学 位 論 文 審 査 の 要 旨

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学 位 論 文 題 名

Development of catalysts and capture-reduction processes for N_2O abatement
（N_2O 除去に向けた分解触媒と捕集・還元プロセスの開発）

Nitrous oxide (N_2O) is a potent greenhouse gas, making its abatement a pressing environmental challenge. Thermal decomposition of N_2O offers a straightforward solution, yet this approach requires extremely high temperatures (ca. > 800 ° C). Currently, direct decomposition and reduction approaches are the mainstream abatement technologies with industrial applications. Between these, direct catalytic decomposition is particularly attractive owing to its efficiency and the absence of external reducing agents, which lowers operational costs and leakage risk. However, under realistic conditions, catalytic performance for direct N_2O decomposition suffers from severe deactivation in the presence of co-existing gases such as O_2. Although various materials have been explored for direct N_2O decomposition, sufficient activity is typically achieved at temperatures above 350 ° C, and highly active systems in the presence of O_2 often rely on costly Rh-based catalysts. These limitations motivate the development of more active and cost-effective catalytic systems for low-temperature N_2O removal.

Chapter 1 introduces the background of the study and outlines the objectives of this dissertation. It provides a broad overview highlighting the environmental impact of N_2O and O_2-induced deactivation in reported catalysts. The chapter also reviews current research on N_2O decomposition catalysts under O_2-containing conditions. This discussion highlights the remaining challenges in the field and motivates the research objectives of this thesis.

Chapter 2 presents machine learning (ML)-assisted development of high-performance catalysts for direct N_2O decomposition. ML has recently emerged as a powerful tool for accelerating catalyst discovery in heterogeneous catalysis. However, current approaches face two key limitations: (i) most ML studies are theory-driven, relying heavily on computational datasets such as those derived from density functional theory (DFT), which fail to capture the complexity of heterogeneous catalysis; and (ii) even ML–experiment combined studies are often restricted to narrow chemical spaces and include only one or a few closed-loop ML–experiment iterations, serving mainly as proof-of-

concept demonstrations. To address these challenges, Chapter 2 introduces a ML-assisted discovery strategy using experimentally measured performance under controlled conditions and extensive closed-loop ML–experiment iterations. Starting with an initial dataset of 51 catalysts, we performed 37 cycles of the closed-loop discovery system (ML prediction + experiment) and experimentally tested 633 catalysts. Among them, more than 10 catalysts were identified to exhibit higher activity (lower T_{20} value, the temperature required for 20% N_2O conversion during the light-off experiment) than the originally best catalyst, Rh(1)–Pd(2)/ZrO_2_RC-100 with a T_{20} value of 378 ° C. The composition of the best catalyst identified by this approach was Rh(1)–Pd(2)/ZrO_2_EP with a T_{20} value of 355 ° C.

Chapter 3 describes a continuous N_2O capture and reduction to N_2 using Ca-zeolite adsorbent and Pd/La/Al_2O_3 reduction catalyst. Despite the improvements afforded by ML-identified catalysts, achieving high N_2O conversion in complex exhaust-gas mixtures still requires temperatures above 300 ° C. Such high reaction temperatures not only consume large amounts of energy but also limit the applicability of these techniques. In Chapter 3, inspired by the chemical-looping strategy, we developed an N_2O capture and reduction system that uses CaO-incorporated zeolites (Ca-zeolites) as N_2O adsorbents and Pd nanoparticles on La-containing Al_2O_3 (Pd/La/Al_2O_3) as the reduction catalyst. This new process is suitable for continuous operation under temperature-swing cycling between 50 and 150 ° C. The N_2O capture capacity and subsequent reduction ability were maintained for at least 15 h (10 cycles). Notably, this process can be performed at low temperatures (below 150 ° C) via a simple temperature-swing operation in the presence of O_2.

Chapter 4 demonstrated the development of enhanced N_2O capture and reduction system and efficient adsorbents that work under O_2-CO_2-rich conditions. Although Ca-zeolite enables the effective N_2O capture in the presence of O_2, its performance was significantly impeded in the presence of CO_2 with the N_2O capture capacity reduced by over 90%. Moreover, selectively capturing N_2O in the presence of CO_2 remains challenging as N_2O and CO_2 share similar molecular size and physical properties. In Chapter 4, we investigated a series of materials to test N_2O adsorption and found that Cu oxides supported on CHA-type zeolite (Cu/CHA) is an efficient N_2O adsorbent in environments containing both O_2 and CO_2. Using the Cu/CHA adsorbent, we developed an N_2O capture and reduction system that could operate effectively in the presence of O_2 and CO_2 at low temperatures (below 150 ° C) for at least 12 h.

The final Chapter summarizes the important results. This work develops catalysts and capture–reduction processes for N_2O abatement by integrating catalyst design and process engineering. A closed-loop ML–based strategy enabled the discovery of highly active catalysts for direct N_2O decomposition and the roles of individual components in the ML-identified best catalyst were clarified. To address the high temperatures required under realistic exhaust conditions, a low-temperature N_2O capture and reduction system was developed using zeolite-based adsorbents and Pd/La/Al_2O_3 as the reduction catalyst. The system achieved stable N_2O capture and conversion under O_2-CO_2-rich conditions through a simple temperature-swing operation.

Thus, the author is qualified to receive the PhD degree in engineering, Hokkaido University.