24AU015-17 Quantum leap

Activity and Characteristics of Ni-Based Hybrid Catalysts with Promoters for Ammonia Methanation

Reiji Sunamoto[a], Hiroki Miyaoka[a], Takayuki Ichikawa[a] and Hitoshi Saima[a]

[a]*Hiroshima University, Higashi-Hiroshima, Japan*

Keywords: carbon dioxide, ammonia, methane

Background:

As one of the carbon recycle techniques, we propose ammonia methanation, which directly synthesizes methane from carbon dioxide and ammonia. Ammonia methanation (1) is a combination of the Sabatier reaction (methane synthesis) (2) and ammonia decomposition (3).

$$CO_2 + 8/3\,NH_3 \rightarrow CH_4 + 4/3\,N_2 + 2H_2O \quad \Delta H = -42.5\ \text{kJ} \tag{1}$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad \Delta H = -165.0\ \text{kJ} \tag{2}$$

$$8/3\,NH_3 \rightarrow 4/3\,N_2 + 4H_2 \quad \Delta H = -122.5\ \text{kJ} \tag{3}$$

Since the heat generation from ammonia methanation is about 1/4 compared with that of the Sabatier reaction (2), conventional adiabatic reactors can be used. On the other hand, the issue of ammonia methanation is that suitable catalysts to accelerate both reactions should be designed effectively. In a previous study, ammonia methanation was conducted using a hybrid catalyst consisting of Ni/Al_2O_3 for ammonia decomposition and Ni/CeO_2 for methane synthesis, achieving about 60% of methane yield at 500°C and 0.4 MPa. The ammonia decomposition rate in this condition was about 57%.[1] In this study, effective ammonia decomposition catalysts with promoters are prepared to enhance the catalysis at low-temperature regions, and their catalytic activity is investigated.

Experimental Methods:

Ni/Al_2O_3 (Ni: 10 wt%) was used as a catalyst for ammonia decomposition. Alkaline metals, which are K, Li, Na, K, Rb, and Cs, were added to the catalyst as promoters, where the number of promoters was 2 wt% to the Ni catalyst. The hybrid catalyst was prepared by mixing Ni-Ba/ Al_2O_3 and Ni/CeO_2(Ni: 20wt%) as a catalyst for ammonia methanation. The catalysts are characterized by X-ray absorption spectroscopy. (Quantum leap)

Results and discussion:

The results of ammonia decomposition at 500 °C by using the prepared catalysts with alkaline metals are shown as follows,

$$Ni/Al_2O_3\ (75\%) > K\ (71\%) > Na\ (67\%) > Cs\ (64\%) \approx Rb\ (63\%) > Li\ (51\%)$$

Ni/Al_2O_3 without a promoter showed the highest ammonia decomposition rate. Among the alkaline metal species, K showed the highest ammonia decomposition rate. A plot of the relationship between ammonia decomposition rate and electronegativity for catalysts with alkaline metal species showed a volcanic-type trend (Fig. 1). From the results, it was expected that the peak is in the region of 0.82~0.93, and the corresponding element is only Ba. Therefore, the catalyst with Ba was prepared, and its catalysis for the ammonia decomposition reaction was evaluated. As shown in Figure 1, the Ba-added catalysts showed the highest catalytic activity with a 77% decomposition rate. Fig.2 shows the XANES spectra. The spectrum

of Ni-Ba was slightly shifted to the oxidation side and different from the spectra of other catalysts. This chemical state might contribute to the highest catalytic activity of Ni-Ba.

The results of ammonia methanation experiments are shown in Fig. 3. The highest methane yield, 73%, was obtained by using the Ni catalyst at 550 °C and 0.5 MPa.

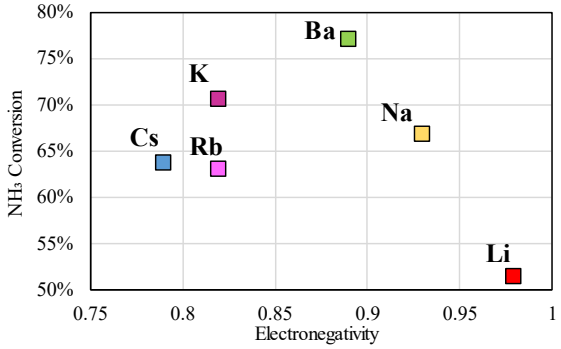

FIGURE 1. Relationship between ammonia decomposition rate and electronegativity

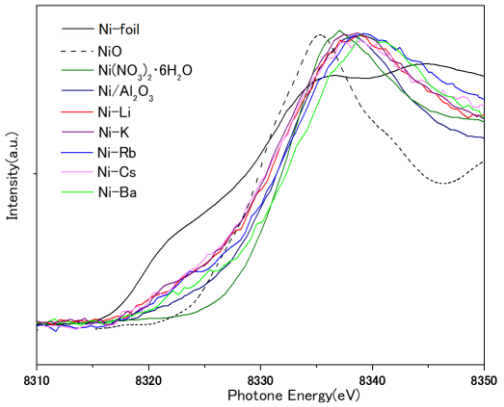

FIGURE 2. XANES spectra of the Ni-K edge.

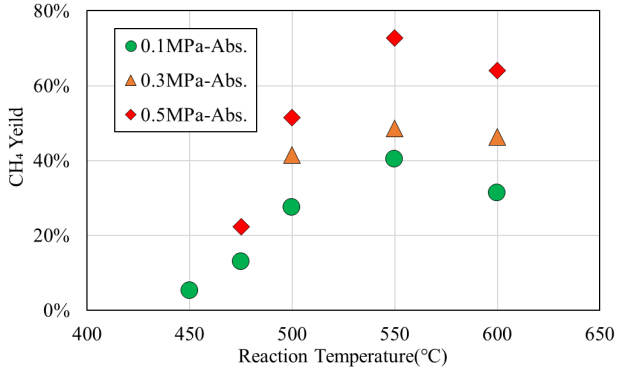

FIGURE 3. Methane yield of ammonia methanation with hybrid catalysts of Ni-Ba/Al_2O_3 and Ni/CeO_2

REFERENCES

1. Hitoshi Saima, Reiji Sunamoto, Hiroki Miyaoka, and Takayuki Ichikawa, *Ammonia Methanation of Carbon Dioxide with a Hybrid Catalyst*, JOURNAL OF CHEMICAL ENGINEERING OF JAPAN, 2023, Volume 56.