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Catalytic Combustion of Carbon Monoxide over $YBa_2Cu_3O_x$ Electroconductive Catalyst

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Yittrium barium copper oxide ($YBa_2Cu_3O_x$), known as high-Tc superconductor was used as an electroconductive catalyst and its characteristics in carbon monoxide oxidation were investigated. When direct current of 3 V was charged, $YBa_2Cu_3O_x$ was heated to about 450 °C, at which it catalyzed CO oxidation.

Catalysts are recently gaining wide roles in many fields, particularly in environmental technologies. Accordingly, requirements for catalyst performance are getting harder. Removal of hydrocarbons emitted from automobile in the period of cold start is one of the most difficult tasks for catalyst to perform. If a solid has a proper electric conductivity to heat its body quickly to a temperature where it can work as a catalyst, a new catalytic system would be realized. We should call such a catalyst an electroconductive catalyst. Such a catalyst may work as a combustion catalyst to clean up the cold-start-exhausts of automobile.

$YBa_2Cu_3O_x$, known as high-Tc superconductor has recently gathered attention not only due to its electric and magnetic characteristics but also due to its intrinsic catalytic activity for oxidation.[1-7] The purpose of this study is to investigate the self-heating property of $YBa_2Cu_3O_x$ induced by DC voltage charged and its catalytic activity for CO oxidation.

$YBa_2Cu_3O_x$ catalyst was prepared by a conventional solid state reaction: Powders of Y_2O_3, $BaCO_3$ and CuO were thoroughly ground in a mortal at a molar ratio of 1:2:3. The mixture was heated in air at 940 °C for 1 h, ground again, and this procedure of heating and grinding was repeated. It was then heated at 940 °C for 4 h to yield black powder. X-ray diffraction analysis using a RAD I-C, CuKα, Rigaku Co.,Ltd., revealed that the powder consisted of a single phase of YBa_2Cu_3Ox. The specific surface area measured by the BET method (N_2 adsorption) was 0.8 $m^2\ g^{-1}$.

Approximately 5 g of the $YBa_2Cu_3O_x$ powder was pressed under 500 kg cm^{-2} for 2 min into a pellet (13

mmϕ × 8 mm length), which was sintered at 940 °C for 1 h. The catalyst temperature during activity tests was measured by use of thermocouple inserted through a hole (3 mmϕ) made in the center of this sintered pellet. Electrodes were connected to the sintered pellet as follows: Silver electroconductive paint (DOTITE Type K-1056, Fujikura Kasei Co., Ltd.) was spread on both top and bottom surfaces of the pellet, dried in air at 650 °C for 10 min, and silver wires (1 mmϕ) were attached to the both surfaces of the pellet with silver paint and then with alumina adhesive (CERAMABOND™ 503, Aremco Product Inc.) for reinforcement. After attachment of silver electrodes as shown above, $YBa_2Cu_3O_x$ was used in reaction. No catalytic activity was exerted by the silver conductive paint, silver wires, and alumina adhesive.

Catalytic activity for CO combustion was measured in a continuous flow reactor operated under atmospheric pressure. The structure of the reactor is shown in Fig. 1. The composition of reactant gas was 2% CO, 1% O_2, and He balance. The total gas flow rate was 100 cm^3 min^{-1}. Prior to a measurement, the catalyst was heated in a stream of He at 400 °C for 1 h.

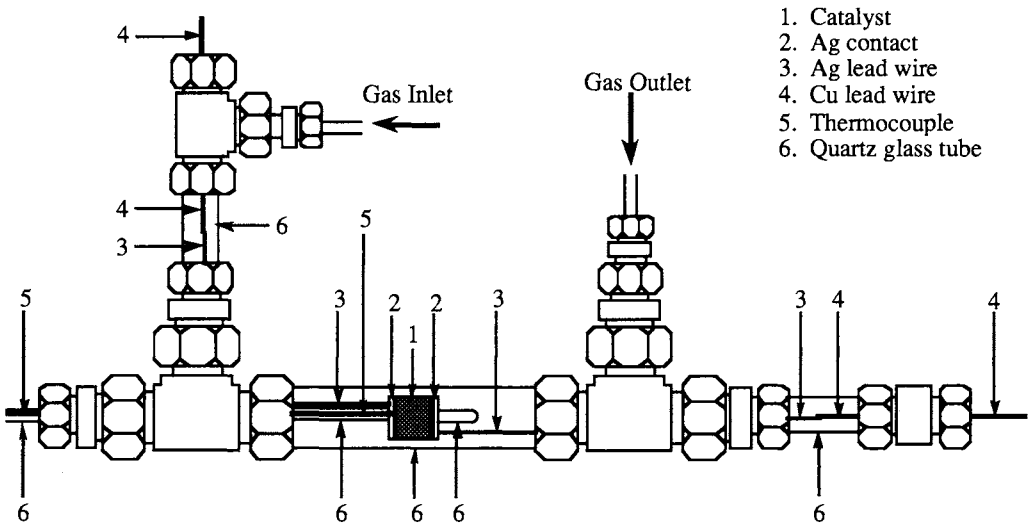

Fig. 1. Schematic diagram of experimental reactor.

