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Inhibition of NO Decomposition Activity of Perovskite-type Oxides by Coexisting Carbon Dioxide

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Catalytic activity of La-based perovskites, $La_{0.8}Sr_{0.2}CoO_3$ as a representative example, for the direct NO decomposition above 500 °C was decreased by the coexistence of gaseous carbon dioxide. The effect of carbon dioxide was more severe than the well-known impact of oxygen, though it was reversible at 800 °C.

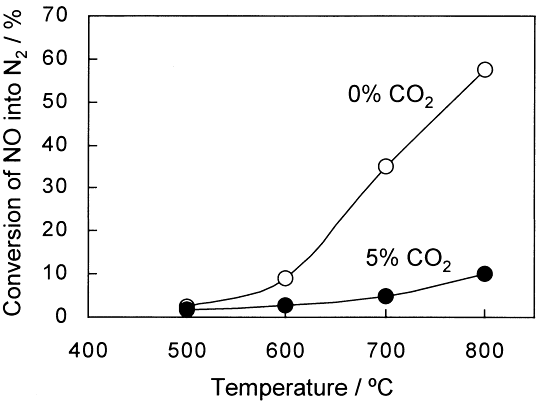

Fig. 1. Catalytic decomposition of NO over $La_{0.8}Sr_{0.2}CoO_3$ with and without coexisting CO_2 (5%).

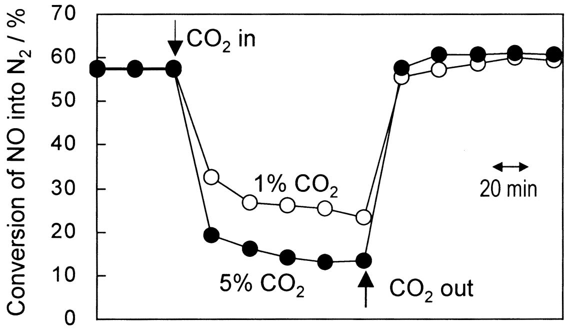

Fig. 2. Response of the NO decomposition activity of $La_{0.8}Sr_{0.2}CoO_3$ at 800 °C to the introduction and removal of CO_2.

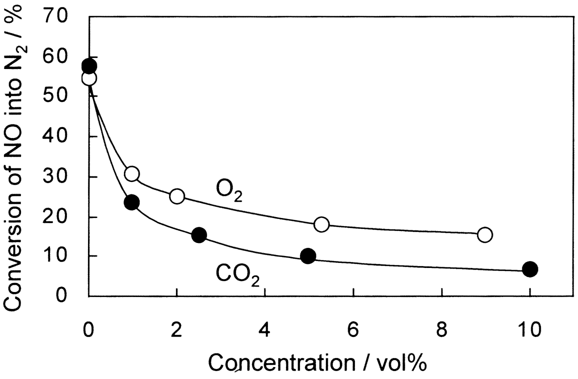

Fig. 3. Effects of partial pressures of O_2 and CO_2 in the feed gas on the conversion of NO into N_2 over $La_{0.8}Sr_{0.2}CoO_3$ at 800 °C. $P(O_2)$ dependence was taken from Ref. 5.

The direct decomposition of NO into N_2 and O_2 ($2NO \rightarrow N_2 + O_2$) is a thermodynamically acceptable reaction and the simplest $deNO_x$ one; a wide variety of catalysts, including metals, oxides and ion-exchange zeolites, have been so far investigated for the reaction.[1] It is well known that coexisting gaseous oxygen, a product of NO decomposition, causes a decrease in the activity of almost all the NO decomposition catalysts, and this is one of crucial reasons why the direct NO decomposition process has not been put into any practical applications. Before the NO decomposition process will be used for exhaust treatment of combustion facilities, it is indispensable to study the effects of other coexisting gases, such as CO_2 and H_2O. Here, we investigated the effect of CO_2 on the NO decomposition activity of perovskites, which are known to be high-temperature catalysts.[2-5] The inhibitory action of CO_2 was already reported on the CO oxidation activity of $LaMn_{1-x}Cu_xO_3$ perovksites,[6] and the present study revealed that CO_2 also decreased the NO decomposition activity more severely than O_2. Since CO_2 is inevitably present in the combustion exhausts, the present results pose a tough but challenging problem for the development of catalytic process of NO decomposition.

Temperature dependences of the NO decomposition reaction in the absence and presence of 5% CO_2 are depicted in Fig. 1 for $La_{0.8}Sr_{0.2}CoO_3$, which is one of most active NO decomposition catalysts in perovskite-type oxides.[2-5] It is clearly seen that coexisting CO_2 brought about serious reduction of the NO decomposition activity in the whole temperature range examined. Figure 2 shows the response of the NO decomposition activity of $La_{0.8}Sr_{0.2}CoO_3$ at 800 °C to the introduction and removal of CO_2 with keeping the NO concentration constant. The activity decreased by the introduction of CO_2, and the removal of CO_2 from the reaction gas caused the recovery of the activity, indicating that the inhibitory action of CO_2 is reversible at this temperature. Figure 2 also shows that the activity is lower for the higher concentrations of CO_2. The dependence of the NO decomposition activity of $La_{0.8}Sr_{0.2}CoO_3$ at 800 °C on the CO_2 concentration is depicted in Fig. 3 together with the O_2 partial pressure dependence.[5] The reversible deterioration of the NO decomposition activity by coexisting O_2 is a well-known phenomenon, but it was found that CO_2 inhibited the reaction more severely than O_2. The apparent reaction orders

