Synthesis of the Palladium Catalyst with the Supercritical CO$_2$-Impregnation Method Realized in the Static Mode

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Abstract

Results of research of supercritical fluid CO$_2$-impregnation process (the static mode) within a problem of synthesis of the palladium catalyst are given. The kinetics of process is characterized in the pressure range from 15.0 to 35.0 MPa on temperatures 308.15°K, 313.15°K, 318.15°K, 323.15°K, 328.15°K and 333.15°K. Results of surface assessment and activity measurements of the catalyst samples synthesized by supercritical CO$_2$-impregnation of aluminum oxide suggest competitiveness of the discussed approach in comparison to traditional methods.

Keywords

Supercritical Carbon Dioxide, Aluminum Oxide, Impregnation, Palladium Catalyst, Activity

1. Introduction

Technical progress of many industries, such as chemical, oil-extracting and oil processing, is closely connected with use of catalysts. The great value in life of modern society has been connected to such products of chemical industry as sulfuric acid, ammonia and nitric acid. Many branches of a national economy consume these substances or substances received on their basis. Meanwhile, large-scale production of these products became poss-

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ible only with the discovering of the corresponding catalysts and development of ways of their application. Catalysts acquired tremendous importance in solving purification of exhaust gases from various contaminants.

Catalysts promote increase in reaction speed and decrease in temperature conditions of its realization due to reduction of activation energy. As a consequence of this, a cost of product considerably decreases and, as a rule, its quality improves [1].

Processes of selective hydrogenation of liquid and gaseous fractions of oil pyrolysis in Russia, and abroad are traditionally carried out in the presence of selective palladium catalysts. Usage of the non-optimal catalyst leads to high technological losses and, in particular, to loss of ethylene as a result of non-selective hydrogenation [2]. In this regard, selective hydrogenation catalysts are constantly updated and improved, including decrease of precious metal concentrations in the catalysts. Modern catalysts of acetylene hydrogenation in ethane-ethylene fraction (EEF) contain 0.01% - 0.05% wt. of palladium. G83 and G58B catalysts (Süd-Chemie AG Lenbachplatz 6 Munich, 80333, Germany), contain 0.015% and 0.035% of palladium, respectively.

The catalysts production has become the independent, rapidly developing industry, requiring increasing energy consumption [3]. In catalysts production, the defining characteristic is not prime cost, but activity and stability of the catalyst in their work. The use of supercritical fluids as extractants and solvents in the above-noted processes is one of the most promising ways to improve the processes of regeneration of spent-catalysts and synthesis of new catalytic systems [4]-[6] will be discussed. Thus, if the case of this approach to regeneration is a subject of researches and even commercial realization for several decades [7]-[12], the problem of catalysts synthesis with the use of supercritical fluid-environments was shown only in several research publications [9] [13].

The analysis of research publications shows the existence of a large number of precious metal-organic complexes, sufficiently well soluble in supercritical carbon dioxide [14] [15]. For the catalysts synthesis with the use of supercritical fluid impregnation method, the following conditions are also desirable: relatively easy complex formation, its stability and low decomposition temperature.

The palladium chloride benzonitrile complex $PdCl_2(C_6H_5CN)_2$, which solubility in SC-CO$_2$ is given in earlier published works [9] [16]. **Figure 1** meets all above-mentioned requirements.

