



Account/Revue

Recent progress in catalytic NO decomposition

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ABSTRACT

Recent progress in catalytic direct NO decomposition is overviewed, focusing on metal oxide-based catalysts. Since the discovery of the Cu-ZSM-5 catalyst in the early 1990s, various kinds of catalytic materials such as perovskites, C-type cubic rare earth oxides, and alkaline earth based oxides have been reported to effectively catalyze direct NO decomposition. Although the activities of conventional catalysts are poor in the presence of coexisting O₂ and CO₂, some of the catalysts reviewed in this article possess significant tolerance toward these coexisting gases. The active sites for direct NO decomposition are different depending on the types of metal oxide-based catalysts. In the case of perovskite type oxides, oxide anion vacancies act as catalytically active sites on which NO molecules are adsorbed. C-type cubic rare earth oxides contain oxide anion vacancies with large cavity space, enabling easy access of NO molecules and their subsequent adsorption. Surface basic sites on alkaline earth based oxides participate in NO decomposition as active sites on which NO molecules are adsorbed as NO₂ species. The reaction mechanisms of direct NO decomposition are also discussed.

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1. Introduction

Because nitrogen oxides (NO_x), which are thermally formed by radical chain mechanisms proposed by Zeldovich at high temperatures above 1200 °C [1], emitted from combustion facilities are harmful to human health and the global environment, the removal of NO_x from exhaust gas is necessary. Catalysis plays an important role in reducing NO_x. For example, three-way catalysts (TWCs) have already been practically applied to the purification of exhaust gases emitted from gasoline-powered vehicles. TWCs can simultaneously reduce NO and oxidize CO and hydrocarbons at a theoretical air/fuel (A/F) ratio of around 14.6. Selective catalytic reduction of NO_x using urea or ammonia is a leading technology to reduce NO_x emission from diesel

exhaust. In this reaction, NO_x are efficiently reduced by ammonia in the presence of excess O₂.

On the other hand, direct NO decomposition (2NO → N₂ + O₂), which needs no reductants, is well known as the most desirable reaction for NO_x removal. Since the enthalpy of formation for NO is large and positive, ΔH_{f(298 K)}⁰ = 90.2 kJ mol⁻¹ [2,3], NO molecules are thermodynamically unstable and can be decomposed into N₂ and O₂. However, despite the thermodynamic instability, direct NO decomposition is a kinetically slow reaction because of its high activation energy (~335 kJ mol⁻¹) [2,3]. Therefore, the use of a catalyst is an effective strategy for NO decomposition to proceed, and the development of highly active catalysts still remains a challenging subject of study for the solution of NO_x problems.

Numerous studies have been performed so far on catalytic NO decomposition, and a wide variety of catalytic materials have been found, such as noble metals, metal oxides, and zeolites [4,5]. In this review article, we

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overview recent progress in catalytic NO decomposition especially focusing on metal oxide-based catalysts.

2. Historical perspective on catalytic NO decomposition

Direct NO decomposition with catalysts has been extensively studied since the first report in the beginning of the 20th century by Jellinek [6], who revealed that precious metals such as platinum and iridium can catalyze NO decomposition at temperatures as low as 670 °C. Research activities reported before the 1980's are summarized in a number of excellent reviews [3–5,7,8].

Most of the early studies were performed focusing on the kinetics of NO decomposition. For instance, Amirnazmi et al. [9] studied NO decomposition over Pt/Al₂O₃, and found that the kinetics follow the equation: $r = N k(\text{NO}) / [1 + \alpha K(\text{O}_2)]$, where k is a reaction rate constant, K is an adsorption equilibrium constant, and α is a conversion factor. This equation means that the reaction is a first order with respect to NO and oxygen inhibits the reaction. As for metal oxide catalysts, Winter [10] measured the NO decomposition rates on 40 metal oxides, and proposed that the NO decomposition rate is closely dependent on the rate of the O₂ desorption step. Boreskov [11] also measured the catalytic activities of the 4th-period transition metal oxides for various catalytic reactions including NO decomposition and CH₄ oxidation, and revealed a close correlation between the activity for NO decomposition and that for homonuclear exchange of oxygen isotopes. These findings suggest that an effective strategy for the development of highly active NO decomposition catalysts is to create catalytically active sites effectively promoting the O₂ desorption step.

