Reactions of the Monoxides of Carbon and Nitrogen over the Superconducting Lanthanoid Mixed Oxide $YBa_2Cu_3O_y$

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Large quantities of NO and CO were rapidly absorbed (or intercalated) by $YBa_2Cu_3O_y$ during the reaction of NO with CO at 573 K; NO was taken up initially, then CO absorption and N_2 formation took place, and finally the stationary catalytic reaction, $NO + CO \rightarrow 1/2N_2 + CO_2$, proceeded.

The lanthanoid mixed oxide $YBa_2Cu_3O_y$ has attracted attention as a superconducting material, and extensive studies of its electronic properties and structure have been reported.[1—3] However, little is known of its catalytic properties or chemical reactivity. The reaction $NO + CO \rightarrow 1/2N_2 + CO_2$ over Cu-containing catalysts has been studied.[4,5] We have investigated the reaction of NO with CO over $YBa_2Cu_3O_y$, and have observed the uptake of large quantities of NO and CO during the reaction.

The oxide $YBa_2CU_3O_y$ was prepared as follows. A mixture of CuO, Y_2O_3, and $BaCO_3$ was calcined at 1193 K overnight in air, and the product was ground to a powder in an agate pestle and then pressed into a disc. The disc was calcined again at 1193 K overnight in air, then cooled in air to room temperature during *ca.* 10 h. The product was re-pulverised before use as a catalyst. The formation of orthorhombic $YBa_2Cu_3O_y$[2] was confirmed by *X*-ray diffraction. It has been reported that the value of y in $YBa_2Cu_3O_y$[2] thus prepared ranges from 6.5 to 6.9.[3]

It was confirmed that this substance showed superconductivity at about 90 K. The surface area was measured by the Brunauer–Emmett–Teller (BET) method to be 0.7 $m^2 g^{-1}$. Our experiments with NO/CO were carried out in a closed circulation system at 298—773 K. The oxide $YBa_2Cu_3O_y$ (200 mg) (1 g corresponds to 1.50×10^{-3} mol at $y = 7$) was used as a mixture with SiC powder (250 mg) for each experiment. The NO/CO reaction was carried out at *ca.* 8 kPa (NO : CO 1 : 1). The procedure was as follows: in run (1) $YBa_2Cu_3O_y$ was exposed to the reaction gas at 573 K after evacuation at the same temperature for 1 h; in run (2) $YBa_2Cu_3O_y$ was exposed to the gas at 298 K after evacuation at 298 K for 20 min, and then the temperature was gradually increased to 573 K and kept there. Small portions of gases desorbed or reacted were taken out intermittently with the aid of a glass sampler and analysed by g.l.c. In an experiment with NO alone, after NO uptake was measured at 573 K (initial pressure 8—17 kPa), the temperature was increased stepwise to 773 K. At each temperature the gas desorbed was collected

Table 1. Uptake of NO and CO by $YBa_2Cu_3O_y$.[a]

Pretreatment	10^3(Uptake of NO) /mol g^{-1}	10^3(NO desorbed)[b] /mol g^{-1}			10^4(Uptake of CO)[c] /mol g^{-1}	10^4(CO desorbed)[b] /mol g^{-1}
Temperature/K	573	573	673	773	573	<773
Evacuation at 573 K	2.9	0.55	2.7	2.9	7.0	0
for 1 h		(19)	(93)	(100)		
Evacuation at 298 K	3.4	0	0.5	2.2[d]	9.0	0
for 20 min		(0)	(15)	(65)		

[a] Uptakes were measured in separate experiments using NO alone or CO alone. [b] Total amounts desorbed below the temperature indicated; % recovery as NO in parentheses. [c] Difference between amounts of CO decrease and CO_2 formed. [d] N_2 (4.8×10^{-4} mol g^{-1}) was formed in addition to NO.