2. Experimental

Synthesis of a palladium chloride benzonitril complex is carried out according to the method described in [17]. For synthesis the following materials are used: carbon dioxide CAS # 124-38-9 with 99.995%, volume maintenance of CO$_2$ (Russian State standard No. 8050-85, certificate of quality No. 2052, supplier EcoFarm Ltd., Kazan, Sybyrsky trakt str, 34, http://www.ecopharm.ru/); palladium chloride CAS # 7647-10-1, purity of 99.99% (supplier EcoFarm Ltd., Kazan, Sybyrsky trakt str, 34, http://www.ecopharm.ru/) and the pure for analysis benzonitril CAS # 100-47-0 with the main component maintenance (not less) than 99.7% (supplier EcoFarm Ltd., Kazan, Sybyrsky trakt str, 34, http://www.ecopharm.ru/).
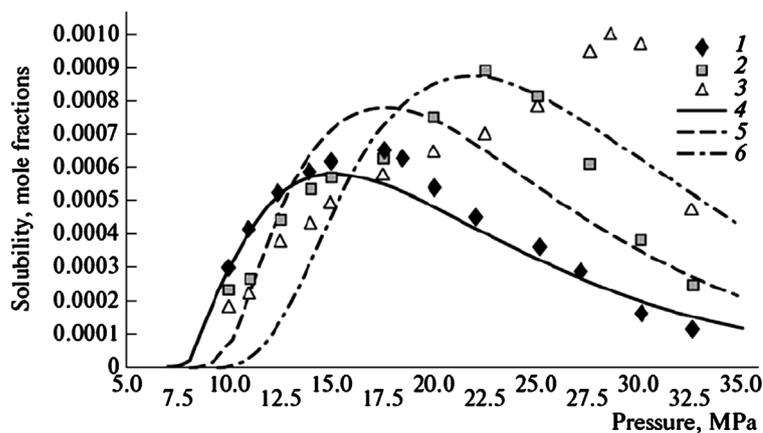
Figure 1. Solubility of palladium chloride benzonitrile complex in SC-CO$_2$ at (1) 308.15, (2) 318.15 and (3) 328.15˚K; (4-6) description (calculations) [9] [16].

Kinetics research of SC-CO$_2$-impregnation process and aluminum oxide impregnation by a benzonitril complex on the basis of palladium chloride has been carried out on experimental unit. Schematic diagram is given in **Figure 2**.

The above-noted experimental unit is realized on the basis of the supercritical fluid extraction experimental unit R-401 made by Reaction Engineering Ink, (Reaction Engineering Inc., Munwin-dong, Gwacheon-si Gyeonggi-do 427-090 Korea, http://reactioneng.co.kr/).

Experimental unit includes the liquid pump for CO$_2$ supply with the maximum productivity of 100 mL/min and with a maximum pressure of 40 MPa, two high pressure cells, used as a saturating cell and impregnation cell with the corresponding volumes in 1.5 and 0.5 liters, and also a separator. The temperature control system of the unit provides heating and maintenance of temperature of cells up to 100˚C. Experimental unit provides possibilities for carbon dioxide recirculation in the closed system "pump-saturating cell" and sharp pressure dumping in the impregnation cell.

Supercritical fluid CO$_2$-impregnation process in the static mode is carried out as follows.

The sample of palladium chloride benzonitrile complex is placed in saturating cell, and sample of Al$_2$O$_3$ CAS # 1344-28-1 (the catalyst carrier, supplier EcoFarm Ltd., Kazan, Sybyrsky trakt str, 34, http://www.ecopharm.ru/) in the impregnation cell, respectively. Initially within 10 - 20 min the stream of CO$_2$ recirculates only between the pump and the saturating cell with the purpose of carbon dioxide saturation by a palladium chloride benzolnitrile complex. After that solution of the above-named complex in supercritical carbon dioxide moves to the high pressure impregnation cell where system "impregnation material solution—the impregnated matrix" is kept in supercritical conditions for 15 - 20 minutes for achievement of the corresponding balance. After this time, sharp pressure dumping carried out. As a result, the carbon dioxide dissolving ability falls, and impregnation material evenly drops out in volume of all matrix.

Efficiency of impregnation process is estimated by weight method on increase in mass of the catalyst carrier's sample after experiment completion.

