Catalysis Letters 16 (1992) 443–446

Plasma-induced nitrogen chemisorption on a ruthenium black catalyst: formation of NH_3 by hydrogenation of the chemisorbed nitrogen

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Received 9 July 1992; accepted 11 September 1992

Nitrogen was chemisorbed on a ruthenium black catalyst by a plasma discharge of N_2. Temperature-programmed desorption of nitrogen showed a broad peak at around 300°C which showed a dependence on the duration and the wattage of the discharge. The chemisorbed nitrogen species was reacted with hydrogen to form NH_3 even at room temperature.

Keywords: Plasma-induced chemisorption; nitrogen chemisorption; Ru black catalyst; production of ammonia; the reactivity of chemisorbed nitrogen

1. Introduction

It is well known that N_2 does not adsorb on noble metals such as Pt and Pd at and above room temperature [1]. However, it was found that N_2 chemisorption occurred on the metal ribbons or the single crystal surfaces if the gas was atomized by electron bombardment [2], by a hot W filament [1,3] or by a high-frequency discharge [4]. It has proved to be a most interesting system with novel and unexpected features such as atomic nitrogen-induced chemisorption of N_2 [1,5] and hydrogenation of chemisorbed nitrogen [2]. Nevertheless, no work has been reported on a practical catalyst with a high surface area to study catalytic behaviors of chemisorbed nitrogen. We will report here plasma-induced nitrogen chemisorption on a Ru black catalyst to study the reactivity of chemisorbed nitrogen with hydrogen. Although Ru, if promoted by aluminum and K, is a promising catalyst system for synthesis of NH_3 from N_2 and H_2 [6], N_2 does not appreciably chemisorb on pure Ru powder [6] or Ru(0001) [7].

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2. Experimental

The plasma-discharged adsorption and temperature-programmed desorption (TPD) measurements were performed in a flow reactor system connected to both a thermal-conductivity detector (TCD) and a quadrupole mass spectrometer (QMS, ANELVA TE-150). The flow rate (30 cm^3/min for H_2, 60 cm^3/min for He and O_2) at atmospheric pressure was controlled and monitored by mass flow controllers. A 0.5 g Ru black catalyst (BET surface area: 5 m^2/g) was placed in a quartz tube reactor (30 mm ∅), where a stable plasma discharge of N_2 (the N_2 pressure = 0.6 Torr) was obtained using a rf (13.56 MHz, 30 or 60 W) power source. After the plasma-induced adsorption at room temperature, the TPD of N_2 was monitored as the catalyst temperature was raised up to 570 or 710°C (20°C/min) in purified helium flow. The catalyst was pretreated in O_2 flow at 400°C, and reduced in H_2 flow at 400°C followed by the helium purge at 710°C.

3. Results and discussion

Fig. 1 shows the TPD profile of nitrogen chemisorbed by the plasma discharge of N_2. It should be noted that no chemisorption of nitrogen was observed after N_2 flow (30 cm^3/min at atmospheric pressure) at and above room temperature without the plasma excitation. It was confirmed by both QMS signal ($m/e = 14, 28$) and the TCD response that only N_2 was desorbed from the catalyst during the TPD in the He flow. A single peak at around 270°C was

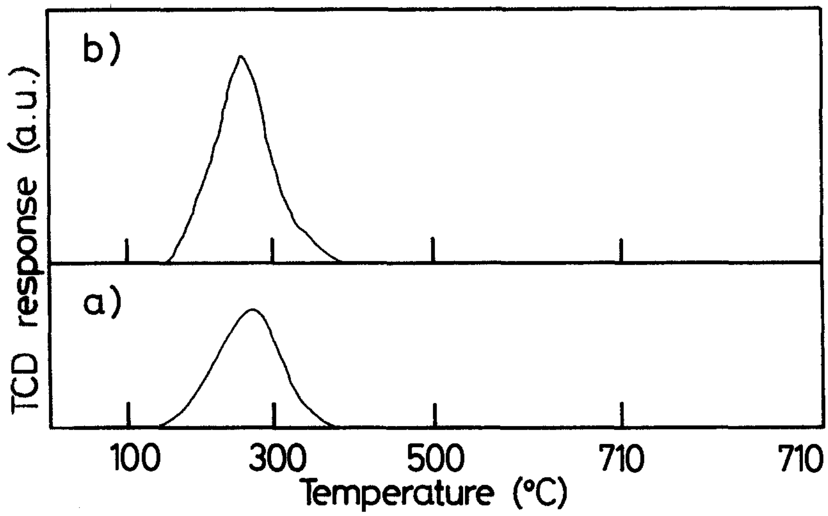

Fig. 1. TPD spectra of nitrogen from the Ru surface after plasma-induced adsorption of N_2. (a) 30 W, 5 min; (b) 30 W, 30 min.

