

High catalytic performance of magnesium cations-added limonite in the decomposition of ammonia in a simulated syngas-rich fuel gas



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ABSTRACT

Catalytic decomposition of 2000 ppm NH₃ with an Australian limonite ore, which is composed mostly of goethite (α -FeOOH), has been studied from a viewpoint of hot gas cleanup with a vertical, cylindrical quartz reactor at 750–850 °C under a high space velocity of 45,000 h⁻¹. It has already been reported that the limonite achieves the almost complete decomposition of NH₃ in inert He at 500 °C and shows very stable performance in the reaction at 750 °C in the coexistence of 50–500 ppm H₂S or at 850 °C in the presence of fuel gas components produced in an air-blown coal gasification process. In the coexistence of a high concentration of syngas (50% CO/25% H₂) produced with an O₂-blown coal gasifier, the limonite is deactivated almost completely because of the remarkable occurrence of carbon deposition from the CO. On the other hand, the addition of small amounts of CO₂ and H₂O, which are always included in actual coal-derived fuel gas, to the syngas improves the activity of the limonite, and conversions of NH₃-N₂ at 750 and 850 °C become about 65% and almost 100% without carbon deposition, respectively. When several limonite-based catalysts with alkali metal and alkaline earth metal cations are prepared by the impregnation method and then used in the NH₃ decomposition at 750 °C in 50% CO/25% H₂/5% CO₂/3% H₂O, fine particles of MgO derived from Mg cations can work more effectively as the promoter, and the 3 mass% Mg-added limonite maintains the high and stable NH₃ conversion of almost 100% for 25 h. In this case, no significant carbon deposition takes place. It is probable that MgO with strong basicity suppresses the carbon formation from CO, and that the limonite-based composite catalyst thus shows the superior performance in the decomposition of NH₃ in syngas-rich fuel gas that simulates product gas in O₂-blown coal gasification.

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1. Introduction

It has been well-accepted that an integrated gasification combined cycle (IGCC) or fuel cell (IGFC) system is one of the most promising clean coal technologies in the future [1–3]. A hot gas cleanup method to remove a low concentration of NH₃ from raw fuel gas produced in high-temperature coal gasification, in place of the wet scrubbing method, has also attracted increasing attention as one option to increase further the power generation efficiency of IGCC and IGFC [4–8]. A large number of catalysts, such as Ni-based [6,9–13], Mo-based [6,10] and Ru-based [6,10] catalysts, have thus been developed to efficiently decompose NH₃-N₂ and H₂, and inexpensive Fe-containing materials have also been studied as the catalyst sources [9,14–20].

It has been reported that ferrous dolomite (5 mass% Fe) and sintered iron ore (59 mass% Fe) provide NH₃ conversions of 75–85% at 900 °C in the decomposition of 2200–2400 ppm NH₃ in product gas (19–25% CO/18–19% H₂/9–14% CO₂/2–3% CH₄) from an air-blown gasifier [9]. It has also been shown that carbon-supported Fe nanoparticles (2 mass% Fe) and brown coal char (2 mass% Fe) are effective as the catalyst materials for NH₃ decomposition in a stream of fuel gas components (20% CO/10% H₂/7% CO₂ and 13% CO/13% H₂/7% CO₂/1% CH₄) [15,16]. We have recently found that α -FeOOH-rich limonite (56 mass% Fe) can maintain conversion of NH₃-N₂ at the high level of almost 100% at 750 °C in the coexistence of 50–500 ppm H₂S or >90% at 750–850 °C in a simulated fuel gas (20% CO/10% H₂/10% CO₂ or 3% H₂O) [18,19], but it is deactivated considerably in the coexistence of a CO-rich (50%) gas [20]. It is thus necessary to develop a CO-tolerable catalyst that can give higher performance even in a large concentration of syngas, such as 50% CO/25% H₂, because 75–90% of syngas can be produced in O₂-blown type gasification processes [6,8,21,22]. To our knowledge,

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the high performance of any catalyst materials in the NH_3 decomposition in the coexistence of such a large syngas concentration has not been reported so far.

In the present paper, therefore, we first investigate in detail the catalytic performance of an Australian limonite in the decomposition of 2000 ppm NH_3 in a syngas-rich fuel gas that simulates product gas from an O_2 -blown gasifier, and then examine the influence of addition of alkali metal and alkaline earth metal cations to the limonite on conversion of $\text{NH}_3\text{-N}_2$.

2. Experimental

2.1. Catalyst materials and preparation

Limonite ore from Australia was used as a catalyst material in this work. The as-received sample is composed of approximately 90 mass% of $\alpha\text{-FeOOH}$, 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%. The size fraction was less than $250\ \mu\text{m}$, and the BET surface area was determined to be $20\ \text{m}^2/\text{g}$ by the conventional N_2 adsorption method. Several limonite samples with alkali metal (K) and alkaline earth metal (Mg and Ca) cations added were also prepared mainly by the impregnation method using an aqueous solution of the corresponding acetate at room temperature, followed by air calcination at $500\ ^\circ\text{C}$. Metal loading was 1–3 mass%. As shown below, all of these materials were subjected to H_2 reduction at $500\ ^\circ\text{C}$ before use.

