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Ammonia synthesis over yttrium-doped barium zirconate and cerate-based perovskite-type oxide supported ruthenium catalysts

Naohiro Shimoda^a, Yutaka Kimura^a, Yusuke Kobayashi^a, Jun Kubota^b, Shigeo Satokawa^{a,*}

^a Department of Materials and Life Science, Faculty of Science and Technology, Seikei University, 3-3-1 Kichijoji-kitamachi, Musashino-shi, Tokyo, 180-8633, Japan

^b Department of Chemical Engineering, Fukuoka University, 8-19-1 Nanakuma, Jonan-ku, Fukuoka, 814-0180, Japan

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ABSTRACT

The performance of yttrium-doped barium zirconate and cerate-based perovskite-type oxide supported ruthenium catalysts for the thermal catalytic NH₃ synthesis process has been studied; these materials are expected to be applied as electrode catalysts for the electrochemical synthesis process of ammonia (NH₃), namely, NH₃ electrolysis. The BaZr_{0.9}Y_{0.1}O_{3-δ} (BZY10, with Y substituting for 10 mol% Zr in BaZrO₃)-supported Ru catalyst (Ru/BZY10) exhibited a high NH₃ synthesis rate (4.00 mmol h⁻¹ g_{cat.}⁻¹) under the following reaction conditions: S.V. = 36 L h⁻¹ g_{cat.}⁻¹, T = 400 °C, P = 0.1 MPa. Furthermore, the calcination at 1200 °C of BZY10 enhanced the catalytic performance of Ru/BZY10 (4.63 mmol h⁻¹ g_{cat.}⁻¹ at 400 °C). Considering the NH₃ synthesis rate per Ru amount, the optimal amount of Ru loading was 2.0 wt%. Furthermore, the addition of K and Cs to Ru/BZY10 can further improve the catalyst performance, which is found to be comparable to that of the other reported catalysts and is due to the electron-donating effect to active sites of Ru species. Based on various characterizations, we conclude that the particle size of Ru, the presence of BaCO₃ and BaO crystalline phases, and the coverage of Ba species strongly affect the catalyst performance.

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Introduction

Hydrogen (H₂) is a promising material as an energy storage medium of renewable energy forms such as water power, wind power, and solar power. However, the storage and transport of H₂ is highly problematic [1]. Therefore, the development of energy storage and transport technologies using new energy carriers that can substitute for H₂ is important for the effective utilization of surplus power

generated from the renewable energy sources. Among the various energy carrier substances containing H₂, ammonia (NH₃) has a central role in the future of the hydrogen economy based on fuel cell systems due to its high energy density, absence of carbon, and easy liquefaction. When NH₃ is used as a hydrogen carrier, although there still remains a problem in the technique of completely decomposing NH₃ to take out H₂ [2,3], it is considered that NH₃ is more advantageous than other candidates as a carbon-free energy carrier. In addition,

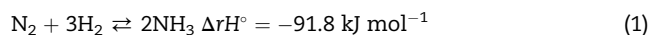
* Corresponding author.

E-mail address: satokawa@st.seikei.ac.jp (S. Satokawa).

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NH₃ is one of the most produced chemicals and is used as a raw material of chemical fertilizers, nitrate acid, and the other organic compounds [4,5]. In industrial production, NH₃ is synthesized by the Haber-Bosch process (Eq. (1)) with the production amount of over 100 million tons per year. However, this process requires the severe reaction conditions of high pressure (15–25 MPa) and high temperature (400–500 °C), leading to high energy consumption.



A well-known catalyst based on Fe₃O₄ promoted with Al₂O₃, K₂O, CaO, and SiO₂ is often used as the catalyst for the Haber-Bosch process [5–7]. Recently, as a NH₃ synthesis catalyst, Guo and Chen et al. have reported that transition metal and LiH composite catalysts show high performance [8]. Additionally, Ru-based catalysts have also been developed, realizing the NH₃ synthesis under more moderate conditions over the past few decades. In particular, a Cs–Ru/MgO catalyst developed by Aika et al. shows quite high performance comparable to that of Fe-based catalysts [9–12]. Recently, the electroneutral material supported Ru catalyst has been reported by Hosono et al. They have developed CaO·Al₂O₃ (C12A7e[−]) as a support which can reduce the inhibition of NH₃ synthesis by hydrogen poisoning and can promote the dissociation of the adsorbed nitrogen molecules by electron donation to Ru [13,14]. Furthermore, it has been reported very recently that a Ru-based catalyst using the novel Ca(NH₂)₂-support material shows high NH₃ synthesis activity [15,16]. Rare earth metal oxides, such as Pr₆O₁₁ [17], and various composite oxides, such as perovskite and spinel-type oxides [18,19], have been researched as potential support for Ru catalysts for NH₃ synthesis. Among these oxides, it was reported that Ru catalysts supported by various ion-conducting oxides, such as BaZrO₃ [20], BaCeO₃ [21], and BaCe_{0.9}Y_{0.1}O_{3-δ} [22], demonstrate high performance. It is presumed that the electron-donating effect of the supports to the Ru species leads to high catalytic activity. However, the reactions in these reports were conducted only under 3.0 MPa of reaction pressure, and there is no report that examined under the mild condition of 0.1 MPa.

