NO Removal by Absorption into BaO–CuO Binary Oxides

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Rapid absorption of NO into BaO–CuO mixed oxides is effective for NO removal from the gas phase, and is significantly accelerated by the presence of oxygen.

The development of efficient and simple processes for NO removal is an important problem. Although many metal oxide systems have been studied as catalysts for decomposition of NO,[1—3] practical catalysts have not been developed so far. In particular, catalytic decomposition of NO is easily suppressed by the presence of oxygen, which is believed to occupy the active site on the catalyst surface for NO adsorption. Some metal oxides absorb a large amount of NO,[4,5] and such NO absorbants provide another approach for removal of NO, especially at low concentrations (< 1000 ppm). We now report rapid NO removal at low concentrations by absorption into BaO–CuO binary oxides.

The binary oxides of alkaline earth–Cu systems are prepared from the corresponding nitrates or acetates. Aqueous solutions of the nitrates or acetates were evaporated to dryness and the residue calcined in air at 1023 K for 5 h. The crystal phase of the sample thus obtained was determined by powder X-ray diffraction (XRD). NO removal over the metal oxides was evaluated in a conventional flow system. A gaseous mixture of NO (1000 ppm) and nitrogen was fed to the oxide bed at a flow rate of 100 cm^3 min^{-1} (space velocity, SV = 6000 h^{-1}). NO removal in the effluent gas was measured by a NO_x analyser using chemiluminescence.

NO removal over equimolar binary oxides of the alkaline earth–Cu system was examined as a function of temperature. Two BaO–CuO samples (BaO–CuO and BaO–13CuO) showed complete NO removal at 450—650 K (Figure 1). When the temperature was raised above 680 K, however, a large amount of NO was liberated from the BaO–CuO samples. Since the amount of NO liberated, which is several times larger than that estimated from adsorption onto surface, was equal to the cumulative amount of NO removed, the NO removal observed up to *ca.* 680 K must result from absorption into the BaO–CuO samples. NO removal over other alkaline earth–Cu systems (SrO–CuO, CaO–CuO) was negligible, however, up to 1000 K, and NO removal by absorption appears to be characteristic for the BaO–CuO system. XRD measurements showed that the samples contained $BaCuO_2$ and $BaCuO_{2.5}$ (Figure 2a). $BaCuO_2$ samples have crystal structures based on corner- or edge-sharing CuO_4 square planes with complex non-stoicheiometry.[6] $BaCuO_{2.5}$ contains octahedrally co-ordinated Cu^{3+} ions[7].

The effect of oxygen on the NO removal was examined over the BaO–CuO sample (Figure 1). When the inlet gas contained 10 vol % of O_2, liberation of NO was observed only above 790 K. Oxygen not only increased the temperature for NO liberation but also promoted NO absorption. This is important for practical applications.

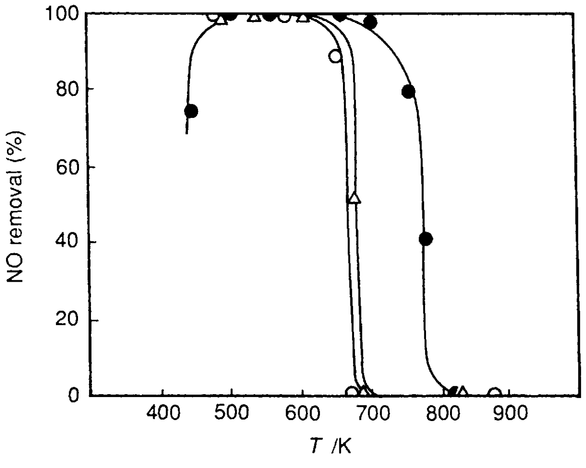

Figure 1. Temperature dependence of NO removal over BaO–CuO binary oxides: △, BaO–13CuO (1000 ppm NO/N_2); ○, BaO–CuO (1000 ppm NO/N_2); ●, BaO–CuO (1000 ppm NO/N_2 + 10% O_2).

