



Influence of nitrogen impurity for steam methane reforming over noble metal catalysts



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ABSTRACT

Ammonia by-production for steam methane reforming over alpha alumina (α -Al₂O₃) supported noble metal catalysts was investigated using the methane containing nitrogen feedstock for residential fuel cell. Ammonia is poisonous substance for carbon monoxide preferential oxidation (CO-PROX) catalyst, Pt electrode, and proton exchange membrane (PEM) in the polymer electrolyte fuel cell system. The ammonia concentrations in the reformed gases at 700 °C under SV = 10,000 h⁻¹ condition over commercial Ni and Ru catalysts were 20 ppm and 81 ppm, respectively. In the case of the Ru catalyst, ammonia concentration almost reached the chemical equilibrium value at 700 °C. Ammonia formation performance over 0.5 wt% metal (Rh, Pt, Ir, and Ru) supported on α -Al₂O₃ catalyst prepared by the impregnation method was compared at 700 °C under SV = 2,500 h⁻¹ condition; the ammonia concentrations in the reformed gases over the Rh, Pt, and Ir catalysts were below 0.1 ppm. The order of ammonia formed amount over the catalysts was as follows: Ru >> Rh, Pt, Ir. The ammonia formation can be substantially suppressed during steam reforming of methane containing nitrogen over the Rh, Pt, and Ir catalysts.

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1. Introduction

Recently, attractive attention to hydrogen production and utilization has been focused as energy saving and reduction of CO₂ emission technologies. A fuel cell co-generation system is one of the most promising methods for clean and efficient energy utilization and it is hoped for stationary and mobile source applications [2]. In particular, polymer electrolyte fuel cell (PEFC) has been enthusiastically developed by many companies and institutions [3–6]. Steam reforming [7–10], partial oxidation [11], auto-thermal reforming [10,12–14], and dry reforming [15–17] of various fuels have been studied as hydrogen production methods. Among them, the highest concentration of hydrogen in the reformed gas is obtained by steam reforming of fuels. Methane [8,9,15–17], methanol [18], dimethyl ether [19], and bio-oil [20] are commonly used as fuels and feed stocks for steam reforming. In particular, the steam reforming of natural gas which mainly consists of methane, is a popular chemical reaction for a residential PEFC system. The reformed gas is followed by water gas shift (WGS) and preferential oxidation of carbon monoxide (CO-PROX) reactions to lower the CO concentration. Two steps of CO purification reactions (CO < 10 ppm) are needed to prevent CO poisoning of electrode catalysts.

Nitrogen is one of common impurities in pipeline distributed natural gas (PNG) in Europe and North America and the concentration of nitrogen in PNG is up to 6% [21]. It is generally known that nitrogen is stable; however there is a serious risk that ammonia (NH₃) can be formed from the nitrogen impurity contained in natural gas by the reaction with reformed hydrogen during the steam reforming process. Some researchers reported that NH₃ in reformed gas causes the degradation of CO-PROX catalyst [22], Pt electrode [23] and proton exchange membrane [24] of PEFC system. To prevent the NH₃ poisoning, the NH₃ removal process must be installed as a post-treatment of the steam reforming process. However, this method requires the regular maintenance at the installation sites by technicians and leads to an increase in the total cost of fuel cell systems. Therefore, the preferred method which can suppress the NH₃ formation (AMF) over the steam reforming catalyst needs to be developed for the fuel cell systems using the PNG as fuel.

It is well known that the alumina (Al₂O₃) supported group VIII-X metal catalysts are active for steam methane reforming (SMR). The supported Ni and Ru catalysts are commonly used as SMR catalyst in industry and residential applications. The supported noble metal catalysts, e.g., Rh, Pt, and Ir are also active for SMR and the effects of metal dispersion and support materials on the catalytic performance for SMR have been also discussed in previous studies [25,26]. However, there are no studies on NH₃ by-production during steam reforming of methane with the nitrogen impurity (N₂-SMR) over conventional

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Ni and Ru based catalysts except for a few patent applications using Rh-Pt/Al₂O₃ catalyst [26–29].

