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Hydrogenation of plasma-excited nitrogen over an alumina catalyst for ammonia synthesis

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ABSTRACT

Ammonia (NH₃) is a potential hydrogen carrier as alternative fuel and feedstock for hydrogen production. In this study, plasma synthesis of NH₃ was conducted in a packed-bed dielectric barrier discharge (DBD) reactor using Al₂O₃ as the catalyst. In order to explore the mechanism of hydrogenation of plasma-excited nitrogen for NH₃ synthesis, the whole NH₃ synthesis process was divided into three steps including N₂ activation, hydrogenation of plasma-excited N(a), and desorption of NH₃(a) from catalyst. The effects of reaction conditions on the three steps and corresponding NH₃ production were examined. Results showed that more plasma-excited nitrogen species were formed through N₂ activation at higher N₂ flow rate, discharge time and discharge power for N₂ activation. Hydrogenation of plasma-excited N(a) to form NH₃(a) was improved by more discharge time at the second step. Higher discharge temperature for N(a) hydrogenation favored NH₃(a) desorption from catalyst and increased NH₃ production at the second step, with the total NH₃ yield slightly changed. In addition, one-step NH₃ synthesis in plasma was investigated and compared with the three-step process. The results will provide reference for catalyst and reactor design in plasma synthesis of ammonia.

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Introduction

Ammonia (NH₃) is the second most widely produced chemical in the world and plays an extremely important role on the economy [1,2]. It is not only a key raw material for agriculture and industry but also a potential hydrogen (H) carrier as alternative fuel for vehicles due to its high energy density, clean combustion property and high hydrogen content [3–5]. In addition, ammonia can be used as an anode substrate for

hydrogen (H₂) generation in bioelectrochemical systems and internal combustion engines [6–8]. Because of the high stability of nitrogen (N₂), NH₃ is industrially synthesized from N₂ and H₂ through the Haber-Bosch (HB) process under high temperature and pressure [9–12]. As an alternative pathway, N₂ and H₂ can be efficiently activated by non-equilibrium plasma and converted to NH₃ on a certain catalyst at ambient conditions. Many studies on NH₃ synthesis using non-equilibrium plasma technology were reported [13–17].

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N_2 exists mainly in the form of metastable N_2^* when being excited by non-equilibrium plasma [18,19]. Using the techniques of temperature-programmed desorption (TPD), Fourier-transform infrared (FTIR) spectroscopy and isotope exchange reaction (IER) of nitrogen, Mizushima et al. (2007) found that the N_2^* was dissociated and chemisorbed on alumina (Al_2O_3) to form atomic N(a) (the suffix “(a)” denotes species adsorbed to an adsorbent), which was then hydrogenated to NH_3 by H_2 plasma [20]. Kunimori et al. (1992) reported that the plasma-excited dissociative N(a) was chemisorbed on Ru catalyst by electron impacts in radio frequency (RF) plasma at room temperature and reduced pressure. N(a) was hydrogenated to NH_3 under an atmospheric H_2 flow at room temperature [21]. In addition, chemical reactivity of plasma-excited atomic N(a) on oxides such as MgO [22,23], TiO_2 [18] and Al_2O_3 [20,24] was found. It is widely accepted that the formation of NH_3 after the generation of atomic N(a) could follow two possible pathways. The first pathway mainly involves hydrogenation of N(a) to form NH_x radicals as predominant precursors for the production of $NH_3(a)$ on the catalyst surface. $NH_3(a)$ is then desorbed and diffused from catalyst surface to gas phase. The second pathway suggests the reaction of N(a) with plasma-excited hydrogen species such as atomic H and metastable H_2^* to directly synthesize NH_3 in plasma phase [20,25–27].

