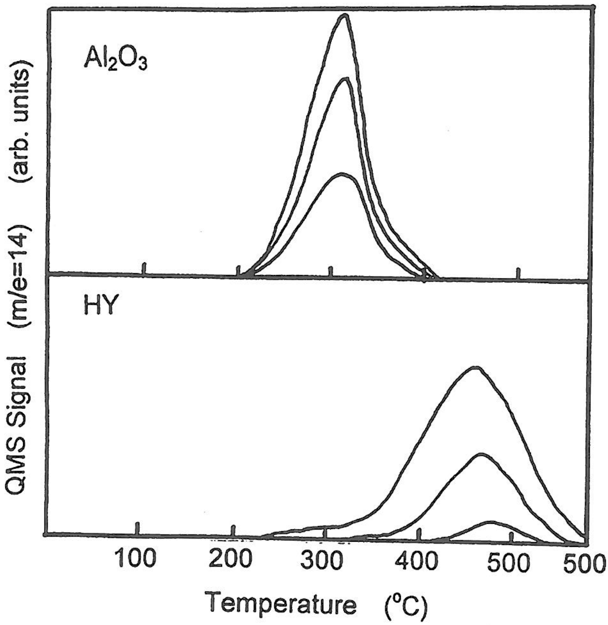

Fig. 1 TPD spectra of N_2 from the Al_2O_3 and HY surfaces after the plasma-excited N_2 treatment.

Table 1 The products of the reaction of plasma-excited N_2 with oxide catalysts

Sample	Adsorbed nitrogen (μmol)	Selectivity (%)		
		N_2	NH_3	NO
HY[1)]	2.5	89	11	0
Al_2O_3[2)]	5.8	57	39	4
TiO_2[2)]	5.4	5	74	21

1) evac. at 300°C for 1h., 2) evac. at 200°C for 1h., N_2 plasma 30W for 0.5h at r.t.

indicate that the behavior of nitrogen chemisorption strongly depends on the oxide catalysts. As shown in the Fig. 1, the T_{max} of the TPD peak was not changed for the different amounts of chemisorbed nitrogen in the case of Al_2O_3, while the T_{max} was changed in the case of HY (coverage-dependent). The features of the TPD spectra (Fig. 1) may suggest a first-order desorption for Al_2O_3 and a second-order desorption for HY, respectively [8].

2. The chemical interaction between the plasma-excited nitrogen and surface OH groups on oxide catalysts

After the samples were preheated, the N_2 plasma reactions were performed at room temperature. The amounts of products desorbed from each sample after heating up to 450°C are shown in Table 1.

We found that NH_3 was formed by the plasma N_2 treatment at room temperature. These results suggest that the plasma excited nitrogen reacted with the surfaces of oxide catalysts. To demonstrate the chemical reaction of the plasma-excited nitrogen with the surface OH groups, the amount of surface OH groups on Al_2O_3 was controlled by a change of preheating temperature [9]. The amounts of produced NH_3 as a function of the sample preheating temperature is shown in Fig. 2. The result indicates the good correlation between the amount of produced ammonia and the amount of surface hydroxyl groups on Al_2O_3.

Figure 3 shows IR spectra in the hydroxyl region (ν_{OH}) of the TiO_2, Al_2O_3 and HY. The observed bands of Al_2O_3 (3750, 3680 cm^{-1}), TiO_2 (3735, 3670 cm^{-1}) and HY (3650, 3560 cm^{-1}) are due to dominant isolated hydroxyl groups [10,11,12]. The band at 3580 cm^{-1} (Al_2O_3) is due to H-bonded hydroxyl groups, and the band at 3745 cm^{-1} (HY) is silanol [10, 12]. The intensity of the ν_{OH} bands of all these samples decreased during the plasma-excited nitrogen treatment, as shown in Fig. 3. The decreases in the intensities of the ν_{OH} bands mainly at 3680 cm^{-1} (Al_2O_3), at 3735 and 3670 cm^{-1} (TiO_2) and at 3650 and 3560 cm^{-1} (HY) were observed. However, the decrease in the intensity of the silanol (3745 cm^{-1}; Si-OH) on HY sample was not observed (Fig. 3). This result shows that Si-OH is inactive for the plasma-excited nitrogen, which agreed well with the TPD result on SiO_2.

