Catalysis of nickel nanoparticles with high thermal stability for ammonia decomposition

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ARTICLE INFO

ABSTRACT

Catalytic properties of nickel (Ni) nanoparticles for thermal ammonia decomposition were investigated. The nanoparticles were synthesized from $Ni(C_5H_5)_2$ in/on pores of zeolite with an aim to prevent diffusion and sintering of the nanoparticles at high temperature. The Ni nanoparticles were smaller than 5 nm and maintained their nano-size after the NH_3 decomposition reaction at 500 °C, whereas Ni particles synthesized by a conventional impregnation method formed large particles, such as 50 nm, after the reaction. The Ni nanoparticles showed much higher activity than Ni particles synthesized by the conventional impregnation method. By the investigation of kinetic properties, it was confirmed that the frequency factor was related to the high catalytic activity. Therefore, both high dispersion level and high thermal stability brought Ni nanoparticles the enhancement of their catalysis.

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1. Introduction

Ammonia (NH_3) is a promising hydrogen (H_2) carrier because of following reasons [1,2]. First reason is the high H_2 content of 17.8 mass% in NH_3. The second one is an ease to liquefy NH_3 by relatively low pressure of 0.857 MPa at 20 °C, where the values of volumetric density of H_2 in liquid NH_3, liquid H_2, and gaseous H_2 compressed at 70 MPa are 108, 71, and 39 g L^{-1}, respectively [1,3]. Therefore, NH_3 enables us to easily carry and store a huge amount of H_2. The third one is that infrastructures to produce, store, and carry NH_3 have been universally established because huge amounts of NH_3 are now produced as fertilizer by Haber–Bosch process. In addition, after H_2 release from NH_3 by the following reaction,

$$2NH_3 \rightarrow 3H_2 + N_2, \tag{1}$$

it is not necessary to collect nitrogen (N_2) as the byproduct because it can be released to the air. Actually, in the case of organic hydride, considerable costs and energies are required to collect the byproduct [4].

Some studies about catalysts to decompose NH_3 and generate H_2 have been carried out [5–13]. Yin et al. investigated catalysis of noble metals, such as Ru, Rh, and Pt, and base metals, such as Ni and Fe, supported on carbon nano-tubes (CNT) [12,13]. Among them,

Ru is the most active catalyst for NH_3 decomposition [12]. In addition, Hill and Torrente-Murciano reported that addition of Cs as a promoter significantly enhanced the catalytic performance of Ru on CNT [14]. Though Ru has a quite high performance as a catalyst for NH_3 decomposition, it also has disadvantages of little resources and high costs. So the development of catalysts using base metals is industrially important in terms of saving resources and reducing costs. As the catalyst of base metal, Ni showed catalytic properties for NH_3 decomposition although its activity was much lower than that of Ru [13]. In order to improve the catalytic activity of Ni for the NH_3 decomposition, we focused on technologies to control the size of Ni particles, because it is reported that the size of catalysts has a great effect on their activities [15,16]. In particular, control of the size to be smaller than 5 nm brought the catalyst a significant enhancement of its activity [16]. However, the extremely small nanoparticles have a problem of deactivation because they sinter into larger particles when they are used at higher temperature than 400 °C for NH_3 decomposition [17]. The thermal stability of the nanoparticles basically depends on the melting point of their materials; sintering of Ni particles, whose melting point is 1455 °C, is easier than that of Ru particles, whose melting point is 2334 °C. Therefore, improvements of both dispersion level and thermal stability enable Ni to be applied to practical catalysts for NH_3 decomposition. To improve the dispersion levels, catalysts with core–shell structure have been investigated, and they showed high performance for NH_3 decomposition [18,19]. However, most of them have diameter larger than 10 nm, and controlling their sizes

smaller than 5 nm has not been achieved yet [18,19]. Cao et al. investigated NH_3 decomposition by a mesoporous catalyst of modified red mud and Ni prepared by a precipitation method [20]. In their report, images of microscope show that NiO disperses homogeneously on the support. The size and dispersion of Ni metal after reduction and NH_3 decomposition reactions are not mentioned and the thermal stability of the catalyst is not discussed [20]. There are quite few reports about controlling size of base metal catalysts with metallic state and extremely small size, such as smaller than 5 nm, at high temperature. In our group, Ni nanoparticles with high thermal stability were successfully synthesized by adsorption and decomposition of Ni organometallic compounds, nickelocene ($Ni(C_5H_5)_2$), in micropores of zeolite [21]. The synthesized Ni nanoparticles kept the size smaller than 5 nm even after heating at 400 °C, whereas Ni particles supported on the zeolite by a conventional incipient wetness impregnation process sintered into larger particle than 10 nm at the same condition. It is considered that the nanoparticles are synthesized in/on pores of zeolite, and the micropores prevented diffusing and sintering of the nanoparticles at the high temperature. Therefore, it is expected that the Ni nanoparticles reveal high catalytic performance by the nano-size and high dispersion state preserved even at high temperature.

In this study, the thermally stable Ni nanoparticles synthesized by this method were applied as catalyst for NH_3 decomposition, and their catalysis and stability were investigated.