3. Results and Discussion

Search of optimum parameters of process implementation assumes experimental realization of stages of saturation SC-CO$_2$ with impregnation material and actually of a firm matrix impregnation at a wide variation of such key parameters, as temperature and pressure, carbon dioxide flow rate and duration of samples being kept in the impregnation cell before sharp pressure dumping.
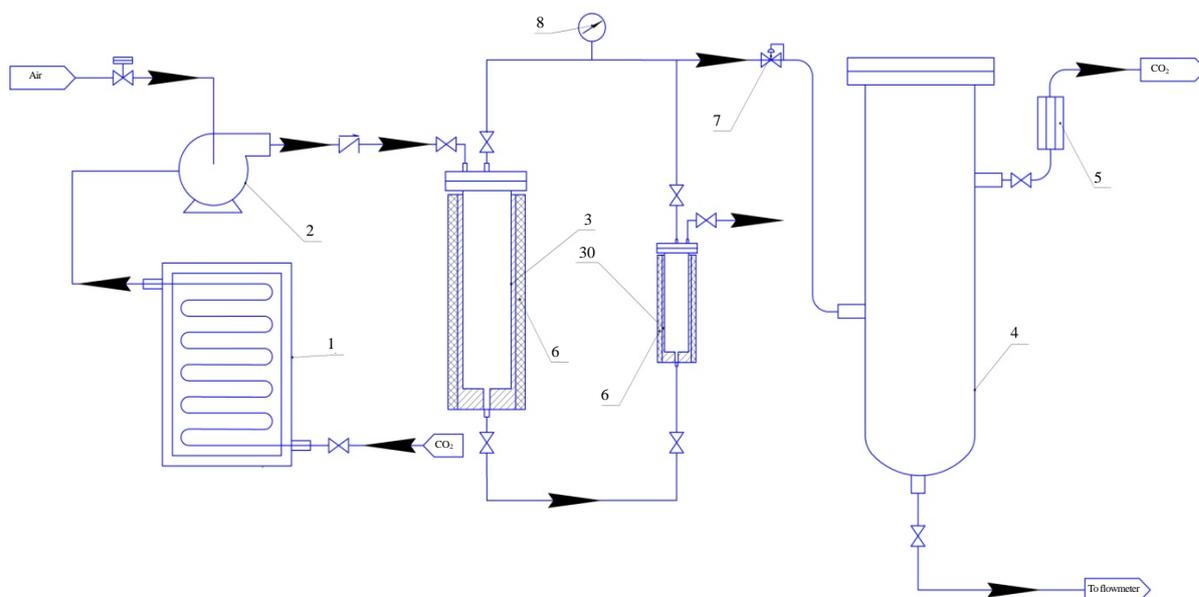
Figure 2. Schematic diagram of impregnation experimental unit: 1—refrigerator, 2—pneumatic pump, 3—saturating cell with the electric heater and thermal insulation (6), 3a—impregnation cell with the electric heater and thermal insulation (6), 4—separator, 5—flowmeter, 7—back pressure regulator, 8—the model manometer.

Key characteristics of the impregnation process realized at the temperature range 308.15˚K - 333.15˚K and pressure of 17.5 MPa are presented in **Table 1**. It is interesting to note that the choice of pressure value was largely accidental, rather than deliberate or, especially, connected with nature of solubility change of a palladium chloride benzolnitrile complex in SC-CO_2 (**Figure 1**). But it is nevertheless important to note that this value practically was equal to value of pressure in the second crossover point for the discussed binary system that has to effect on results of SC-CO_2-impregnation process as appropriate.

Table 1. Increase in mass of the catalyst carrier as a result of SC-CO_2-impregnation process, % to the initial weight (17.5 MPa).

Temperature, ˚K	CO_2 flow rate (recilculation), ml/min	Endurance duration min.			
		5	10	15	20
308.15	1	0.1493	0.2102	0.2595	0.2732
	5	0.1461	0.2058	0.2541	0.2675
	10	0.1152	0.1622	0.2003	0.2108
	15	0.0833	0.1173	0.1448	0.1524
	20	0.0701	0.0987	0.1219	0.1283
313.15	1	0.1756	0.2473	0.3053	0.3214
	5	0.1713	0.2412	0.2978	0.3135
	10	0.1406	0.1981	0.2445	0.2574
	15	0.1017	0.1432	0.1768	0.1861
	20	0.0774	0.1090	0.1345	0.1416
318.15	1	0.1995	0.2810	0.3469	0.3652
	5	0.1943	0.2737	0.3379	0.3557
	10	0.1683	0.2371	0.2927	0.3081
	15	0.1521	0.2142	0.2645	0.2784
	20	0.1171	0.1649	0.2036	0.2143
323.15	1	0.1642	0.1741	0.1845	0.1956
	5	0.1607	0.1703	0.1805	0.1914
	10	0.1267	0.1343	0.1423	0.1509
	15	0.0916	0.0971	0.1029	0.1091
	20	0.0771	0.0817	0.0866	0.0918
328.15	1	0.1672	0.1772	0.1879	0.1992
	5	0.1636	0.1734	0.1839	0.1949
	10	0.1290	0.1368	0.1450	0.1537
	15	0.0933	0.0989	0.1048	0.1111
	20	0.0785	0.0832	0.0882	0.0935
333.15	1	0.1702	0.1804	0.1912	0.2027
	5	0.1666	0.1765	0.1871	0.1984
	10	0.1313	0.1392	0.1476	0.1564
	15	0.0950	0.1007	0.1067	0.1131
	20	0.0799	0.0847	0.0898	0.0952

Comments to **Table 1**:

-As carbon dioxide flow rate in recirculation solvent saturation system with impregnation material increases, efficiency of impregnation processes with the same duration naturally falls. Higher flow rates leads to smaller time of contact in system "the dissolved material-solvent" and smaller concentration of a palladium chloride benzonitrile complex in the carbon dioxide directed to the impregnation cell. Preferable range of CO_2 flow rate is from 1 to 5 ml/min.

