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Highly Active $Cs_2O/Ru/Pr_6O_{11}$ as a Catalyst for Ammonia Decomposition

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The use of a new catalyst, namely, $Cs_2O/5$ wt % Ru/Pr_6O_{11} (mole ratio of Cs to Ru: 1), in which Ru is supported on strong basic Pr_6O_{11} and the strong basic promoter Cs_2O is added, resulted in almost complete NH_3 consumption at 673 K and an NH_3 conversion of 14% even at temperatures as low as 523 K.

Recently, NH_3 has been regarded as a potential H_2-storage material that can be used in a PEFC (proton-exchange membrane fuel cell), owing to the following reasons:[1] (i) the H_2-storage capacity (17.7%) and energy density ($3000\,W\,h\,kg^{-1}$) of NH_3 are higher than those of methanol and other fuels, (ii) NH_3 is in the liquid form at room temperature and at a pressure of around 8 atm, and hence, it is easy to store, (iii) CO_2, which causes global warming, and CO, which degrades cell electrodes when it is converted to H_2 and N_2, are not produced, and (iv) the concentration of unconverted NH_3 can be reduced to less than 200 ppb by using suitable absorbers.[2] In addition, NH_3 is catalytically decomposed ($NH_3 \rightarrow 0.5N_2 + 1.5H_2$) at 673 K (equilibrium conversion: 99%); at this temperature, common industrial waste heat is available.[3] Supported Ru catalysts doped with alkaline metal oxide promoters are widely known to be active catalysts,[1] and GC (graphitic carbon)[4] and CNTs (carbon nanotubes) have been reported to be the most effective supports. However, in the case of on-site generation of H_2 for use in PEFC applications, in which the system is shutdown and restarted daily, a catalytic support made of flammable carbon may not be suitable. Therefore, in this study, we have developed new Ru catalysts that are supported by rare-earth oxides and promoted with alkaline metal oxides. The objective of this study is to realize an energy-saving process based on the use of industrial waste heat by ensuring that NH_3 is almost completely consumed at 673 K.

Supported Ru catalysts were prepared according to a procedure described elsewhere.[5] Supports such as Pr_6O_{11} and La_2O_3, which were prepared in-house,[6] MgO (the reference catalyst of the Catalysis Society of Japan, JRC-MGO-500A), Al_2O_3 (JRC-ALO-3), and SiO_2–Al_2O_3 (Catalysts & Chemicals Industries Co., Ltd.) calcined at 973 K were impregnated with $Ru_3(CO)_{12}$ (Wako Pure Chemical Industries) in THF (tetrahydrofuran) solution. The Ru loading was set to 1 or 5 wt %. The $Ru_3(CO)_{12}$–THF–support system was stirred for 12 h, evacuated in a rotary evaporator, and dried at 343 K overnight. It was heated to 623 K under He for 5 h in order to remove the CO ligand from the Ru precursor.

Alkaline metal oxides doped with 5 wt % Ru/Pr_6O_{11} were prepared by wet impregnation using 5 wt % Ru/Pr_6O_{11}, a decarbonylated aqueous solution of $CsNO_3$ purchased from Kanto Chemical, and $RbNO_3$, KNO_3, $NaNO_3$, and $LiNO_3$, which were purchased from Wako Pure Chemical Industries. The mole ratio of the alkaline metal to Ru was set to 1. The samples were dried at 343 K overnight and then heated at 773 K in flowing H_2 to remove NO_3^-. The Brunauer–Emmett–Teller surface areas of the catalysts are listed in Table S1.[6]

The obtained catalyst powders were pressed into pellets at 52 MPa for 5 min. The pellets were crushed and sieved to obtain grains with diameters between 250 and 500 µm, and 200 mg of catalyst was loaded into a tubular quartz reactor (i.d. = 7 mm). The catalysts were reduced in an atmosphere of pure H_2 at 773 K for 1 h at a rate of $10\,K\,min^{-1}$ and then purged with pure Ar and cooled to 473 K. At 473 K, pure NH_3 ($10\,mL\,min^{-1}$, $SV = 3000\,mL\,h^{-1}\,g^{-1}$) was passed over the catalyst. After the temperature of the catalyst was kept constant for 0.5 h in order to measure its activity, the catalyst was heated to 523 K. This procedure was repeated until the catalyst was heated up to 773 K. The reaction products were analyzed by using a gas chromatograph with a thermal conductivity detector that was equipped with an active carbon column.

