Brief information about the project

Name of the project	AP09058656 «Development of scientific foundations of metal complex hydroalkoxycarbonylation of C_4-C_{10} olefins of oil refining»
Relevance	The problem of rational use of large-scale by-products of oil refineries (OR) - C_4-C_{10} olefins of process gases - is very relevant and has great practical significance. The Project proposes the development of the scientific basis for the synthesis of practically valuable esters of carboxylic acids by carbonylation of C_4-C_{10} olefins of OR process gases with carbon monoxide and alcohols in the presence of metal complex catalysts at low pressure of carbon monoxide.
Purpose	To develop the scientific foundations of metal-complex hydroalkoxycarbonylation of C_4-C_{10} olefins of petroleum refining used for the synthesis of practically valuable esters of carboxylic acids – biologically active drugs, scented substances, solvents, etc.
Objectives	*Task I.* Development of highly efficient catalytic systems based on transition metal complexes with organophosphorus ligands and various stabilizers and promoters have been developed for the reaction of hydroalkoxycarbonylation of C_4-C_{10} olefins under mild conditions of the process (CO pressure not higher than 2,0 MPa, temperature is not higher than 100 °C). *Task II.* Determination of optimal parameters of the hydroalkoxycarbonylation reaction of C_4-C_{10} olefins at low carbon monoxide pressures ($\leq$ 2.0 MPa) in the presence of developed effective catalytic systems based on transition metal complexes with organophosphorus ligands and various stabilizers and promoters have been determined. The kinetics and mechanism of the reaction under study are investigated. *Task III.* Possibilities of reuse of metal-complex catalysts for the reaction of hydroalkoxycarbonylation of olefins and methods of their regeneration to reduce the cost of the process. *Task IV.* To develop standard laboratory and technological regulations for the production of practically valuable aromatic substances based on carboxylic acid esters from olefins of oil refining process gases.
Expected and achieved results	**Expected results:** - 2 articles will be published in international peer-reviewed journals from the first three quartiles (Q1, Q2, Q3) of the Web of Science database. - 3 articles will be published in journals recommended by the Committee for Quality Assurance in Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan (CQASE ME RK) - One textbook will be published in the publishing house “Qazaq Universiteti”

	- One document of protection will be received in the form of a Patent of the Republic of Kazakhstan **Achieved results:** - For the first time, the comparative catalytic activity of a number of Pd phosphine complexes and free ligands in three-component reaction systems of hydroethoxycarbonylation of octene-1 was carried out, and optimal conditions (T=120^{0}C, P_{CO}=5.0 MPa, τ=5 hours) of the process in the presence of the $PdCl_2(PPh_3)_2$-PPh_3-$AlCl_3$ system were determined, under which the yield of the target products reached 88.5%. - The catalytic activity of the three-component $PdCl_2(PPh_3)_2$-PPh_3-$AlCl_3$ system containing AlCl3 as a promoter has been established in the hydroethoxycarbonylation reaction of pentene-1. The reaction proceeds with the formation of two isomeric products of linear (ethyl ether of capronic acid (EECA)) and branched structure (ethyl ether of 2-methylvaleric acid (EE-2-MVA)). Optimal reaction conditions were found under which the yields of the target products (the sum of isomeric esters of EECA and EE-2-MVA) reached 74.72%. - The activity of various alcohols in the reaction of hydroalkoxycarbonylation of hexene-1 in the presence of two catalytic systems has been studied: 1. $Pd(PPh_3)_4$-PPh_3-TsOH (menthol, cyclohexanol, ethanol, propanol, iso-propanol, butanol, isobutanol, benzyl alcohol) and 2. $PdCl_2(PPh_3)_2$-PPh_3-$AlCl_3$ (ethanol, propanol-1, butanol-1, isoamyl alcohol, isobutanol, pentanol-1, allyl and tretbutyl alcohol). The optimal parameters of the process (temperature, pressure and reaction duration) for the reaction of hydropropoxycarbonylation and hydrobutoxycarbonylation of hexene-1 have been established at which the yields of the target products reach 91.78% and 91.55%, respectively. - The activity of the $PdCl_2(PPh_3)_2$-PPh_3-$AlCl_3$ catalytic system containing $AlCl_3$ as a promoter in the cyclohexene hydroethoxycarbonylation reaction was investigated, optimal parameters were determined: $[C_6H_{10}]$:$[C_2H_5OH]$:[Pd]:$[PPh_3]$:$[AlCl_3]$ = 870:435:1:6:8, P_{CO} = 2.5 MPa, T = 120 °C, τ = 6 h. With these parameters, the yield of cyclohexanecarboxylic acid ethyl ether was 85.2%. - The optimal parameters of the cyclopentene hydroethoxycarbonylation process by the three-component $PdCl_2(PPh_3)_2$-PPh_3-$AlCl_3$ system have been determined. At the molar ratio of the initial reagent $[C_5H_8]$:$[C_2H_5OH]$=2:1, with a molar ratio of the component of the catalytic system [Pd]:$[PPh_3]$:$[AlCl_3]$ in a ratio of 1:6:10 and at T=120 °C, P_{CO} = 25 atm. and with a reaction duration of τ =6 hours,