CO combustion was carried out by either heating the catalyst pellet with charging a constant voltage by use of a DC power source (EX-375-L, Takasago Corporation), or in an electric furnace under isothermal condition. Exit gas from the reactor was analyzed by use of an on-line gas chromatography (GC-8AIT, Shimadzu Corporation). Chromatographic separation was achieved using an active carbon column (80/100 mesh, 2 m, G.L.Science Inc.).

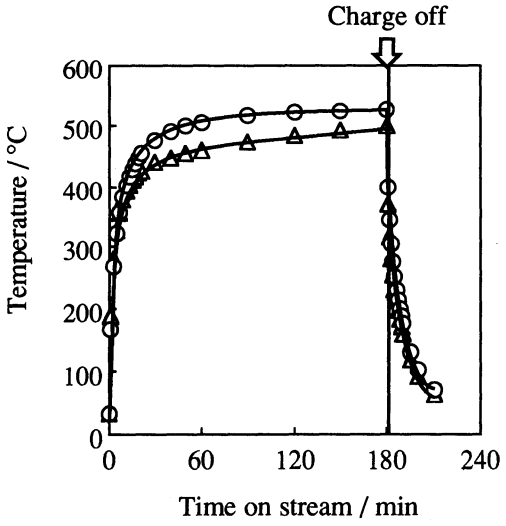

Fig. 2. Time on stream variation in temperature of $YBa_2Cu_3O_x$ under the charge of 3 V.
○ , CO 2% + O_2 1% / He ; △ , He .

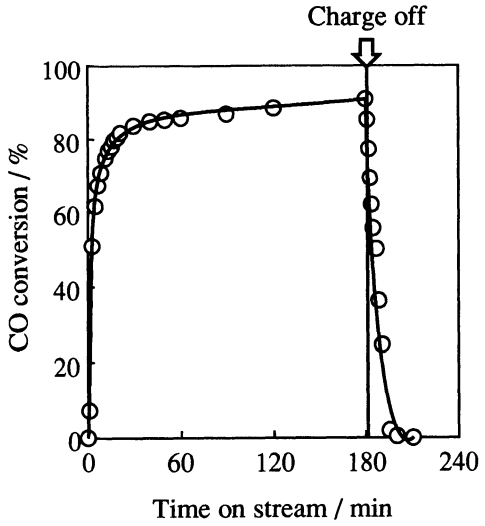

Fig. 3. Time on stream variation in CO conversion. Same reaction conditions as in Fig. 2.

A solid, which can work as an electroconductive catalyst, requires a proper electric conductivity to be heated to a temperature high enough for catalytic reaction. Figure 2 shows the self-heating property of $YBa_2Cu_3O_x$ as measured by the temperature of catalyst body as a function of time on stream. When electric current passed through $YBa_2Cu_3O_x$ under DC bias of 3 V, the temperature rapidly increased and reached a steady state. The difference in catalyst temperature observed in reactant gas flow and in He flow is attributed to the reaction heat of CO oxidation. Figure 3 shows the catalytic activity simultaneously observed being expressed by CO conversion. The CO

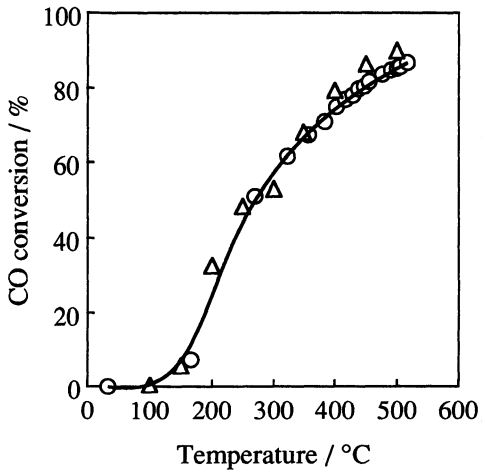

Fig. 4. Catalytic activitiy of $YBa_2Cu_3O_x$ for the combustion of CO.
○ , Under the DC bias of 3 V ;
△ , Under isothermal condition .

conversion increased quickly when charged. These results show that $YBa_2Cu_3O_x$ satisfy previously mentioned requirements for electroconductive catalyst.

The catalytic activity of $YBa_2Cu_3O_x$ under isothermal condition was measured and compared with the results observed for the same catalyst under DC bias of 3 V in Fig. 4 as a function of reaction temperature. There was no appreciable difference in the level of CO conversion with and without electric current. This means that the catalytic activity is a sole function of catalyst temperature, and the rise in temperature of the catalyst solid is caused by the Joule's heat. In other words, there is no effect of the local electric fields caused by electric current upon the catalysis of $YBa_2Cu_3O_x$. Consequently, it is deduced that the two important features required for electroconductive catalyst, namely electric conductivity to heat up the catalyst body and catalytic activity, can be discussed independently.

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