To measure the temperature-programmed desorption (TPD) profiles of CO_2, 200 mg of the catalysts was reduced at 773 K for 1 h and exposed to CO_2/He (1%/99%) at 323 K for 1 h. Pure He was fed to the fresh catalysts at ambient temperature, and then the oven temperature was increased at a rate of $10\,K\,min^{-1}$. The CO_2-ion intensity was continuously monitored using a quadrupole mass spectrometer.

Figure 1 shows the temperature-dependence of NH_3 conversion for supported 1 and 5 wt % Ru catalysts. The activities of Ru/La_2O_3 and Ru/Pr_6O_{11} were the highest among supported 1 wt % Ru catalysts, and the activities of the other catalysts decreased in the following order: MgO, Al_2O_3, SiO_2–Al_2O_3.

To understand why Ru/Pr_6O_{11} and Ru/La_2O_3 exhibited high activity, the catalysts were characterized by CO_2-TPD (Figure 2). The intensity of the CO_2 desorption peak was much greater for Ru/La_2O_3 and Ru/Pr_6O_{11} than for popular basic MgO supports and the other oxide supports, indicating that basic sites were highly abundant on Ru/La_2O_3 and Ru/Pr_6O_{11}. Note that the amount of CO_2 desorbed at high temperatures above 673 K was

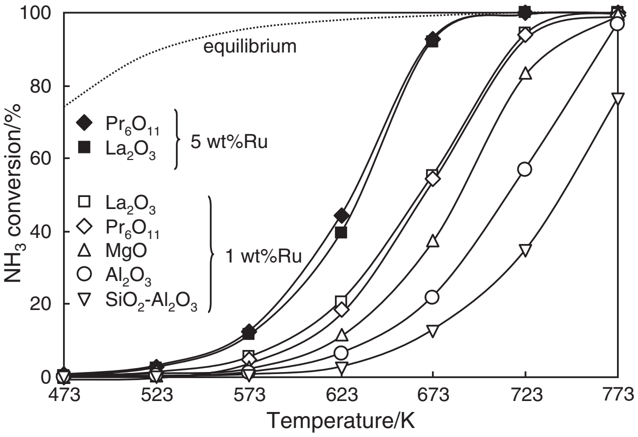

Figure 1. NH_3 conversion vs. temperature for NH_3 decomposition for 1 and 5 wt % Ru catalysts.

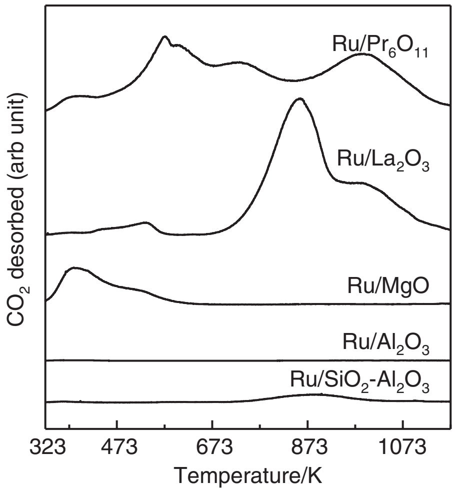

Figure 2. Temperature-programmed desorption profiles of CO_2 over 1 wt % Ru catalysts.

greater in the case of Ru/La_2O_3 than in the case of Ru/Pr_6O_{11}; this CO_2 desorption can be attributed to the presence of basic sites. Despite the above-mentioned trend, the total amount of CO_2 desorption, which was proportional to the number of basic sites, was greater in the case of Ru/Pr_6O_{11} (588 $\mu mol\,g^{-1}$) than in the case of Ru/La_2O_3 (498 $\mu mol\,g^{-1}$). Such a trend in the basicity of the catalyst is consistent with the trend in activity; in particular, the high activity of Ru/Pr_6O_{11} and Ru/La_2O_3 was ascribed to the strong basicity of the catalytic supports. Ru dispersion may be considered to be a crucial factor that determines catalytic activity. However, the value of CO/Ru estimated by CO chemisorption at 273 K ranged from 0.50 to 0.67; thus, the values were similar for all the catalysts. Hence, we believe that the basicity of the support is the most critical factor that determined catalytic activity. It is well known that the basic component having low electronegativity enhances the desorption of nitrogen diatoms and decreases the apparent activation energy of the decomposition reaction; this enhances the activity of Ru catalysts.[1]

In order to increase the NH_3 conversion, we increased the Ru loading of Ru/Pr_6O_{11} and Ru/La_2O_3 up to 5 wt %. As shown in Figure 1, the activities per catalyst weight of both catalysts increased, and the NH_3 conversion at 673 K increased to more than 91%. Note that a further increase in the Ru loading, i.e., an increase up to 10 wt %, did not result in any further increase in NH_3 conversion, probably because of the sintering of the Ru particles.

