Self-heating of Supported Ru Catalysts as a Trigger for Hydrogen Production by Ammonia Oxidative Decomposition from Room Temperature

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Abstract: We demonstrate hydrogen production by exposing NH_3 and O_2 at room temperature to acidic $RuO_2/\gamma\text{-}Al_2O_3$ or reduced $RuO_2/Ce_{0.5}Zr_{0.5}O_2$ catalyst. In these process, the catalysts are heated from room temperature to catalytic auto-ignition temperature of NH_3 oxidative decomposition and thus the reaction begin, because adsorption of NH_3 onto the catalyst and oxidation of $Ru/Ce_{0.5}Zr_{0.5}O_{2-x}$ are exothermic.

Keywords: hydrogen carrier, ammonia, hydrogen production.

1. Introduction

Hydrogen produced from renewable energy has received a lot of attentions as a clean energy source and development of a hydrogen storage and transportation system using hydrogen carrier has been greatly demanded. Among different kinds of hydrogen carrier, NH_3 is regarded as one of the promising candidates, due to high hydrogen capacity, high energy density, low production cost, and ease of liquification at room temperature. Furthermore, a carbon-free hydrogen storage and transportation system could be realized by using NH_3 as hydrogen carrier. In this system, hydrogen produced from NH_3 is used in engines, turbines and fuel cells. However, use of NH_3 as a hydrogen carrier, peculiarly for transportable devices and household, has been limited owing to lack of an efficient process for producing hydrogen from NH_3.

To solve this problem, it is necessary to develop a process that can be initiated rapidly, produces hydrogen from NH_3 at a high rate, and does not need external heat supply. NH_3 oxidative decomposition (Eq. 1) is a combination of NH_3 combustion (Eq. 2) and NH_3 decomposition (Eq. 3) and thus the heat generated by NH_3 combustion is utilized for NH_3 decomposition, which results in high hydrogen formation rate. Furthermore, after ignition of NH_3 oxidative decomposition at catalytic auto-ignition temperature, the catalyst is automatically heated to reaction temperature due to exothermic nature of the reaction and then the reaction proceeds spontaneously. Therefore, challenge is how to heat the catalyst from room temperature to catalytic auto-ignition temperature of NH_3 oxidative decomposition. In this research, we have discovered that the heat generated by self-heating of the catalyst heats the catalyst rapidly. Our results demonstrated that two kinds of heats are available for self-heating, i.e. heat produced by NH_3 adsorption on the catalyst[1] and oxidation of the reduced catalyst. With this process, hydrogen is produced by only supplying NH_3 and oxygen at room temperature to pre-treated oxide-supported Ru catalysts.

$NH_3\ (g) + 0.25O_2\ (g) \rightarrow H_2\ (g) + 0.5N_2\ (g) + 0.5H_2O\ (g)\quad \Delta H = -75\ \text{kJ mol}^{-1}$ (Eq. 1)
$NH_3\ (g) + 0.75O_2\ (g) \rightarrow 0.5N_2\ (g) + 1.5H_2O\ (g)\quad \Delta H = -317\ \text{kJ mol}^{-1}$ (Eq. 2)
$NH_3\ (g) + 0.25O_2\ (g) \rightarrow H_2\ (g) + 0.5N_2\ (g) + 0.5H_2O\ (g)\quad \Delta H = -75\ \text{kJ mol}^{-1}$ (Eq. 3)

We also succeeded in construction of cyclic process where NH_3 oxidative decomposition is triggered repeatedly without pre-treatment from 2nd cyvle.

2. Experimental

$RuO_2/\gamma\text{-}Al_2O_3$ and $RuO_2/Ce_{0.5}Zr_{0.5}O_2$ were prepared by wet impregnation method.

After the pre-treatment shown in SS3, triggering tests were carried out under quasi-adiabatic conditions. An $NH_3/O_2/He$ ($NH_3/O_2/He$ ratio, 150:37.5:20.8 ml min^{-1};GHSV, 62.5 $\text{Lh}^{-1}\text{g}^{-1}$) gas mixture was then fed at room temperature to the catalyst. We set the gas composition assuming the Eq. 1. The composition of the exit gas was monitored with a quadrupole mass spectrometer. After 30 min, the composition of the dried exit gas was analyzed with a thermal conductivity detector.

