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Influence of basic dopants on the activity of Ru/Pr₆O₁₁ for hydrogen production by ammonia decomposition

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ABSTRACT

Basic oxides such as alkali metal oxides, alkaline earth metal oxides, and rare earth oxides were added to Ru/Pr₆O₁₁, and the activity of the catalysts with respect to hydrogen production by ammonia decomposition was investigated. Ru/Pr₆O₁₁ doped with alkali metal oxides, except for Li₂O, achieved higher NH₃ conversions than bare Ru/Pr₆O₁₁. Cs₂O, the most basic of the alkali metal oxides, was the most effective dopant. In contrast, other dopants with lower basicity than the alkali metal oxides achieved lower NH₃ conversions than bare Ru/Pr₆O₁₁. Changing the Cs/Ru molar ratio revealed that the best Cs/Ru ratio was 0.5–2; the reaction was effectively promoted without negative effects from coverage of the Ru surface by the Cs₂O. Varying the order of loading the Ru and Cs₂O onto Pr₆O₁₁ revealed that loading Ru onto Cs₂O/Pr₆O₁₁ was an effective way to enhance NH₃ conversion, and coverage of the Ru surface was reduced.

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Introduction

As fossil fuel reserves continue to decrease, the prospects are improving for use of energy from renewable sources, such as the sun and wind [1]. However, the places where renewable energy can be produced are limited, and energy must therefore be stored and transported, for example in the form of hydrogen compounds by a so-called hydrogen carrier [2,3].

Ammonia is regarded as one of the likely hydrogen carriers. Increasing attention is being given to the fact that ammonia may be catalytically decomposed to produce hydrogen, which is then supplied to a proton-exchange membrane fuel cell (PEFC) or to a hydrogen engine. This increasing attention reflects the facts that [4–9] (i) the H₂-storage capacity (17.6 wt%) and energy density (3000 Wh kg⁻¹) are higher for ammonia than for methanol and other fuels; (ii) ammonia is a liquid at 20 °C and a pressure of about 0.8 MPa, and hence it is easily

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stored; (iii) CO₂, which causes global warming, and CO, which degrades cell electrodes, are not produced when ammonia is converted to hydrogen and nitrogen; and (iv) the concentration of unconverted ammonia can be reduced to less than 200 ppb by using suitable absorbers [10]. Furthermore, ammonia is thermodynamically decomposed at 400 °C (equilibrium conversion: 99%), a temperature at which hydrocarbon steam reforming results in low hydrocarbon conversion and hydrogen yields.

Supported Ru catalysts doped with basic oxides (i.e., alkali metal oxides) are widely known to be active catalysts for ammonia decomposition [5,11], and GC (graphitic carbon) [11] and CNTs (carbon nanotubes) [12,13] have been reported to be effective carriers of Ru. However, in the cases of on-site generation of hydrogen for PEFCs or use in hydrogen engines, the system is shut down and restarted daily, and catalytic supports that are flammable may not be suitable [14]. In contrast, we have developed highly active Ru catalysts supported on Pr₆O₁₁; these catalysts are highly basic, and their NH₃ decomposition activity is greatly enhanced with the addition of Cs₂O (Cs/Ru = 1 in molar ratio) [14]. A Cs₂O/Ru/Pr₆O₁₁ catalyst can achieve equilibrium NH₃ conversion of 99% at 400 °C, the temperature of which was easily obtained from industrial waste heat.

As mentioned above, compounds with basic characteristics promote ammonia decomposition over Ru/Pr₆O₁₁ [14]. However, only alkaline metal oxide was used as additives and influence of its loading was not studied. In this study, we therefore examined the effects of basic additives such as alkali metal oxides, alkaline earth metal oxides, and rare earth oxides. The results indicated that the most effective additive was Cs₂O, and we therefore clarified the effect of Cs₂O by investigating the influence of the Cs₂O loading and the procedure for preparing the Ru/Pr₆O₁₁ promoted with Cs₂O.

