Study on Catalytic Alkane Oxidations by B12 Complex as Homogenous and Heterogenous Catalyst

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論 文 名　：Study on Catalytic Alkane Oxidations by B_{12} Complex as Homogenous and Heterogenous Catalyst（均一系および不均一系触媒としての B_{12} 錯体によるアルカン酸化反応に関する研究）

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論　文　内　容　の　要　旨

Oxidation of aliphatic C-H bonds is an important chemical transformation that is widely practiced in nature and in synthetic chemistry. In this work, alkane oxidation reaction with *m*-chloroperbenzoic acid catalyzed by B_{12} complex was investigated. B_{12} complex was explored as an oxidation catalyst, and the detailed mechanistic studies for oxidation of alkanes with *m*-chloroperbenzoic acid catalyzed by B_{12} complex was conducted and proposed, and it was supported by theoretical studies. Moreover, the B_{12}-immobilized catalysts were developed and used in alkane oxidations, and the obviously improved catalytic efficiency could be obtained after the B_{12} complex incorporated to monolith structure. It gave an essential example for mechanism of cobalt complex catalyzed alkane oxidation and offered a potential commercial use of B_{12} immobilized catalyst in this reaction.

In chapter 1, the alkane oxidations with C-H activation and the examples in catalytic alkane oxidation with transition metal complex and *m*-chloroperbenzoic acid have been described briefly. The introduction of B_{12} derivatives and the examples of immobilized B_{12} catalysts have been given concisely. B_{12} has unique structure of cobalt center with monoanionic corrin ligand and partially saturated structure, and it usually works as a catalyst in reduction reaction based on its easy stabilization of low oxidation states of the central cobalt. Therefore, to explore the value of B_{12} in catalytic oxidation reaction is attractive and challenging, and impressive advances of mechanistic studies are expected to make in B_{12}-mediated radical reactions in the field of oxidation reaction.

In chapter 2, the alkane oxidation reaction was conducted by using B_{12} derivative as catalyst and *m*-chloroperbenzoic acid as oxidant. We focused on the mechanism of this reaction. The reaction intermediate, Co(III)-*m*CPBA adduct, was monitored and characterized by several spectroscopic measurements such as UV-vis, ESR, ESI-MS and IR. The rate determining step and the kinetic deuterium isotope effect could be known from some kinetic studies. Isotope-labeling experiments and radical trapping experiments were also carried out for the investigation of the mechanism. Both Co(III)-oxyl species and *m*-chlorobenzoyloxyl radical could abstract hydrogen atom from alkane substrate to form alkyl radical. Then the alkyl radical could react with oxygen under aerobic condition to produce the oxygenate products,

alcohol and ketone, by Russell mechanism. Other pathways of rebound mechanism and Hartwig's mechanism are dominant for alcohol formation in anaerobic condition. The density functional theory calculations were performed to support the proposed mechanism. This work showed potential utility of B_{12} complex for oxidation catalysis, and gave an important example for the mechanism of cobalt complex with *m*-chloroperbenzoic acid in alkane oxidation reactions.

In chapter 3, the heterogenous catalysts composed of B_{12} derivative with a polymer and mesoporous silica have been prepared and applied in alkane oxidation reactions. When the B_{12}-supported monolith was used as catalyst, a highly improved catalytic efficiency could be noticed compared to the monomeric B_{12} catalyst, while B_{12}-supported mesoporous silica show almost same catalytic efficiency with monomeric B_{12} catalyst. Catalytic oxidation of other common alkanes were investigated and compared both in monolith and mesoporous silica system, and B_{12}-supported monolith exhibited a better performance in every alkane case. This work explored the immobilization of B_{12} catalyst and provide a potential application of B_{12} complex as catalyst in alkane oxidation reactions.

In chapter 4, the summary of this work and perspective of the future work have been depicted. Such environmentally benign vitamin B_{12} derivative was first explored as oxidation catalyst in alkane oxidation reaction. Further utilize of the B_{12} derivative for automated and practical application is worth expecting.