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Uptake of NO Gas by $YBa_2Cu_3O_y$

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A large quantity (2.5 - 3 in molar ratio) of NO was taken up from gas phase by $YBa_2Cu_3O_y$ (y=6.88) at 573 K, and desorbed mostly as NO at 773 K. The rate of uptake at 573 K increased with the increase in the concentration of coexisting O_2 upto 8%, or by treating the sample in N_2 above 850 K. The addition of Pd (0.1%) to $YBa_2Cu_3O_y$ greatly accelerated the rate of NO uptake.

Recently $YBa_2Cu_3O_y$ attracted considerable attention as a superconducting material.[1,2] We applied $YBa_2Cu_3O_y$ as a catalyst for the catalytic decomposition of NO ($2NO \rightarrow N_2 + O_2$), and found remarkable and almost reversible uptake of NO by $YBa_2Cu_3O_y$. $YBa_2Cu_3O_y$ was prepared by heating the mixture of CuO, Y_2O_3 and $BaCO_3$ at 1196 K for 10 h in air after heating at 1073 K for 5 h, and then cooled to room temperature for 12 h. The X-ray diffraction pattern agreed with the literature.[2] The value of y was 6.88, as determined by an oxygen analyzer (Horiba EMGA - 2800). The surface area was measured by BET method to be 0.9 $m^2\ g^{-1}$. The reaction of NO over $YBa_2Cu_3O_y$ was investigated either by a conventional flow or by a closed circulation system. In the case of the former system, the sample powder (1.0 g) mixed with quartz sand (total volume: 2.4 cm^3) was used, and a mixture of O_2 (0 - 17%), NO (20 - 80 ppm), and N_2 (balance) was fed with the space velocity (SV) of 12000 - 155000 h^{-1}, the concentration at the exit being measured by a NO_x analyzer (Yanaco ECL - 77A).

Figure 1 shows the variation of the concentration of NO at the exit of the reactor which was fed over $YBa_2Cu_3O_y$ in the flow system. The concentrations of NO and O_2 at the inlet of the reactor were 50 ppm and 8%, respectively. As the

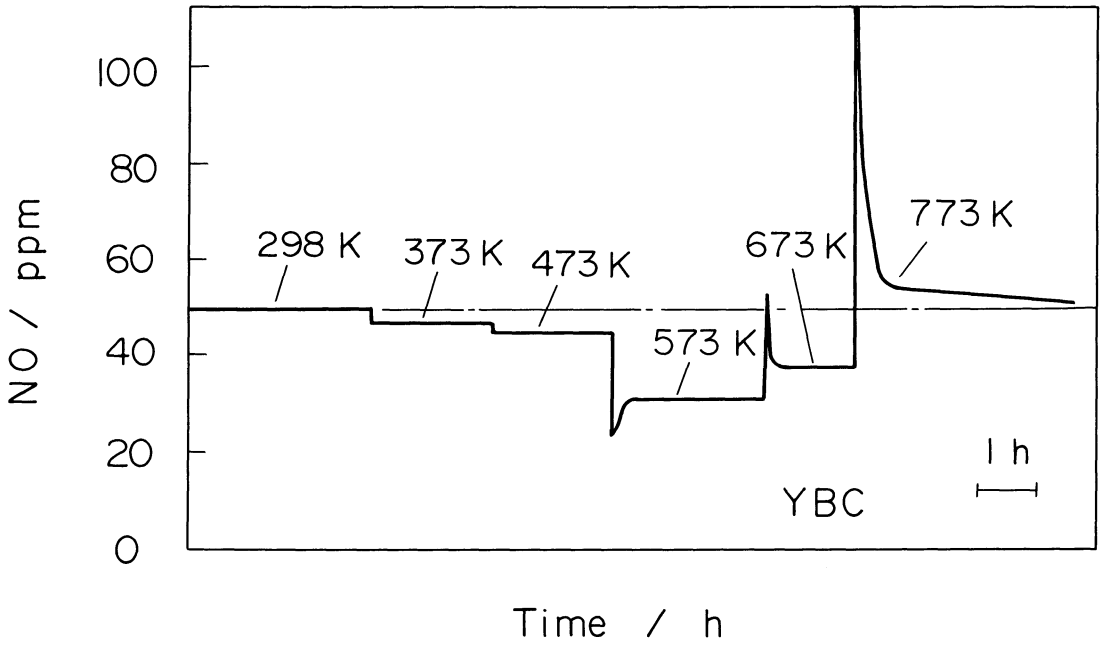

Fig. 1. The variation of the concentration of NO at the exist of the reactor, when the temperature was increased stepwise. (SV 12000 h^{-1}, NO 50 ppm, O_2 8%, N_2 balance)

