

Dopant effects on crystal structure and NO decomposition activity of yttrium based mixed oxides

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論 文 名 : Dopant effects on crystal structure and NO decomposition activity of yttrium based mixed oxides (イットリウム系複合酸化物における添加物が結晶構造と NO の直接分解活性の向上に及ぼす影響)

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論 文 内 容 の 要 旨

The direct decomposition of nitrogen oxides (NO_x) is an ideal way to remove NO_x pollution created by chemical industries and automobiles. Although intense studies have been conducted for developing active NO decomposition catalysts, the activities under co-existing gases (O_2 , H_2O or CO_2) is still not high to the practical application level. Therefore, the key issue for NO direct decomposition is to find a catalyst that is active under practical used condition. In this thesis, we focused on two kinds of perovskite like yttrium-based oxides, $\text{Ba}_3\text{Y}_4\text{O}_9$ and SrY_2O_4 , for achieving high active catalysts for NO decomposition. Dopant effects in $\text{Ba}_3\text{Y}_4\text{O}_9$ on NO decomposition activity were studied systematically and it is found that metal doping is effective for increased stability and activity because of the increase in oxygen vacancy amount and removal of surface NO_x species. The content of each chapter is summarized as follows.

In chapter 1, the background and current state of the de NO_x process for exhaust gas from engines is reviewed. Moreover, the challenges of research in NO decomposition and research objectives of this study were presented.

In chapter 2, single metal doping effect on $\text{Ba}_3\text{Y}_4\text{O}_9$ was studied and it is found that 10 mol% Cu doped sample showed the highest NO decomposition activity. N_2 and O_2 yield of 81% and 93%, respectively was achieved at 700 °C. Cu doped $\text{Ba}_3\text{Y}_4\text{O}_9$ shows the high activity and stability under 1% O_2 co-feeding condition. Temperature programmed desorption (TPD) results indicated that doping with Cu increased the amount of surface oxygen vacancies and mobility of the lattice oxygen resulting in an increase of NO adsorption and the promotion of the removal of NO_x species. In-situ FT-IR measurement suggests that doping Cu was weakened the removal of NO_3^- species, thus promoting the decomposition of NO_3^- species at low temperatures, which resulted in high NO decomposition activity.

In chapter 3, the effects of Sc and Cu co-doping in $\text{Ba}_3\text{Y}_4\text{O}_9$ on NO decomposition were studied and it was found that Sc and Cu co-doping highly effective for increasing both catalytic activity and lattice stability of $\text{Ba}_3\text{Y}_4\text{O}_9$. Optimized catalyst, i.e. $\text{Ba}_3\text{Y}_3\text{Sc}_{0.6}\text{Cu}_{0.4}\text{O}_9$, showed the highest activity in NO decomposition with N_2 and O_2 yields of 90% and 99% respectively at 700 °C among the examined $\text{Ba}_3\text{Y}_4\text{O}_9$. The crystal structure of $\text{Ba}_3\text{Y}_4\text{O}_9$ was completely decomposed in the case of pristine or Cu doped one after NO decomposition under the co-existence of O_2 or H_2O . In contrast, Sc and Cu co-doped $\text{Ba}_3\text{Y}_4\text{O}_9$ showed almost no phase

change after reactions. The increased crystal phase stability means better regeneration of active sites, leading to further easier removal of surface adsorbed NO_2^- or NO_3^- species. As a result, it became clear that the co-doping of Cu and Sc in $\text{Ba}_3\text{Y}_4\text{O}_9$ is promising for high NO direct decomposition activity even under O_2 and H_2O coexistence atmosphere.

In chapter 4, to achieve high NO decomposition under CO_2 co-existence condition, effects of doping and loading were studied on SrY_2O_4 to NO decomposition. 5 mol% BaO loaded SrY_2O_4 showed the highest activity in NO decomposition with N_2 and O_2 yields of 66.2% and 54.2% respectively at 850 °C among the Y based oxide studied. BaO loaded catalyst shows the high activity and good stability under 1% O_2 or CO_2 co-feeding condition. TPD results revealed that BaO loading weakening NO, O_2 , and CO_2 adsorption. In particular, NO desorption amount at low temperatures was much increased by BaO loading and so loaded BaO might be formed nitrate species. For NO decomposition reaction, NO adsorption and desorption are the rate-determining steps and so positive effects of BaO loading can be assigned to an increased amount of NO.

Finally, the general conclusions of this thesis were summarized, and prospects for future development were proposed. Active sites such as oxygen vacancies play an important role during the NO decomposition process. The approaches of introducing oxygen vacancies, weakening oxygen adsorption strength, and moderate basic sites could lead to finding more active catalysts in the future.