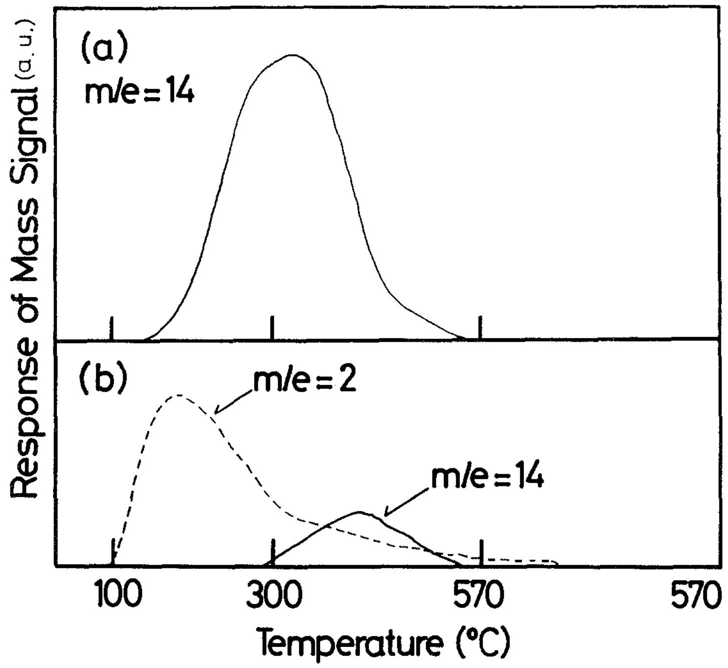

Fig. 2. TPD spectra of nitrogen ($m/e = 14$) and hydrogen ($m/e = 2$) from the Ru surface. (a) N_2 discharge: 60 W, 30 min; (b) after the N_2 discharge at the same condition as (a), H_2 flow at r.t. for 30 min.

observed in fig. 1a. By increasing the duration of the N_2 discharge (30 W, 30 min), the peak became a little larger, but appeared to reach a steady-state intensity (fig. 1b). Assuming the exponential factor to be 1×10^{13}/s for the N_2 desorption rate [8], the activation energy for the desorption was evaluated to be 164 kJ/mol. The high desorption energy would suggest that the peak may be attributed to the dissociated chemisorbed nitrogen N(a) [1,3,4]. The N_2 desorption peak became broader at around 300°C as the wattage (60 W) of the N_2 discharge was increased, as shown in fig. 2a. The amount of N_2 desorbed was estimated to be $\approx 6.6 \times 10^{-6}$ mol/g Ru from the TCD response. Based on the BET surface area, $\approx$ 10% of the Ru surface was covered by the chemisorbed nitrogen N(a).

After the nitrogen chemisorption, the catalyst was exposed in H_2 flow at room temperature, during which a liquid nitrogen trap was used to trap the NH_3 that was produced, which was subsequently quantified by gas chromatography (GC). As shown in fig. 2b, both N_2 and H_2 desorption was observed in the TPD run after the H_2 flow. The amount of N_2 desorption was diminished significantly, while NH_3 was detected in the trap by GC (see table 1). The result indicates that most of the chemisorbed nitrogen on the Ru surface was hydrogenated to NH_3. The data in table 1 show that the hydrogenation reaction occurred during the H_2 flow at room temperature, and only a trace amount of

Table 1
Plasma-induced nitrogen chemisorption on the Ru black catalyst (0.5 g) and the reactivity of the chemisorbed nitrogen with hydrogen

Procedure	Desorbed N_2 (mol)	Product NH_3 (mol)
A N_2 chemisorption [a]	3.3×10^{-6} [b]	–
B N_2 chemisorption [a] + H_2 flow at r.t.	–	5.7×10^{-6} [c]
C after B, He flow up to 570°C	0.4×10^{-6} [b]	0.1×10^{-6} [d]

[a] N_2 discharge: 60 W, 30 min.
[b] During the TPD run.
[c] Before the TPD run.
[d] After the TPD run.

NH_3 was formed by the surface reaction between N(a) and the chemisorbed hydrogen during the TPD run.

Hydrogenation of N(a) to NH_x(a) ($x = 1$ or 2) has been reported on noble metals such as Pd [2,9]. However, no formation of product NH_3 (i.e. no further hydrogenation of NH_x) has been reported when the H_2 partial pressure was low (from 10^{-7} to 10^{-6} Torr) [2,9]. The present result has demonstrated that NH_3 is formed by the hydrogenation of N(a) on the Ru surface even at room temperature under the atmospheric H_2 flow. The high chemical reactivity of N(a), once formed by the activated chemisorption, on metal surfaces deserves further attention to expand into more detailed studies including the characterization of the chemisorbed nitrogen.

Acknowledgement

This work was supported in part by the Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture (No. 04241202).

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