STRUCTURE OF Pd/C COMPOSITES AND THEIR CATALYTIC PROPERTIES IN HYDROGENATION OF DIENE CARBOXYLATES

Verner E. V.^{1,2}, Subotin V. V.^{1,2}, Vashchenko B. V.^{1,3}, Asaula V. M.², Ivanytsya M. O.^{1,2},

Shvets O. V.², Ostapchuk E. N.,^{1,3} Grygorenko O. O.^{1,3}, Ryabukhin S. V.^{1,3,4}, Volochnyuk D. M.^{1,3,4}, Kolotilov S. V.^{1,2,3}

¹Enamine Ltd., Kyiv, Ukraine

²L. V. Pisarzhevskii Institute of Physical Chemistry of the National Academy of Sciences of Ukraine, Kyiv, Ukraine

³Taras Shevchenko National University of Kyiv, Kyiv, Ukraine

⁴Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Kyiv, Ukraine

vernereduard2103@gmail.com

A series of palladium-containing composites, i.e. four Pd/C and three "Pd(OH)2"/C (Pearlman's catalysts, where Pd(OH)₂ indicated hydrated PdO), was prepared using modified common approaches to deposition of Pd or PdO on the charcoal. The composites were characterized by transmission and scanning electron microscopy (TEM and SEM), powder Xray diffraction, and low-temperature N2 adsorption.

All the composites were tested in the catalytic hydrogenation of diene carboxylates with 5,6-dihydropyridine-1(2H)-carboxylates the isolated-ring scaffold, e. g. with 2-(alkoxycarbonyl)cyclopent-1-en-1-yl and hex-1-en-1-yl substituents at C(4)-position (Fig. 1). It was found that the composites, containing Pd nanoparticles (NPs) of 5-40 nm size were the most efficient catalysts for the hydrogenation of dienes, providing the reduced products with up to 90 % yields at $p(H_2) = 100$ atm, T = 30 °C for 24 h. The method of Pd NPs formation had more effect on the catalyst performance than the size of the NPs: the composites formed by adsorption of Pd^{2+} on the charcoal followed by reduction to metallic Pd had significantly higher performance in the hydrogenation of dienes compared to the composites, prepared by precipitation of hydrated PdO on the charcoal followed by its reduction. The catalytic performance of Pearlman's catalysts (Pd(OH)₂/C) in the hydrogenation of dienes was comparable to or lower than the performance of the Pd/C systems.

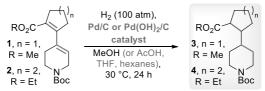


Fig. 1. The catalytic hydrogenation of N-Boc protected 5,6-dihydropyridine-1(2H)carboxylates 1 and 2 bearing additional 2-(alkoxycarbonyl)cyclopent-1-en-1-yl and hex-1-en-1-yl substituents at C(4)-position, respectively

The yield of the products in the hydrogenation of dienes increased in the following order of solvents: THF < hexanes << MeOH, which correlates with an increase in the solubility of H2.