Density Functional Theory (DFT) Study On Ligand Candidates For Cobalt Catalysts To Optimize Branching Selectivity And Esterification In The Carbonylative Polymerization Of Undecenol

([1]*Waseda University,* [2]*Bandung Institute of Technology*) ○Cedric Purwanto,[1] Aditya Wibawa Sakti,[1] Hiromi Nakai,[1] Abel Faeyza Natawardaja,[1] Nova Pratiwi Indriyani[2]

Keywords: Carbonylation, Biodegradable Thermoplastic, Aliphatic Polyester, Density Functional Theory (DFT), Cobalt, 10-undecen-1-ol

Cobalt tetracarbonyl hydride $HCo(CO)_4$ is a catalyst widely used in hydroformylation reactions to synthesize biodegradable polymers(1). Previous studies have also shown that it can catalyze the carbonylative polymerization of polyesters(2). This study proposes a method using undec-10-en-1-ol, a monomer derived from castor oil. We discuss the elucidation of the reaction mechanism for the carbonylative polymerization of undecenol into aliphatic polydodecyloate at the DFT level using wB97X-D/6-311+G(d) after preoptimization using XTB. Computational details were selected after benchmarking carbonyl dissociation energies across different basissets. Experimental results from our collaborators showed catalytic activity of 486 g mol^{-1}cat^{-1}h^{-1} at a syngas pressure of 22 bar. The purpose of this study is to modify the cobalt catalyst to optimize both selectivity and yield.

The reaction starts with the insertion of the $HCo(CO)_4$ catalyst into undecenol. Depending on whether the hydrogen atom of the catalyst points towards the C_1 or C_2 position of the undecenol, a branched or a linear polymer will be synthesized, respectively. The DFT calculation results show that the linear polymer is kinetically and thermodynamically preferable than the branched one. To further promote the synthesis of the linear polymer, the catalyst ligands are modified with $P(OPh)_3$, PPh_3, and PMe_3, to increase steric hindrance of the non-hydrogen ligands of the catalysts.

These ligand variations also impact the esterification step, which has shown to have high activation energies from the DFT results. After analysis of the Fukui indexes of the different ligands, variations in electrophilicity of the different ligands explain the lower esterification energies when using the catalyst variations.

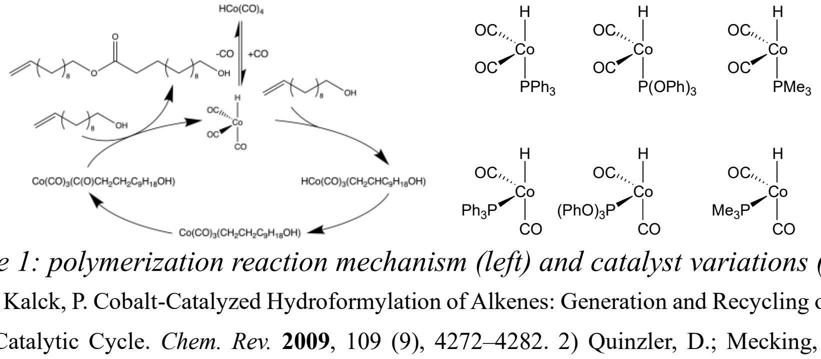

Figure 1: polymerization reaction mechanism (left) and catalyst variations (right)

1) Hebrard, F.; Kalck, P. Cobalt-Catalyzed Hydroformylation of Alkenes: Generation and Recycling of the Carbonyl Species, and Catalytic Cycle. *Chem. Rev.* **2009**, 109 (9), 4272–4282. 2) Quinzler, D.; Mecking, S. Renewable Resource-Based Poly(Dodecyloate) by Carbonylation Polymerization. *Chem. Commun.* **2009**, No. 36, 5400.1