In this paper, the catalytic performances for SMR and AMF during N₂-SMR over α -Al₂O₃ supported Rh, Pt, Ir, and Ru catalysts have been reported for the first time and have been also compared with those over the commercial Ru/ α -Al₂O₃ and Ni/ α -Al₂O₃ catalysts.

2. Experimental

2.1. Catalyst preparation

The catalysts used in this work were prepared by the conventional impregnation method with aqueous solution containing active metal sources. An α -Al₂O₃ support was prepared by calcination of boehmite provided from Sasol (Catapal B) in air at 1300 °C for 2 h. The boehmite powder was pressed into pellet, crushed, and sieved to obtain the appropriate pellet size within 150–250 μ m prior to the calcination process. The α -Al₂O₃ pellets were dipped in distilled water and the slurry was stirred for 1 h under reduced pressure by a rotary evaporator. As active metal source, a rhodium (III) nitrate nitric acid solution and an iridium (IV) nitrate solution were purchased by Furuya Metal Co. Ltd. A diamminedinitroplatinum (II) nitrate solution and a ruthenium (III) nitrate solution were purchased by Kojima Chemicals Co. Ltd. and Tanaka Holdings Co. Ltd., respectively. The active metal solution was added into the slurry and the mixture was stirred for 2 h under atmospheric pressure. Water solvent was evaporated at 80 °C under reduced pressure by a rotary evaporator and the obtained solid product was dried in air at 110 °C overnight and calcined in air at 500 °C for 2 h. Metal loading was adjusted to 0.5–2.0 wt.% in all catalysts used in the present study. As commercial catalysts, 12wt%Ni/ α -Al₂O₃ (FCR-4-02) and 2.0 wt%Ru/ α -Al₂O₃ (RUA) catalysts supplied by Clariant Catalysts K.K. (sphere type with 2 mm in diameter) were used, which they were crushed and sieved to obtain the appropriate pellet size within 150–250 μ m.

2.2. Catalytic performance test

The catalytic performance test of N₂-SMR was carried out using two types of fixed-bed flow reactors under atmospheric pressure; one has quartz tube reactor (I.D. 6 mm) and the other has SUS tube reactor (I.D. 10 mm). The commercial and prepared catalysts (0.05–2.00 g) were used for the performance test. In the case of the FCR-4-02, the catalyst was reduced in 10%₂H₂/N₂ gas flow (100 mL min⁻¹) at 500 °C for 30 min prior to the performance test. A feed gas composition was N₂/CH₄/H₂O = 1/4/10 and total flow rate was 75 or 150 mL min⁻¹. The catalytic performance was evaluated at the temperature range of 400–700 °C. In the case of FCR-4-02 and RUA, both the SMR and AMF performances were evaluated under the same condition; W/F = 10.2 g-cat. h mol-CH₄⁻¹ (GHSV = 10,000 h⁻¹). In the case of the prepared noble metal catalysts, the SMR performance test was conducted under the W/F = 0.51 g-cat. h mol-CH₄⁻¹ (GHSV = 200,000 h⁻¹) condition to compare the SMR performances of various catalysts more specifically. While, the amount of NH₃ formed during N₂-SMR was measured under the 40.3 g-cat. h mol-CH₄⁻¹ (GHSV = 2,500 h⁻¹) condition because NH₃ concentration in the outlet gas was less than detection limits under the GHSV = 10,000 h⁻¹ condition over Rh, Pt, and Ir catalysts.

The by-produced NH₃ contained in the outlet gas was collected by a H₃BO₃ aqueous solution (5 g L⁻¹) and the obtained solution was analyzed by an ion chromatograph (HIC NH₃-6 A, Shimadzu) equipped with Shim-pack IC-GC3 guard column and Shim-pack IC-C3 column (Shimadzu) to determine the concentration of NH₃ formed. The concentrations of other produced gases (H₂, N₂, CH₄, CO, and CO₂) were measured by a gas chromatograph equipped with a thermal conductivity detector (Shimadzu, GC-14B) after the steam was removed from the produced gaseous mixture by an ice-cold trap.

