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.

Keywords:

Hydrogen carrier, Ammonia decomposition, Hydrogen production, Pr₆O₁₁, Ru catalyst, Cs₂O

1. 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 Whkg⁻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 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 NH_3 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 $\text{Ru/Pr}_6\text{O}_{11}$ [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 Cs_2O , and we therefore clarified the effect of Cs_2O by investigating the influence of the Cs_2O loading and the procedure for preparing the $\text{Ru/Pr}_6\text{O}_{11}$ promoted with Cs_2O .

2. Materials and Methods

2.1 Preparation of catalysts

Supported Ru catalysts were prepared according to the procedure described in an earlier report [14]. Pr_6O_{11} supports were precipitated at room temperature from a suspension that was prepared by adding a solution of $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Kanto Chemical) to a 25 wt% NH_3 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 Pr_6O_{11} was impregnated with $\text{Ru}_3(\text{CO})_{12}$ (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 $\text{Ru}_3(\text{CO})_{12}$.

$\text{Ru/Pr}_6\text{O}_{11}$ catalysts doped with various oxides were prepared by wet impregnation [14] using 5 wt% $\text{Ru/Pr}_6\text{O}_{11}$ and aqueous solutions of (i) CsNO_3 and $\text{Pr}(\text{NO}_3)_3$ purchased from Kanto Chemical Co. Ltd.; (ii) RbNO_3 , KNO_3 , NaNO_3 , LiNO_3 , $\text{Ba}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$,

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.

2.2 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.

2.3 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.

3. Results and Discussion

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

Fig. 1 – NH₃ conversion vs. temperature for NH₃ decomposition over 5 wt% Ru/Pr₆O₁₁ catalysts doped with (A) alkali metal oxides, (B) alkaline earth metal oxides, and (C) rare earth oxides.

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 measured. The plots, reproduced from our earlier report [14], are shown in Fig. 1A. Ru/Pr₆O₁₁ doped with alkali metal oxides, except for Li₂O, achieved higher conversions of NH₃ than did bare Ru/Pr₆O₁₁. The difference of NH₃ conversion was pronounced at 350 °C and decreased in the order Cs₂O, Rb₂O, K₂O, and Na₂O as added catalysts. This order was in agreement with the order of the basic nature of the alkali metal oxides; i.e., dopants with stronger basicity promoted ammonia decomposition more effectively.

The effect of doping with alkaline earth metal oxides on the NH₃ conversion of Ru/Pr₆O₁₁ is shown in Fig. 1B. All the catalysts that included alkaline earth metal oxides achieved lower NH₃ conversions than bare Ru/Pr₆O₁₁. Note that with an increase of the basicity of the alkaline earth metal oxides, NH₃ conversion decreased. As was the case for Ru/Pr₆O₁₁ doped with alkaline earth metal oxides, NH₃ conversions of Ru/Pr₆O₁₁ doped with rare earth metal oxides were lower than those achieved with bare Ru/Pr₆O₁₁ (Fig. 1C).

Fig. 2 – NH₃ conversion at 350 ° C for 5 wt% Ru/Pr₆O₁₁ doped with various oxides (dopant/Ru ratio = 1) vs. partial charge of doped oxide.

To evaluate basicity of the catalyst, we carried out temperature-programmed desorption of ammonia. However, the measurements were not succeeded. This is due to unstable nature of the alkali metal oxide above 350 °C for K₂O, 400 °C for Rb₂O, and 400 °C for Cs₂O [15]. Figure 2 shows NH₃ conversions at 350 °C as a function of the partial charge of the dopants. The partial charge of the oxides is one indicator of the basicity of the oxides [16], and smaller values mean that the oxide is more strongly basic. The values have been successfully used to evaluate basicity of the supported Ru catalysts for ammonia synthesis [17, 18]. Note that partial charge of Pr₆O₁₁ is –0.48 to –0.55. When the partial charge of the oxide was less than –0.81, NH₃ conversions of the corresponding catalysts were higher than that of bare Ru/Pr₆O₁₁, and the conversions increased as the partial charge of the oxides decreased. It was therefore apparent that Ru/Pr₆O₁₁ doped with Cs₂O, which is the strongest base, has the highest activity for NH₃ decomposition among the catalysts tested. On the other hand, when the partial charge of the oxide was greater than or equal to –0.8, the NH₃ conversions of the corresponding catalysts were lower than that of bare Ru/Pr₆O₁₁. Here the catalysts were prepared by wet impregnation of the each nitrate on Ru/Pr₆O₁₁. Therefore, we assume that part of the Ru surface was covered by the additives, number of the Ru active site was decreased, and thus NH₃ conversion was decreased.

3.2 Influence of Cs/Ru ratio on the decomposition of ammonia over Cs₂O/Ru/Pr₆O₁₁

Fig. 3 – NH₃ conversion vs. temperature for NH₃ decomposition over Cs₂O/5 wt % Ru/Pr₆O₁₁ with different Cs/Ru molar ratios. Lower panel shows NH₃ conversion at 350 °C as a function of the Cs/Ru molar ratio.

