学 位 論 文 審 査 の 要 旨

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学 位 論 文 題 名

In situ/operando spectroscopic studies on selective catalytic reduction mechanisms of NO and N_2O

（*In situ/operando* 分光法による NO と N_2O の選択還元の反応機構研究）

Meeting increasingly stringent NOx and N_2O emissions limits across on-road, stationary, and maritime sectors demands catalysts that remain active and selective under the hardest parts of real operation: cold starts and frequent transients in oxygen-rich, steam- and SO_x-containing feeds, where conventional selective catalytic reduction (SCR) formulations suffer slow light-off, parasitic NH_3 oxidation, and NOx slip. Progress is limited not only by materials gaps but also by diagnostic blind spots: the kinetically relevant surface species are short-lived, low-coverage, and phase-locked to cycling feeds, making them invisible to steady-state characterization.

This dissertation addresses both challenges by advancing an operando-first framework—modulation-excitation (ME) IR with phase-sensitive detection to isolate reactive manifolds from spectators; complementary UV–vis to resolve ligand-to-metal charge-transfer and charge transfer between metal indicative of redox states; and X-ray absorption spectroscopy to quantify valence and coordination dynamics—with time resolution matched to realistic perturbations and chemometric deconvolution to retrieve rates, phases, and sequences of intermediates. By coupling these measurements to microkinetic and DFT analyses, time-resolved fingerprints were converted into actionable design rules for SCR of NOx and N_2O abatement. This research gives detailed insight into the mechanisms of NOx-SCR and N_2O abatement and guides the rational design of novel catalysts.

Chapter 1 provides the general background and objectives of this thesis.

In Chapter 2, an O_3-assisted, unsteady-state De-NOx strategy on Cu-CHA to address cold-start windows is developed based on the combing results of *in situ/operando* FTIR and DFT. Density functional theory (DFT) calculations indicate that catalyst-free oxidation of NO by O_3 proceeds readily at room temperature, yielding NO_2 at an O_3/NO ratio of 0.5, whereas higher oxidant ratios (>0.5) favor the formation of N_2O_5 via pathways with very low activation barriers (≈2 kJ mol^{-1}). Complementary *in situ/operando* FTIR measurements show that exposing Cu-CHA to 0.16% NO + 0.08% O_3 at 100 ° C leads to efficient NOx storage as nitrate species bound to Cu^{2+} sites,

which subsequently react with NH_3 to generate N_2 and NH_4NO_3; above 200 ° C, the accumulated NH_4NO_3 further reacts with NO to produce N_2. NH_3 adsorbed on Cu-CHA is also oxidized by excess O_3 (0.7%), yielding N_2 and N_2O below 150 ° C with a characteristic N_2O/N_2 ratio of 0.75, whereas lower O_3 levels (0.08%) suppress both oxidation rates to <100 ppm. Moreover, oxidation of adsorbed NH_3 by NO + O_3 selectively forms N_2 at low temperature. These combined mechanistic insights provide a foundation for engineering unsteady-state lean deNOx strategies that exploit the controlled desorption and reaction of stored NOx with NH_3, or the reduction of NOx using captured NH_3 species.

During Chapter 3, I construct an integrated picture of the reduction half-cycle (RHC) / oxidation half-cycle (OHC) for NH_3–SCR on sulfate-modified CeO_2. Under the employed reaction conditions, SO_4^{2-} and $S_2O_7^{2-}$ are identified as the predominant surface sulfate species on the catalyst. Mechanistically, Ce^{4+}–(OH^-) ensembles, likely positioned in proximity to these sulfate groups, undergo reduction by NO and NH_3 to generate N_2 and H_2O while forming Ce^{3+} sites, establishing the reduction half-cycle. Modulation-excitation (ME) DRIFTS and XANES resolves this half-cycle as initiating with NO activation on Ce^{4+}–(OH^-) to produce an NO^+ intermediate, followed by Ce^{3+} formation and concomitant release of gaseous HONO. The transient HONO is rapidly trapped by NH_3, proceeding through NH_4NO_2 intermediates to yield N_2 and H_2O. The resulting Ce3+ species are subsequently reoxidized by O_2, thereby closing the oxidation half-cycle and completing a sulfate-tuned Ce^{4+}/Ce^{3+} redox loop that drives low-temperature NO reduction.

In Chapter 4, I elucidate CO-SCR of N_2O over Fe-β under excess O_2. Fe-exchanged ß zeolite (Fe0.9ß) exhibits high efficiency for the selective reduction of N_2O by CO even under O_2-rich conditions. Steady-state kinetics provide quantitative evidence that CO markedly accelerates N_2O reduction, and that N_2O reacts with CO substantially more readily than O_2 over Fe0.9ß. Reaction-order analysis further demonstrates that both CO and N_2O participate directly in the kinetically relevant elementary steps. *In situ/operando* UV–Vis and XAS collectively reveal a redox-driven catalytic cycle in which Fe(III)–αO species (likely Fe(III)–O^-) are reduced by CO to produce CO_2 and Fe(II), followed by preferential reoxidation of Fe(II) by N_2O to regenerate Fe(III)–αO. Spectro-kinetic quantification confirms that regeneration of Fe(III)–αO by N_2O proceeds faster than by O_2 on CO-reduced Fe0.9ß, providing a mechanistic basis for the observed selectivity toward CO + N_2O conversion while suppressing the competing CO oxidation pathway in excess O_2.

Chapter 5 is the general conclusion. This study extensively explores cross-cutting design rules for NOx and N_2O SCR catalysis. (1) For low temperature NH_3-SCR, transient capture-and-convert tactics (O_3-enabled NO oxidation) to preload reactive reservoirs on zeolites. (2) For N_2O SCR on Fe-zeolites, faster oxidation of Fe(II) species by the selective oxidants (N_2O) than the non-selective oxidant (O_2) is the key design concept. (3) For NH_3-SCR on CeO_2-based catalysts, acid–redox cooperativity and vacancy-stabilized anions (e.g., sulfate/ceria) to accelerate the RHC is the key design concept. These concepts are the fundamental guidance for the development of environmental catalysts, providing a mechanism-driven map for practical emission control.

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