As discussed above, the increase in basicity was proven to result in an increase in the catalytic activity for NH_3 decomposition. Hence, basic promoters, i.e., alkaline metal oxides (mole ratio of alkaline metal to Ru: 1), were added to 5 wt % Ru/Pr_6O_{11} and Ru/La_2O_3; then, the catalytic activities were measured. The results are shown in Figure 3. Ru/Pr_6O_{11} promoted with Cs_2O, Rb_2O, K_2O, and Na_2O resulted in higher NH_3 conversion at 623 K than did unpromoted Ru/Pr_6O_{11}; the activity decreased in the following order: Cs_2O, Rb_2O, K_2O, Na_2O. Hence, the order of the activities of the catalysts is in agreement with the order of the basicities of the promoter. Note that the drastic enhancement of the activity by the addition of Cs_2O was also observed in 5 wt % Ru/La_2O_3, and the activity of Cs_2O/5 wt % Ru/La_2O_3 was comparable to that of Cs_2O/5 wt % Ru/Pr_6O_{11}. Surprisingly, the NH_3 conversion in the presence of Cs_2O/5 wt % Ru/Pr_6O_{11} was 99% at 673 K, 73% at 623 K, and 14% at 523 K. Further, the activity of Cs_2O/5 wt % Ru/Pr_6O_{11} was stable at 623 K for 120 h (Figure S1).[6] As alkaline metal oxides were prepared by wet impregnation of the alkaline metal nitrate on 5 wt % Ru/Pr_6O_{11}, a part of the Ru surface would be covered by the promoters. In fact, the value of CO/Ru for Cs_2O/5 wt % Ru/Pr_6O_{11} (0.10) was lower than that for 5 wt % Ru/Pr_6O_{11} (0.33). In the case of stronger basic promoters such as Cs_2O, Rb_2O, and K_2O, it is assumed that the effect of the promoters dominates the decrease in the number of active Ru surface sites. On the other hand, in the case of weaker basic promoters such as Li_2O, the effect of the promoter may be negated by the decrease in the number of active sites.

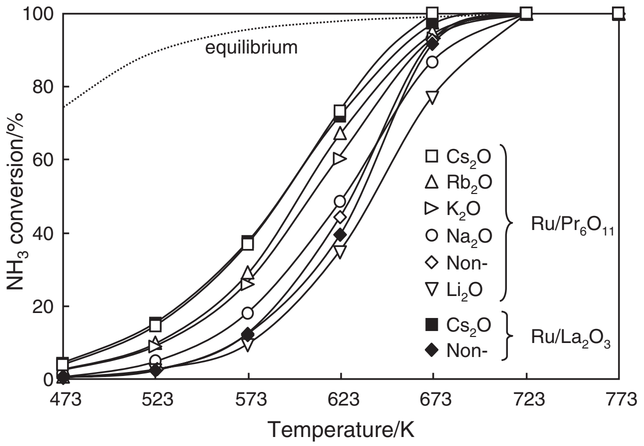

Figure 3. NH_3 conversion vs. temperature for NH_3 decomposition for alkaline-metal-oxide-doped 5 wt % Ru/Pr_6O_{11} and Ru/La_2O_3 catalysts.

In summary, we demonstrated that the use of Cs_2O/5 wt % Ru/Pr_6O_{11} resulted not only in almost complete NH_3 consumption at 673 K, where industrial waste heat is available but also helped to achieve a surprisingly high NH_3 conversion of 14%, even at 523 K. The high activity of Cs_2O/5 wt % Ru/Pr_6O_{11} at low temperatures is advantageous for on-site generation of H_2 for use in PEFC applications. Therefore, the present study is closely related to the development of a desired sustainable society. In particular, H_2 is produced by solar energy in an area that receives plenty of sunlight. Then, H_2 is transported in the form of NH_3 to areas in which electricity is consumed; here, electricity is generated using PEFCs equipped with an NH_3 cracker.

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