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High catalytic performance of fine particles of metallic iron formed from limonite in the decomposition of a low concentration of ammonia

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Catalytic NH_3 decomposition with limonite rich in α-FeOOH has been studied as a hot gas cleanup method to remove a low concentration of NH_3 from fuel gas produced in coal gasification. Fine particles of metallic Fe formed from α-FeOOH achieve the almost complete decomposition of 2000 ppm NH_3 to N_2 at 500°C under a high space velocity of 45,000 h^{-1} and show the stable catalytic performance for 50 h. The predominant catalytic mechanism involving the formation and subsequent decomposition of Fe nitrides may be proposed on the basis of the XRD and TPD results.

KEY WORDS: ammonia decomposition; hot gas cleanup; limonite; metallic iron; iron nitrides

1. Introduction

An integrated gasification combined cycle (IGCC) under development is expectable to be one of the most environmentally acceptable technologies to generate electric power from coal and biomass. A hot gas cleanup method to remove a small concentration of NH_3, typically 1000–5000 ppm (in volume), from fuel gas produced in a high temperature gasification process for IGCC can improve the thermal efficiency and environmental performance [1,2]. Catalytic decomposition of NH_3 to N_2 and H_2 may be the most efficient method for this purpose [1] and has thus attracted increasing attention [3–5]. Although it has been reported that Ni-, Mo-, and Ru-based catalysts show NH_3 conversions of ≥70% in the decomposition of several thousands ppm NH_3 at high temperatures of 700–960°C under total pressures of 0.1–2.0 MPa [1,3,6–9], inexpensive Fe-containing materials may be promising as the catalyst sources.

According to earlier studies under ambient pressure, ferrous dolomite and sintered iron ore catalyzed this reaction at 900°C [6], and Fe oxide on TiO_2 monolith support provided high NH_3 conversion of 95% at 800°C [4]. We have also shown that nanoscale metallic Fe supported on coal char, which can simply be produced by heating fine FeOOH particles precipitated on brown coal in inert gas [10,11], is capable of achieving the complete decomposition of 2000 ppm NH_3 to N_2 at 750°C [12,13]. However, these reaction temperatures are high and may thus be reduced to ≤600°C, because, in a hot gas cleanup system proposed for IGCC [1], the removal of H_2S from fuel gas prior to the catalytic decomposition of NH_3 is carried out usually with Zn ferrite and titanate at 450–600°C.

To our knowledge, the high catalytic performance of Fe materials in the NH_3 decomposition at such a low temperature range from the viewpoint of hot gas cleanup has not been reported so far. This paper demonstrates that low-valued iron ore (limonite) rich in goethite (α-FeOOH) can achieve the almost complete decomposition of 2000 ppm NH_3 to N_2 at 500°C under a high space velocity of 45,000 h^{-1}, and it also proposes the reaction mechanism involving the formation of fine particles of metallic Fe from the limonite.

2. Experimental

2.1. Catalyst materials and preparation

An Australian limonite was used as a catalyst precursor in the present study, because it was reported to be transformed into a highly dispersed Fe catalyst [14]. The as received limonite is composed of about 90 mass% of α-FeOOH, and the metal composition on a dry basis is: Fe, 55.6; Si, 2.3; Al, 1.4; Ca, 0.2; Mg, 0.1 mass%. About 90% of the limonite had the size fraction of $< 250\ \mu m$, and the BET surface area was 20 $m^2\ g^{-1}$. The limonite was first reduced with pure H_2 at 500°C and then supplied to NH_3 decomposition without exposure to laboratory air. The detailed procedure is described below.

