

アルデヒド存在下での銅錯体を触媒とするアルカンの自動酸化反応機構

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Autoxidation Mechanism of Alkanes Catalyzed by Copper Complexes in the Presence of Aldehyde ○RIN Itoh¹, Kohei Yamaguchi¹, Hideki Sugimoto¹, Shinobu Itoh¹ (1. Osaka University)

We have been investigating the autoxidation mechanism of alkanes catalyzed by copper acetate in the presence of aldehydes. However, the role of copper catalyst has remained unclear. In this study, catalytic activity of copper(II) complexes supported by a series of multidentate amine ligands was examined, and the effects of the supporting ligand structure, geometry of the copper center, and the external ligands on the catalytic activity were systematically investigated. Among the copper complexes examined, copper(II) complexes of Me₆tren (*N,N,N',N',N'',N''*-hexamethyl-tris(2-aminoethyl)amine) exhibited the highest catalytic activity, where the axial ligand was also found to influence the catalytic activity. Based on the correlations of the catalytic activity with the τ_5 value and redox potential ($E_{1/2}$) of the copper(II) complexes, the role of the copper(II) complexes is discussed.

Keywords: Copper complex; Autoxidation of alkane; Aldehyde; Ligand effect; Structure-reactivity relationship

我々はこれまでに、酢酸銅を触媒とするアルデヒド存在下におけるアルカンの自動酸化反応¹について検討を行い、酸化反応機構の詳細について考察を行って来た。しかし、銅触媒の役割については不明な点が多く残されていた。本研究では、アミン系多座配位子に支持された一連の銅(II)錯体を用いて検討を行い、配位子の構造や銅中心の配位構造および外部配位子の効果を明らかにした。検討した銅(II)錯体の中では、Me₆tren (*N,N,N',N',N'',N''*-hexamethyl-tris(2-aminoethyl)amine)配位子に支持された銅(II)錯体 (Figure 1) が最も高い触媒活性を示し、軸配位子(X)も触媒活性に影響を及ぼす事がわかった。用いた銅(II)錯体の τ_5 値や酸化還元電位($E_{1/2}$)と触媒活性との相関関係を明らかにし、銅錯体の役割について考察を加えた。

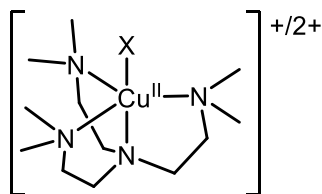


Figure 1. $[\text{Cu}^{\text{II}}(\text{Me}_6\text{tren})\text{X}]^{n+}$ ($\text{X} = \text{F}^-, \text{Cl}^-, \text{Br}^-, \text{CH}_3\text{CN}, \text{AcO}^-, \text{PhCOO}^-$)

1. S.-I. Murahashi and co-workers, *Tetrahedron Letters*, **2013**, 54, 2706–2709.