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Catalytic decomposition of pyridine gas with fine particles of metallic iron formed from limonite

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ABSTRACT

Catalytic decomposition of 100 ppmv pyridine (C_5H_5N) with an Australian limonite ore, composed mainly of goethite (α-FeOOH), has been examined for hot gas cleanup with a fixed-bed quartz reactor at 300–500 °C under a large space velocity of 51,000 h^{-1}. When α-FeOOH in the limonite is reduced with pure H_2 at 500 °C, the transformation into nanoscale particles of metallic iron (α-Fe) occurs, and the catalyst achieves almost complete C_5H_5N decomposition in inert He at 500 °C and provides an N_2 yield greater than 80% for at least 10 h. The limonite also exhibits a high catalytic activity at 500 °C, even without H_2 reduction. Based on the results of N 1s X-ray photoelectron spectroscopy and temperature-programmed desorption measurements, it is probable that the limonite-catalyzed formation of N_2 from pyridine proceeds through cycle mechanisms involving α-Fe and iron nitride species.

1. Introduction

An advanced integrated gasification combined cycle (A-IGCC), for coal gasification at temperatures below 900 °C using steam directly from a heat recovery steam generator after a gas turbine unit, has the potential to achieve a very high generation efficiency greater than 53%, which corresponds to a greater than 30% reduction in CO_2 emissions compared with conventional pulverized coal-fired plants [1]. Coal-derived fuel gas is composed mainly of syngas (CO and H_2) with low concentrations of CO_2, CH_4, and H_2O and can also contain undesirable impurities such as HCl, HF, H_2S, COS, NH_3, HCN, particulates, alkali metals, and trace elements [2–5]. A cold gas cleaning process using wet scrubbers is a proven technology for removing these gaseous and solid impurities from the fuel gas before combustion and is applied in many IGCC plants [6–8]. However, the wet process results in a loss of heat energy of the hot raw gas and requires a high capital cost for large wastewater treatment facilities. A hot gas clean-up method that purifies fuel gas at temperatures higher than 300 °C can further improve the power generation efficiency of A-IGCC [3,4,9,10].

The decomposition of NH_3, which is the main precursor of NO_x emitted from a gas turbine, has been investigated using inexpensive iron catalysts, instead of Ni- or Ru-based catalyst reported previously [2,11–16]. Results showed that fine particles of metallic iron (α-Fe) formed from low-rank iron ore (limonite) can achieve almost complete decomposition of 2000 ppmv NH_3 diluted with inert gas at 500 °C and show stable activity in the presence of fuel gas components at 850 °C [13–16]. Fuel gas produced via low-temperature coal gasification contains not only impurities and particulates but also significant amounts of tarry materials. The nitrogen in tar (tar-N) predominantly takes heterocyclic N-forms such as pyridinic-N and pyrrolic-N [17–21]. The present authors' research group has recently found that 2–7 mass% Fe catalysts supported on cellulose-derived carbons provide N_2 yields of 40–45% after the almost complete decomposition of pulse-injected pyridine at 650–700 °C [22]. In the present study, therefore, the catalytic performance of an Australian limonite is examined for the decomposition of pyridine (C_5H_5N) at different temperatures in inert gas, followed by an investigation into the transformation reaction of C_5H_5N into N_2 to develop a novel hot gas clean-up method for removing the tar-N as N_2.

2. Experimental

2.1. Catalyst materials and preparation

A natural Australian limonite ore comprising approximately 70% of goethite (α-FeOOH) was employed as a catalyst precursor. The metal composition of the dried limonite was: Fe, 44; Si, 9.4; Al, 7.2; Mg, 0.15; and Ca, 0.07 mass%. The as-received limonite was sieved to obtain a size fraction of 250–500 µm. The BET-specific surface area was 40 m^2/g. Commercially available reagents of hematite

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(α-Fe_2O_3) (99.9% pure) and magnetite (Fe_3O_4) (>98% pure), which were obtained from Wako Pure Chemical Industries, Ltd, also were used as references. All catalyst materials were subjected to H_2 reduction at 500 °C before C_5H_5N decomposition experiments, unless otherwise noted.

2.2. Pyridine decomposition and gas analysis

Catalytic C_5H_5N decomposition was conducted with a flow-type fixed-bed quartz reactor (8 mm i.d.) under ambient pressure. Details of the experimental system have been described elsewhere [11]. The temperature was controlled by a K-type thermocouple attached to the exterior surface of the reactor. Approximately 0.25 g of the catalyst material was loaded into the reactor with quartz wool; a flow of high-purity He (>99.99995%) then was began until the concentration of N_2 in the entire system had decreased to less than 20 ppmv. After performing precautions against leakage, the reactor was heated electrically up to 500 °C, followed by replacement of the He with pure H_2 (>99.9999%) for 2 h. After reduction, the atmosphere was restored to He, and the reactor was held at a constant temperature of 300–500 °C. The C_5H_5N decomposition experiment began by passing 100 ppmv C_5H_5N diluted with high-purity He over the catalyst bed, at a space velocity of 51,000 h^{-1}. The amount of N_2 produced via C_5H_5N decomposition was determined at 3 min intervals by high-speed micro gas chromatography (GC) (Agilent), with a thermal conductivity detector. Concentration of C_5H_5N, HCN, and NH_3 was determined at intervals of 2 min with a photoacoustic multi-gas monitor (Innova). The C_5H_5N conversion was calculated using the amount of C_5H_5N before and after reaction. The yield of N_2, HCN, and NH_3 was estimated using the amounts of C_5H_5N fed and N_2, HCN, or NH_3 formed, respectively, and was expressed as a percent of nitrogen.

