学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Development of Multimetallic Alloy Catalysts Efficient for CO_2 Utilization by Dry Reforming of Hydrocarbons

（炭化水素のドライリフォーミングによる CO_2 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 CO_2 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 CO_2 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, $(Ni_{0.5}Co_{0.5})_3Ge/SiO_2$, in which a part of Ni atoms of intermetallic Ni_3Ge was substituted with Co without changing the parent Ni_3Ge structure, as evidenced by the combination of high-angle annular dark-field-scanning transmission electron microscopy-energy-dispersive system, X-ray diffraction, and X-ray absorption fine-structure analysis. $(Ni_{0.5}Co_{0.5})_3Ge/SiO_2$ 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 CO_2 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, $(Ni_{0.5}Co_{0.5})_3Ge/SiO_2$ catalyst showed a sufficiently high catalytic activity, coke resistance, and renewability in CO_2 reforming of methane reaction. **Chapter 3** summarizes a binary intermetallic Ni_3Ga supported on CeO_2 works as an effective catalyst for CO_2-assisted dry reforming of benzene (DRB: $C_6H_6 + 6CO_2 \rightarrow 3H_2 + 12CO$). The combination of high-angle annular dark-field scanning transmission microscopy and X-ray absorption fine structure analysis confirmed the formation of the Ni_3Ga intermetallic structure. The CO_2 conversion of Ni_3Ga/CeO_2 catalyst was two-fold that of the corresponding monometallic catalyst, which might be attributed to the synergetic effect of higher CO_2 adsorption or activation of Ni–Ga alloy and CeO_2 support. Moreover, Ga plays a crucial role in improving catalytic activity and minimizing coke formation. Therefore, the Ni_3Ga/CeO_2 catalyst exhibited significantly enhanced CO_2 utilization ability and product yield.

In summary, the activity and stability in conversion of CO_2 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 CO_2 dry reforming of hydrocarbons.