Three-way catalysis over self-regenerating Ni-Cu alloy catalysts

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Abstract: Ni-Cu alloy catalyst prepared by H_2 pretreatment at high temperature is active for three-way catalysis for a model automobile exhaust gas (CO, C_3H_6, NO, and O_2) to CO_2 and N_2, and maintained high activity under a lean condition. The catalyst was also reactivated under a rich condition. STEM-EDX, XRD, and *operando* XAS studies revealed reformation of Ni-Cu alloy under the reaction condition.

Keywords: Three-way catalytic converter, base metal

1. Introduction

Automotive emission control has been one of the most important global environmental issues for more than half a century. The three-way catalysts (TWC) has been used to convert harmful CO, unburnt hydrocarbons and NO_x into CO_2 or N_2 from 1970s for a practical use. Platinum group metal elements such as Rh, Pd, and Pt are frequently used as essential components of TWCs, but we have to reduce/replace the usage of the PGM elements to tackle increasing demand for automobiles all over the world. In this study, we applied Ni-Cu alloy catalysts to three-way catalysis under a model automobile exhaust gas at a lab-level without water vapor and found them very active for NO_x reduction not only under stoichiometric condition, but also under rich or lean condition with high durability.

2. Experimental

10 wt% Ni/Al_2O_3, 10 wt% Cu/Al_2O_3 and 10 wt% Ni_xCu_y/Al_2O_3 (x:y = 75:25, 50:50, 25:75) were prepared by an impregnation method. Appropriate amounts of Ni and/or Cu precursor (0.1 g as total metal basis) were poured into an evaporating dish as stock solution prepared from their nitrates, followed by an addition of γ-Al_2O_3 (JRC-ALO-7, 0.9 g) into the solution. Each mixture was heated with a water bath to 80 °C and continuously stirred with a glass rod to dryness. The dried samples were calcined at 500 °C for 5 h. The catalysts were characterized by XRD, STEM-EDX, XAS, temperature programmed oxidation and H_2-TPR. Three-way catalytic reaction was carried out using a fixed bed flow reactor at atmospheric pressure. A 200 mg of catalyst sample (25/50 mesh) was placed into a tubular quartz reactor. The catalyst was pretreated under 5% H_2/He at 900 °C for 1 h. After the pretreatment, the catalyst bed was cooled to room temperature and heated to 500 °C again. The three-way catalytic reaction started with an introduction of lean condition model exhaust gas (NO 1000 ppm, CO 1000 ppm, C_3H_6 250 ppm, O_2 1462.5 ppm, He balance, 100 mL min^{-1}) into the catalyst bed. After 2.5 hours, the model exhaust gas was changed to rich condition (NO 1000 ppm, CO 1000 ppm, C_3H_6 250 ppm, O_2 675 ppm, He balance, 100 mL min^{-1}) and changed to lean and rich condition repeatedly every 2.5 hours. The eluent gas was analyzed by a micro-GC.

3. Results and discussion

Figure 1 shows three-way catalytic reaction results over the 10 wt% Cu/Al_2O_3, Ni/Al_2O_3 and $Cu_{50}Ni_{50}/Al_2O_3$ catalysts. At the very beginning under the lean condition, all of them showed high activity on NO_x reduction. The Cu/Al_2O_3 catalyst abruptly lost its activity under the lean condition. On the other hand, the Ni/Al_2O_3 catalyst maintained high activity on NO_x reduction under the first lean condition for

about 1.5 h, but lost its activity by 20% under the rich condition between 2:30 and 5:00 and by 80% under the second lean condition. However, the $Cu_{50}Ni_{50}/Al_2O_3$ catalyst maintained high activity on NO_x reduction under the first reduction for about 1 h and recovered under the rich condition repeatedly. Thus, the $Cu_{50}Ni_{50}/Al_2O_3$ catalyst is a kind of self-regenerating[1] TWC.

