学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称　　博士（工学）　　氏名　Ma Jiamin 馬 嘉敏

学 位 論 文 題 名

Development of Highly Efficient Catalysts for Acetylene Semi-hydrogenation Based on Multinary Non-Noble Alloys

（アセチレン部分水素化に有効な卑金属多元素合金触媒の開発）

The development of efficient non-noble metal-based catalysts to be alternative of noble metal for acetylene semihydrogenation has attracted much attention recently. However, there are challenges in obtaining high activity, selectivity and stability based on the conventional metal catalysts. To address this issue, structure manipulation was revealed on (1) high-entropy intermetallics (HEIs), a multi-metallic alloy with five or more elements with specific crystal structure derived from the parent binary intermetallic; (2) pseudo-binary alloy, a ternary alloy described as $(A_{1-x}A'_x)_mB_n$, where a part of active metal A is substituted by a similar third element A'; (3) the introduction of light elements into alloy; (4) metal oxides.

Chapter 2 presented a novel catalyst design based on high-entropy intermetallics (HEI), which provide thermally stable isolated Ni without excess counterpart metals and achieve exceptionally high performance. Intermetallic NiGa was multi-metalized to a (NiFeCu)(GaGe), where the Ni and Ga sites were partially substituted with Fe/Cu and Ge, respectively, without altering the parent CsCl-type structure. The NiFeCuGaGe/SiO_2 HEI catalyst completely inhibited ethylene overhydrogenation even at complete acetylene conversion and exhibited five-times higher activity than other 3d-transition-metal-based catalysts. The significant improvement of catalytic activity is assigned to the lower energy barrier of acetylene hydrogenation and facilitated the adsorption/activation of hydrogen. The drastic enhancement of ethylene selectivity can be attributed to the reduction in the surface energy of the most stable (110) plane resulting from surface relaxation, which remarkably promoted ethylene desorption. The role of multi-metallization on the enhancement was attributed to geometric effects but not to an electronic effect. In **Chapter 3**, I further designed a pseudo-binary alloy which was highly active, selective, and durable at low temperature. A series of $(Ni_{1-x}Cu_x)_3Ga/TiO_2$ catalysts exhibiting $L1_2$-type pseudo-binary alloy structures with various Cu contents (x = 0.2, 0.25, 0.33, 0.5, 0.6, and 0.75) were prepared for active site tuning. The optimal catalyst, $(Ni_{0.8}Cu_{0.2})_3Ga/TiO_2$, exhibited outstandingly high catalytic activity among the reported 3d transition metal-based systems and excellent ethylene selectivity (96%) and long-term stability (100 h) with near full conversion even at 150°C. A mechanistic study revealed that Ni_2Cu hollow sites on the (111) significantly destabilized the multifold coordination of adsorbates, such as 3-

fold vinyl, thereby lowering the energy barrier of acetylene hydrogenation. This destabilization also weakened the strong adsorption of acetylene, which (1) further accelerated the hydrogenation process by increasing hydrogen coverage and (2) improved ethylene selectivity by suppressing the direct hydrogenation pathway via the ethylidene intermediate. Thus, acetylene semihydrogenation at low temperatures can be performed using Ni-based materials. In **Chapter 4**, the catalytic activity was further enhanced on the silica-decoration Ni-Zn alloy without lowering its selectivity. Ni–Zn alloy nanoparticles on SiO_2 were further decorated by additional silica, which significantly increased the acetylene conversion (15%–97%) without decreasing the ethylene selectivity (ca. 80%) at 200°C under a remarkably high GHSV (128000 mL g^{-1} h^{-1}). In **Chapter 5**, I report on another strategy for structure regulation based on metal oxide In_2O_3. At first, In_2O_3 was supported on SiO_2 for higher efficiency to form In_2O_3/SiO_2, which was active for acetylene semihydrogenation, but deactivation occurred within a few hours probably due to by-production of poisonous species. When In_2O_3/SiO_2 was further doped with a small amount of Co (0.5 wt%), the acetylene conversion and ethylene selectivity remained high (approximately 70%). For the Co/ In_2O_3/SiO_2 catalyst, the hydrogen pretreatment temperature had strong influence on the catalytic performance, in which reduction by H_2 at 250°C resulted in the best stability. A temperature-programmed reduction study suggested that metallic Co species contributed to inhibiting the formation of poisonous by-products, thereby improving stability.

In summary, the innovative catalyst design concepts in this study not only developed highly efficient catalysts for acetylene semihydrogenation, but also provided a fresh perspective on how to design and tune multi-metallic catalysts. The insights obtained in this study accelerated the development of multi-metallic catalysts and industrial processes for the purification of acetylene.