Different amounts of Cs₂O were loaded onto Ru/Pr₆O₁₁, and results of the activity tests are shown in Fig. 3. NH₃ conversion over Ru/Pr₆O₁₁ at 350 °C increased from 45% to 76% with the addition of Cs₂O at a Cs/Ru molar ratio of 0.5. Further addition of Cs₂O up to a Cs/Ru ratio of 2 had little effect on NH₃ conversion. Nevertheless, Ru/Pr₆O₁₁ doped at a Cs/Ru ratio of 5 achieved a lower NH₃ conversion of 58%. To understand the cause of the change of NH₃ conversion as a function of Cs/Ru, we performed CO chemisorption measurements. The CO/Ru values are shown in Table 1. With an increase of the Cs/Ru ratio, the CO/Ru ratio decreased, but the turnover frequency (TOF) increased. Here Cs₂O/Ru/Pr₆O₁₁ was prepared by

wet impregnation of the CsNO_3 on $\text{Ru/Pr}_6\text{O}_{11}$. Therefore this result indicates that part of the Ru surface was covered by the added Cs_2O , and the covered area of the Ru surface increased with an increase of the Cs/Ru ratio. In contrast, the TOF increased with an increase of the Cs/Ru ratio, probably because of an increase in electron donation from Cs_2O to Ru. It is well known that basic components work as electron donor to Ru, which was proved by decrease in N-N stretching frequencies of adsorbed dinitrogen on Ru with the addition of Cs_2O to $\text{Ru/Al}_2\text{O}_3$ and Ru/MgO [17, 18]. Yin SF *et al.* reported the electron donation decreases the apparent activation energy of the NH_3 decomposition reaction; this enhances the activity of the Ru catalyst [5]. Such enhancement of the TOF for $\text{Ru/Pr}_6\text{O}_{11}$ doped at Cs/Ru ratios of 0.5–2 maximized NH_3 conversion compared to that of bare $\text{Ru/Pr}_6\text{O}_{11}$, whereas too much coverage of the Ru surface by Cs_2O (Cs/Ru = 5) resulted in a decrease of NH_3 conversion.

Table 1 – Results of CO chemisorption and activity tests for supported $\text{Ru/Pr}_6\text{O}_{11}$ and $\text{Ru/Pr}_6\text{O}_{11}$ doped with Cs_2O

Catalyst	Cs/Ru mole ratio	CO/Ru	TOF (s^{-1})	NH_3 conversion at 350 °C (°C)
$\text{Cs}_2\text{O/Ru/Pr}_6\text{O}_{11}$	0	0.33	0.10	45
	0.5	0.21	0.27	76
	5	0.04	1.01	58
$\text{Ru/Cs}_2\text{O/Pr}_6\text{O}_{11}$	0.5	0.24	0.30	93

3.3 Influence of the procedure for loading Cs_2O and Ru onto Pr_6O_{11}

Fig. 4 – NH₃ conversion vs. temperature for NH₃ decomposition over Cs₂O/Ru/Pr₆O₁₁ and Ru/Cs₂O/Pr₆O₁₁ (Cs/Ru molar ratio = 0.5).

At this point in the study, Cs₂O had been loaded onto Ru/Pr₆O₁₁. In this case, NH₃ conversion increased because of the effect of electron donation by Cs₂O, but part of the Ru surface was covered with Cs₂O. To reduce this coverage of the Ru surface by Cs₂O, Cs₂O was first loaded onto Pr₆O₁₁, and Ru was subsequently loaded onto Cs₂O/Pr₆O₁₁. It is apparent in Fig. 4 that newly prepared Ru/Cs₂O/Pr₆O₁₁ exhibited much higher NH₃ conversion than did Cs₂O/Ru/Pr₆O₁₁, and the NH₃ conversion of the catalyst was 93% at 350 °C. The CO/Ru ratio and TOF at 350 °C of these catalysts are shown in Table 1. It is apparent that the CO/Ru ratio was improved, and the TOF increased slightly as a result of the change in the preparation procedure, the result being a higher NH₃ conversion over Ru/Cs₂O/Pr₆O₁₁.

4. Conclusions

We prepared Ru/Pr₆O₁₁ catalysts doped with various kinds of basic oxides and investigated the catalytic activity of the catalysts with respect to ammonia decomposition for renewable

hydrogen production. Ru/Pr₆O₁₁ doped with Cs₂O, which is the strongest base, showed the highest NH₃ conversion among the catalysts. Changing the ratio of Cs to Ru revealed that doping with Cs₂O enhanced the TOF, but covering only a part of the Ru surface and choice of an appropriate Cs/Ru ratio (0.5–2) increased NH₃ conversion. Such enhancement of TOF was ascribed to the effect of electron donation to Ru. Furthermore, the preparation procedure was changed from sequential loading of Cs₂O onto Ru/Pr₆O₁₁ to sequential loading of Ru onto Cs₂O/Pr₆O₁₁. This change enhanced NH₃ conversion at 350 °C over Ru/Cs₂O/Pr₆O₁₁ from 76% to 93%. This enhancement was ascribed to efficient reduction of the area of the Ru surface covered by Cs₂O.

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Captions

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