Under these circumstances, Iwamoto et al. developed highly active copper ion exchanged Y zeolites (Cu–Y) [12], based on the finding that oxygen species adsorbed on Cu^{II} cations exchanged into zeolites can desorb at temperatures as low as 300 °C [13]. They also reported that excessively copper ion exchanged ZSM-5 zeolites (Cu-ZSM5) showed quite high NO decomposition activity in the temperature range of 350–600 °C [14]. According to their further studies [15–17], Cu⁺ ions in the zeolite produced at elevated temperatures act as catalytically active sites and NO decomposition proceeds via the formation of NO^{δ-} or (NO)₂^{δ-} species on Cu⁺ and the reversible redox cycle between Cu²⁺ and Cu⁺.

Since the discovery of the Cu-ZSM-5 catalyst, extensive studies have been performed to improve its NO decomposition activity [18–21]. For instance, Părvulescu et al. [22,23] reported that the addition of Sm into Cu-ZSM-5 promotes the O₂ desorption step along with the stabilization of the Cu^I–O–Cu^{II} redox sites, resulting in the enhancement of NO decomposition activity. Yahiro et al. [24] also investigated the effect of coexisting rare earth elements such as La, Ce, Pr, Nd, Sm, and Gd on the activity of Cu-ZSM-5. Among the rare earth elements, Sm and Gd were found to act as promoters for NO decomposition over Cu-ZSM-5. They attributed the promotional effect to the stabilization of Cu⁺ active sites to enhance NO adsorption.

In addition to Cu-ZSM-5 catalysts, metal oxides with weak metal–oxygen bonds, such as cobalt oxide [25–27], oxygen-deficient Sr–Fe oxides [28] and perovskite-type compounds [29–31], have been investigated. Fig. 1 shows a rough comparison of the relative catalytic activities reported so far [32]. It is of interest that the key components for direct NO decomposition are Cu and Co, the combination of which with other components would enhance NO decomposition activity. Although Cu-ZSM-5 is still the most active catalyst as can be seen in Fig. 1, some composite oxides such as perovskite show comparable activity in the high temperature region. Therefore, designing and controlling the catalytically active sites may lead to highly active NO decomposition catalysts because of infinite combinations of metal components for composite mixed oxides. In the next section, recent advances in metal oxide-based NO decomposition catalysts will be overviewed.

3. Advances in metal oxide-based NO decomposition catalysts

Many kinds of metal oxides have been reported to effectively catalyze direct NO decomposition. It is of interest that N₂ and O₂ are always formed at a steady state with an O₂/N₂ ratio of approximately unity. The formation of N₂O is almost negligible in NO decomposition over these metal oxide-based catalysts. Recent advances in four different types of metal oxide-based catalysts will be reviewed.

3.1. Perovskite-type oxides

Perovskite-type materials are the oxides having ABO₃ and/or A₂BO₄ structures shown in Fig. 2, where A is a large cation that is coordinated by twelve O²⁻ ions and B is a small cation located at the center of the octahedron. Perovskite-type oxides show good performance for direct NO decomposition, as reviewed by Zhu and Thomas [33], by Imanaka and Masui [34] and by Royer et al. [35]. Major

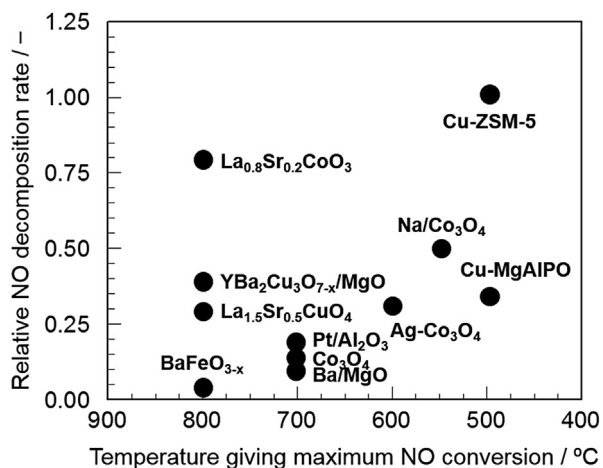


Fig. 1. Comparison of the activity of various catalysts reported so far for direct NO decomposition [32].

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