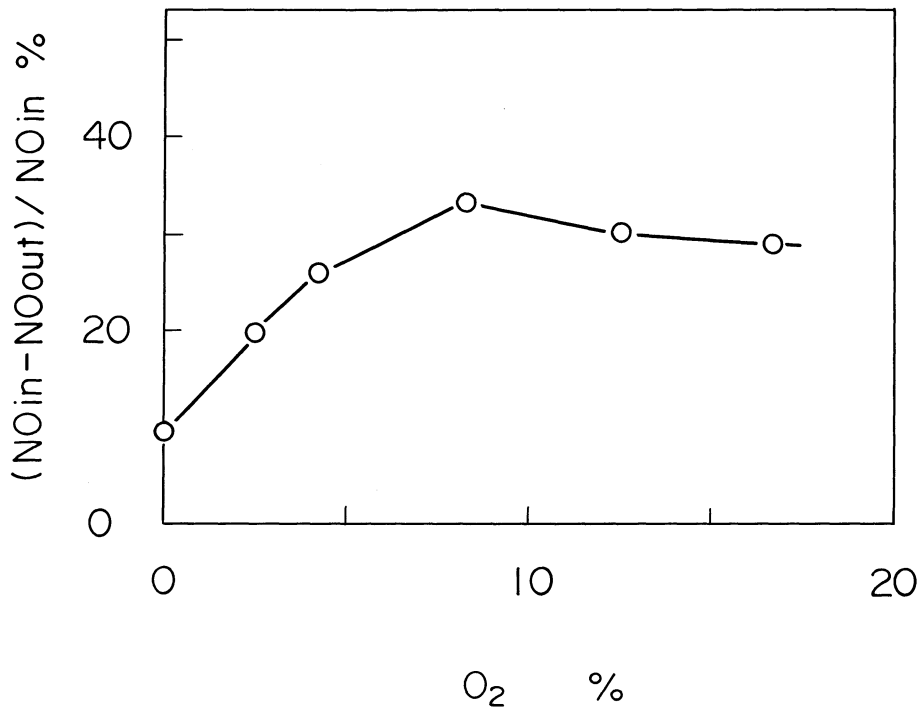

Fig. 2. The elimination ratio of NO vs. the concentration of O_2 at the inlet in the flow system.(SV 12000 h^{-1}, NO 50 ppm, N_2 balance)

temperature increased stepwise, the concentration of total No_x (= NO + NO_2) at the exit decreased with increasing temperature, and had a minimum value at 573 K. Then, it increased again, showing a sharp rise at 773 K. This result may be explained by adsorption at lower temperature and desorption at 773 K over $YBa_2Cu_3O_y$.

So, we quantitatively measured the uptake of NO by $YBa_2Cu_3O_y$, which had been evacuated at room temperature, by using the closed gas circulating system. The uptake of NO at 573 K, which was measured at 200 Torr of NO (1 Torr = 133.3 Pa) in the absence of O_2, amounted to 2.5 - 3 mole per unit mole of $YBa_2Cu_3O_y$. When the temperature of that was raised to 773 K, most of NO was recovered as NO together with a small amount of N_2. The uptake was sensitive to the pretreatment; when the sample was treated at 573 K in O_2, the uptake in the closed gas circulating system was very slow. The uptake of NO was not observed for either $BaCO_3$, CuO, or Y_2O_3 and only a little for BaY_2CuO_5. The large quantity of the NO uptake can never be explained by the adsorption on the surface, if one considers the small surface area. So, this is absorption into the solid bulk or reaction of the solid bulk such as formation of metal nitrates. Anyhow, we believe that nearly reversible uptake of a tremendous amount of NO is a very novel phenomenon of $YBa_2Cu_3O_y$.

To examine the possible application for the elimination of low concentration NO, we studied in more detail this phenomenon. The elimination ratio of NO which is defined by $(NO_{in} - NO_{out})/NO_{in}$ where NO_{in} and NO_{out} represent concentrations of

Table 1. Crystal structure and nonstoichiometry, y, and the NO elimination ratio of $YBa_2Cu_3O_y$ in after treatment under N_2 gas atmosphere

	N_2 treated temperature			
	Original	673 K	873 K	1073 K
y	6.88	6.62	6.30	6.10
Crystal structure[a)]	ortho.	ortho.	tetra.	tetra.
$\frac{No_{in} - No_{out}}{No_{in}}$ [b)]	0.23	0.25	0.28	0.45

a) ortho.; orthorhombic, tetra.; tetragonal.

b) No_{in} and NO_{out} represent the NO concentration at the inlet and that at the outlet, respectively.

NO at inlet and outlet of the reactor, respectively, was examined in the flow system as a function of the concentration of NO at the inlet. The ratio was constant regardless of the concentration of NO, indicating that the rate of uptake was proportional to the NO pressure. The capacity of NO uptake was so large as compared to the NO fed that the NO concentration at the outlet did not change with time. Figure 2 shows the effect of O_2. The elimination ratio increased with increasing O_2 concentration upto 8% in the flow system. In all the range of O_2 concentration, the desorbed gas at 773 K was mainly NO, and the fraction of NO in total NO_x little changed.

Table 1 summarizes the effects of the annealing of $YBa_2Cu_3O_y$ in N_2 gas for 2 h. The elimination ratio increased with the increase in the annealing temperature in the flow system. The value of y decreased with increasing temperature, and the crystal structure was transformed from orthorhombic to tetragonal at 873 K. The increase in the rate of the uptake with the increase in the annealing temperature was thus likely due to the increase of oxygen vacancy.

We further examined the effects of the addition of Pd to $YBa_2Cu_3O_y$. Pd was supported by impregnation with an aqueous solution of $(NH_4)_2PdCl_4$ (0.1 wt%) and calcined at 673 K for 1 h. The removal of NO was complete at first at 573 K in the flow system, and decreased only slightly with time, under the same conditions as in Fig. 1.

References

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