Experimental

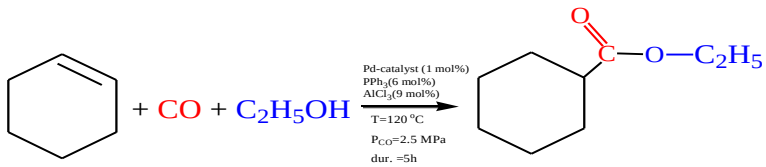
Primary reagents, features and methods of their study. Reagents produced by SIGMA-ALDRICH (bis(triphenylphosphine)palladium (II) dichloride, cyclohexene (purity 99 %), triphenylphosphine, aluminium trichloride), absolute ethyl alcohol, carbon monoxide reagent without superrefining (CO) were used as primary reagents.

Equipments. Experiments were conducted in a steel laboratory autoclave reactor (capacity 100 ml) equipped with a mixer and heater. The target product (ethyl ester of cyclohexanecarboxylic acid) was identified by gas chromatography on an Agilent 7890A/5975C mass-spectrometer (USA). Chromatography conditions were as follows: gas chromatograph 7890A with mass-selective detector 5975C produced by Agilent, helium mobile phase (gas carrier), evaporation temperature 300 ºC, flow shift (Split) 1000:1. Also, column heating with initial oven temperature 40 °C (1 min), temperature increase 5 ºC per minute and final value 250 ºC that is maintained for 1 minute were used. Total analysis time was 44 minutes and mass detector ionization was carried out by electron impact method. A capillary chromatographic column HP-FFAP was also used; the column length was 30 m, the inner diameter was 0.25 mm, the stationary phase was nitrophthalic acid modified with polyethylene glycol.

Hydroethoxycarbonylation of cyclohexene. 0.08 g (1.14×10^{-4} mol) $PdCl_2(PPh_3)_2$, 0.180 g (6.84×10^{-4} mol) PPh_3, 0.122 g (9.12×10^{-4} mol) $AlCl_3$, 2.289 g (4.96×10^{-2} mol) ethanol and 4.067 g (4.96×10^{-2} mol) of cyclohexene were placed into a steel autoclave reactor (100 ml) equipped with a mixer and carbon monoxide injection device. Ratio of primary reagents and components of catalyst system was $[C_6H_{10}]:[C_2H_5OH]:[PdCl_2(PPh_3)_2]:[PPh_3]:[AlCl_3]$ = 435:435:1:6:9. The reactor was sealed. To remove air inside of it, it is blown through with carbon monoxide three times and filled with carbon monoxide until pressure reaches 1.5 MPa. Then, mixer and heater are turned on and within 1 hour temperature is increased up to 120 °C, and carbon monoxide pressure grew up to 2.5 MPa. At a given temperature and pressure the reaction mixture is intensively stirred for 5 hours. Then it is cooled to room temperature and reaction mixture fractionation is carried out at atmospheric pressure. As a result of distillation, 6.244 g (80.7 %) of ethyl ester of cyclohexanecarboxylic acid was obtained.

Results and discussion

The reaction of cyclohexene hydroethoxycarbonylation in the presence of $PdCl_2(PPh_3)_2$–PPh_3–$AlCl_3$ catalyst system has the following form:



The activity of the three-component catalytic system $PdCl_2(PPh_3)_2$–PPh_3–$AlCl_3$, which contains $AlCl_3$ as a promoter, was studied in the hydroethoxycarbonylation of cyclohexene at low pressure (P_{CO} = 2.5 MPa) of carbon monoxide. A high catalytic activity of the catalytic system with respect to this reaction was found. Cyclohexanecarboxylic acid ethyl ester formation reaction was confirmed by reference data for such characteristics as GC/MS analysis, boiling point, and refractive index.

The effect of the reaction conditions (temperature, CO pressure, molar ratio of primary reagents, ratio of the components of the catalytic system and reaction time) on the yield of the target product has been established (Table 1).

Table 1 shows the results of the influence of various conditions on the yield of ethyl ester of cyclohexanecarboxylic acid as the target product of the reaction of hydroethoxycarbonylation of cyclohexene in the presence of the system $PdCl_2(PPh_3)_2$–PPh_3–$AlCl_3$. Temperature, pressure of carbon monoxide, reaction time, and the amount of $AlCl_3$ in the $PdCl_2(PPh_3)_2$–PPh_3–$AlCl_3$ catalytic system were the main factors determining the outcome of the process. An increase in the reaction temperature from 110 to 130 °C led to an increase in the yield of target products from 65.8 to 80.7 %. A further increase in temperature reduces the yield of target products due to catalyst deactivation (formation of palladium on carbon). The graphs of the yield of the target products depending on the pressure of carbon monoxide and the duration of the reaction also have an extreme form. Optimal conditions are P_{CO} = 2.5 MPa, τ = 5 h. A further increase in the pressure of carbon monoxide to 3.0 MPa sharply reduces the yield of the target products. Apparently, that is due to competition between the