

Development of honeycomb-type Ru-based catalyst for NH₃ decomposition, with mass processing ability of raw materials

Masaki Kawase^a, Kimihito Suzuki^b, Ryo Watanabe^a, Choji Fukuhara^{a*}

^a Graduate school of Integrated Science and Technology, Shizuoka University, 3-5-1 Johoku Naka-ku Hamamatsu-shi, 432-8561, Japan

^b Nippon Steel & Sumitomo Metal Co., 20-1 Shintomi, Futtsu, Chiba, 293-8511, Japan

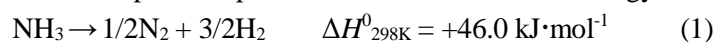
*Corresponding author: +81-53-478-1171, fukuhara.choji@shizuoka.ac.jp

Abstract: The purpose of this study is to develop a structured catalyst for NH₃ decomposition, which has advantage in a large amount of raw materials processing. The Ru/CeO₂ structured catalyst was successfully prepared on a stainless-steel honeycomb-substrate by wash-coating, showing a high performance. Furthermore, by investigating the addition effect of alkali metal (Li, Na, K, Cs), the Cs- and K-promoted honeycomb catalysts showed more high decomposition performance. It was thought that electron donation from alkali metal promoted the bonding process of nitrogen atoms and the desorption process of nitrogen molecular, thus improved the decomposition activity.

Keywords: Structured catalyst, Alkali metal addition, NH₃ decomposition

1. Introduction

The process of decomposing NH₃ (*eq.1*), included in the coke oven gas (COG) of the steelwork manufacturing, is expected to be developed from the viewpoint of environmental conservation. Conveniently, hydrogen produced by such decomposition process can be used as clean energy. The key point of developing



such process are (i) effective supplying of thermal energy, (ii) fine controlling of material gas flow and (iii) provision of a large amount of gas processing capacity to the decomposition field. The structured catalyst system having the catalyst component loaded on the honeycomb-metal-substrate brings about an effective exchanging thermal energy by conductional heat transfer and reducing the pressure drop for easy controlling a large amount of raw materials processing.

In this study, basing on our knowledge for preparing structured catalyst, a honeycomb-type catalyst for decomposing NH₃ was developed. The Ru/CeO₂ structured catalyst could be successfully prepared by wash-coating on a stainless-steel substrate, indicating a high decomposition performance. The addition effect of alkali metal (Li, Na, K, Cs) was also examined, and it was found that the Cs- and K-promoted honeycomb catalysts indicated more high decomposition performance by the electron donation from alkali metal species.

2. Experimental

The honeycomb-type structured catalysts were prepared by wash-coating method. For preparing a slurry coating solution, granular Ru/CeO₂ component was firstly prepared by impregnation method, using Ru(NO₃)₃ and CeO₂ (JRC-CEO-2). In case of adding alkali metal component on Ru/CeO₂, alkali nitrate agent (LiNO₃, NaNO₃, KNO₃, CsNO₃) were added into the solution. After evaporating at 80°C, followed by drying at 120 °C for 2 h and calcining at 500°C for 5 h, the obtained granular component was grained and suspended in 2-propanol to prepare a slurry solution. The loading amount of Ru and alkali metal were 10 wt% and 5 wt%, respectively. Using such slurry, the stainless steel honeycomb substrate (19φ x 50L, 400 cpsi) was repeatedly dipped to form the catalyst layer on the substrate surface, with the amount of 100 mg or 300 mg.

The NH₃ decomposition property of the prepared honeycomb catalyst was investigated using a conventional flow reactor. After being reduced the prepared catalyst in H₂ stream at 450°C for 1 h, NH₃ gas diluted by He (NH₃:He=1:2 mol/mol) was fed with F/W: 3,000-15,000 mL/(g·h).

3. Results and discussion

Fig. 1 shows decomposing performance of the Ru/CeO₂ structured catalyst, compared to some granular type Ru-based catalysts reported in the references^{2,3}. The prepared honeycomb catalyst exhibited the high activity at F/W 3000 mL/(g·h). Furthermore, even at higher feeding flow rate, the activity was still maintained about 70% or more. The selectivity of N₂ was 100% in all reaction condition. The honeycomb type catalyst with high decomposing performance was successively prepared on stainless-steel substrate by wash-coating in this time. The reason for such high performance might be caused by using CeO₂ support. Namely, the CeO₂ material has an advantage of an electron donation property⁴. Such electron donation from CeO₂ to Ru metal would accelerate the rate-determining step of the bonding nitrogen atoms and desorption of N₂ molecules.