2.2. Ammonia decomposition and gas analysis

Catalytic decomposition of NH_3 was carried out isothermally with a cylindrical quartz reactor (8 mm i.d.) under atmospheric pressure [13]. After 0.40 g of the

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limonite was charged into the reactor, high purity He ($\geq$99.99995%) was passed for an appropriate time to ensure that the concentration of N_2 as an impurity in the outlet gas was <20 ppm. The reactor was then heated electrically, and at 500°C the limonite was reduced with pure H_2 for 2 h. After reduction, the atmosphere was restored to the He, and the reactor was finally held at a constant temperature (300–500°C). The decomposition run started by passing 2000 ppm NH_3 diluted with high purity He over the reduced catalyst, the space velocity being 45,000 h^{-1}.

The amount of N_2 formed was analyzed at 2.5 min intervals with a high-speed micro gas chromatograph (Hewlett Packard), and the concentration of NH_3 fed or unreacted was determined at 3 min intervals with a photoacoustic multi-gas monitor (Innova) [13]. Conversion of NH_3 to N_2 was calculated by using the amounts of NH_3 fed and N_2 formed.

2.3. *Catalyst characterization*

The X-ray diffraction (XRD) measurements of the limonite samples as received, after H_2 reduction and after NH_3 decomposition were made with Mn-filtered Fe Kα radiation. The reduced or used limonite always generated a lot of heat upon recovery from the reactor due to the highly exothermic oxidation of metallic Fe. To avoid the occurrence of the rapid oxidation and minimize the effect of laboratory air on the XRD forms, only the surface layer of the reduced or used catalyst was first passivated with 1 vol.% O_2/He at room temperature, and the resulting sample was then recovered from the reactor.

In a temperature-programmed desorption (TPD) run, the limonite held in the reactor after NH_3 decomposition at 300°C was first quenched to room temperature in a stream of high purity He (100 mL(STP) min^{-1}) and then heated at 5°C min^{-1} up to 950°C. The concentration of N_2 evolved in this process was monitored by using the micro GC. Commercially available bulk Fe_3N (99.9% pure) (Kojundo Chemical Lab. Co.) was also employed in place of the used limonite for comparison. Some samples after TPD were also subjected to the XRD measurements.

3. Results and discussion

3.1. *States of limonite catalysts before NH_3 decomposition*

Figure 1 shows the XRD profiles for the limonite samples. The as received limonite provided the XRD peaks attributable to α-FeOOH (goethite). When the limonite was first H_2-reduced at 500°C and then O_2-passivated at room temperature, as seen in figure 1b, the clear diffraction lines of α-Fe appeared, whereas no XRD signals of any Fe oxides, such as hematite, magnetite and wustite, were detectable, indicating the complete reduction of goethite to metallic Fe. The average crystalline size of α-Fe was estimated to be as small as 23 nm by the Debye–Scherrer method. Such a high degree of Fe dispersion may also be supported by the observation that the H_2-reduced limonite without O_2 passivation always generated the intense heat due to the rapid oxidation of fine particles of metallic Fe when exposed to laboratory air. It is evident that the fresh limonite catalyst supplied to the NH_3 decomposition run exists as the finely-dispersed form.