Fig. 4 shows IR spectra in the 3450-3150 cm^{-1} region of the HY and TiO_2 samples during the N_2 plasma treatment. Exposure of the each sample to the plasma-excited N_2 at room temperature results in the appearance of new peaks in the 3450-3150 cm^{-1} region. The increase in the intensities of these peaks correlated well with the decrease in the intensities of the ν_{OH} peaks in Fig. 3. The three peaks

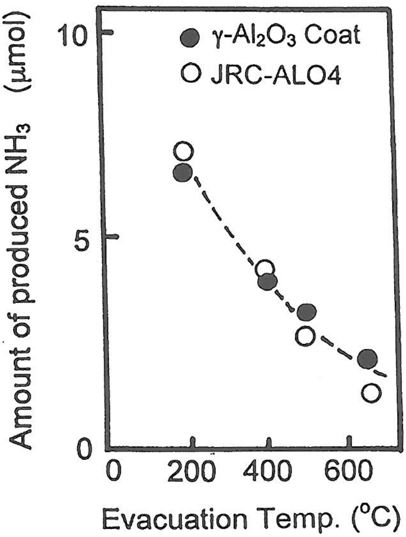

Fig. 2 The correlation between the amount of produced NH_3 and the amount of surface OH on Al_2O_3.

(3401, 3345 and 3230 cm^{-1}) on HY surface may be assigned to NH_3(a) and/or NH_4^+ [13]. The eight peaks in the 3450-3150 cm^{-1} region on TiO_2 surface were assigned to NH_3(a) and/or NH_x(a) (x=1 or 2) [2]. In fact, the similar peaks at these regions were observed in the study of NH_3 adsorption on HY and TiO_2, respectively [13,14]. The change in ν_{NH} band region (3400-3150 cm^{-1}) of Al_2O_3 could not be observed because of the large adsorption of hydroxyl groups.

Fig. 5 shows XPS spectra of nitrogen

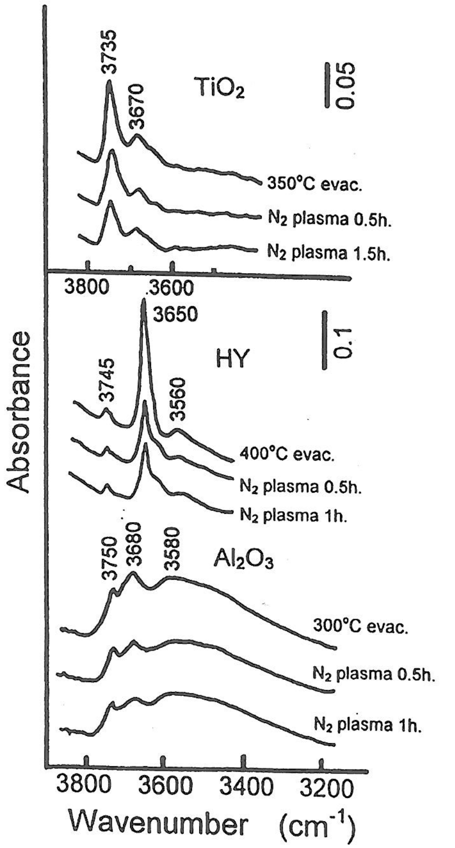

Fig. 3 IR spectra in the ν_{OH} region of oxide catalysts during the N_2 plasma-surface interaction.

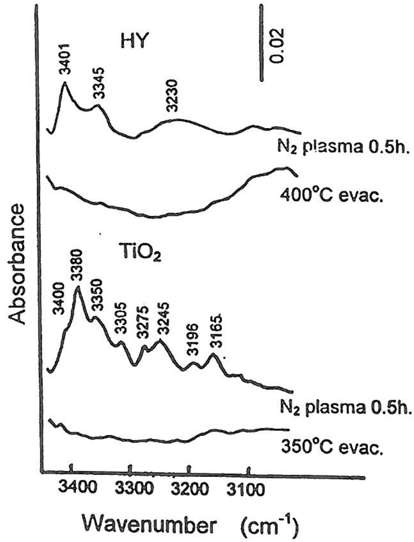

Fig. 4 IR spectra in the ν_{NH} region of the HY and TiO_2 during the N_2 plasma-surface interaction.

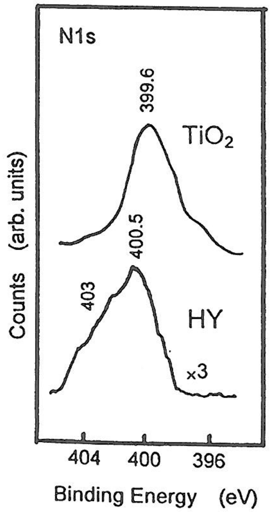

Fig. 5 The N1s XPS spectra of TiO_2 and HY samples after the N_2 plasma treatment.

