チタンーセリウム混合触媒系による可視光照射下でのカルボン酸の脱炭酸ー酸素化反応

(阪大院基礎工[1]・阪大院工[2]) ○玉木 颯太[1]・草本 哲郎[1]・劔 隼人[2]

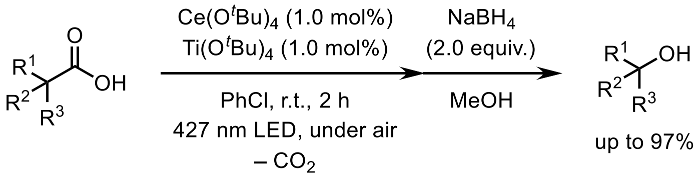
Catalytic Decarboxylative Oxygenation of Carboxylic Acids by Titanium and Cerium Combined Catalysts under Visible Light Irradiation

([1]*Graduate School of Engineering Science, Osaka University*, [2]*Graduate School of Engineering, Osaka University*) ○Sota Tamaki,[1] Tetsuro Kusamoto,[1] Hayato Tsurugi[2]

Photo-induced homolysis of a metal-ligand bond is an efficient strategy for generating organic radicals in a selective manner under mild reaction conditions, which is a key step to develop photocatalytic organic transformations.[1] We previously reported that cerium(IV) carboxylate complexes served as photocatalysts for decarboxylative oxygenation of carboxylic acids under blue LED irradiation, in which homolysis of the cerium(IV)-carboxylate bond generated carboxyl radicals.[2] We herein report efficient titanium and cerium combined catalysts for decarboxylative oxygenation under visible light irradiation in the presence of air. The photocatalytic activity was strongly affected by the ratio of titanium to cerium: titanium alkoxide was inactive under visible light irradiation, whereas the addition of an equivalent of cerium alkoxide to titanium alkoxide showed the highest catalytic activity among the reactions with different ratios of the two metals, in which cerium(IV) and titanium(IV) containing clusters are formed with a 1:1 ratio of the two metals. In addition, the catalytic activity of the mixed-metal clusters is higher than the previously reported cerium(IV) clusters. Optimization of the reaction conditions and the scope of substrates are disclosed in this presentation.

Keywords: *Cerium; Titanium; Carboxylic Acid; Photo-catalytic Reaction; Decarboxylation*

遷移金属錯体の光励起を伴う金属ー配位子結合の均等開裂は、温和な条件下で選択的に有機ラジカルを発生させる手法として、触媒反応への応用が活発に研究されている[1)]。われわれは以前に、オキソ架橋 6 核セリウムカルボキシラート錯体におけるセリウムー酸素結合が青色 LED 光の照射下で均等開裂を起こし、カルボキシルラジカルの生成と脱炭酸による有機ラジカル生成を経て、空気雰囲気下において酸素酸化体を与えることを報告している[2)]。今回、セリウムアルコキシドに対して任意の比でチタンアルコキシドを加えた触媒系によりカルボン酸の脱炭酸酸素酸化反応を検討したところ、セリウムとチタンの比が 1:1 の場合に触媒活性が最も高くなることを見出した。さらに、光照射前の反応混合物の質量分析を行うことで、セリウムとチタンが 1:1 の比で含む金属クラスター錯体が生成することを明らかにした。本発表では、反応条件の最適化と基質適用範囲についても報告する。



1) Bhattacharyya, A.; Reiser, O. *et al. Angew. Chem., Int. Ed.* **2021**, *60*, 21100.

2) Tsurugi, H.; Satoh, T.; Mashima, K. *et al. J. Am. Chem. Soc.* **2020**, *142*, 5668.