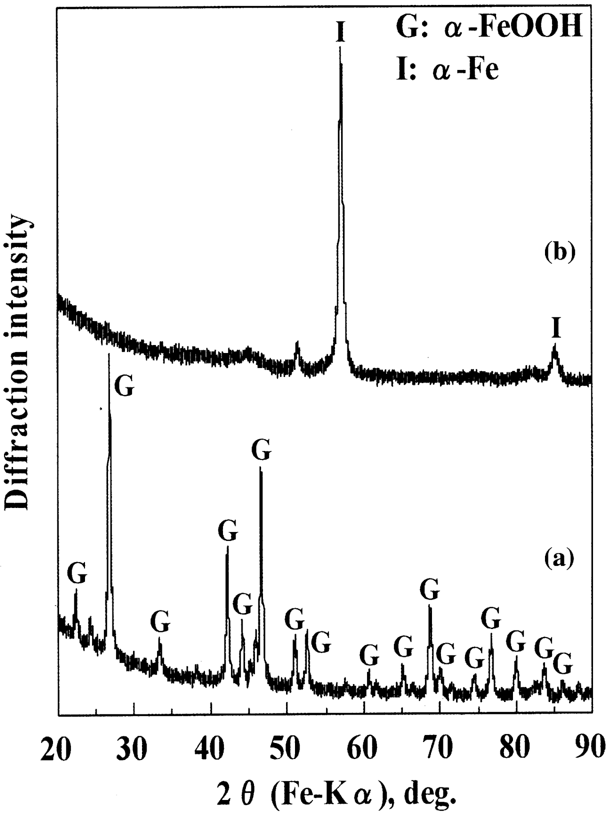

Figure 1. XRD profiles for limonite samples as-received (a) and after H_2 reduction at 500°C followed by O_2 passivation (b).

3.2. *Catalytic activity of limonite in NH_3 decomposition*

Figure 2 shows conversion of NH_3 to N_2 against time on stream at 300–450°C. In a blank test with quartz wool alone at 750°C, the conversion was <1%, which means that thermal decomposition of NH_3 can be neglected under the present conditions. As seen in figure 2, the limonite was almost inactive at 300°C, but it promoted the decomposition reaction even at a low temperature of 350°C, and the catalytic activity increased dramatically with increasing temperature. Although the induction period was observed at 350–450°C, it was shorter at a higher temperature. The NH_3 conversion at a steady state was 8% at 350°C, 42% at 400°C and 88% at 450°C. The apparent activation energy was calculated to be about 100 kJ mol^{-1} from such a temperature dependency of the reaction rate.

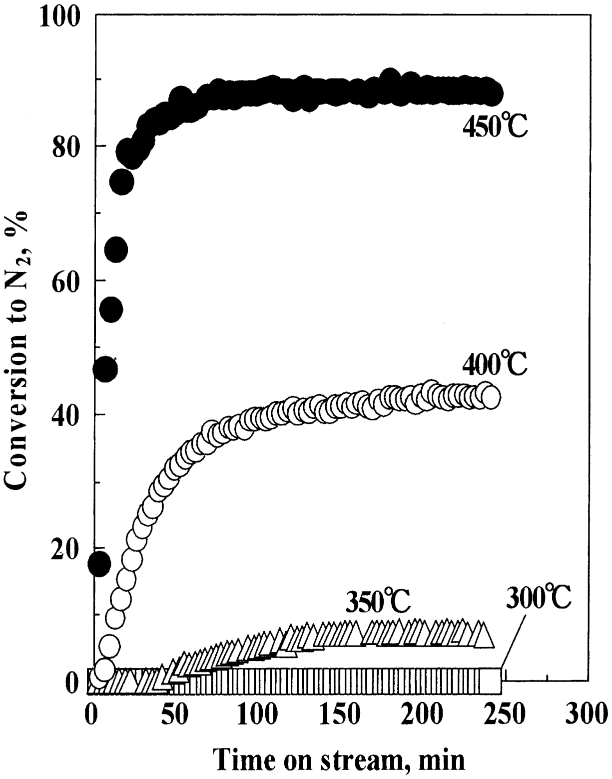

Figure 2. Conversion of NH_3 to N_2 against time on stream over limonite catalysts at different temperatures.

The reaction profile for a long run for 50 h at 500°C is shown in figure 3, where both conversion of NH_3 to N_2 and the concentration of NH_3 in the reactor outlet are plotted as a function of time on stream. The induction period observed at ≤ 450°C in figure 2 disappeared, and the limonite achieved the high conversion of 99.9% at the start of the reaction and showed the stable catalytic performance for 50 h. As seen in figure 3, the concentration of NH_3 in the exit gas was always less than the detection limit of 1 ppm.