Generally, the NH_3 synthesis in plasma can be divided into three successive steps, including N_2 activation on catalyst in the plasma, hydrogenation of plasma-excited N(a) by H_2 plasma to form $NH_3(a)$, and desorption of $NH_3(a)$ from catalyst. To investigate the three steps separately is important to the understanding of hydrogenation of plasma-excited nitrogen and optimization of plasma synthesis of ammonia. However, most previous studies focused on the development of novel and effective catalysts, yet few reports on the effects of reaction conditions on the three steps and corresponding NH_3 production were found. In this study, hydrogenation of plasma-excited N(a) was examined in a packed-bed DBD plasma reactor filled with Al_2O_3 as the catalyst. The effects of discharge time for N_2 activation and N(a) hydrogenation, N_2 flow rate, discharge power for N_2 activation, and discharge temperature for N(a) hydrogenation on NH_3 synthesis were investigated.

Experimental

Experimental setup

The schematic diagram of the experimental setup is shown in Fig. 1. The gas flows of H_2 and N_2 , regulated by the gas flow meters, were mixed in a buffer tank and then introduced into the packed-bed DBD reactor. NH_3 produced in the plasma was absorbed by H_2SO_4 solution. During the experiments, the temperature of the DBD reactor was controlled by a temperature controller.

DBD plasma reactor

The packed-bed DBD reactor consisted of a quartz tube with an inner diameter of 13 mm and thickness of 1 mm and a

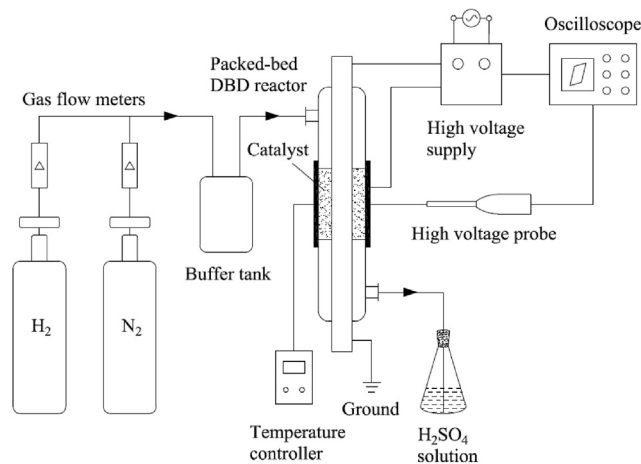


Fig. 1 – Schematic diagram of the experimental setup.

nested and coaxial stainless-steel rod with an outer diameter of 10 mm as the internal electrode. A stainless-steel mesh was wrapped around the quartz tube as the external electrode. Al_2O_3 used as the catalyst and the dielectric material was filled in between the quartz tube and stainless-steel rod. The diameter, specific surface area, and pore size of Al_2O_3 particles were 0.3–0.5 mm, 121.3 m^2/g and 28.7 nm, respectively. The quantity of Al_2O_3 used for each test was 0.5 g. A high voltage generated by a 9.2 kHz power supply (Nanjing Suman Electronics Co., Ltd.) was applied to the external electrode, with the stainless-steel rod as the ground electrode. The discharge distance between the two electrodes was 2 mm and the discharge length was 14 mm.

The discharge power for the packed-bed DBD reactor was determined using the charge-voltage (Q - U) Lissajous figure [28,29]. The voltage (U) applied to the DBD reactor was measured with a 1000:1 high voltage probe (P6015A, Tektronix), with the signal detected and shown in a digital oscilloscope (DPO 3052, Tektronix). A 0.47 μF capacitor (C) was connected with the DBD reactor in series to determine the quantity of electric charge stored in the reactor. The voltage of the capacitor (U_C) was measured using a 1:1 voltage probe (P6139A, Tektronix). The area of the Q - U Lissajous figure represents the discharge energy per cycle (E). Thus, the average discharge power (P , W) can be calculated through the discharge energy per cycle multiplied by the power frequency (f) [30], as shown in the following equation:

$$P = f \times E = f \times \int_0^T U(t) d(U_C(t) \times C) \quad (1)$$

Three-step NH_3 synthesis in plasma

In order to study the hydrogenation of plasma-excited N(a) on catalyst, the NH_3 synthesis over Al_2O_3 in the DBD plasma reactor was conducted following three successive steps, i.e. N_2 activation for the generation of plasma-excited N(a) on Al_2O_3 , hydrogenation of N(a) to form $NH_3(a)$, and desorption of $NH_3(a)$ from Al_2O_3 .

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