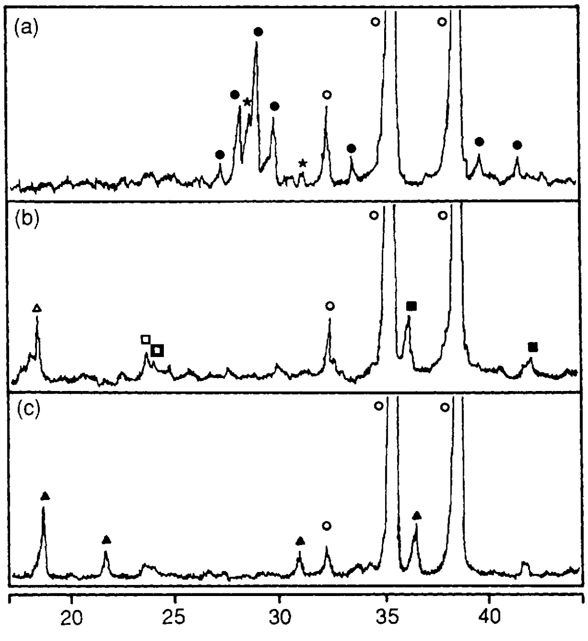

Figure 2. X-Ray diffraction of the BaO–CuO sample: (a) before and after NO absorption; (b) in the absence of O_2; (c) in the presence of O_2: ●, $BaCuO_2$; ★, $BaCuO_{2.5}$; ○, CuO; ■, Cu_2O; △, $Ba(NO_2)_2$; ▲, $Ba(NO_3)_2$; □, $BaCO_3$.

Crystallographic aspects of the NO removal over the BaO–CuO system were examined by XRD measurement. Figure 2 shows the XRD patterns for the sample (BaO–13CuO) as-prepared and after NO absorption in a volumetric vacuum system. Since these diffraction patterns are complicated, containing many peaks, only the typical regions are presented. The XRD patterns of the sample after the NO absorption were free from reflections from $Cu(NO_3)_2$ or $Cu(NO_2)_2$. When 10^4 Pa of NO was introduced in the absence of O_2, the BaO–CuO sample absorbed *ca.* 0.5 mol/mol of NO. Although most of the diffraction peaks which appeared after NO absorption were weak, traces of $Ba(NO_2)_2$, Cu_2O, and $BaCO_3$ were detected with simultaneous disappearance of mixed oxides of the Ba–Cu system (Figure 2b). Thus, the NO absorption may occur, qualitatively, as in reaction (1). The Cu_2O in the product probably arises from charge compensation in order to produce barium nitrite, because no oxygen is provided from gas phase in this case. The $BaCO_3$ phase observed in XRD was formed by the reaction between BaO and CO_2 in air.

$$BaCuO_2 + BaCuO_{2.5} \xrightarrow{NO} Ba(NO_2)_2 + BaO + Cu_2O + CuO \quad (1)$$

When the NO absorption was carried out in the presence of O_2, $Ba(NO_3)_2$ appeared instead of Ba–Cu mixed oxides (Figure 2c) after half the equimolar amount of NO had been absorbed. The Ba–Cu–O phases seem to be converted into a mixture of $Ba(NO_3)_3$ and CuO [reaction (2)]. This reaction is different from reaction (1) in producing barium nitrate and in the absence of BaO and Cu_2O as products, because the oxygen in the gas phase participates in the absorption reaction. The effect of oxygen on the temperature dependence of NO removal (Figure 1) appears to be associated with the thermal stability of barium nitrate, the decomposition temperature of which is $>$ *ca.* 970 K.

$$BaCuO_2 + BaCuO_{2.5} \xrightarrow{NO + O_2} 2\,Ba(NO_3)_2 + 2\,CuO \quad (2)$$

Since the NO absorption caused no crystallographic change in the original phases other than $BaCuO_2$ and $BaCuO_{2.5}$, these mixed oxides are likely to play a key role in NO removal from the gas phase. Although the catalytic decomposition of NO is always suppressed by the presence of oxygen, NO absorption into BaO–CuO can be enhanced by oxygen which promotes the nitrate formation.

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