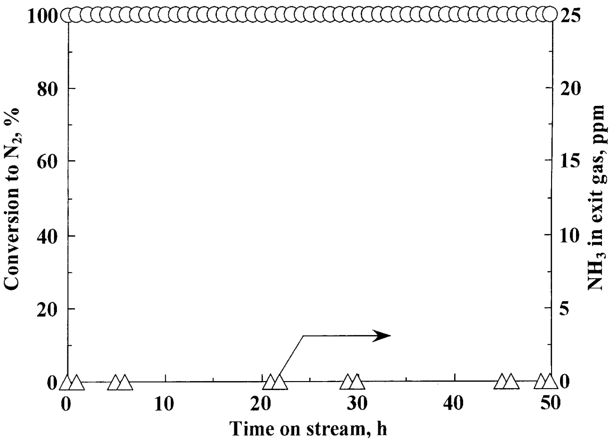

Figure 3. Time changes in NH_3 conversion and its concentration in exit gas in a 50 h run at 500°C.

Thus, the limonite catalyst realized the almost complete decomposition of 2000 ppm NH_3 at a much lower temperature, compared with other Fe-containing materials studied earlier from the viewpoint of the hot gas cleaning, such as ferrous dolomite [6], sintered iron ore [6], Fe oxide on TiO_2 monolith support [4], and metallic Fe supported on coal char [13]. The conversion to N_2 was 75–90% at 900°C over the former two materials [6], 15% at 500°C with the monolith catalyst [4], and 20% at 550°C for the char-supported Fe [13], the space velocity being smaller [4,6] than or the same [13] as that in the present work. Although the decomposition of a higher concentration of NH_3 of more than 5 vol.% with fused Fe catalysts with some promoters has been studied at 400–500°C in relation to the kinetics of NH_3 synthesis, the conversion to N_2 can be estimated to be very low under the high space velocity of 45,000 h^{-1} used in this study [15,16]. Small amounts of Al and Ca present in the limonite might have promotion effects on the catalytic activity of metallic Fe, because it is well known that the fused catalysts for NH_3 synthesis are promoted by these components. To make clear this point will be the subject of future work.

The turn-over frequency for the limonite catalyst was calculated by determining surface Fe atoms using the CO chemisorption method, and the value at 400°C was estimated to be 2.7×10^{-2} s^{-1}, which was comparable to those (1.5–1.6×10^{-2} s^{-1}) in the decomposition of 20% NH_3 at 400°C with fused and carbon-supported Fe catalysts promoted by potassium [15,17].

3.3. *Iron forms of limonite catalysts after NH_3 decomposition*

Figure 4 shows the XRD patterns for the three catalysts recovered after NH_3 decomposition for 4 h followed by O_2 passivation. After the reaction at 300°C, α-Fe observed in the H_2-reduced limonite disappeared, but instead the distinct diffraction lines of Fe_4N were detectable, and the weak XRD peaks of Fe_3N were also present. The average size of Fe_4N was as small as 18 nm. The formation of these nitrides means the reaction of α-Fe with NH_3. As shown in figure 4b, at 400°C, Fe_4N still existed as the main species, whereas the presence of Fe_3N seemed to disappear, and the XRD signals of α-Fe appeared newly.

When the temperature was raised further to 500°C, as seen in figure 4c, Fe_4N disappeared completely, and α-Fe was the only crystalline Fe species, showing the decomposition of Fe_4N to α-Fe. Some XRD peaks remained unidentified in figure 4 and may be attributable to aluminosilicates present in the original limonite. The crystalline sizes of α-Fe after the 4 and 50 h runs were estimated to be 26 and 27 nm, respectively. These values reveal no significant agglomeration of metallic Fe particles in the process of NH_3 decomposition. The unchanged catalyst dispersion and the stable catalytic performance observed in figure 3 demonstrate that there is no deactivation of the present limonite.