2.2. Ammonia decomposition and gas analysis

All decomposition experiments were carried out with a vertical, cylindrical quartz reactor at ambient pressure. The apparatus and procedure have been mentioned in detail previously [15,16] and is thus simply explained below. The catalyst charged into the reactor was first exposed to a stream of high-purity He ($\geq 99.99995\%$) for an appropriate time to ensure that the concentration of N_2 as an impurity in the outlet gas was less than 20 ppm. After such precautions against leakage, the reactor was heated up to $500\ ^\circ\text{C}$, and high-purity He was then replaced by pure H_2 to reduce the catalyst. After reduction at $500\ ^\circ\text{C}$, the reactor was reheated in the He and held at a constant temperature. A mixture of 2000 ppm NH_3 and inert He or fuel gas components was finally passed through a thin layer (8 mm) of the reduced catalyst to start the decomposition run. The standard conditions are: limonite reduction: 2 h at $500\ ^\circ\text{C}$; NH_3 concentration: 2000 ppm; NH_3 decomposition: 4 h at $750\text{--}850\ ^\circ\text{C}$; space velocity: $45,000\ \text{h}^{-1}$; apparent contact time between gas and catalyst, 0.080 s.

The amounts of N_2 produced and fuel gas components fed were determined at 2.5 min intervals with a high-speed micro gas chromatograph with a thermal conductivity detector (Hewlett-Packard), and the concentration of NH_3 gas unreacted was measured at 3 min intervals with a photoacoustic multi-gas monitor (Innova) [15,16]. In the run in the coexistence of H_2O , the NH_3 was analyzed with a standard detector tube (Gastec). Nitrogen mass balances with all runs fell within the reasonable range of $100 \pm 6\%$. Conversion of $\text{NH}_3\text{-N}_2$ was estimated by using the amounts of NH_3 supplied and N_2 formed.

2.3. Catalyst characterization

The powder X-ray diffraction (XRD) measurements of several limonite samples after H_2 reduction, air calcination and NH_3 decomposition were made with Mn-filtered $\text{Fe-K}\alpha$ radiation. When the reduced or used catalyst was exposed to laboratory air upon recovery from the reactor, the highly-exothermic oxidation of nano-order particles of metallic iron took place, which resulted in

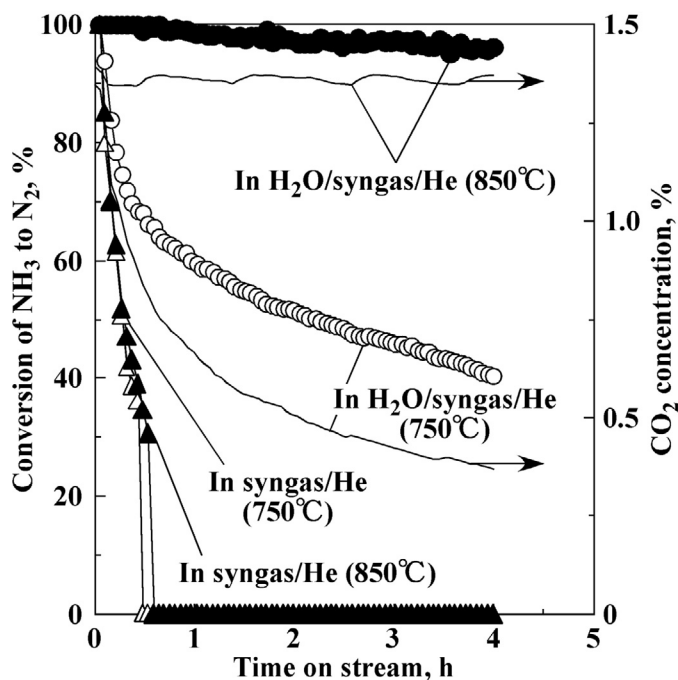


Fig. 1. Conversion of $\text{NH}_3\text{-N}_2$ and CO_2 concentration in the decomposition of 2000 ppm NH_3 in a syngas-rich gas of 50% $\text{CO}/25\% \text{H}_2$ without and with 3% H_2O at $750\text{--}850\ ^\circ\text{C}$.

the undesirable changes of the crystalline forms. To avoid and minimize the effect of the rapid oxidation on the XRD results, only the surface layer of the catalyst was first passivated with 1% O_2/He at room temperature, and the resulting sample was then recovered for the XRD analysis.

3. Results and discussion

3.1. Catalytic effect of as-received limonite

Fig. 1 shows conversion of $\text{NH}_3\text{-N}_2$ against time on stream during NH_3 decomposition at $750\text{--}850\ ^\circ\text{C}$ in the presence of a high concentration of syngas (50% $\text{CO}/25\% \text{H}_2$) without and with 3% H_2O added. The initial conversion was as large as almost 100% in all cases. The conversion in the coexistence of the syngas alone dropped steeply with increasing time on stream, regardless of the temperature, and it became nearly 0% after 30 min (Fig. 1), showing the almost complete deactivation of the limonite catalyst. Since carbonaceous materials were deposited on the limonite together with appreciable formation of CO_2 under the conditions applied [23], it is likely that the carbon deposition by the following disproportionation of CO in syngas is responsible for the catalyst deactivation observed.



As shown in Fig. 1, the addition of 3% H_2O –50% $\text{CO}/25\% \text{H}_2$ improved the activity of the limonite, and the extent of the improvement depended strongly on the reaction time and temperature: the conversion lowered gradually with time at $750\ ^\circ\text{C}$, whereas, at $850\ ^\circ\text{C}$, the limonite maintained the high conversion of more than 95% under the present conditions. The difference in the conversion between 750 and $850\ ^\circ\text{C}$ was thus larger at a longer time and reached about 55% after 4 h. The coexistence of the H_2O at $850\ ^\circ\text{C}$ also suppressed the carbon deposition apparently, though carbonaceous materials were formed considerably at $750\ ^\circ\text{C}$.

Fig. 1 also presents the concentration of CO_2 evolved during NH_3 decomposition in the 3% H_2O -containing syngas. Significant

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