非ヘム型ルテニウム触媒を用いた C – H 酸化反応の酸応答性挙動解析と新規触媒開発

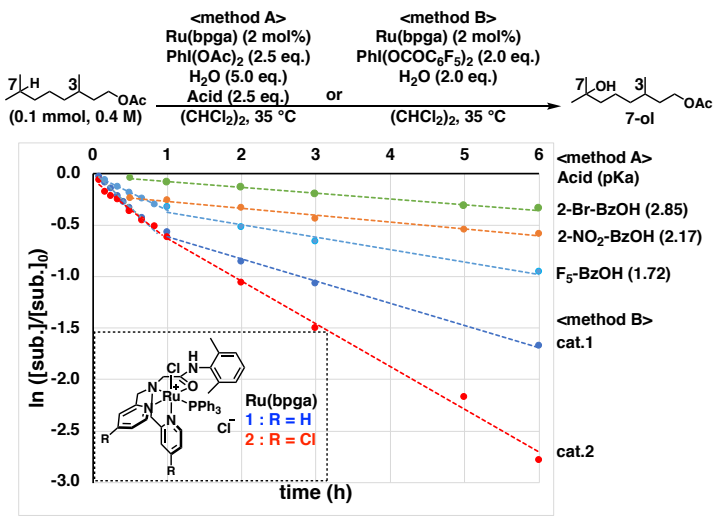
（九大院理[1]・九大基幹[2]・九大 I2CNER[3]）○下田 菜々子[1]・土居内 大樹[1]・内田 竜也[1,2,3]

Development of non-heme type ruthenium-catalyzed C–H bond oxidation based on mechanistic studies of carboxylic acid responsiveness ([1]*Graduate School of Science, Kyushu University*, [2]*Faculty of Arts and Science, Kyushu University*, [3]*International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University*) ○Nanako Shimoda,[1] Daiki Doiuchi,[1] Tatsuya Uchida[1,2,3]

C–H oxidation is a useful and straightforward tool for the construction of the oxygen functional groups such as hydroxy and carbonyl groups. Recently, we found that non-heme type Ru(bpga) complex **1** is an efficient catalyst for the site-selective C–H oxidation. During these studies, interesting additional effects of carboxylic acids, the elevation of reaction rates with the correlation of carboxylic acid's acidity, were observed. Following this study, to the mechanistic insight of the reaction, we followed the detail of the additional effect of carboxylic acids in the reaction. Based on these investigations, it was thought that carboxylic acids are hydrogen-bonding donors to ruthenium(oxo) intermediate and ligated to the ruthenium ion. Furthermore, it was indicated that the deactivation process includes the oxidation of ligand. Based on these considerations, we succeeded in preparing the more robust and effective catalyst for the site-selective C–H oxidation.

Keywords : C–H Oxidation; Catalytic Oxidation; Site-Selective Oxidation; Ruthenium catalyst

C–H 酸化反応は、ヒドロキシル基などの酸素官能基を直接導入できるステップエコノミーに優れた有用な合成反応である。最近、我々は、非ヘム型ルテニウム錯体 **1** が位置選択的な C-H 酸化反応の優れた触媒となることを見出している [1)]。同反応は、系中のカルボン酸の酸性度の向上に伴い、反応活性が上昇する傾向が観測されている [2)]。今回、各種カルボン酸存在条件下における反応機構解析を進め、カルボン酸の効果について明らかとすると共に、触媒活性の失活過程の一部に配位子の酸化が関与することも明らかとした。さらに、これらの知見を基に、ピリジン部位に電子求引基を導入し、触媒耐久性と反応性を共に向上させたルテニウム錯体 **2** を開発した。



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