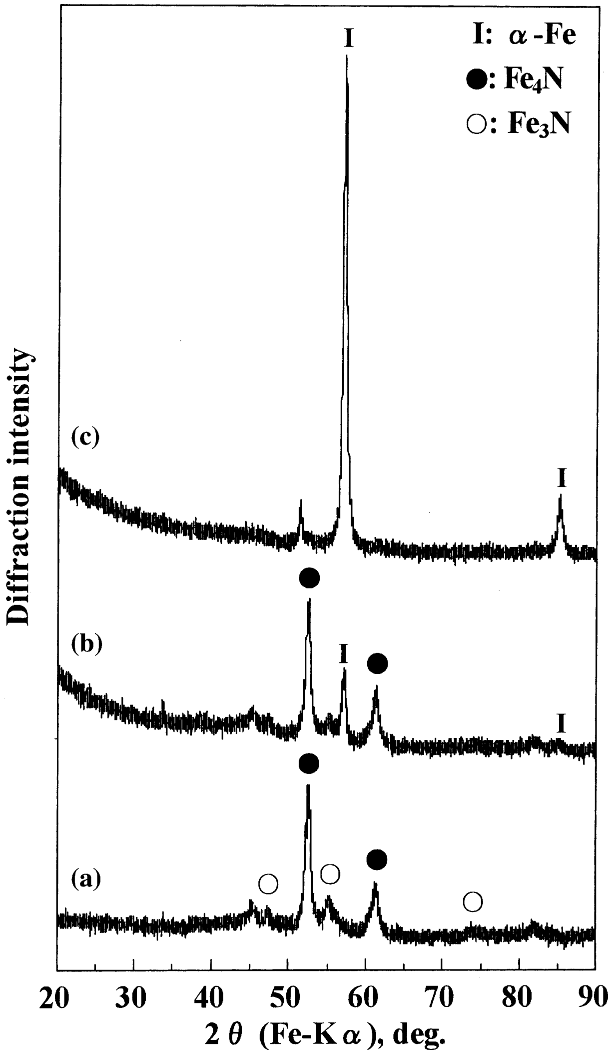

Figure 4. XRD profiles for limonite catalysts after NH_3 decomposition at 300°C (a), 400°C (b) and 500°C (c).

The comparison of the catalytic activity (figures 2 and 3) and the Fe forms (figure 4) in the temperature region of 300–500°C may indicate that the catalysis of NH_3 decomposition by the limonite relates closely to the formation and subsequent decomposition of Fe nitrides. The next section addresses this point.

3.4. Evolution of N_2 during TPD and changes in Fe forms after TPD

It can be expected that the changes from Fe_4N and Fe_3N into α-Fe with the reaction temperature observed in figure 4 accompany N_2 formation. To examine this point, the catalyst quenched after the run at 300°C was subjected to the TPD experiment in a stream of high purity He. The rate of N_2 evolved is plotted against the TPD temperature in figure 5. The N_2 evolution started at about 350°C, and the rate profile exhibited the shoulder and main peaks at 420 and 580°C, respectively. It is evident that the decomposition of Fe_4N and Fe_3N into N_2 occurs at elevated temperatures. The rate drop observed beyond 580°C in figure 5 should thus be responsible for the decreased content of these nitrides.

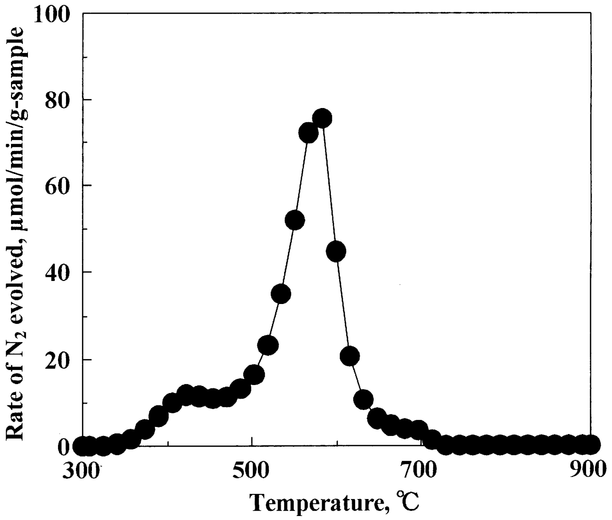

Figure 5. Rate profile for N_2 evolved during TPD of the limonite after NH_3 decomposition at 300°C.

