Effect of washing condition with ammonia aqueous solution on the properties and catalytic performances of the prepared Ru-based catalysts for ammonia decomposition

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Abstract: Ru/ZrO_2 catalysts were prepared using incipient wetness method followed by washing with ammonia aqueous solution to remove Cl derived from Ru precursor. In the preparation procedure, time, temperature, and stirring rate for washing step were changed. The characterization results indicated that almost complete removal of Cl existed on the catalyst was attained, while Ru loss *via* the formation of Ru-amine complex was suppressed when washing step was conducted at 60ºC for 1 h under stirring rate of 100 rpm. The prepared Ru catalyst showed high activity for ammonia decomposition at 673 K with GHSV of 2000 mL-NH_3 g_{cat}^{-1} h^{-1}.
Keywords: **N**H_3 decomposition, Ru-based spherical catalyst, washing condition

1. Introduction

Hydrogen is expected to be an energy carrier because it has high energy conversion and generates only water at the combustion.[1] There are still challenges in developing methods to store and transport H_2 from production sites to the end-user.[1-2] Our research group focused on NH_3 as a hydrogen energy carrier because it has high hydrogen storage capacity and is easily liquefied under the mild condition.[3-5]Although various types of catalysts for ammonia decomposition were reported in the literatures, in our previous studies[6], Ru/CeO_2, Ru/MgO, and Ru/ZrO_2 catalysts prepared by a chemical reduction method using $NaBH_4$ as a reducing agent were found to exhibit high activity for ammonia decomposition in a low temperature region. However, these catalysts with irregulated shape could not be used directly for the membrane reactor because they damaged for Pd thin film layer physically. It was thought that the spherical shape catalyst should be prepared in order to avoid this physical damage for Pd membrane. Therefore, first the method for preparing Ru-based spherical catalyst was found using ZrO_2 spherical support as an example in the present study, and then the optimal washing condition with ammonia aqueous solution was obtained by changing several factors. Finally, Ru-based spherical catalyst prepared under the optimal condition was tested for ammonia decomposition, and the relationship between the properties and the performances of prepared spherical catalysts for ammonia decomposition was discussed.

2. Experimental

Ru/ZrO_2 catalysts were prepared by the incipient wetness impregnation method using the zirconia spherical support (65.4 m^2 g^{-1}, 2.5 mm) and aqueous solution of $RuCl_3 \cdot 3H_2O$ (Kanto Chemical Co.). The obtained catalysts were subsequently washed with 0.01M ammonia aqueous solution at room temperature (RT) or 333 K for 0~2 h under stirring rate of 100 rpm. The catalyst washed at RT or 333 K is denoted as Ru/ZrO_2-1 or Ru/ZrO_2-2, respectively. Ru loading amount was adjusted to 5 wt%. The prepared catalysts were characterized by X-ray fluorescence spectrometry (XRF) and H_2 pulse chemical adsorption technique.

Catalytic tests were conducted with the atmospheric flow experimental system. The catalyst was treated in an Ar flow at 773 K for 1 h followed by reduction with 100% H_2 at 723 K for 2 h. After reduction, the catalyst was cooled to the reaction temperature and 100% NH_3 was passed through the catalyst bed. The effluent gases were analyzed by GC-TCD, and NH_3 conversion was calculated based on the analysis results.

3. Results and discussion

Table 1 shows the XRF results of Ru/ZrO_2 catalysts prepared under various washing conditions. The results suggested that washing time of 2 h is necessary to remove Cl sufficiently from the catalyst surface at RT, whereas that of 1 h is enough to remove Cl at 333 K. A higher temperature and a shorter time for washing the catalyst resulted in the suppression of Ru loss from the catalyst surface because the formation of the Ru-amine complex was prevented. It was determined that the temperature at 333 K, time of 1 h, and stirring rate of 100 rpm was the optimal washing condition to remove Cl completely and keep sufficient amount of Ru loading.

Table 1 XRF results of the Ru/ZrO_2 spherical catalysts

	Ru/ZrO_2-1			Ru/ZrO_2-2	
Washing time [h]	0	1	2	1	2
Ru [wt%]	5.25	4.42	4.51	5.18	4.81
Cl [wt%]	4.96	1.03	0.25	0.12	0.09

Figure 1 shows the catalytic performances of Ru/ZrO_2 spherical catalysts prepared under various washing conditions for NH_3 decomposition reaction at 673 K with GHSV of 2000 mL-NH_3 g_{cat}^{-1} h^{-1}. It could be seen that the NH_3 conversion was increased with an increase in washing time from 0 to 2 h for the Ru/ZrO_2-1 catalysts. As it is well known that the presence of Cl from Ru precursor retards the NH_3 decomposition reaction, the residual Cl amount on the catalyst (Table 1) might affected the NH_3 conversion. In contrast, relatively high catalytic activity (80%) was observed for Ru/ZrO_2-2 catalyst conducted with washing process for only 1 h. This is probably because the almost complete removal of Cl derived from Ru precursor and the sufficient amount of Ru loading on the catalyst (Table 1) were attained for this catalyst.

4. Conclusion

XRF results indicated that the temperature at 333 K, time of 1 h, and stirring rate of 100 rpm was optimal washing condition to remove Cl derived from Ru precursor completely and to keep the sufficient amount of Ru loading. The catalyst prepared under optimal washing condition showed a higher activity for NH_3 decomposition reaction than the catalyst washed at room temperature for 1 h. This is because of the amount of Cl remained on the catalyst and the amount of Ru loaded on the catalyst.

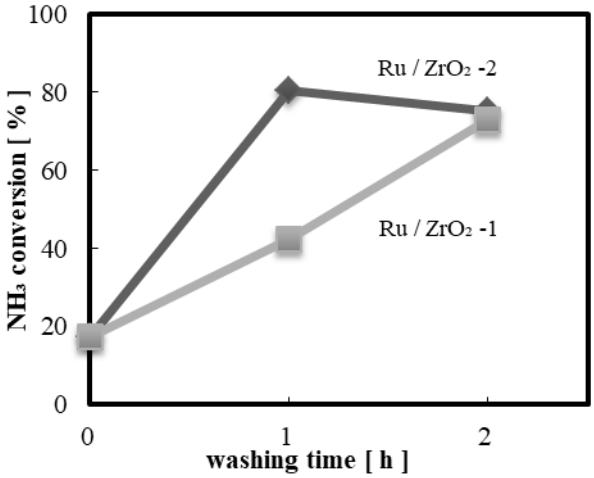

Figure 1 Catalytic activity of Ru/ZrO_2 spherical catalysts for the NH_3 decomposition reaction at 673 K with GHSV of 2000 mL-NH_3 g_{cat}^{-1} h^{-1}.

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