3. Results and discussion

The $RuO_2/\gamma\text{-}Al_2O_3$ catalyst was treated in He at 300°C to remove adsorbate and create NH_3 adsorption site and then the catalyst was cooled to room temperature. After supplying the $NH_3/O_2/He$ mixture, H_2 production rate increased to 33 $Lh^{-1}g^{-1}$ within 30 s and catalyst bed temperature rose to 522 °C at the same time[1]. After the reaction for 30 min, O_2 was consumed completely: NH_3 conversion was 93% and hydrogen yield was near the maximum value, 67 % (Fig. 1A). These results demonstrate that NH_3 oxidative decomposition is triggered in a very short time without any external heat input and proceeds spontaneously. After 35 min, the reaction was terminated by substitution of He for the $NH_3/O_2/He$ mixture, and the catalyst was cooled to room temperature. O_2 was then briefly supplied over the catalyst to oxidize the Ru metal formed during the reaction, and an $NH_3/O_2/He$ mixture was fed to the catalyst. This purge-feed sequence was repeated three more times. For all cycles, the oxidative decomposition of ammonia was repeatedly triggered at room temperature, and high H_2 yields as well as high NH_3 and O_2 conversions were maintained. After the second cycle, ammonia was apparently desorbed *in situ* (regeneration of NH_3 adsorption sites) during the reaction.

On the other hand, $RuO_2/Ce_{0.5}Zr_{0.5}O_2$ catalyst was treated in H_2 at room temperature to reduce the catalyst. After supplying the $NH_3/O_2/He$ mixture, catalyst bed temperature increased drastically and H_2 production starts. After the reaction for 30 min, O_2 as well as NH_3 were consumed completely and H_2 yield reached 67 % (Fig. 1B). These results elucidate that NH_3 oxidative decomposition is triggered without any external heat input. After 35 min, the reaction was terminated by stopping the flow of O_2 and He in $NH_3/O_2/He$ mixture, and the catalyst was cooled to room temperature. Then, an $NH_3/O_2/He$ mixture was fed to the catalyst. This purge-feed sequence was repeated three more times. For all cycles, the oxidative decomposition of ammonia was repeatedly triggered at room temperature. After the second cycle, the catalyst was reduced to $Ru/Ce_{0.5}Zr_{0.5}O_{2-x}$ *in situ* during the reaction.

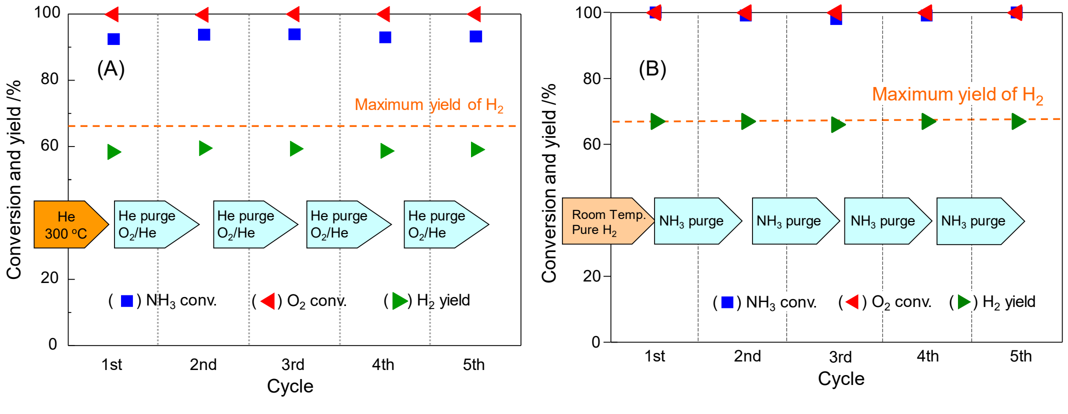

Figure 1. Cycle tests of NH_3 oxidative decomposition from room temperature over (A) $RuO_2/\gamma\text{-}Al_2O_3$ and (B) $RuO_2/Ce_{0.5}Zr_{0.5}O_2$.

4. Conclusions

Our results indicate that self-heating of the catalyst at room temperature is used as a trigger for the NH_3 oxidative decomposition. To heat the catalyst to the catalytic auto-ignition temperature, we successfully used the heat evolved by ammonia adsorption onto $RuO_2/\gamma\text{-}Al_2O_3$ or oxidation of $Ru/Ce_{0.5}Zr_{0.5}O_{2-x}$. This study demonstrates the concept of self-heating of catalysts, which is a novel strategy for the cold-start process for hydrogen production from ammonia and other reactions.

Reference

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