2.3. Catalyst characterization

The spent catalysts tested for N₂-SMR at 700 °C for 18 h under the GHSV = 2500 h⁻¹ were characterized by the following methods. The crystalline phase of catalysts was determined by powder X-ray diffraction (XRD, Ultima IV, Rigaku) equipped with the D/teX Ultra detector (Ni-filtered Cu K α radiation) at voltage of 40 kV and current of 40 mA. The step scans were taken over the 2 θ range of 20–70° in steps 0.010° and scan speed was 0.2° min⁻¹. The crystallite size of each metal phase was determined using Scherrer equation (K = 0.94). The specific surface area of each catalyst was determined by nitrogen adsorption and desorption measurement at liquid nitrogen temperature (–196 °C) using BELSORP mini II (MicrotracBEL). The samples were initially dried at 150 °C for 2 h under vacuum in order to vaporize adsorption water on sample surface. The specific surface area was determined by the Brunauer-Emmett-Teller (BET) method. The morphology of noble metals in the catalysts was observed using transmission electron microscope (TEM, JEM-2100F, JEOL). The operating voltage, emission current, and dark current were 200 kV, 230 μ A, and 93–97 μ A, respectively. The catalysts were crushed to powder and dispersed in ethanol with ultrasonic, followed by transferring into a copper grid. The diameter of metal particles supported on the α -Al₂O₃ was measured from the TEM images obtained. Average metal particle size was calculated from the observed metal particles which were 50–100 particles. The average size was defined as follows:

$$d_{average} = \frac{\sum d}{n} \quad (n = 50-100).$$

where $d_{average}$ represents average diameter of metal particles and n represents the number of metal particles.

3. Results and discussion

3.1. Catalytic performance of commercial catalysts

The catalytic performance for N₂-SMR over FCR-4-02 and RUA catalysts under the GHSV = 10,000 h⁻¹ condition are shown in Fig. 1(A). The methane (CH₄) conversions for N₂-SMR over FCR-4-02 and RUA increased with increasing in the reaction temperature and they reached to the chemical equilibrium limits of SMR at the temperature range of 400–700 °C. We confirmed that both FCR-4-02 and RUA exhibit the sufficient catalytic performances for N₂-SMR under the almost realistic reaction condition.

The by-produced NH₃ concentrations in the reformed gas for N₂-SMR over FCR-4-02 and RUA are shown in Fig. 1(B). The NH₃ by-production was hardly detected at below 500 °C for both catalysts. However, in the case of RUA, NH₃ concentration increased with an increase in reaction temperature above 500 °C and 20 ppm of NH₃ was formed at 600 °C. Furthermore, the NH₃ concentration reached the chemical equilibrium limit (81 ppm) at 700 °C. And noted that the SMR process is generally operated at more than 700 °C because the preferred CH₄ conversion cannot be obtained at less than 700 °C. In addition, Ru based catalyst is well known as an NH₃ synthesis catalyst [30–32]. Therefore, NH₃ is considered to be sequentially formed from the reformed hydrogen and the nitrogen impurity during N₂-SMR over Ru catalyst. On the other hand, the NH₃ concentration in the reformed gas over FCR-4-02 was 20 ppm at 700 °C. The AMF performance of FCR-4-02 was clearly lower than that of RUA. However, the residue of a few ppm of NH₃ in the reformed gas causes the degradation of CO-PROX and electrode catalysts in PEFC systems [22–24]. Thus, the AMF during N₂-SMR is a severe problem for the actual operation of natural gas fueled PEFC systems. From these results, we have focused on α -Al₂O₃ supported noble metal (Rh, Pt, and Ir) catalysts as new SMR catalysts which can suppress the NH₃ by-production during N₂-SMR.

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