N1s from the TiO_2 and HY samples after the N_2 plasma treatment for 0.5 h at room temperature. The N1s spectrum of the TiO_2 sample has a broad peak mainly at 399.6 eV and at 397.0 eV. These peaks are assigned to the NH_3(a) and N(a), respectively [15,16]. The N1s spectrum of the HY sample has at least two peaks at 403.0 and 400.5 eV. These two peaks are assigned to the NH_4^+(a) and NH_3(a), respectively [17]. These XPS results were good agreement with the IR results that the hydrogenated species (NH_x(a), NH_4^+(a) and NH_3(a)) were formed on the oxide surfaces by the N_2 plasma treatment.

3. The adsorbed states of nitrogen on oxide catalysts

The results in Table 1 show that the chemical reactivities with N_2 plasma were different among the surface OH groups on Al_2O_3, TiO_2 and HY. The desorption products from Al_2O_3 were mainly N_2 and NH_3. The species of the chemisorbed nitrogen on Al_2O_3 may be mainly N_2(a) and NH_3(a). In practice, the ν_{NN} band of a molecular N_2(a) was observed at ca.2260 cm^{-1} [4]; and the TPD spectra of N_2 showed the typical behavior for a first-order desorption (Fig. 1). However, we do not exclude the presence of N(a) and NH_x(a) on Al_2O_3.

The desorption products from TiO_2 were mainly NH_3 and NO. This result suggests that the plasma-excited nitrogen was adsorbed dissociatively on TiO_2, because no ν_{NN} bands were observed [2]. No significant N_2 TPD peak was observed, because the greater part of adsorbed N(a) reacted with surface OH groups on TiO_2 to form NH_3 at room temperature and the amount of NH_3(a) increased during the heat treatment to 350°C [2]. These results were supported by XPS and IR data.

The desorption products from HY were mainly N_2 and little NH_3 (Table 1). NH_4^+(a) and NH_3(a) species on the HY were observed by XPS and IR measurements. The thermal behavior of these species on the HY was very interesting, because the decrease in the intensities of the ν_{NH} peaks correlated well with the regeneration of the ν_{OH} peak after heating the sample up to 400°C [18]. These results show that the decomposition of NH_4^+ and/or NH_3(a) species occurred on the HY zeolite sample and that the surface hydroxyl groups were reproduced during the heat treatment. On the other hand, in the usual study of NH_3 adsorption, the decomposition of NH_3(a) (adsorbed on Bronsted and/or Lewis acid site) on Y-zeolites has not been observed during heat treatment [19]. Namely, this result may indicate that peculiar surface species are formed on the HY by the N_2 plasma treatment.

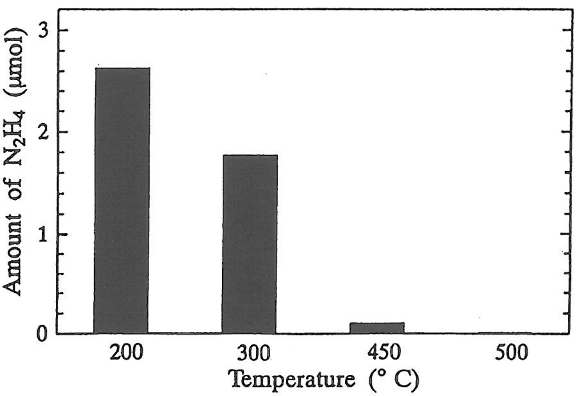

Fig. 6 The total amount of produced N_2H_4 as a function of the $Mg(OH)_2$ sample pretreatment temperature.

4. Hydrazine formation on MgO

Hydrazine (N_2H_4) and ammonia (NH_3) were produced on the $Mg(OH)_2$ sample after the N_2 plasma treatment (30W for

0.5h.). The ratio of N_2H_4 (μmol) : NH_3 (μmol) was approximately 1:3 (after preheating the sample at 200°C). The effect of pretreatment of $Mg(OH)_2$ sample on the amount of produced N_2H_4 is shown in Fig. 6. The amount of produced hydrazine decreased with increasing the preheating temperature of the sample. It was suggested that the amount of hydroxyl groups on $Mg(OH)_2$ was decreased significantly by increasing the pretreatment temperature (e.g., 450°C). Miyahara [3] suggested that activated molecular N_2^* was adsorbed on oxides such as MgO, and protonated by the surface OH groups to form N_2H_4 (the Shilov's mechanism [20]). In the case of the MgO sample, only NH_3 was detected even after the sample preheating at 200°C (N_2H_4< 0.01μmol). Moreover, the amount of produced NH_3 on the MgO was half of the $Mg(OH)_2$ after the pretreatment at 200°C. These results suggest the formation of hydrazine may be very sensitive to the nature of MgO surface (e.g., surface crystal state and/or surface OH property).

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