Materials and methods

Preparation of catalysts

Supported Ru catalysts were prepared according to the procedure described in an earlier report [14]. Pr₆O₁₁ supports were precipitated at room temperature from a suspension that was prepared by adding a solution of Pr(NO₃)₃·6H₂O (Kanto Chemical) to a 25 wt% NH₃ solution. The precipitates were kept in suspension overnight with stirring; they were then filtered, washed with distilled water, dried overnight at 70 °C, and calcined at 700 °C in static air. The calcined Pr₆O₁₁ was impregnated with Ru₃(CO)₁₂ (Tanaka Kikinzoku Kogyo) in a solution of tetrahydrofuran. The Ru loading was set to 5 wt%. The solution was stirred for 12 h, evacuated in a rotary evaporator, and dried overnight at 70 °C. The precipitate was heated to 350 °C in He for 5 h to remove the CO ligand from the Ru₃(CO)₁₂.

Ru/Pr₆O₁₁ catalysts doped with various oxides were prepared by wet impregnation [14] using 5 wt% Ru/Pr₆O₁₁ and aqueous solutions of (i) CsNO₃ and Pr(NO₃)₃ purchased from Kanto Chemical Co. Ltd.; (ii) RbNO₃, KNO₃, NaNO₃, LiNO₃, Ba(NO₃)₂, Sr(NO₃)₂, Ca(NO₃)₂, Mg(NO₃)₂, La(NO₃)₃, and Yb(NO₃)₃ purchased from Wako Pure Chemical Industries, Ltd.; (iii)

Gd(NO₃)₃ purchased from Mitsuwa Chemistry Co., Ltd.; and (iv) Sm(NO₃)₃ purchased from Kishida Chemical Co., Ltd. The molar ratio of these elements to Ru was normally set to 1. However, in the case of CsNO₃, the molar ratio of Cs to Ru was varied from 0.25 to 5. These samples were dried at 70 °C overnight and treated in H₂ at 500 °C for 1 h to remove NO₃⁻.

For the preparation of Ru/Pr₆O₁₁ promoted with Cs₂O, another preparation method was also employed. First, Cs₂O/Pr₆O₁₁ was prepared by wet impregnation using calcined Pr₆O₁₁ and an aqueous solution of CsNO₃. This sample was dried at 70 °C overnight and treated in H₂ at 500 °C for 1 h to remove NO₃⁻. The Cs₂O/Pr₆O₁₁ was impregnated with Ru₃(CO)₁₂ in a solution of tetrahydrofuran. The solution was stirred, evacuated, and dried overnight at 70 °C. The precipitate was treated in He at 350 °C for 5 h. The molar ratio of Cs to Ru was fixed at 0.5.

Characterization of catalysts

The specific surface areas of the catalysts were measured with a BELSORP-mini (BEL Japan, Japan) at -196 °C with N₂, and the results are listed in Table S1.

The amount of CO chemisorbed at 0 °C (a measure of the number of Ru atoms on the surface) was determined by pulse methods. The catalysts were treated in situ in H₂ at 500 °C for 1 h and cooled to 0 °C in an ice bath under He. At 0 °C, CO was pulsed over the catalysts. The amount of CO taken up was measured with a thermal conductivity detector.

Tests of catalyst activity

The procedure for testing activity, which has been described in our earlier report [14], was as follows. Powders of the catalyst were pressed into pellets at 52 MPa for 5 min. They were then crushed and sieved to obtain grains with diameters of 250–500 microns, and an aliquot of 200 mg of catalyst was loaded into a tubular quartz reactor (i.d. = 7 mm). The catalysts were reduced in pure H₂ at 500 °C for 1 h at a rate of 10 °C min⁻¹ and then purged with pure Ar and cooled to 200 °C. At 200 °C, pure NH₃ (10 mL min⁻¹, space velocity (SV) = 3000 mL h⁻¹ g⁻¹) was passed over the catalyst. The temperature of the catalyst was kept constant for 0.5 h to measure its activity. The catalyst was then heated by 50 °C. This procedure was repeated until the catalyst had been heated to 500 °C. The reaction products were analyzed by using a gas chromatograph with a thermal conductivity detector (GC-8A, Shimadzu) equipped with an active carbon column.

Results and discussion

Influence of the kinds of dopants on the decomposition of ammonia over Ru/Pr₆O₁₁

The Ru/Pr₆O₁₁ was treated with various kinds of basic oxide dopants. The molar ratio of dopant to Ru was 1, and the temperature dependences of the NH₃ conversions of the catalysts were compared. First, alkali metal oxides were doped into Ru/Pr₆O₁₁, and NH₃ decomposition activities were

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