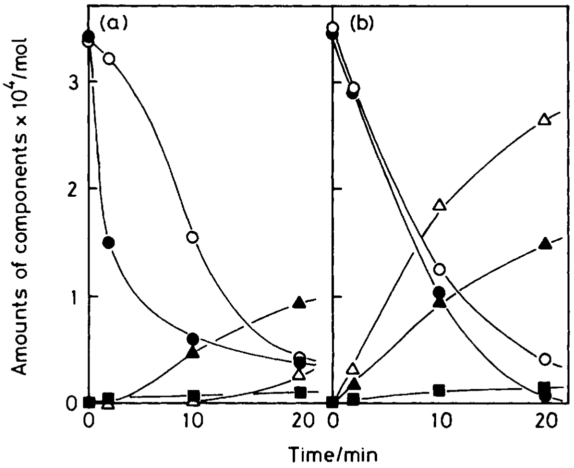

Figure 1. Reactions of NO and CO at 573 K; ●, ▲, and ■ correspond to amounts of NO, N_2, and N_2O, respectively; ○ and △ correspond to amounts of CO and CO_2, respectively; (a) reaction course at 573 K; (b) course at 573 K when the reaction of NO and CO was repeated.

in a liquid nitrogen trap (except for N_2). In an experiment with CO alone, after the rapid CO uptake at 573 K had been measured (initial pressure 13—15 kPa), the system was evacuated at 573 K for a short period (1—3 min). It was confirmed that neither CO nor CO_2 was desorbed during this evacuation. The temperature was then increased stepwise to 773 K without a trap.

When NO reacted with CO at 573 K over $YBa_2Cu_3O_y$ which had been evacuated for 1 h at the same temperature [run (1)], a large amount of NO was initially taken up rapidly, then CO uptake took place accompanied by N_2 formation. This was followed by CO_2 evolution. Finally the stationary catalytic reaction $NO + CO \rightarrow 1/2N_2 + CO_2$ proceeded. In run (2), in which the $YBa_2Cu_3O_y$ had been evacuated at 298 K, very little reaction took place below 573 K. The reaction proceeded at 573 K in a similar way to that in run (1), except that the induction period was a little longer for run (2). Figure 1 shows the course of run (2) at 573 K. The amount of NO uptake after 2 min in run (2) was 1.0×10^{-3} mol g^{-1}, which corresponds to a molar ratio of 0.7 with respect to $YBa_2Cu_3O_y$, and also to 120 times the monolayer of $YBa_2Cu_3O_y$ (assuming that the cross section of NO is 14 Å^2). Neither N_2 nor N_2O was formed in this period. Such a large uptake cannot be explained only by adsorption on the surface; a large amount of NO must have been absorbed by intercalation or reaction in the catalyst bulk.

The amount of CO uptake [run (2)] after 10 min (9.5×10^{-4} mol g^{-1}) was almost the same as that of NO uptake in the first 2 min. Thus a large amount of CO was also absorbed in the catalyst bulk. In the meantime, no CO_2 was formed; this reaction began later. The eventual reaction products were mostly N_2 and CO_2. In the run shown in Figure 1(b), the amount of NO uptake was comparable with that of CO uptake, and N_2 and CO_2 were formed in approximately stoicheiometric ratio in accordance with the reaction $NO + CO \rightarrow 1/2N_2 + CO_2$. When the $YBa_2Cu_3O_y$ was pretreated with O_2 at 573 K, the reaction was very slow.

The amounts of NO and CO uptake by $YBa_2Cu_3O_y$, measured separately, are summarized in Table 1. When the $YBa_2Cu_3O_y$ had been evacuated at 573 K for 1 h, the NO uptake was 2.9×10^{-3} mol g^{-1} at 573 K in 1.5 h. This amount represents a molar ratio of about 2 with respect to $YBa_2Cu_3O_y$. During this uptake only small amounts of N_2 and N_2O were observed. The NO molecules thus absorbed were almost completely recovered as NO by increasing the temperature to 673 K. When $YBa_2Cu_3O_y$ was exposed to NO after evacuation at 298 K, the behaviour was different. The NO uptake at 573 K was a little greater (3.4×10^{-3} mol g^{-1}), and the recovered gas at 673 K was a mixture of NO and N_2; 65% and 28% of NO absorbed were desorbed at 773 K as NO and N_2, respectively. It is clear that a large amount of NO was reversibly absorbed into the catalyst bulk.

On the other hand, CO was taken up at 573 K with simultaneous formation of CO_2. The difference between CO decrease and CO_2 formation was 7.0—9.0×10^{-4} mol g^{-1} (about two-thirds of the total CO uptake), which approximately corresponds to the CO uptake in the initial stage of the CO/NO reaction. The CO molecules held by $YBa_2Cu_3O_y$ were not desorbed below 773 K. The CO absorbed appears to be held more strongly than the NO absorbed in the $YBa_2Cu_3O_y$ bulk.

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