HETEROBIMETALLIC Ru(II)-Ni(II) COMPLEXES AS PROMISING CATALYSTS FOR COUPLING MECHANISTICALLY INCOMPATIBLE CATALYTIC REACTIONS: ROMP AND ETHYLENE OLIGOMERIZATION

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Late transition metal complexes have been used to catalyze many reactions. Among them, complexes based on Ni^{II} or Ru^{II} have attracted much attention. Ni^{II} shows high activity in catalysis, mainly in ethylene polymerization and oligomerization due the easily activation of olefins, besides to act as a Lewis acid in the presence of olefins. On the other hand, Ru^{II} can be coordinated to a great number of ligands, what must change its behavior in catalysis. Due its good π-donnor effect, this metal is a good alternative for Ring-Openning Methathesis Polymerization (ROMP). The use of heterobimetallic complexes as homogeneous catalysts aims to expand the catalytic scope, besides increases their reactivity via an electronic or mechanistical synergism [1]. In this work, we reported the synthesis, characterization, and catalytic activity of Ru^{II}-Ni^{II} heterobimetallic complexes to act in two mechanisms: ethylene oligomerization and ROMP. Thus, four new heterobimetallic complexes [Ph(PPh_3)Ni(N,O)pip-Ru(*p*-cymene)Cl_2] (**1**), [Ph(PPh_3)Ni(N,O-tert-butyl)pip-Ru(*p*-cymene)Cl_2] (**2**), [Ph(PPh_3)Ni(N,O)py-Ru(*p*-cymene)Cl_2] (**3**), and [Ph(PPh_3)Ni(N,O-tert-butyl)py-Ru(*p*-cymene)Cl_2] (**4**) were obtained by the reaction of the appropriated ruthenium precursor, [(Ph)Ni(PPh_3)$_2$Cl], and the desired aldehyde in an 1:1:1 ratio. The complexes were fully characterized by spectroscopy techniques as FTIR, UV-Vis, and ^1H and $^{31}P\{^1H\}$, besides cyclic voltammetry (CV). All bimetallic species showed an irreversible process assigned to the $Ni^{II/III}$ redox pair, and reversible processes related to the $Ru^{II/III}$ pair. A shift on oxidation potential in the Ru fragment was observed as compared to the Ru monometallic species (precursor) and it could be attributed to a synergic effect between **Ru**-**Ni**. The complex **2** (Ru fragment) was able to polymerize norbornene (NBE) reaching 80% in 60 minutes of conversion using with [NBE]/[Ru] = 5000 and [EDA]/[Ru] = 10 in chloroform at 50° C, while monometallic Ru polymerized NBE with 40% conversion using the same conditions [2]. The complex **2** (Ni fragment) oligomerized ethylene using ethylaluminium sesquichloride (EASC) in a molar ratio Al/[Ni] of 2100, toluene as solvent, 220 psi of ethylene, and 25° C, reaching a turnover frequency about 150 s^{-1}. The major part of products was C4 chains, with lower amount of C6 (around 25% related to the C4).

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[2] MASSON, Gustavo HC et al. Ruthenium–nickel heterobimetallic complex as a bifunctional catalyst for ROMP of norbornene and ethylene polymerization. New Journal of Chemistry, v. 45, n. 26, p. 11466-11473, 2021.