学 位 論 文 審 査 の 要 旨

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学 位 論 文 題 名

Development of high-performance catalysts for low temperature CO_2 hydrogenation to methanol

（低温におけるCO_2水素化によるメタノール合成に有効な固体触媒の開発）

Methanol is widely used as a fuel, solvent, and key feedstock for the production of numerous industrially important chemicals such as formaldehyde, acetic acid, and olefins. Owing to its versatility and increasing demand in various industries, the global methanol market is expected to experience steady growth at a rate of around 4-5% annually. Currently, methanol is mainly produced from fossil-based feedstocks via syngas ($CO + H_2$) conversion. However, with the growing demand for carbon neutrality, sustainable methanol production routes, particularly through carbon dioxide (CO_2) hydrogenation, are attracting widespread attention. This process not only reduces CO_2 emission but also enables the sustainable production of fuels and chemicals. Industrial-scale methanol production via direct CO_2 hydrogenation has been accomplished using copper-based catalysts under severe reaction conditions (5-10 MPa; >220 ° C). Despite this success, the process is limited by the low equilibrium conversion of CO_2 to methanol, needing extensive recycling of the effluent stream after product separation. Operating at lower temperatures presents clear advantages, such as the potential for higher CO_2 conversion and reduced operating costs. However, achieving efficient methanol synthesis under such mild conditions (<180 ° C) remains a major challenge. Although the reaction is exothermic in nature, the intrinsic inertness of CO_2 poses a barrier for its hydrogenation below 200 ° C, resulting in poor methanol productivity. Therefore, developing highly active catalysts capable of promoting CO_2 hydrogenation to methanol at low temperatures is essential. The present research focuses on developing high-performance catalysts for efficient methanol synthesis through CO_2 hydrogenation under low-temperature conditions.

Chapter 1 presents the background of the study and outlines the objectives of this dissertation. It provides a broad overview highlighting the importance of methanol and its production via CO_2 hydrogenation using heterogeneous catalysts, along with relevant thermodynamic considerations. The chapter also reviews current research on catalyst design for CO_2 hydrogenation to methanol. This discussion leads to the identification of the existing challenges in the field and the formulation of the research objectives of this thesis.

Chapter 2 describes the development of highly active catalysts for low temperature CO_2 hydrogenation to

methanol using machine learning (ML) approach in batch reactors. Starting with an initial dataset containing 80 catalysts, a total of 580 distinct catalysts were screened over 43 iterations (ML predictions combined with experimental validation in batch reactors), leading to the identification of 33 catalysts that outperformed the previously reported highly active Pt(3)/Mo(20)/TiO_2 catalyst. The best-performing catalyst, Pt(5)/Mo(8)–Re(1)–W(0.7)/TiO_2, achieved a high methanol production rate of 1.46 mmol g^{-1} h^{-1} (at 150 ° C) in a batch reactor and an even higher rate of 1.8 mmol g^{-1} h^{-1} in a flow reactor (150 ° C, 4 MPa, 8 L g_{cat}^{-1} h^{-1} and H_2/CO_2 = 3). *In situ/operando* spectroscopic analyses were conducted to elucidate the roles of individual catalyst components during methanol synthesis. The detailed investigation revealed that Pt facilitated H_2 dissociation, partially reduced Mo oxides were responsible for forming oxygenated intermediates, acidic W sites enhanced methanol desorption from the catalyst surface, and Re promoted the conversion of formate to methanol, thereby accelerating the overall methanol formation process.

Chapter 3 presents the development of Nb promoted Pt/MoOx/TiO_2 catalysts for low-temperature CO_2 hydrogenation to methanol in flow system. Chapter 1 revealed the importance of additive oxides to promote the methanol productivity in batch reactors. In particular, the incorporation of elements such as Nb, Yb, V, and Zr to the Pt/MoOx/TiO_2 system proved to be effective. However, to achieve practical applicability, it remains essential to develop efficient catalyst systems for high methanol productivity in flow system and to conduct a systematic investigation into the promotional effects of these additives. Out of the additives selected, Nb promoted Pt(5)/Mo(10)–Nb(1)/TiO_2 showed the best optimized methanol formation rate of 3.8 mmol g_{cat}^{-1} h^{-1} at 150 ° C. *In situ/operando* spectroscopic analyses revealed that Pt predominantly facilitated H_2 dissociation, while partially reduced MoO_x species contributed to oxygenate formation. Notably, the incorporation of highly dispersed Nb species enhanced the desorption of methanol and suppressed its decomposition. Moreover, Nb helped in the mitigation of CO poisoning of Pt by making it more electron deficient via electronic charge transfer process.

In Chapter 4, I developed more efficient catalysts by using ML prediction and experimental validation in a flow system. Using ML prediction and human intuition, many catalysts were developed with higher methanol formation rate than previously highly active catalysts. Pt(5)/Mo(8)–Cr(0.7)–V(0.7)–La(0.7)–Re(1)/TiO_2 was obtained as the best catalyst with a methanol formation rate of 6.5 mmol g_{cat}^{-1} h^{-1}. The performance of this catalyst was one of the best ever reported at low-temperatures (<180 ° C). Detailed characterizations supported the role Pt and partially reduced MoO_x as discussed in the previous chapters. Re helped in the conversion of formate to methoxy while La promoted CO_2 activation. Cr was helpful for the stabilization of intermediates while V promoted facile desorption of methanol from the catalyst surface.

The final Chapter summarizes the important results. This dissertation has explored the development of highly efficient heterogeneous catalysts for methanol synthesis from CO_2 hydrogenation under low-temperature conditions. Starting with ML guided study in batch reactors, ultimately highly active catalysts for flow system were developed. While the ML studies provided general guidelines for catalyst design, extensive characterizations and *in situ/operando* spectroscopic analyses were carried out to understand the structure of active sites and mechanism. This not only enhanced the understanding of the structure-activity relationships but also provided guidance for catalyst design to develop new catalysts for producing high-value chemicals from renewable raw materials.

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