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Decomposition of Nitric Oxide over Y-Ba-Cu-O Mixed Oxide Catalysts

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Y-Ba-Cu-O mixed oxide catalysts supported on MgO were found to have higher catalytic activity for NO decomposition than a commercial Pt supported catalyst at 800 °C. XPS analysis suggests that the decomposition of NO is facilitated by the redox cycle of Cu.

Catalytic decomposition of nitric oxide (NO) is one of the simplest methods for NOx removal. However, a catalyst that can catalyze the direct decomposition of NO rapidly under mild conditions has not yet been developed. Supported noble metal catalysts in a reduced state have been known to be active, but the oxygen generated from the decomposition of NO significantly poisons the catalytic activity.1,2) Several kinds of oxide catalysts are also known to be active. However, they are less active than noble metal catalysts. Reaction rates for NO decomposition on these oxides are related to the exchange of oxygen between gaseous reactants and the catalyst.3) This suggests that oxygen-deficient structures which have mobile lattice oxygen should be suitable for NO decomposition.

Very recently, new oxygen-deficient perovskite-like compounds, $LnBa_2Cu_3O_{7-y}$, with a high superconductivity transition temperature were synthesized.4,5) One of the Cu-O planes perpendicular to the c-axis of these compounds has oxygen sites with low occupancy that is variable with temperature and/or oxygen partial pressure.6) The present study was aimed at utilizing the oxygen defects as the catalytically active sites for NO decomposition.

$YBa_2Cu_3O_{7-y}$ perovskite-like compounds were prepared by calcining a mixture of Y_2O_3, $BaCO_3$, and CuO at 950 °C for 40 h. The X-ray diffraction (XRD) pattern of the calcined material was the same as that reported in the literature.5) The powder was pulverized in a ball mill in order to improve the surface area. Scanning electron microscope (SEM) observation revealed that a resulting material had a particle size between 0.2 - 1.0 μm, corresponding to a surface area of several m^2/g. The XRD of the pulverized

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material revealed little of the original perovskite pattern, in spite of the relatively large particle size. This is likely due to a mechanochemical reaction during pulverization that significantly modifies the XRD detectable surface. The Y-Ba-Cu-O/MgO catalyst was prepared by impregnating a MgO powder (Wako Pure Chemical Industries, Heavy, Surface area: c.a. 4 m^2/g) with a petroleum benzine solution of mixed naphthenic acid salts of Co, Ba, and Y, followed by filtering and calcining in air at 850 °C for 30 min. This procedure (impregnation, filtration and calcination) was repeated 10 times. The prepared catalyst, containing 2.75% of CuO, 1.62% of BaO, 1.40% of Y_2O_3 (ICP emission spectroscopy), gave XRD peaks arising only from MgO. All catalytic reactions were carried out using a conventional flow reaction system. As standard conditions, the gas mixture (3%NO/He) flow rate was 20 cm^3/min and the amount of catalyst used was 0.5 g or 2.5 g. A gas chromatograph equipped with molecular sieve 5A was used in the analysis of the gas products. All of the NO conversion values reported were calculated based on the yield of N_2 due to extensive reaction of unconverted NO with oxygen ($NO + 1/2O_2 \rightarrow NO_2$) after exiting the catalyst bed.

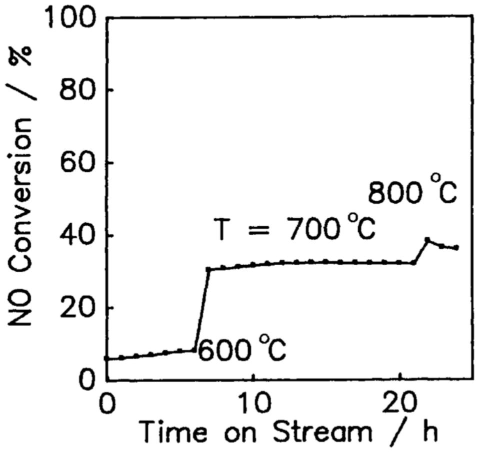

Fig. 1. NO Decomposition over Y–Ba–Cu–O (2.5 g).

Figure 1 shows the results for catalytic NO decomposition over the pulverized $YBa_2Cu_3O_{7-y}$ ceramic catalysts. The conversion reaches approximately 30% at 700 °C. When the temperature is increased up to 800 °C, the conversion improves a little but decreases with time on stream. Sintering of the catalyst particles during the reaction was suggested by SEM observation. Little decomposition of NO was observed over $BaCuO_2$ or $Cu_2Y_2O_5$ under the same conditions. Thus, $YBa_2Cu_3O_{7-y}$ has catalytically active sites for NO decomposition, but they are deactivated by sintering at 800 °C.

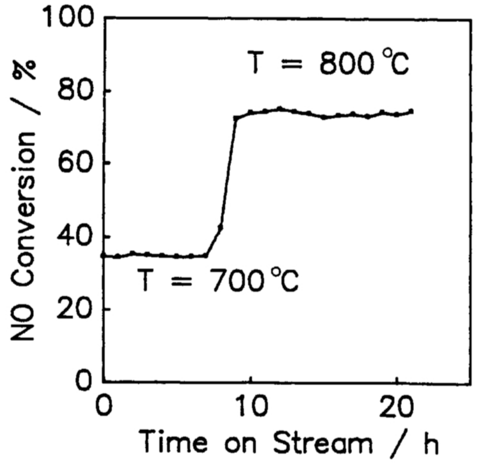

Fig. 2. NO Decomposition over Y–Ba–Cu–O/MgO Catalyst (2.5 g).

