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博士の専攻分野の名称 博士（工学） 氏名 DU PENGFEI

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学 位 論 文 題 名

Development of high-performance catalysts for EtOH synthesis via CO₂ hydrogenation and
syngas conversion

(CO₂水素化と合成ガス変換によるEtOH合成触媒の開発)

Ethanol is used as a fuel additive and as a solvent or starting reagent in many chemical products. Due to the widespread demand for ethanol across various sectors, the global ethanol market is projected to grow rapidly at a rate of 5.6%. Currently, bioethanol is the primary source of ethanol used in industry and is a leading renewable biofuel, produced primarily from agricultural sources such as potatoes, lignocellulosic biomass, and corn starch. Although some progress has been made in coal-to-ethanol processes, the exploration of more efficient catalytic methods—such as syngas (CO+H₂) conversion and CO₂ hydrogenation remains crucial. Of particular interest is the hydrogenation of CO₂ to ethanol, which not only mitigates CO₂ emissions but also offers a renewable fuel and valuable chemical feedstock. This research aims to develop high-performance catalysts for ethanol synthesis through CO₂ hydrogenation and syngas conversion.

Chapter 1 outlines the scope and objectives of this work. Chapter 2 presents an efficient catalyst, K–Fe–Cu–Zn/ZrO₂ (KFeCuZn/ZrO₂), which enhances the EtOH space time yield (STY_{EtOH}) to 5.4 mmol g_{cat}⁻¹ h⁻¹, under optimized conditions (360 °C, 4 MPa, and 12 L g_{cat}⁻¹ h⁻¹). *In situ/operando* spectroscopic techniques and various characterizations revealed the essential roles of K and Fe in EtOH synthesis. The introduction of Cu accelerated the formation of CH₃CH₂O*, which is an important intermediate in EtOH production. Additionally, Zn inhibited EtOH decomposition, thereby improving the efficiency of EtOH synthesis.

Despite the promising performance of KFeCuZn/ZrO₂, it falls short of industrial requirements, necessitating the development of more advanced catalysts. Chapter 3 shows a machine learning (ML) approach to accelerate catalyst discovery. Starting with an initial dataset of 58 catalysts (274 data points), 24 iterations (ML predictions and experimental validation) were conducted, resulting in the evaluation of 555 catalysts (2477 data points). This ML-based strategy led to the discovery of a Pd(0.8)–Au(0.3)/K(2.5)–Sr(1)–Fe(20)–Zn(4)–Cd(2)–Yb(1)–Re(1)/CeO₂(25%)–ZrO₂ catalyst with the highest STY_{EtOH} of 8.2 mmol g_{cat}⁻¹ h⁻¹. More than 70 highly active catalysts were identified through this data-driven approach, and detailed

characterizations were performed to clarify the specific contributions of each component.

In Chapter 4, syngas conversion to ethanol was explored as an alternative synthesis pathway. A $\text{RhO}_x/\text{Li}_2\text{O}/\text{MgO}$ catalyst demonstrated excellent performance, achieving 20% ethanol selectivity and an STY_{EtOH} of $12.2 \text{ mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$ with a CO conversion rate of 35%. This catalyst outperformed other Rh-based catalytic systems. Characterizations and theoretical studies highlighted the significance of Li_2O –Rh interactions on the MgO surface in modulating CO adsorption, which is critical for ethanol production. Chapter 5 is a general conclusion. This study extensively explored highly efficient catalysts for ethanol synthesis via CO_2 hydrogenation and syngas conversion. This not only advances the understanding of catalytic mechanisms but also provides a catalyst design guideline for the development of novel catalysts to produce value-added chemicals from low-cost and renewable feedstocks.

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