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学 位 論 文 審 査 の 要 旨

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学 位 論 文 題 名

Development of Highly Efficient Multimetallic Alloy Catalysts for Alkane Dehydrogenation (アルカン脱水素に有効な多元素合金触媒の開発)

Alkane dehydrogenation is an important molecular transformation in various applications. However, due to its endothermicity, alkane dehydrogenation requires high temperatures to obtain sufficient alkene yield, in which severe catalyst deactivation by coking and/or sintering inevitably occurs in short periods. In this context, developing an innovative dehydrogenation catalyst that exhibits outstanding catalytic performance at high operation temperatures is incredibly beneficial. In this thesis, two approaches have been explored using intermetallic compounds as starting materials, i.e., (i) multimetallization (pseudo-binary alloys and high-entropy intermetallics (HEIs)), (ii) surface modification (geometric and electronic decorations).

Chapter 2 shows that the $\text{Pt}_3(\text{Fe}_{0.75}\text{Zn}_{0.25})$ pseudo binary alloys exhibited an outstanding catalytic performance in the dehydrogenation of methylcyclohexane (MCH), which is an emerging topic and a promising platform for the hydrogen production/carriage application. The partial substitution of Fe in Pt_3Fe by Zn, which showed a high catalytic performance among a series of Pt-based intermetallics, with a third metal was applied to form the pseudo-binary alloys. The $\text{Pt}_3(\text{Fe}_{0.75}\text{Zn}_{0.25})$ catalyst exhibited an outstandingly high catalytic performance. The mechanistic study revealed that the Fe enhanced decoking ability and Zn promoted toluene desorption. In **Chapter 3**, the surface modification of PtGa intermetallic using Pb was applied to serve only isolated Pt sites as active sites for propane dehydrogenation (PDH), which has attracted tremendous interest as a strategy for satisfying the growing global demand for propylene. PtGa displays three-fold-Pt ensembles and isolated Pt atom at the surface, the former of which can be selectively blocked and disabled by Pb deposition. The isolated Pt effectively inhibited the side reactions and drastically improved the stability. In **Chapter 4**, the author further modified the PtGa–Pb catalyst via dispersing Ca species which affords an electron-enriched isolated Pt site, around the nanoparticles. PtGa–Ca–Pb exhibited almost no deactivation for up to one month for the first time. In **Chapter 5**, another approach to isolate the Pt atoms was explored, namely, HEIs. The Pt isolated by the inert metals in HEI exhibited an outstandingly high catalytic stability, even at 600°C, for the first time, almost no deactivation of the catalyst was observed for two months. Detailed mechanic study demonstrated that the site-isolation drastically enhanced the desorption of propylene, eventually suppressing the further C–H scission from generated propylene, and entropy effects enhanced the thermal stability, suppressing nanoparticle aggregation.

In summary, the author has successfully developed the innovative alloy catalysts for the dehydrogenation of alkanes. The insights obtained in the thesis provide direction for the development of truly efficient catalysts for alkane dehydrogenation and other challenging reactions.

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