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学 位 論 文 審 査 の 要 旨

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Development of Multimetallic Alloy Catalysts Efficient for CO₂ utilization by Dry Reforming of Hydrocarbons
(炭化水素のドライリフォーミングによる CO₂ 利用に有効な多元素合金触媒の開発)

Reforming reactions may have one of greatest commercial potentials among many CO₂ conversion routes. However, it still has many challenges for the catalysts design such as carbon deposition and metal sintering. Therefore, developing a catalyst with high reactant activity, excellent stability and sintering resistance for CO₂ reforming of hydrocarbons is essential. To meet these requirements, the modification of structure and active sites by alloying is very promising.

Chapter 2 presents a novel catalyst design based on a pseudo-binary alloy structure, (Ni_{0.5}Co_{0.5})₃Ge/SiO₂, in which a part of Ni atoms of intermetallic Ni₃Ge was substituted with Co without changing the parent Ni₃Ge structure, as evidenced by the combination of HAADF-STEM-EDX, XRD, and XAFS analyses. (Ni_{0.5}Co_{0.5})₃Ge/SiO₂ exhibited a remarkably high coke resistance, an outstandingly long catalyst life (1000 h) at 700 °C even below the equilibrium conversion. Additionally, the used catalyst could be easily regenerated by a simple and soft oxidation procedure and the initial conversion in the second run was completely recovered in the third run. Alloying Ni with Ge not only inhibits carbon formation, but also promotes CO formation via the CHO intermediate pathway that involves no carbon formation. The dopant Co acts as an efficient site for CO₂ adsorption and activation, which supplies more oxygen atoms to promote carbon combustion. The combination of Ge and Co allows to minimize the coke accumulation, thus achieving outstandingly high stability for long-term operation. Therefore, (Ni_{0.5}Co_{0.5})₃Ge/SiO₂ catalyst showed a sufficiently high catalytic activity, coke resistance, and renewability in CO₂ reforming of methane reaction.

Chapter 3 summarizes a binary intermetallic Ni₃Ga supported on CeO₂ works as an effective catalyst for CO₂-assisted dry reforming of benzene (DRB: C₆H₆ + 6CO₂ → 3H₂ + 12CO). The combination of HAADF-STEM-EDX and XAFS analyses confirmed the formation of the Ni₃Ga intermetallic structure. The CO₂ conversion of Ni₃Ga/CeO₂ catalyst was two-fold that of the corresponding monometallic catalyst, which might be attributed to the synergetic effect of higher CO₂ adsorption or activation of Ni–Ga alloy and CeO₂ support. Moreover, Ga plays a crucial role in improving catalytic activity and minimizing coke formation. Therefore, the Ni₃Ga/CeO₂ catalyst exhibited significantly enhanced CO₂ utilization ability and product yield.

In summary, the activity and stability in conversion of CO₂ and hydrocarbons were drastically enhanced based on the delicate design of catalysts structure and modification of active sites by alloying. The findings of this study provide a new perspective to prolong Ni-based catalysts lifespan and advancing the development of CO₂ dry reforming of hydrocarbons.

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