The Haber-Bosch process is a thermal catalytic process that can effectively produce NH₃ using the heterogeneous catalysts in an industrial large-scale plant [23]. For the future, considering that the surplus power generated at thermal and nuclear power plants must be stored effectively as an energy carrier, the development of a new NH₃ synthesis process that can flexibly respond to the unsteady supply of electric power is required. In recent years, electrolysis of NH₃ using proton conducting solid electrolyte has been studied as an alternative process [5,24]. However, the rate of NH₃ synthesis is insufficient due to the low activity of the electrode catalyst for the N₂ dissociation step on cathodes. Recently, some cermet-type electrodes, such as Ni–BaCe_{1-x}Gd_xO_{3-δ} [25] and Ni–BaCe_{1-x}Y_xO_{3-δ} [26], have been reported for a cathode; however, the obtained NH₃ formation rate is still not high enough. To solve this problem, the use of La_{0.5}Sr_{0.5}Ti_{0.6}Ru_{0.4}O_{3-δ}–BaCe_{0.9}Y_{0.1}O_{3-δ} [27] and Ni–BaCe_{0.8}Y_{0.1}Ru_{0.1}O_{3-δ} [28] that contain Ru for enhancing the N₂ dissociation in the NH₃ synthesis process has been studied.

Based on previous work, we have focused on Ru catalysts using perovskite-type oxides, such as BaZrO₃ and BaCeO₃, as a support. These perovskites exhibit high proton conductivity and can be employed as cathode and electrolyte materials. In addition, it was reported that the substitution of Y for Ce or Zr improves the proton conductivity of BaZrO₃ and BaCeO₃ [29]. Therefore, we report here the catalytic performance of Ru catalysts using Y doped BaZrO₃ and BaCeO₃, namely, BaZr_{1-x}Y_xO_{3-δ} and BaCe_{1-x}Y_xO_{3-δ}, for NH₃ synthesis under standard pressure. Furthermore, various factors related to catalyst development, including Y substitution amount, support calcination temperature, Ru source, Ru loading amount, addition of alkali metals (K and Cs) and alkali-earth metal (Ba), have been studied to improve the catalytic performance.

Experimental

Preparation of perovskite-type oxides

As support materials, several perovskite-type oxides were prepared by the co-precipitation method using ammonium oxalate. First, Ba(NO₃)₂ (Wako Pure Chemical), ZrO(NO₃)₂·2H₂O (Wako Pure Chemical), Ce(NO₃)₂·6H₂O (Kanto Chemical), and Y(NO₃)₃·6H₂O (Kanto Chemical) were dissolved into distilled water at a desired molar ratio. Next, this mixture was slowly dropped into a 0.2 M ammonium oxalate (Wako Pure Chemical) aqueous solution. After the stirring for 0.5 h at room temperature, the precipitant was filtered and washed by distilled water. The obtained sample was dried in air at 90 °C overnight. Then, the specimen was crushed and ground in a mortar and was finally calcined in air at 1000 °C for 12 h. The prepared support oxides are denoted as BZYx and BCYx, where x denotes the Y substitute molar ratio for Zr and Ce in BaZr_{1-x}Y_xO_{3-δ} and BaCe_{1-x}Y_xO_{3-δ}, respectively. In addition, some perovskite-type oxides were re-calcined in air at 1200 °C, 1400 °C, and 1600 °C for 10 h (denoted as BZY10-T, T refers to the calcination temperature).

Preparation of supported Ru catalysts

All perovskite-type oxide supported Ru catalysts were prepared by the conventional impregnation method [30]. The obtained perovskite-type oxides were impregnated with a tetrahydrofuran (THF, Kanto Chemical) solution containing Ru₃(CO)₁₂ (Kanto Chemical). The suspension was stirred under ambient conditions for 4 h, and the THF solvent was then removed using a rotary evaporator at 80 °C. The obtained powder was then dried in air at 110 °C overnight. Next, the sample was pressed into a pellet, crushed, and sieved to obtain the appropriate pellet size in 150–250 μm range. The pretreatments in which the Ru₃(CO)₁₂ cluster was decomposed in N₂ flow (60 mL min^{−1}) at 500 °C for 3 h and reduced in H₂ flow (60 mL min^{−1}) at 400 °C for 2 h in the reactor prior to the NH₃ synthesis. For a comparison, BaZr_{0.9}Y_{0.1}O_{3-δ}-supported Ru catalysts were also prepared using RuCl₃ and Ru(NO₃)₃ (in HNO₃ solution) as Ru source. For all catalysts, the metal loading was adjusted to 2.0 wt% unless noted otherwise.

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