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Catalytic Oxidation of Organic substrates by a Ruthenium(II) Polypyridyl complex

以二價金屬釕的多吡啶絡合物為催化劑催化氧化有機化合物的研究

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Abstract

The use of recyclable catalysts and water as solvent for the oxidation of organic compounds is appealing in the context of green chemistry. The objectives of this thesis are to develop a polymer-supported ruthenium catalyst for oxidation of organic compounds in aqueous media. This thesis is divided into two parts. Part I is concerned with the catalytic activities of a ruthenium(II) polypyridyl complex, *cis*-$[Ru^{II}(2,9\text{-}Me_2phen)_2(H_2O)_2](PF_6)_2$ (2,9-Me_2phen = 2,9-dimethyl-1,10-phenanthroline) toward oxidation of various organic compounds in aqueous media. Part II describes the preparation of recyclable polymer-supported ruthenium catalysts and their application for the oxidative degradation of environmental pollutants.

In Part I, the catalytic activities of *cis*-$[Ru^{II}(2,9\text{-}Me_2phen)_2(H_2O)_2]^{2+}$ (**Ru^{II}**) toward the oxidation of organic compounds using various terminal oxidants in aqueous media was described. Among various terminal oxidants, Ce(IV) gave the best yields, and reaction was completed within 15 min. For example, using 1 mol % of **Ru^{II}**, alcohols and alkenes were oxidized to ketones or carboxylic acids with excellent yields (up to 100 %) using Ce(IV) as terminal oxidant. Notably, in the oxidation of cyclohexanol to cyclohexanone, a turnover number (TON) of > 10,000 could be achieved under ambient conditions.

In part II, two polymer-supported ruthenium catalysts have been prepared by

immobilizing **Ru^{II}** onto the cation exchange resins Dowex-50W and Chelex-100, and their catalytic activities have been examined. No significant deterioration of product yields were found when **Ru^{II}** was supported onto these polymers. The Dowex-50W supported ruthenium catalyst (**Ru^{II}-Dowex**) showed higher stability than the Chelex-100 supported catalyst since no leaching of ruthenium was found. In the case of oxidation of cyclohexanol and cyclohexene, a TON of over 10,000 can be achieved. **Ru^{II}-Dowex** could be reused by simple filtration and displayed no loss of activity.

In addition, the potential use of these polymer-supported ruthenium catalysts for the oxidative degradation of organic pollutants in water was studied using bisphenol A, an emerging endocrine disruptor, as a substrate; and the environmentally friendly H_2O_2 as oxidant. These polymer-supported catalysts are found to be efficient for the degradation of bisphenol A in aqueous solution by H_2O_2 under ambient conditions. The intermediates and products formed during the oxidative degradation of bisphenol A by these catalytic systems have been identified and a mechanism is proposed. The supported catalysts are easily recovered by simple filtration and display no loss of activity when recycled.

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Abbreviations

TPP	tetraphenylporphyrinato anion
TPFPP	tetra(perfluorophenyl)porphyrinato anion
TTPPP	tetra(2,4,6-triphenylphenyl)porphyrinato
tpa	tris(2-pyridylmethyl)amine
tacn	1,4,7-triazacyclononane
t-BuOH	*tert*-butanol
DMF	dimethylformamide
2,9-Me_2phen	2,9-dimethyl-1,10-phenanthroline
O_2	diozxygen
H_2O_2	hydrogen peroxide
TBHP	*tert*-butyl hydroperoxide
PhIO	iodosylbenzene
Oxone®	$2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$
Ce^{IV}	cerium(IV) ammonium nitrate
Ru^{II}	*cis*-[Ru^{II}(2,9-Me_2phen)$_2$(H_2O)$_2$](PF_6)$_2$
BPA	bisphenol A