

Effect of reduction condition of Ni/Al₂O₃ catalyst for suppression of ammonia by-production during steam reforming of nitrogen contaminated methane

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Introduction

Fuel cell systems are one of the most promising methods for clean and efficient energy utilization. Natural gas is a useful fuel for stationary applications of fuel cell systems. Steam reforming of natural gas is a popular chemical process on hydrogen production for residential polymer electrolyte fuel cell systems. In some cases, natural gas contains nitrogen as a popular contaminant and the assumed maximum nitrogen concentration is 20%. When such natural gas is fed to PEFC systems, it has a fear of ammonia (NH₃) formation over steam reforming catalyst. Because it is reported that the NH₃ contamination in the reformed gas causes the deterioration of preferential CO oxidation catalyst and the electrode catalyst [1, 2]. Supported Ni and Ru catalysts are commonly used as a natural gas steam reforming catalyst in industry [3]. It is well known that the CH₄ steam reforming activity of Ru catalyst is higher than that of Ni catalyst [4]. However, NH₃ synthesis activity of Ru catalyst is also higher than that of Ni catalyst [4].

In this study, the effect of reduction condition of Ni catalyst for the CH₄ steam reforming activity and the NH₃ formation activity over alumina supported Ni catalyst was investigated.

Materials and Methods

The support material (α -Al₂O₃) was obtained by the calcination of boehmite (Catapal B alumina, Sasol) at 1300°C for 2 h in air. The Ni/Al₂O₃ catalyst was prepared by a conventional impregnation method using aqueous solution of a Ni(NO₃)₂·6H₂O. The obtained solid sample was calcined at 500°C for 2 h in air. The Ni content was adjusted to 12wt% after reduction treatment. The catalytic activity test was carried out in a fixed bed flow reactor. The calcined sample was reduced in 10% H₂/N₂ gas stream at 500°C, 600°C or 700°C for 30 min prior to the activity test. A reaction gas composed of 20% N₂ and 80% CH₄ was fed in the reaction tube and the gas flow rate was 50 mL min⁻¹. Steam was fed in the reaction tube separately and steam carbon (S/C) ratio was adjusted to 2.5. Catalyst weight for methane steam reforming activity test was 0.05 g (GHSV = 60,000 h⁻¹) and it for NH₃ formation activity test was 1.0 g (GHSV = 3,000 h⁻¹). The produced gas components (H₂, N₂, CH₄, CO, and CO₂) were analyzed by using a gas chromatograph (Shimadzu, GC-14B). The concentration of NH₃ was analyzed by ion chromatography method. The outlet gas was introduced in H₃BO₃ aqueous solution (5 g L⁻¹) for 18 h and the obtained solution was analyzed by an ion chromatograph (Shimadzu, HIC-6A).

Results and Discussion

Figure 1a shows the CH₄ conversion over Ni/Al₂O₃ catalysts pretreated at different reduction temperatures. A dotted line indicates a chemical equilibrium curve for CH₄

conversion at S/C = 2.5. The CH₄ conversion of each catalyst was low enough from equilibrium curve from 500°C to 700°C and has a nearly same value at each reaction temperature. It means that the CH₄ steam reforming rate of Ni/Al₂O₃ catalyst was almost same in spite of different reduction temperatures. The apparent CH₄ steam reforming rate was about 2.5 mmol s⁻¹ g-metal⁻¹ at 700°C in all catalysts. Figure 1b shows the NH₃ concentration in the outlet gas reacted over Ni/Al₂O₃ catalysts pretreated at different reduction temperatures. The NH₃ concentration increased with the increase of reaction temperature and the NH₃ concentrations obtained over 12wt%Ni/Al₂O₃ catalysts reduced at 500°C, 600°C and 700°C were 20.8 ppm, 13.4 ppm and 8.9 ppm, respectively. Therefore, the NH₃ formation rate was suppressed by the increase of reduction temperature of Ni/Al₂O₃ catalyst. It is suggested that the degree of reduction of Ni metal controls the apparent NH₃ formation rate over Ni/Al₂O₃ catalyst.

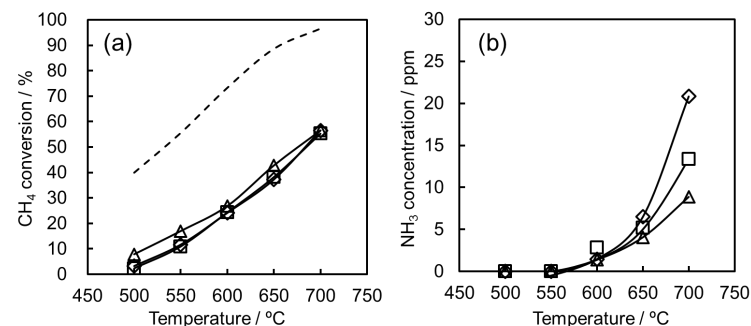


Figure 1. Experimental results of (a) the methane conversion (GHSV = 60,000 h⁻¹) and (b) the ammonia concentration (GHSV = 3,000 h⁻¹) over 12wt%Ni/ α -Al₂O₃ catalysts after reduced at 500°C (Δ), 600°C (\square) and 700°C (\diamond). A dotted line indicates chemical equilibrium curve for methane conversion at S/C = 2.5.

Significance

High temperature reduction of catalyst is effective to suppress NH₃ by-production during steam reforming of nitrogen contaminated methane over Ni/Al₂O₃ catalyst.

References

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