学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Development of high-performance catalysts for EtOH synthesis via CO_2 hydrogenation and syngas conversion

（CO_2 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 ($CO+H_2$) conversion and CO_2 hydrogenation remains crucial. Of particular interest is the hydrogenation of CO_2 to ethanol, which not only mitigates CO_2 emissions but also offers a renewable fuel and valuable chemical feedstock. This research aims to develop high-performance catalysts for ethanol synthesis through CO_2 hydrogenation and syngas conversion.

Chapter 1 outlines the scope and objectives of this work. Chapter 2 presents an efficient catalyst, K–Fe–Cu–Zn/ZrO_2 (KFeCuZn/ZrO_2), 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 $CH_3CH_2O^*$, 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/ZrO_2, 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 effort 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)/CeO_2(25%)-ZrO_2 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 RhO_x/Li_2O/MgO catalyst demonstrated excellent performance, achieving 20% ethanol selectivity and an STY_{EtOH} of 12.2 mmol g_{cat}^{-1} 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 guidline for the development of novel catalysts to produce value-added chemicals from low-cost and reneable feedstocks.