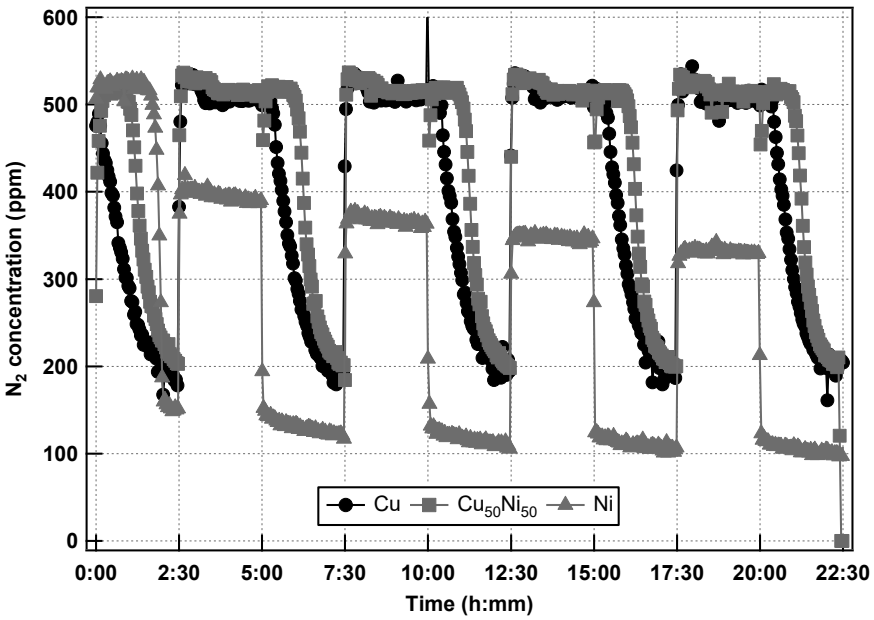

Figure 1. N_2 concentration in eluent gas during three-way catalytic reaction over 10 wt% Ni/Al_2O_3, Cu/Al_2O_3 and $Cu_{50}Ni_{50}/Al_2O_3$.

Figure 2 shows STEM-EDX images of the $Cu_{50}Ni_{50}/Al_2O_3$ catalyst after lean or rich conditions. After the lean condition, the Cu and Ni species are segregated but in contact with each other (Figure 2, upper middle and upper right). After another rich condition, the Cu and Ni reformed alloy particles (Figure 2, lower middle and lower right) as confirmed from XRD patterns. These results indicate both of the Ni and Cu species were reduced to Ni-Cu alloy under the rich condition in the aid of Cu species generating reductant for Ni species.

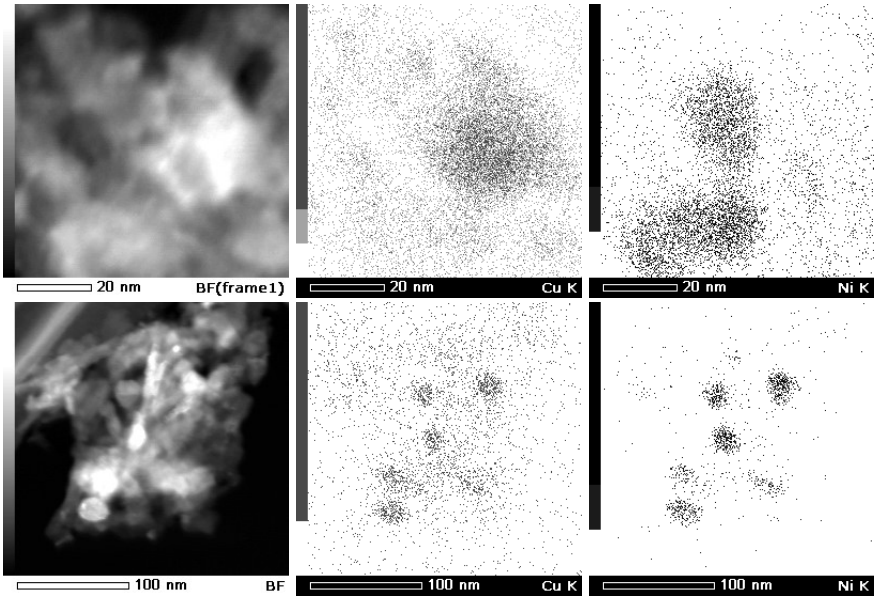

Figure 2. STEM-EDX images of the $Cu_{50}Ni_{50}/Al_2O_3$ catalysts
(Upper: STEM (left), Cu (middle), Ni(right) after lean condition; Lower: STEM (left), Cu (middle), Ni(right) after rich condition)

4. Conclusions

The Ni-Cu alloy catalyst was active for three-way catalysis under a model automobile exhaust gas and dynamically reactivated under the rich condition after the degradation under the lean condition. This feature can be a new insight into the TWC design based on base metals.

References

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