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学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称 博士（工学） 氏名 DUOTIAN CHEN

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Machine-Learning-Assisted Development and Mechanistic Investigation of Multi-Elemental Reverse Water–Gas Shift Catalysts

(機械学習を活用した多元素逆水性ガスシフト触媒の開発および反応機構解明)

This thesis advances a machine-learning-guided strategy for the discovery and optimization of multi-element catalysts for the reverse water–gas shift (RWGS: $\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$), with mechanistic understanding established through kinetic analysis and targeted *in situ/operando* spectroscopy. The central objective is to accelerate catalyst development while maintaining interpretability and generalizability across complex composition spaces, where the combinatorial explosion of possible platinum-group metal (PGM)–additive–support combinations make conventional trial-and-error screening inefficient. In the context of CO_2 utilization, RWGS is a pivotal route to produce CO as a versatile C1 intermediate for downstream synthesis, yet practical implementation requires catalysts that deliver high CO selectivity, strong low-temperature activity, and sustained stability while minimizing PGM usage. To address these requirements, catalyst materials are represented using element-property descriptors (e.g., electronegativity, group number, and thermal conductivity), enabling models to learn structure–composition–performance relationships in a transferable descriptor domain rather than being confined to interpolation within specific training compositions. This representation supports rational extrapolation to previously untested elements and combinations, facilitating principled navigation of high-dimensional composition spaces and enabling catalyst design under realistic constraints on cost, element availability, and experimental throughput. Coupled with a closed-loop prediction–synthesis–testing workflow, the approach iteratively updates models with new experimental evidence and prioritizes candidates with high expected benefit, thereby improving both efficiency and robustness of discovery. Mechanistic insights are anchored to experimentally observable surface states and intermediates under reaction conditions, connecting data-driven predictions to physically meaningful catalytic roles and mechanistic hypotheses. Together, the proposed framework enables efficient exploration of large candidate spaces, provides quantitative guidance for experimental prioritization, and promotes knowledge extraction beyond mere performance ranking. As a result, it accelerates screening, clarifies the division of functions among PGMs, additives, and supports, and distills actionable design rules for low-temperature, CO-selective CO_2 -to-CO conversion under cost and precious-metal limitations.

Chapter 1 motivates the study in the context of rising anthropogenic CO_2 emissions, positions RWGS as a flexible C1 platform reaction for carbon utilization, and reviews recent progress in machine-learning-guided catalyst development. It highlights key challenges in catalysis modeling, including limited extrapolability, sparse and heterogeneous datasets, and the need for interpretability, and introduces the descriptor-based representation and closed-loop experimental strategy adopted throughout this thesis.

Chapter 2 demonstrates extrapolative discovery in a 3 wt.% PGM regime on TiO_2 . Starting from 45 initial samples and

iterating 44 closed-loop cycles to reach 300 compositions, the workflow identifies an unconventional additive set, Pt(3)/Rb(1)–Ba(1)–Mo(0.6)–Nb(0.2)/TiO₂_P25. The catalyst achieves 100% CO selectivity and sustained stability at 250 °C and 1 bar ($\approx$ 300 h on stream), while exhibiting enhanced low-temperature activity compared with baseline formulations. Kinetic analysis indicates that the apparent activation energy is reduced to $\sim$ 45.6 kJ·mol⁻¹, providing quantitative evidence that the model-guided search successfully extrapolates to previously untested elements and multi-element combinations.

Chapter 3 elucidates the reaction mechanism of Pt(3)/Rb(1)–Ba(1)–Mo(0.6)–Nb(0.2)/TiO₂_P25 by integrating kinetics with *in situ/operando* spectroscopy. CO adsorption IR and CO₂-TPD, together with kinetic metrics, indicate improved CO tolerance and enhanced CO₂ activation in the presence of the multi-additive ensemble. *Operando* XAS and AP-XPS track reversible Mo redox behavior under alternating CO₂/H₂ environments, while *operando* IR identifies carbonate/formate-related intermediates, supporting a cooperative mechanism: Mo provides redox functionality, Rb/Ba contribute basic sites to facilitate CO₂ activation, and Nb electronically tunes Pt to mitigate CO poisoning and stabilize active states.

Chapter 4 transfers the derived design rules to $\leq$ 1 wt.% PGM catalysts by jointly optimizing PGMs, additives, and supports across 35 closed-loop iterations (470 compositions). A low-PGM formulation, Pt(0.8)–Ru(0.1)–Pd(0.1)/Mo(0.8)–Ba(1)–Re(1)–Ho(1)–Na(0.4)/TiO₂_STR100N, outperforms the 3 wt.% benchmark in both absolute activity and PGM-normalized performance while maintaining 100% CO selectivity. Statistical analyses identify Mo and Re as influential additives, Pt as a favorable PGM choice under the examined conditions, and reveal a pronounced support effect favoring TiO₂_STR100N in the low-PGM regime, thereby strengthening the generality of the proposed catalyst design principles.

Chapter 5 summarizes the main contributions and provides an outlook toward practical deployment. It emphasizes how multi-element cooperation among PGMs, additives, and supports can be leveraged to achieve low-temperature, CO-selective RWGS, and discusses future opportunities such as expanding operating-condition coverage, improving uncertainty-aware active learning, and integrating *operando*-derived information into data-efficient modeling to further enhance discovery efficiency and mechanistic insight.