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学 位 論 文 題 名

Developing a Highly Efficient Multimetallic Catalyst for CO₂-assisted oxidative dehydrogenation
and dry reforming of propane

(CO₂ によるプロパンの酸化脱水素および改質反応に有効な多元合金触媒の開発)

CO₂-assisted conversion of hydrocarbons has attracted increasing attention due to the high suitability for carbon neutralization. However, achieving high catalytic activity, selectivity, and stability based on the conventional catalyst design concept remains highly challenging. In this thesis, two novel catalyst design concepts have been developed for this challenge: (i) pseudo-binary alloy, where one constituent metal of binary intermetallic A_mB_n is partially replaced with a third metal A' to form (A_{1-x}A'_x)_mB_n, and (ii) high-entropy intermetallic (HEI), which is a multi-metallic alloy having five or more elements and specific crystal structure is derived from the parent binary intermetallic, namely an expansion of (i) to a multinary system .

Chapter 2 showed that Pt–Co–In ternary alloy on CeO₂ exhibited a highly efficient catalyst for CO₂-ODP. Both the C₃H₈ dehydrogenation and CO₂ reduction smoothly proceed on the Pt–Co active site to form 2H and O, as well as the main products: C₃H₆ and CO. Alloying with In enhances the C₃H₆ selectivity due to the ensemble effect and decreases the amount of coke that accumulates on the catalyst surface. The doped Co improves the adsorption strengths of the C and H species, which promotes the activation of C₃H₈ and CO₂. The O atoms oxidize the eliminated H to form H₂O or combust coke on the alloy surface or neighboring CeO₂ sites. Moreover, CeO₂ can facilitate coke combustion via a Mars-van Krevelen-type mechanism, which significantly enhances the coke resistance and catalyst stability. Pt–Co–In/CeO₂ exhibits outstanding catalytic activity, C₃H₆ selectivity, long-term stability, and CO₂ utilization efficiency, all of which are greater than typical values ever reported. In **Chapter 3**, I further designed and prepared a PtSn-based HEIs catalyst for higher coke resistant and thermal stability than those of Pt–Co–In/CeO₂. I focused on intermetallic PtSn and its Pt and Sn sites were partially substituted with Ni/Co and In/Ga, resulting in nanoparticles with a HEI structure of (PtCoNi)(SnInGa). The multi-metallization sufficiently isolates Pt atoms, preventing propylene decomposition and coke formation. The incorporation of Ni and Co significantly enhanced the ability to activate CO₂. Doping In(Ga) into the Sn site improved catalyst stability, probably due to the enhanced entropy effect. The combination of these abilities significantly enhances coke resistance and catalyst lifetime. Furthermore, because of the increased thermal stability, multi-metallization also prevents nanoparticle

sintering. The HEI/CeO_2 catalyst shows much greater catalyst life and specific activity than Pt-Co-In/CeO_2 . In **Chapter 4**, I further applied the Pt-Co-In ternary alloy system to dry reforming of propane (DRP), which has attracted much attention as a syngas production technology for liquid fuels with a low H_2/CO ratio. The $\text{PtCo}_2\text{In}_3/\text{CeO}_2$ for the DRP reaction with high selectivity and stability even over 100 h. The results show that the catalytic behavior of these catalysts is highly sensitive to the amount of cobalt doping. By controlling the amount of cobalt doping, the catalytic activity of $\text{PtCo}_2\text{In}_3/\text{CeO}_2$ catalysts can be improved, and the C-H/C-C bond of propane can be selectively cleaved in the presence of CO_2 .

In summary, the study in this thesis not only provides excellent catalytic performances in conversion of light alkane and CO_2 , but also opens a new window for the design of multi-metallic catalysts for challenging molecular conversions.

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