Abstract

Project Code : MRG5980148

Project Title : The Synthesis of ε -Caprolactone from 1,6-Hexanediol Oxidation Using Air-Stable Ruthenium Complexes as a Catalyst and Molecular Oxygen as a Hydrogen Acceptor

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Project Period : 2 years

Abstract:

The (*p*-cymene)$RuCl_2$(L) and (*p*-cymene)$RuCl_2$(L´) where L = phosphine ligands including PPh_3, PCy_3, $P(OPh)_3$, $PO(Ph)_2(OC_2H_5)$, dppm, and L´ = pyridine ligands including 4-diMepy, 4-Mepy, py, 4-^{t}Bupy, 2,4-Cl_2py, and 4-CF_3py, were prepared and used as a catalyst for 1,6-hexanediol (1,6-HD) oxidation to ε-caprolactone (ε-CL). The x-ray crystallography of (*p*-cymene)$RuCl_2$(4-^{t}Bupy) complex shows the distorted pseudo-tetrahedral structure where the Ru-N bond and angles are quite similar to those pyridine derivatives. The centroid(*p*-cymene)-Ru-Cl angle (pocket site) of (*p*-cymene)$RuCl_2$(L´) complexes is larger than those of (*p*-cymene)$RuCl_2$(L) complexes (127-129, 123-126 Å, respectively). The activity of 1,6-HD oxidation using (*p*-cymene)$RuCl_2$(L) as a catalysts increases from 0.0125, 4.37, 7.25, 14.7, to 192 (x 10^{-3} s^{-1}) for PCy_3, $P(OPh)_3$, $PO(Ph_2)(OC_2H_5)$, PPh_3, and dppm, respectively, despite the decrease in steric hindrance of phosphine ligands. Furthermore, the linear correlation between 1,6-HD conversion and pocket site (centroid(*p*-cymene)-Ru-Cl angle) of (*p*-cymene)$RuCl_2$(L) complexes suggests that the reaction proceeds via the interchange associative mechanism. In sharp contrast, for (*p*-cymene)$RuCl_2$(L´) complexes, the

similar k_{app} (~10 x 10^{-3} s^{-1}) was obtained despite the difference in steric hindrance of pyridine derivative ligands. This leads to the suggestion of interchange dissociative mechanism. Despite the different Ru complexes, ε-CL selectivity only depends on the 1,6-HD conversion. The presence of bases significantly enhanced the reaction activity; however, deactivation of Ru complexes was observed due to a side reaction with metyl *iso*-butyl carbinol (MIBC) produced during the reaction. In addition, the stronger the base the lower the conversion (K_2CO_3 < KOH < KO^{t}Bu) as it promotes the side reaction as relatively faster rate.

Keywords : Oppenaur oxidation, Ruthenium complexes, Caprolactone