-The results given in **Table 1** unambiguously indicate preference of 15 - 20 minute endurance of the impregnated matrix in SC-CO_2-impregnation material solution before a sharp decompression. This duration in opinion of other researchers is sufficient for the supercritical fluid-solution diffusion in all volume of a porous matrix and most often appears in the corresponding publications [4]-[6] [8].

-Difficult nature of impregnation efficiency temperature dependence caused by the above-noted coincidence of pressure value (17.5 MPa) for a data array, presented in the table, with pressure value of the second crossover point for solubility isotherms of a palladium chloride benzolnitrile complex in supercritical carbon dioxide. This pressure value (**Figure 3**) within errors of results of measurements is an interface between two opposite tendencies: solubility decrease with growth of temperature ($P < P^{**}$, where P^{**}—a pressure in the second crossover point) and solubility increases with growth of temperature ($P > P^{**}$). According to tabular data temperature range 313.15°K - 318.15°K represented to be is the most preferable for the impregnation process.

Characteristics of SC-CO_2-impregnation process in the preferable ranges of a carbon dioxide flow rate, temperatures and endurance in the impregnation cell, but in a wide interval of pressure change (15.0 - 35.0 MPa) has been presented in **Table 2**.

On isobars with pressure values of 15.0 MPa and 16.0 MPa decrease in weight change with temperature growth is distinctly traced according to similar nature of solubility change with pressure values smaller than pressure in the second crossover point. While on isobars with the pressure values P = 230 - 350 MPa is exceeding that for the same crossover point, weight change with growth of temperature increases.

The results presented in **Table 2** confirm results of earlier carried out research of palladium chloride benzolnitrile complex solubility in supercritical carbon dioxide [9] [16] (**Figures 4-6**). Earlier stated preferences to ranges of SC-CO_2-impregnation process parameters implementation can be added with the preferable range of pressures from 19.0 - 21.0 MPa.

Activity of the prepared catalysts samples study has been carried out on the microcatalytic experimental unit of flowing type which has been described in [9] [16].
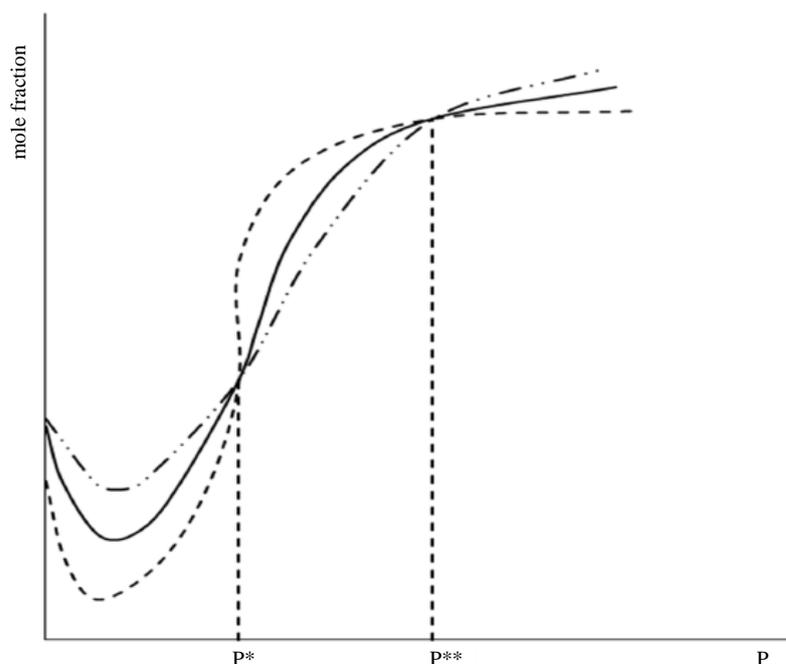
Figure 3. The character of the change of the solubility of the model substance in the on isobars in the super-critical fluid solvent and the crossover points [18] [19].