Subsequently, MgO supported Y-Ba-Cu-O catalysts were studied in order to see the improvement of catalytic properties through a high dispersion and a suppression of sintering. MgO was chosen as the support because unlike other conventional oxide supports such as SiO_2 or Al_2O_3,[7] it dose not react with the components of Y-Ba-Cu-O. Figure 2 shows the change in the catalytic activity of the MgO supported catalyst with temperature and time on stream. At 700 °C the conversion is about 35%, similar to that over the pulverized $YBa_2Cu_3O_{7-y}$ catalyst in Fig. 1. When the temperature is increased up to 800 °C, the conversion reaches approximately 73% and still shows a stable catalytic activity for more than 10 hours.

Figure 3 shows the comparison of the catalytic activities of various catalysts for NO decomposition. Two kinds of catalysts were chosen as references. One was a commercially available 0.5wt.%Pt/Al_2O_3 catalyst (Nippon Engerhard Co. Ltd.). The other was a prepared $La_{0.85}Sr_{0.15}CoO_3$ perovskite catalyst, which was reported to be the most active for NO decomposition among the perovskites examined by Uchijima et al.[8] The Pt/Al_2O_3 catalyst was found to be much more active than the other two catalysts below 700 °C. While, at 800 °C, the order of the catalytic activity changed to be Y-Ba-Cu-O/MgO > Pt/Al_2O_3 > $La_{0.85}Sr_{0.15}CoO_3$. This result suggests that highly active sites for NO decomposition are formed on the Y-Ba-Cu-O/MgO catalyst at 800 °C.

In order to obtain information on the active sites of this catalyst, XPS measurements were carried out on the catalysts used in NO decomposition. Figure 4(a) shows the Cu 2p photoelectron spectrum of the Y-Ba-Cu-O/MgO catalyst cooled under NO/He flow from 800 °C, while Fig. 4(b) shows the spectrum for a similar catalyst cooled under He flow. The stars (*) in Fig. 4 indicate shake-up satellite peaks arising from Cu species

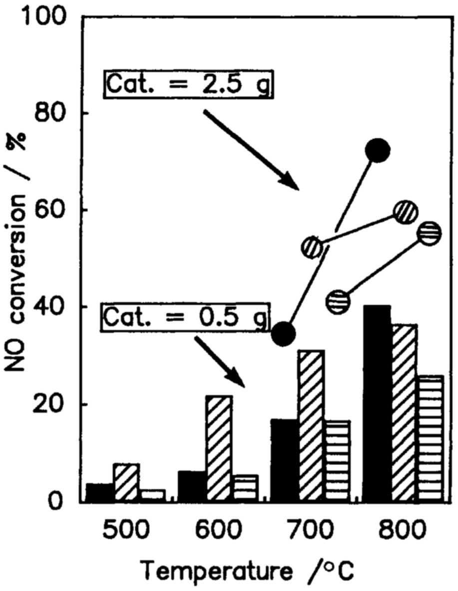

Fig. 3. Comparison of the Catalytic Activity for NO Decomposition.

■ Y-Ba-Cu-O/MgO
▨ Pt/Al_2O_3
▤ $La_{0.85}Sr_{0.15}CoO_3$

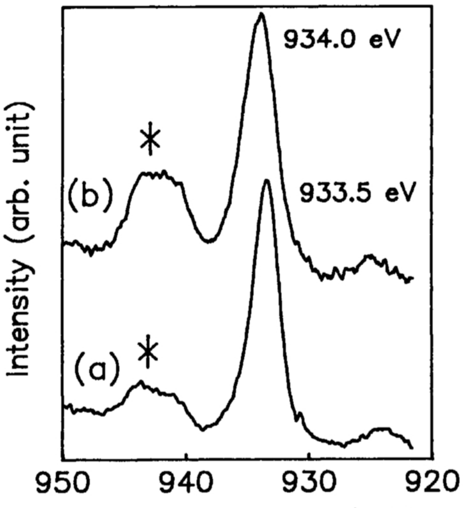

Fig. 4. Cu 2p XPS Spectra of Y-Ba-Cu-O/MgO Catalysts.
(a) Cooled under NO/He flow
(b) Cooled under He flow

with the electronic structure of $3d^9$ (Cu^{2+}). This allows the intensity ratio for the satellite peak relative to the main photoelectron peak to be taken as approximately proportional to the ratio Cu^{2+}/(total Cu) in the compounds. Therefore, the catalyst cooled under He flow (Fig. 4(b)) contains more Cu^{2+} species than that cooled under NO/He flow. This result seems to suggest that NO is adsorbed on Cu^+ sites when cooled under NO/He flow, and prevents Cu^+ from being oxidized to Cu^{2+} as the catalyst is exposed to air prior to XPS measurement. While, Cu^+ sites are free to be oxidized in air when the catalyst is cooled under He flow. Thus, the decomposition of NO is likely to be facilitated by the redox cycle of Cu ($Cu^{2+} \rightleftarrows Cu^+$).

Recently, Tabata et al.[9] reported that a large amount of NO is reversibly taken up by $YBa_2Cu_3O_{7-y}$ ceramics below 400 °C. It can be assumed that the NO adsorption sites on the Y-Ba-Cu-O system are Cu ions adjacent to oxygen vacancies. The decomposition of NO requires higher temperatures (700 to 800 °C), because the decomposition requires the completion of the Cu redox cycle. As suggested by the XRD results of the catalysts studied here, the long-range ordered tri-perovskite structure (as detectable by XRD) is not essential for the presence of the catalytically active Cu sites. The local Y-Ba-O framework seems to provide for a rapid and stable Cu redox cycle. These findings suggest the possibility that a local structure that gives a rapid Cu redox cycle at lower temperatures can provide very active sites for NO decomposition.

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