	ethylcyclopentanecarboxylate was synthesized with a yield of 75.74%. - The mechanism of the hydroethoxycarbonylation reaction of cyclohexene in the presence of a three-component $PdCl_2(PPh_3)_2$-PPh_3-$AlCl_3$ catalytic system is proposed. - Laboratory and technological regulations for the production of cyclohexanecarboxylic acid ethyl ether by the reaction of hydroethoxycarbonylation of cyclohexene in the presence of $PdCl_2(PPh_3)_2$-PPh_3-$AlCl_3$ system have been developed.
Research team members with their identifiers (Scopus Author ID, Researcher ID, ORCID, if available) and links to relevant profiles	The scientific director of the project is ***Kudaibergenov Nurbolat Zharylkasynuly*** (https://orcid.org/0000-0002-4641-6779), Doctor of Philosophy (PhD) in chemistry. ***Zhaksylykova Gulbanu Zhaksylykovna*** (https://orcid.org/0000-0003-2390-0688), candidate of chemical sciences. ***Kanapieva Fatima Mukhidinovna*** (https://orcid.org/0000-0002-9829-3117), Candidate of Chemical Sciences. ***Zykay Meruert Halykkyzy*** (https://orcid.org/0000-0002-4853-9983), Candidate of Chemical Sciences. ***Pietrobon Luca***. Currently he is a PhD candidate at the Ca' Foscari University of Venice (Italy, Venice). ***Meirbekov Nurkanat Ayazbayuly*** (https://orcid.org/0000-0001-6440-3544), Master of Engineering and Technology. 1st year PhD student in the specialty “Chemistry” of al-Farabi KazNU ***Mamyrkhan Diana Batyrkhankyzy***, 1st year master's student in the specialty "Petrochemistry" of al-Farabi KazNU
List of publications with links to them	For 2021 1. Kudaibergenov, N.Zh., Shalmagambetov, K.M., Vavasori, A., Zhaksylykova, G.Zh., Kanapiyeva, F.M., Almatkyzy, P.,Mamyrkhan, D.B., & Bulybayev, M. (2021) The use of Lewis acid AlCl3 as a promoter in the Pd-complex catalytic system of the Циклогексен гидроэтоксикарбонилирование reaction. Bulletin of the University of Karaganda – Chemistry, 102(2), 8-17. https://doi.org/10.31489/2021Ch2/8-17 2. Bulybayev M.E., Almatkyzy P., Mamyrkhan D.B., Kalen G., Zhaksylykova G.Zh. The use of alcohols in pd-complex catalyzed system for the hydroethoxycarbonylation of hexene-1 // Proceedings of the 11th International Beremzhanov congress on chemistry and chemical technology. – 2021. – P.138-139. 3. Алматқызы П., Жаксылыкова Ж. Сызықты олефиндерді әр түрлі спирттермен палладийдің фосфинді комплекстерінің қатысында карбонилдеу // «Фараби әлемі» атты конференция материалдары. – 2021. – С.135.

	4. Shalmagambetov K.M., Kudaibergenov N.Zh Zhaksylykova G.Zh., Almatkyzy P., Mamyrkhan D.B., Bulybayev M., Esenov A. Carbonylation of olefins by carbonmonoxideand alcohols in the presence of Pd-complexcatalytic system // MATEC Web of Conferences. – 2021. – №340. https://doi.org/10.1051/matecconf/202134001023 For 2022 1. Shalmagambetov K.M., Zhaksylykova G.Zh., Kanapiyeva F.M., Kudaibergenov N.J., Abyzbekova G.M. Ethoxycarbonylation of pentene-1 in the presence of PdCl(PPh3)2-PPh3-AlCl3 system. Chem. J. Kaz., 2022, 3(79), 110-119. https://doi.org/10.51580/2022-3/2710-1185.84 2. Алматқызы П., Булыбаев М., Кенжаева А., Жаксылыкова Ж. Сызықты олефиндерді әр түрлі спирттермен палладийдің фосфинді комплекстерінің қатысында карбонилдеу // «Фараби әлемі» атты конференция материалдары. – 2022. – С.109. For 2023 1. Zhaksylykova G. Zh., Shalmagambetov K. M., Kudaibergenov N. Zh., Kanapieva F. M., Bulybaev M.E., N. Bolatkyzy, A. Azimbay. Hydroethoxycarbonylation of cyclopentane in the presence of a three-component PDCL2(PPH3)2-PPH3-ALCL3 system. Нефть и газ. 2023. №3. С.139-152. https://doi.org/10.37878/2708-0080/2023-3.11 2. Zhaksylykova G. Zh., Bolatkyzy N., Bulybaev M.E., Orynbassar B.K., Appaz A.N., Beibitbek G. Investigation of the activity of catalytic systems based on Ni and Co complexes in hydroalkoxycarbonylation reactions. IX International Russian-Kazakhstan International Conference "Chemical Technology of Functional Materials". May 25-27, 2023. P. 239. 3. Kairzhan Shalmagambetov, Andrea Vavasori, Gulbanu Zhaksylykova, Fatima Kanapiyeva, Meruyert Zykay, Nurbolat Kudaibergenov. Lewis acids as co-catalyst in Pd-based catalysed systems of hydroethoxycarbonylation reaction of octene-1 // Open Chemistry. 2023. №21. 20230156. DOI: https://doi.org/10.1515/chem-2023-0156 4. Zhaksylykova, G.; Shalmagambetov, K.; Kanapiyeva, F.; Kudaibergenov, N.; Bulybayev, M.; Zykai, M.; Abyzbekova, G.; Balykbayeva, G. The Role of Alcohols in the Hexene-1 Hydroalkoxycarbonylation Reaction with Catalysts Based on Palladium Complexes. *Catalysts* 2023, 13(12), 1507; https://doi.org/10.3390/catal1312150
Patents	Способ получения этилового эфира циклогексанкарбоновой кислоты. Шалмагамбетов К. М., Жаксылыкова Г. Ж., Канапиева Ф.М., Кудайбергенов Н.Ж., Мамырхан Д.Б. Патент на полезный модель РК. № 6933. 11.03.2022.