To make clear the chemistry of the N_2 formation upon TPD, the XRD measurements of some catalysts after TPD were carried out. The results are summarized in table 1, where the Fe species identified by XRD before TPD are also provided for comparison. When the TPD run of the limonite used at 300°C was stopped at 450°C where the shoulder N_2 peak was observed (figure 5), Fe_3N disappeared, and Fe_4N alone remained in the sample. After the TPD up to 950°C, on the other hand, Fe_4N was transformed completely into α-Fe, irrespective of the kind of the used catalyst. The combination of the results shown in figure 5 and table 1 strongly suggests that the shoulder N_2 peak at 420°C in figure 5 originates from the transformation of Fe_3N into Fe_4N and N_2, whereas the main N_2 formation beyond 500°C does from the decomposition of Fe_4N to metallic Fe and N_2, and the consequent decrease in the content of Fe_4N causes the rate drop after 580 °C.

The transformation of Fe_3N into Fe_4N was confirmed by making the TPD and XRD measurements of bulk Fe_3N as a commercial regent. Figure 6 shows the TPD profile. The N_2 evolution from the bulk compound started at 500°C, and the rate profile provided the two peaks at 600 and 670°C. As shown in table 1, when the TPD run was stopped at 600°C, the XRD peaks of Fe_3N lowered considerably, which resulted in the appearance of Fe_4N. After the TPD up to 950°C, Fe_4N was converted to α-Fe (table 1). The comparison of figures 5 and 6 reveals that Fe_3N present in the limonite used at 300°C undergoes the transformation into Fe_4N at a lower temperature than bulk Fe_3N. This difference is probably attributable to the high dispersion of the Fe_3N species in the catalyst.

Table 1
Changes in Fe species identified by XRD before and after TPD run

Sample	Before TPD run[a] Fe species[b]	After TPD run	
		Temperature/°C	Fe species[b]
Limonite used at 300°C	Fe_3N (w), Fe_4N (s)	450	Fe_4N (s)
Limonite used at 300°C	Fe_3N (w), Fe_4N (s)	950	α-Fe (s)
Limonite used at 400°C	Fe_4N (s), α-Fe (m)	950	α-Fe (s)
Bulk Fe_3N[c]	Fe_3N (s)	600	Fe_3N (w), Fe_4N (s)
Bulk Fe_3N[c]	Fe_3N (s)	950	α-Fe (s)

[a] After NH_3 decomposition followed by O_2 passivation.
[b] XRD intensities designated as w, weak; m, medium; s, strong.
[c] Commercial reagent (99.9% pure).

3.5. Catalytic mechanism of NH_3 decomposition

The results described above strongly suggest that the present NH_3 decomposition with fine particles of α-Fe formed from α-FeOOH in the original limonite proceeds through a mechanism involving Fe nitrides. The Fe-catalyzed NH_3 decomposition has extensively been studied mainly in terms of the mechanisms of NH_3 synthesis with the different kinds of Fe catalysts, and several types of Fe nitrides can be formed [16,18,19]. The formation of Fe_4N and Fe_3N observed in the XRD profiles (figure 4) after the reaction at 300°C can be expressed by the following equations:

$$8Fe + 2NH_3 \rightarrow 2Fe_4N + 3H_2 \quad (1)$$

$$6Fe + 2NH_3 \rightarrow 2Fe_3N + 3H_2 \quad (2)$$

The stronger XRD intensities of Fe_4N in figure 4 show that equation (1) is the predominant reaction. As seen in figure 5, no N_2 evolution from Fe_3N and Fe_4N present in the limonite occurred at 300°C. In other words, these nitrides were thermally stable, and consequently the limonite was inactive apparently in the NH_3 decomposition at 300°C (figure 2). The N_2 formation from the Fe nitrides took place significantly at ≥350°C, and the rate increased with increasing temperature up to 580°C (figure 5). The limonite correspondingly promoted the decomposition of NH_3 into N_2 at ≥350°C, and the conversion to N_2 was larger at a higher temperature (figures 2 and 3). The following equations may be proposed for the N_2 formation from Fe_3N and Fe_4N:

