Mechanism analysis and efficiency improvement of ammonia formation reaction from iron nitride and carbonated water

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Ammonia (NH_3) is an important raw material for nitrogen fertilizers used in agriculture, and it has been identified as a potential hydrogen carrier in recent years. However, NH_3 is mainly synthesized by the Haber–Bosch process, which requires high temperature and pressure. To lower the environmental burden, it is necessary to achieve NH_3 synthesis under milder conditions. In this study, we investigated the generation of NH_3 from iron nitride and carbonated water at ambient temperature and pressure.[1]

Fe_4N powder and a small amount of carbonated water were sealed in a bottle together with 101.3 kPa CO_2. The bottle was stirred at a constant temperature in the range of 298 to 328 K. The gas-phase H_2 and CO_2 and the liquid-phase NH_3 were quantified by gas chromatography every 30 min. After the reaction, the contents of the bottle were dried, and qualitative and quantitative analyses were performed by X-ray diffraction (XRD). In addition, Na_2CO_3 aqueous solution was prepared and used in place of carbonated water, and the same measurements were repeated.

For both NH_3 and H_2, the production rates and final production amounts increased as the reaction temperature increased. At 298 K, the amount of NH_3 300 min after the start of the reaction was almost twice that of H_2. In the reaction, 1 mol of NH_3 is produced from 1 mol of Fe_4N, and 4 mol of Fe can provide 8 electrons. Hence, it was expected that 5 mol of H would be produced in addition to 1 mol of NH_3, i.e., 2.5 mol of H_2 can be produced. It is presumed that the amount of NH_3 produced is higher than that of H_2 because N escaped from the lattice of Fe_4N, which is an interstitial compound, and reacted preferentially with H on the Fe_4N surface.

The activation energy ΔE_a calculated by using the Arrhenius plot of the reaction rate constants obtained at each temperature was 28 and 50 kJ/mol for the formation of NH_3 and H_2, respectively. The smaller ΔE_a also indicated that NH_3 production is more advantageous. The addition of Na_2CO_3 increased the rate of NH_3 formation as well as the amount of NH_3. The addition of carbonate increased both the pH and HCO_3^-concentration, which improved the rate of the redox reaction involving HCO_3^- and the formation of the Fe carbonato complex.

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