2. Experiments

2.1. Synthesis and characterization

Ni nanoparticles were synthesized via the processes which we previously reported [21]. Powder of zeolite Y (Wako chemical, Japan), which includes Na^+ as a cation, was mixed with nickelocene, $Ni(C_5H_5)_2$ (Sigma-Aldrich, USA), in a glove box filled with Ar, and put into a quartz tube. The mixture was heated at 130 °C for 8 h after reducing pressure in the tube to about 5 Pa, and gaseous $Ni(C_5H_5)_2$ was adsorbed in the zeolite. Ultraviolet (UV) light generated by Xe lamp was irradiated to the sample at room temperature until the color of the sample was completely changed to dark. After the UV irradiation, the sample was reduced under H_2 atmosphere at 400 °C for 1 h. The sample synthesized by the above process is named "$CH_{zeolite}$". To compare the catalysis of the synthesized nanoparticles with those of conventional catalysts, Ni supported on zeolite and alumina were also prepared by a conventional incipient wetness impregnation process. Zeolite Y (Wako chemical, Japan) and Al_2O_3 (Sigma–Aldrich, USA) are added to $NiCl_2$ solution. After drying the suspension, powders were calcined at 400 °C for 3 h and reduced at 400 °C for 1 h under H_2 atmosphere. The samples prepared by these impregnation processes were named "$IMP_{zeolite}$" and "$IMP_{Al_2O_3}$", respectively. Microstructure was characterized by transmission electron microscope (TEM, JEM-2010, JEOL, Japan). To determine the size of Ni particles, the sizes of total more than 100 Ni particles for $CH_{zeolite}$ and approximate 20 Ni particles for $IMP_{zeolite}$ and $IMP_{Al_2O_3}$ were measured in more than 5 areas. The composition and the amount of Ni in the samples were analyzed by X-ray fluorescence spectroscopy (ZSX-Primus II, Rigaku, Japan). Crystal structure of the samples was characterized by X-ray diffraction (XRD, Rint-2500V, Rigaku, Japan). Samples were set on Quartz cell and covered with a polyimide film by using Apiezon® H grease in the glove box in order to avoid contact of samples with the air.

2.2. Ammonia decomposition

NH_3 decomposition reaction was carried out in a closed reactor of Inconel® as shown in Fig. S1 with detail explanation about the procedure. 100 mg of the sample was put into the reactor, and heated at 500 °C as the reaction temperature under vacuum condition. NH_3 was introduced up to 0.100 MPa at the reaction temperature, and then pressure variation was monitored. As mentioned above, the decomposition reaction consumes 2 mol of NH_3 and generates 3 mol of H_2 and 1 mol of N_2, that is total amount of gaseous products is 4 mol. Therefore, the increase of pressure indicates the conversion ratio from NH_3 to H_2 and N_2 as described by Eq. (2),

$$\text{Conversion}(\%) = \frac{P - P_0}{P_0} \times 100. \tag{2}$$

P_0 is initial pressure, which is 0.100 MPa. NH_3 decomposition (Eq. (1)) generally progresses as the first-order reaction. However, in this case, the actual conditions of experiments, which are static atmosphere in the closed system, could cause the errors from the theoretical behavior by negative effect of increasing pressure due to the NH_3 decomposition. Thus, it is not appropriate to analyze the whole curve of NH_3 degradation and evaluate reaction rate constant, k. Because it is guessed that the decomposition reaction proceeds without any effects in the initial period of the reaction, the k values can be evaluated by analyzing the initial reaction rate. To evaluate k value from the slope of degradation curves of NH_3 partial pressure (expressed as $[NH_3]$), the curves in the range of $1.00 > [NH_3] > 0.95$ were fitted to an exponential formula "$Y = Y_0 + A \exp(-kx)$" as shown in Fig. S2. In order to estimate an activation energy and a frequency factor of $CH_{zeolite}$ and $IMP_{zeolite}$, Arrhenius plots were carried out by using the k values at 400, 450, 500, and 550 °C. The samples were reduced at 550 °C for 1 h before the reactions for the Arrhenius plot to remove an influence of sintering by elevating temperature on their catalysis. These evaluated values of k, activation energy, and frequency factor are relatively compared to discuss kinetics of catalysts synthesized in this study, however it is difficult to absolutely compare the values with those in other literatures. The NH_3 decomposition at 500 °C for 24 h was repeated 5 times to examine the stability of the catalytic performance. Before each reaction in the repeated tests, the system was cooled to room temperature with degassing, and 0.100 MPa of NH_3 was refilled after heating at 500 °C from the vacuum condition.

3. Results and discussion

Fig. 1 shows TEM images of Ni particles supported on zeolite and alumina after the reduction under H_2 at 400 °C. Ni nanoparticles of $CH_{zeolite}$ were formed with 2–5 nm in diameters. On the $IMP_{zeolite}$ and $IMP_{Al_2O_3}$, the diameters of the synthesized Ni particles were 10–15 nm and about 8–10 nm, respectively. The Ni particles of only $CH_{zeolite}$ have small size below 5 nm and showed the highest dispersion.

From XRD patterns of zeolite after dehydration at 600 °C for 20 h and $CH_{zeolite}$ after reduction at 400 °C, as shown in Fig. 2(a) and (b), respectively, it was found that crystal structure of the zeolite was maintained after the reduction. After the reduction, peaks assigned to Ni metal were not clearly observed because Na-Y zeolite also has a peak near 44° and the Ni nanoparticles possess the nanosize.

Fig. 3 shows conversion rate for NH_3 decomposition reaction at 500 °C of each catalyst as a function of time. $CH_{zeolite}$ showed much higher activity than those of Ni particles prepared by the impregnation processes. Here, although the conversion at 773 K and 1 atm should be reached to 99.74% thermodynamically, the conversion brought by $CH_{zeolite}$ seems to be saturated near 60% [13]. It is considered that the limitation of conversion was caused by negative effects due to reaction conditions such as static atmosphere and increase of total pressure in the closed system. Reaction rate constants k are shown in Table 1 with Ni contents to discuss the catalytic properties in detail. From the comparison of k values, it was found that Ni nanoparticles of $CH_{zeolite}$ showed about