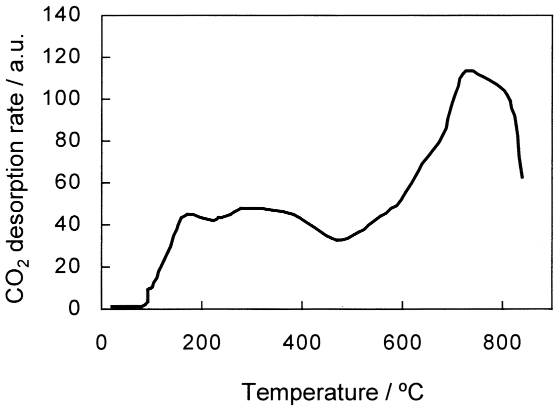

Fig. 4. TPD profile of CO_2 from $La_{0.8}Sr_{0.2}CoO_3$ pre-evacuated at 800 °C. CO_2 adsorption; 500 °C → rt, 100 Torr (1 Torr ≈ 133.322 Pa).

of O_2 and CO_2 were estimated to be -0.3 and -0.6, respectively, for the results shown in Fig. 3. The CO_2 impact (1%) on the other Co- and Mn-containing perovskites, such as $La_{0.6}Sr_{0.4}CoO_3$, $La_{0.4}Sr_{0.6}Co_{0.8}Fe_{0.2}O_3$ and $La_{0.4}Sr_{0.6}Mn_{0.8}B'_{0.2}O_3$ (B′ = Mn, Fe, Co, Ni), were also investigated. $La_{0.8}Sr_{0.2}CoO_3$ was the most tolerant to the CO_2 inhibition, followed by $La_{0.4}Sr_{0.6}Mn_{0.8}Fe_{0.2}O_3$ and $La_{0.4}Sr_{0.6}Mn_{0.8}Co_{0.2}O_3$.

In order to study the origin of the inhibitory action of CO_2, TPD of CO_2 was measured for $La_{0.8}Sr_{0.2}CoO_3$ (Fig. 4). Apart from desorption below 500 °C, the desorption of strong adsorbed species was observed, with the desorption maximum at around 750 °C. It was reported that CO_2 adsorbed on La-based perovskites as carbonate species,[7] and in fact X-ray photoelectron spectroscopy showed the presence of carbonate carbon in C1s region on La-based perovskites which had been kept in an ambient atmosphere and subjected to the XPS measurement without any pretreatments. The presence of strongly adsorbed carbonate species should be related to the basicity of the oxides which originated from rare earth (La) and alkaline earth (Sr) metal ions. The desorption maximum at about 750 °C is enough to understand that the CO_2 impact at 800 °C is reversible.

As previously reported,[4,5] a pair of adjacent oxide ion vacancies serves as the active sites of the direct decomposition of NO on perovskites, and the inhibition of the activity by O_2 is related to the reaction mechanism (oxygen adsorption-desorption equilibrium). The CO_2 impact, on the other hand, is considered to have relation not to the mechanism but to the structure of the active sites. When CO_2 is adsorbed on the surface and interacts with surface oxide ion to form the carbonate species, such a surface carbonate species might hinder the access of NO molecules to the oxide ion vacancies on the surface. In more extreme case, the adsorption of CO_2 at elevated temperatures might modify the structure in the vicinity of the surface into, for example, carbonates of lanthanum and/or strontium and cobalt oxide. It is noted that Cu–ZSM-5 with an ion-exchange level of 100% also suffered the CO_2 inhibition; at 500 °C the conversion of NO into N_2 was 44.1% (0% CO_2) and 19.9% (1% CO_2). In this case, the deactivation might be caused not by the modification of the active sites (Cu ions) but by the competitive adsorption between NO and CO_2.

Experimental

Perovskite-type oxides used in this study were prepared at 850 °C with the same manner as already reported.[3–5] The specific surface area of $La_{0.8}Sr_{0.2}CoO_3$, which was mainly used in this study, was 4.6 $m^2\ g^{-1}$. The catalytic activity for NO decomposition was measured in a fixed-bed flow reactor by feeding a reaction gas, NO(0.9%)–CO_2(0–5%)–He(balance) over 1 g catalyst (W/F = 4.0 $g\ s\ cm^{-3}$). The gaseous composition was analyzed by a TCD-type gas chromatograph (Shimadzu GC-8A) with Molecular Sieve 5A (NO, N_2, O_2) and Porapak Q (N_2O) columns. Temperature programmed desorption (TPD) of CO_2 was carried out by heating a pretreated $La_{0.8}Sr_{0.2}CoO_3$ sample in a helium stream (30 $cm^2\ min^{-1}$) at a rate of 10 °C min^{-1}. The desorbed CO_2 was continuously monitored by a thermal conductivity detector; a quadrupole mass spectrometer (NEVA, TE-600) was occasionally used to identify the desorbed species. The adsorption of CO_2 was carried out by cooling the sample in a CO_2 atmosphere (13 kPa) from 500 °C to room temperature, following evacuation at 800 °C for 30 min. By the evacuation, oxygen thermally desorbed below 850 °C was mostly eliminated, and recording TPD chromatogram of CO_2 was made possible without interference of O_2 desorption.

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