

Hydroethoxycarbonylation of α -Olefins at Low Pressure of Carbon(II) Oxide in the Presence of the $\text{PdCl}_2(\text{PPh}_3)_2\text{-PPh}_3\text{-AlCl}_3$ System

Kh. A. Suerbaev^{a*}, N. Zh. Kudaibergenov^a, and A. Vavasori^b

^a Al-Farabi Kazakh National University, ul. Tole Bi 96A, Almaty, 050012 Kazakhstan

*e-mail: khsuerbaev@mail.ru

^b Ca'Foscari University of Venice, Venice, Italy

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Abstract—High catalytic activity of the $\text{PdCl}_2(\text{PPh}_3)_2\text{-PPh}_3\text{-AlCl}_3$ system containing AlCl_3 as promotor has been demonstrated in the reaction of hydroethoxycarbonylation of hexene-1 and octene-1 at low pressure of carbon(II) oxide (≤ 25 atm). The reaction yields linear and branched products. The optimal conditions of the process have been elaborated. The target products yield is 84.6–93.8%.

Keywords: palladium, triphenylphosphine, aluminum chloride, olefins, carbonylation

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α -Olefins are large-scale industrial products widely used in the production of surfactants, synthetic lubricants, plasticizing alcohols, fatty acids and their derivatives, and a variety of monomers [1]. Esters are among valuable derivatives of fatty acids prepared on the basis of α -olefins. Many esters are applied as odorants in the production of perfumes, cosmetic products, and food essences [2]. Some of them exhibit biological activity and serve as drug components (Validol, Corvalol, etc.) or their precursors [3].

The reaction of hydroalkoxycarbonylation of olefins with carbon(II) oxide and alcohols in the presence of metal complex catalysts is the most important industrial method of synthesis of carboxylic acids esters. Its advantage over other methods are one-pot mild conditions of the process and availability of the starting compounds. The catalysts based on the complexes of VIII group metals exhibit the highest activity in the reaction of hydroalkoxycarbonylation of olefins [4, 5]. Their catalytic activity, stability, and selectivity depend on the nature of the complex forming metal, the composition of the coordination sphere, synthesis conditions, and the presence of external stabilizers and promotors. The catalysts based on phosphine complexes of palladium has been considered to be the most promising so far, owing to the advantageous combination of donor and acceptor

properties of its zero- and bivalent forms [6–10]. Triphenylphosphine is the most widely used stabilizer of the systems based on phosphine palladium complexes, its action being attributed to the stabilization of the main complex composition, preventing the possible deactivation of the catalytically active species via the ligand exchange reaction. Various Brønsted acids are used as external promotors; their role is to facilitate the generation of intermediate hydride complexes of palladium, key components of the catalytic cycle [4–7, 11, 12]. Strong Brønsted acids (like *p*-toluenesulfonic acid and methanesulfonic acid) forming weakly coordinating conjugate anions are the most efficient in this regard. Strongly coordinating anions decelerate the kinetically important stage of incorporation of the reagents (CO and olefin) in the inner sphere of the complex forming metal, whereas weakly coordinating anions leave the Pd site of the catalytic systems more accessible, thus facilitating its interactions with the substrates in the catalytic cycle [13, 14].

Only few papers have reported the use of Lewis acids as promotors of organic substrates carbonylation with carbon(II) oxide in the presence of metal complex catalysts [15–18]. It has been shown in [15] that the $\text{Al}(\text{OTf})_3$ Lewis acid is an efficient promotor of catalytic systems based on the $[\text{Pd}(\text{OAc})_2\text{-PPh}_3]$ complexes in hydromethoxycarbonylation of styrene and