論文 / 著書情報
Article / Book Information

題目(和文)	温和な条件下でのメタノール合成に向けた触媒探索
Title(English)	Search for Catalysts toward Methanol Synthesis at Mild conditions
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Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

（博士課程）
Doctoral Program

論 文 要 旨

THESIS SUMMARY

系・コース： Department of, Graduate major in	材料 系 材料 コース	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of （ 工学 ）
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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

Methanol is mainly used as a raw material for C1 chemistry and as a fuel additive. Recently it also attracts much attention as an energy carrier. Methanol is synthesized by two routes: CO ($CO + 2H_2 \rightarrow CH_3OH$, $\Delta H_{298K} = -90.4$ kJ mol^{-1}) or CO_2 hydrogenation ($CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$, $\Delta H_{298K} = -49.4$ kJ mol^{-1}). Although Cu/ZnO/Al_2O_3 is known to be a highly active catalyst for both reactions, activation of CO and CO_2 at low temperatures is difficult on this catalyst, and therefore requires high temperature and pressure conditions (200 -300 °C, 5-10 MPa). Therefore, it is desirable to develop catalysts that can operate under milder conditions (especially at low temperatures) from the viewpoint of energy savings and the downsizing of plants for on-site methanol synthesis. In this thesis, catalyst candidates for low-temperature methanol synthesis are explored based on two approaches (1. Utilization of catalyst support with electron donating property and hydride ions and 2. Exploration of novel materials). The contents in this thesis are listed below:

Chapter 1: The research background of low-temperature methanol synthesis, the objective of this thesis, and approaches to achieve it were outlined.

Chapter 2: Low-temperature methanol synthesis from CO using Cu-loaded rare-earth hydride (Cu/REH_{2+x}, *RE*=La, Ce, and Y) catalysts was performed and the promotion effect of hydride supports in methanol synthesis reaction was investigated. REH_{2+x} supports clearly enhanced catalytic activity and enabled methanol synthesis at low temperatures below 100°C, where conventional Cu catalysts don't work. The TOF was enhanced by ~20-fold over the Cu/REH_{2+x} catalyst, and the apparent activation energy was reduced to less than half that of that for conventional Cu catalysts. Efficient electron donation from electronically active support to loaded Cu, and lattice H^- ions accelerate the hydrogenation of CO with much lower activation energy. Therefore, these two factors may be regarded as essential for this low-temperature methanol synthesis. These results provided guidelines for the development of catalysts for methanol synthesis under mild conditions.

Chapter 3: Electronic promotion in CO hydrogenation to methanol over Cu-loaded ZnO system by using ZSO as a support, whose electronic properties (work function and carrier concentration) can be tuned continuously by its composition. By using the thermal plasma method, biphasic nanoparticles consisting of crystalline ZnO:Si nanoparticles embedded in the amorphous phase were obtained. ZSO nanoparticles with the Zn-rich composition ($x \leq 0.25$) achieve both a low work function (ca. 3.5 eV) and high carrier concentration, and these unique electronic properties enhanced methanol synthesis activity with lower activation energy (70 kJ mol^{-1}) compared with the Cu/ZnO catalyst (111 kJ mol^{-1}).

On the other hand, Si-rich ZSO ($x \geq 0.50$) with a low work function but low carrier concentration exhibited no promotion effect. These results indicate that not only a low work function but also a high carrier concentration (metallic nature) of the support material are important for effective electron donation from the support to the metal.

Chapter 4: hcp-PdMo intermetallic compound (h-PdMo) stabilized by a small amount of anions was discovered through the synthesis of Pd_2Mo_3N. And its catalytic performance for CO hydrogenation to methanol was investigated. The h-PdMo catalyst can be prepared *via* the facile ammonolysis of an oxide precursor and the catalyst exhibits long-term stability in air. These features are favorable for the practical use of the catalyst. For low-temperature CO hydrogenation to methanol, the h-PdMo/Mo_2N catalyst exhibited significantly improved catalytic activity, with activation energy less than half that of the Pd/Mo_2N catalyst. Furthermore, methanol synthesis activity was enhanced more than 15-fold over the h-PdMo/Mo_2N catalyst compared to an industrial catalyst, Cu/ZnO/Al_2O_3.

Chapter 5: h-PdMo catalyst was applied to CO_2 hydrogenation to methanol, and its catalytic performance and reaction mechanism were investigated. As a result, h-PdMo catalyst showed excellent low-temperature activity for CO_2 hydrogenation to methanol as well as CO hydrogenation, and achieved continuous room-temperature methanol synthesis. The h-PdMo catalyst had a TOF of 0.15 h^{-1} at 0.9 MPa and 25 °C, which is comparable to or higher than that of the state-of-the-art catalysts under higher pressure conditions (4-5 MPa). From the results of kinetic analysis, it was revealed that CO_2 hydrogenation to methanol over the h-PdMo catalyst, proceeds by CO hydrogenation following the RWGS reaction. This finding provides a novel catalyst candidate for low-temperature methanol synthesis and CO_2 conversion process.

Chapter 6: The major conclusion of each chapter is summarized, and future prospect is described.