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Pyridylimine cobalt (II) and nickel (II) complex-functionalized multi-walled carbon nanotubes and their catalytic activities for ethylene oligomerization

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Multi-walled carbon nanotubes (MWCNTs) were covalently functionalized with pyridylimine and its metal complexes. The synthesized compounds were characterized by several analytical techniques. The pyridylimine metal complex-functionalized multi-walled carbon nanotubes [Pyr-M(II)-MWCNTs] were evaluated as catalyst precursors for ethylene oligomerization with methylaluminoxane (MAO) used as an activator at different Al/M [M(II) =Co(II) and Ni(II)] ratios and at two different ethylene pressures. [Pyr-Co(II)-MWCNTs] (C1) and (Pyr-Ni(II)-MWCNTs] (C2) were isolated as solid materials in good yield. Complex C2 was found to be a more effective pre-catalyst than C1 in the presence of MAO. Thus, C2 exhibited a maximum catalytic activity of 1.89×10^6 g mol^{-1}(Ni) h^{-1} bar^{-1} with an Al/Ni ratio of 2000:1 at room temperature with a 5 atm pressure of ethylene, whereas C1 exhibited a maximum activity of 1.87×10^6 g mol^{-1}(Co) h^{-1} bar^{-1} in similar condition. When the Al/Co ratio was increased at a 1 atm pressure of ethylene, the catalytic activity of the pre-catalyst increased, and the process became more selective towards higher oligomers. The catalytic activity and selectivity with 1-decene using C1 were 3.02×10^5 g mol^{-1}(Co) h^1 bar^{-1} and 72%, respectively, with 5 atm ethylene and an Al/Co ratio of 200:1.

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