The electron donation effect was also observed in case of adding alkaline metal as the promoter. Fig. 2 shows the temperature-dependence of NH₃ conversion of Ru/CeO₂ granular catalysts added the alkali metal (Li, Na, K, Cs). Basing on the Ru/CeO₂ catalyst, the addition of Cs and K components accelerated decomposing activities, however the addition of Li and Na did not accelerate. The order of ionization energy of alkali metals is Li > Na > K > Cs. This trend well coincided with the trend of the activity of the alkaline-modified Ru/CeO₂ catalysts. Judging from this result, it was thought that the electron donation promoted the rate-determining step of NH₃ decomposition, however the excess donation bring about negative effect. It may also be the same reason that the Ru/MgO catalyst shown in Fig.1 did not show high activity.

As the catalyst component with high decomposing activity could be prepared, such component was then structured on the stainless steel substrate. Fig.3 shows decomposing activity of K- and Cs-promoted Ru/CeO₂ catalysts, compared with non-promoted catalyst. It was clearly found that the high performance honeycomb type catalysts were successfully prepared. A function of allowing mass treatment of ammonia feedstock will be provided to the reactor by using such structured catalyst.

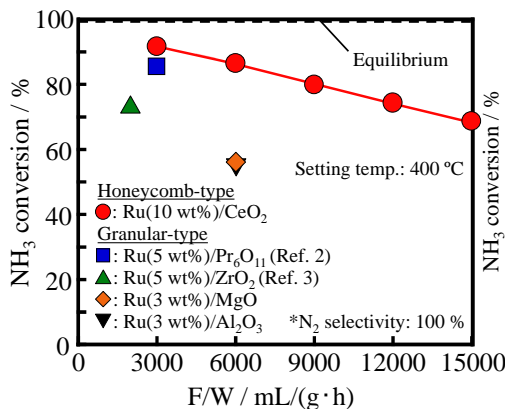


Figure 1. NH₃ decomposition performance over various Ru-supported catalyst.

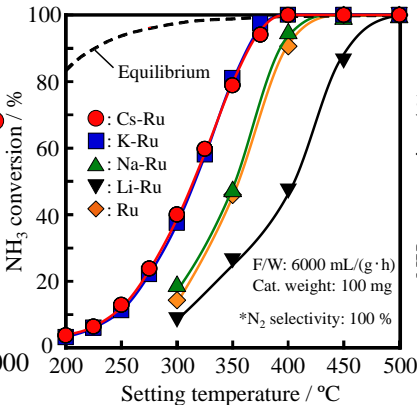


Figure 2. Catalytic property of alkaline-promoted Ru/CeO₂ catalysts.

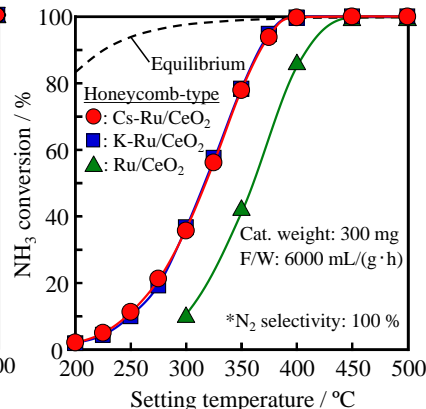


Figure 3. Catalytic performance over Cs- and K-promoted Ru/CeO₂ structured catalysts.

4. Conclusions

The prepared Ru/CeO₂ honeycomb catalyst indicated higher NH₃ decomposing performance compared to the other Ru-based catalyst reported at present. The addition of Cs and K components accelerated the performance of Ru/CeO₂ moreover by the effect of electron donation. The K- and Cs-promoted Ru/CeO₂ honeycomb catalysts were successfully prepared and will provide the function of a large amount of ammonia gas processing.

References

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