$$8Fe_3N \rightarrow 6Fe_4N + N_2 \quad (3)$$

$$2Fe_4N \rightarrow 8Fe + N_2 \quad (4)$$

Equation (3) took place at a lower temperature than equation (4). As seen in figure 4, Fe_4N and α-Fe coexisted at 400°C, whereas, at 500°C, the XRD peaks of Fe_4N completely disappeared, and α-Fe alone remained in the used limonite. The combination of equations (1) and (4) (or equations (2), (3) and (4)) can lead to the following overall equation for NH_3 decomposition:

$$2NH_3 \rightarrow N_2 + 3H_2 \quad (5)$$

According to earlier work on NH_3 synthesis with Fe-based catalysts [16,18,19], the reverse reaction, that is equation (5), may occur on the surface of Fe nitride phases. In order to examine this possibility, 2000 ppm NH_3 was passed over commercial Fe_3N compound (99.9% pure) at 400°C where no significant evolution of N_2 from the nitride itself took place (figure 6). The conversion to N_2 after 100 min over the Fe_3N was about 10%, which was much lower than the value (40%) observed with the limonite (figure 2), suggesting that metallic Fe can work mainly as the catalytically active sites under the present conditions. It is thus likely that the catalytic decomposition of NH_3 with metallic Fe formed from the limonite proceeds predominantly through a cycle mechanism involving the formation of Fe nitrides and the subsequent transformation into N_2 and metallic Fe, and the occurrence of the latter reaction determines the rate of the NH_3 decomposition.

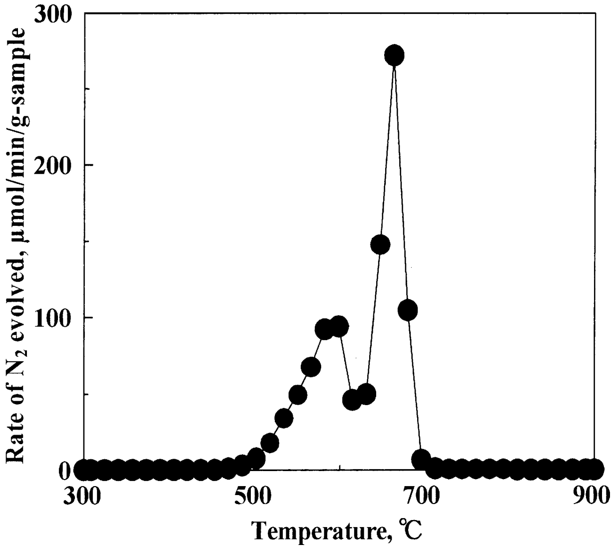

Figure 6. Profile for the rate of N_2 evolution during TPD of commercial Fe_3N.

4. Conclusions

The reduction of α-FeOOH-rich limonite with pure H_2 provides fine particles of α-Fe, and the highly dispersed metallic Fe catalyzes the decomposition of 2000 ppm NH_3 diluted with inert gas at temperatures of ≥350°C under ambient pressure. The Fe catalyst achieves the almost complete decomposition under the conditions of 500°C and high space velocity of 45,000 h^{-1}, and it shows the stable performance in the 50 h run. The XRD and TPD measurements after reaction reveal the transformation of metallic Fe into Fe_3N and Fe_4N at 300°C and the N_2 evolution from these nitrides beyond 350°C, respectively. These observations suggest that the Fe-catalyzed NH_3 decomposition proceeds mainly through a cycle mechanism involving Fe metal and nitrides.

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