2.3. Catalyst characterization

Powder X-ray diffraction (XRD) measurements using Fe-Kα radiation with an Mn filter were performed on catalyst samples as received, after H_2 reduction and after C_5H_5N decomposition to identify crystalline iron forms. To avoid rapid oxidation of α-Fe particles upon exposure to air, the reduced or used catalyst was passivated with 2% O_2/He at room temperature before it was recovered from the reactor [13]. The average crystallite size of α-Fe was calculated using the Debye–Scherrer method. The X-ray photoelectron spectroscopy (XPS) measurements were conducted with a non-monochromatic Mg-Kα source to examine the chemical forms of elemental nitrogen on the surface of the limonite used. The binding energies of the N 1s spectra were referred to the Ag $3d_{5/2}$ peak at 367.9 eV [23]. In the temperature-programmed desorption (TPD) run, the limonite after reaction at 500 °C was first cooled to ambient temperature in a stream of high-purity He and then heated at 5 °C/min up to a maximum temperature of 1000 °C. The concentration of N_2 evolved was monitored using micro GC. Commercially available bulk Fe_3N (99.9% pure) (Kojundo Chemical Lab. Co.) also was used for comparison. The number of catalytically active α-Fe sites for C_5H_5N decomposition was determined using the CO-TPD method [13]. A catalyst material after H_2 reduction at 500 °C was quenched to 100 °C in He, followed by admission of pure CO (>99.95%) flow for 1 h to adsorb CO on the catalyst surface. After physically adsorbed CO was purged in a flow of He, the temperature was increased at 5 °C/min to a maximum of 700 °C for desorption of chemically adsorbed CO. The amount of CO desorbed was analyzed using micro GC. The C, H, and N contents in the limonite after C_5H_5N decomposition were determined according to the Japanese Industrial Standard method (JISM 8813).

3. Results and discussion

3.1. Decomposition of C_5H_5N and formation of N_2

Fig. 1 shows the effects of limonite, Fe_3O_4, and α-Fe_2O_3 as catalyst precursors on C_5H_5N conversion at 500 °C. In a blank experiment with quartz wool alone at 500 °C, conversion was less than 1%, indicating that thermal decomposition of C_5H_5N can be ignored under the present conditions. As seen in Fig. 1, the commercial reagents of α-Fe_2O_3 and Fe_3O_4 were effective as catalyst precursors for the decomposition of C_5H_5N. However, the activity decreased with increasing time on stream. The C_5H_5N conversion with α-Fe_2O_3 and Fe_3O_4 after 4 h reaction was 18% and 50%, respectively. In contrast, the limonite showed the greatest activity and stability and achieved almost complete decomposition of C_5H_5N immediately after the beginning of the reaction. The high performance was constant for a reaction time of over 4 h.

Fig. 2 illustrates C_5H_5N conversion against the time on stream over limonite catalyst at 300–450 °C. The initial conversion was greater than 99%, irrespective of the reaction temperature. At a temperature of 300 °C, the C_5H_5N conversion decreased sharply during the early stage of the reaction to less than 35% after 0.5 h and was less than 5% after 4 h. The trend through the run at 350 °C was similar to the result at 300 °C. The C_5H_5N conversion at 400 °C declined moderately to 30% after 2 h, whereas the conversion after 4 h was about 7%. Conversion at 450 °C was consistently greater

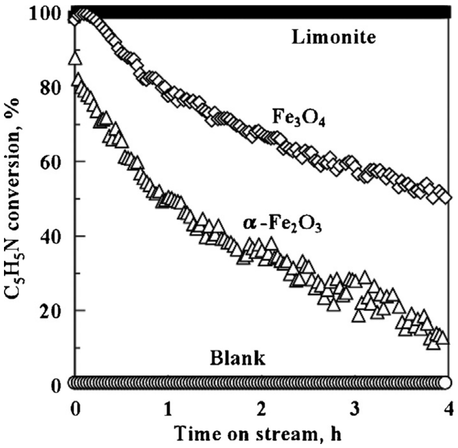

Fig. 1. Effects of limonite, Fe_3O_4, and α-Fe_2O_3 as catalyst precursors on the decomposition of 100 ppmv C_5H_5N at 500 °C.

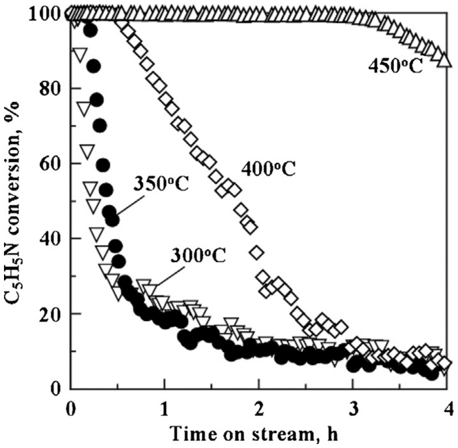

Fig. 2. Changes in C_5H_5N conversion with time over limonite catalysts at different temperatures.