Table 2. Increase in mass of the catalyst carrier as a result of implementation SC-CO₂-impregnation process, % to initial weight.

P, MPa	T, 308.15˚K	T, 313.15˚K	T, 318.15˚K	T, 323.15˚K	T, 328.15˚K	T, 333.15˚K
150	0.2707	0.2613	0.2503	0.2311	0.1898	0.1503
160	0.2762	0.2768	0.2711	0.2515	0.2017	0.1706
170	0.2675	0.2996	0.3057	0.2714	0.2199	0.1984
180	0.2428	0.3135	0.3338	0.2916	0.2402	0.2357
190	0.2238	0.3002	0.3589	0.3117	0.2747	0.2594
200	0.2009	0.2843	0.3632	0.3509	0.3129	0.2793
210	0.1863	0.2594	0.3517	0.3617	0.3386	0.2911
220	0.1751	0.2336	0.3356	0.3542	0.3401	0.3051
230	0.1649	0.2045	0.3148	0.3107	0.3497	0.3199
240	0.1563	0.1742	0.2909	0.2652	0.3095	0.3244
250	0.1497	0.1627	0.2045	0.2395	0.2714	0.3275
260	0.1403	0.1533	0.1982	0.2206	0.2519	0.3204
270	0.1318	0.1425	0.1919	0.2017	0.2193	0.2913
280	0.1233	0.1321	0.1806	0.1828	0.1967	0.2623
290	0.1149	0.1216	0.1794	0.1739	0.1864	0.2332
300	0.1064	0.1112	0.1731	0.1645	0.1751	0.2041
310	0.0979	0.1007	0.1457	0.1526	0.1646	0.1751
320	0.0894	0.0903	0.1261	0.1351	0.1396	0.1460
330	0.0709	0.0798	0.1054	0.1183	0.1224	0.1369
340	0.0602	0.0694	0.0915	0.1069	0.1120	0.1288
350	0.0564	0.0608	0.0842	0.0905	0.1042	0.1159
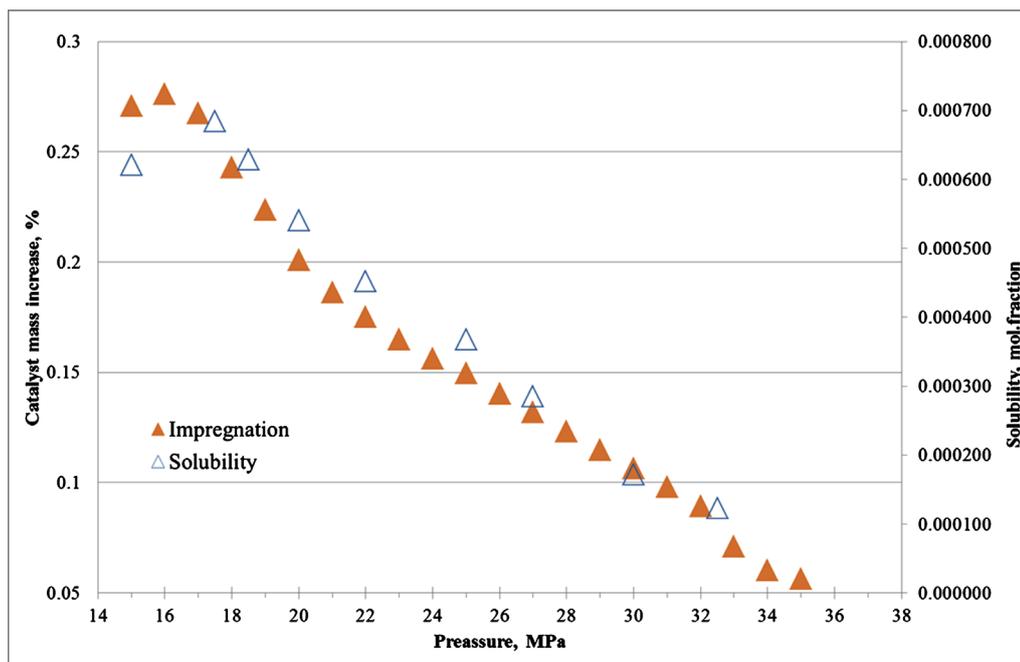
Figure 4. Increase in mass of the catalyst carrier as a result of implementation SC-CO₂-impregnation-process. Comparison to nature of impregnation material solubility change in supercritical carbon dioxide at a temperature T = 308.15˚K.
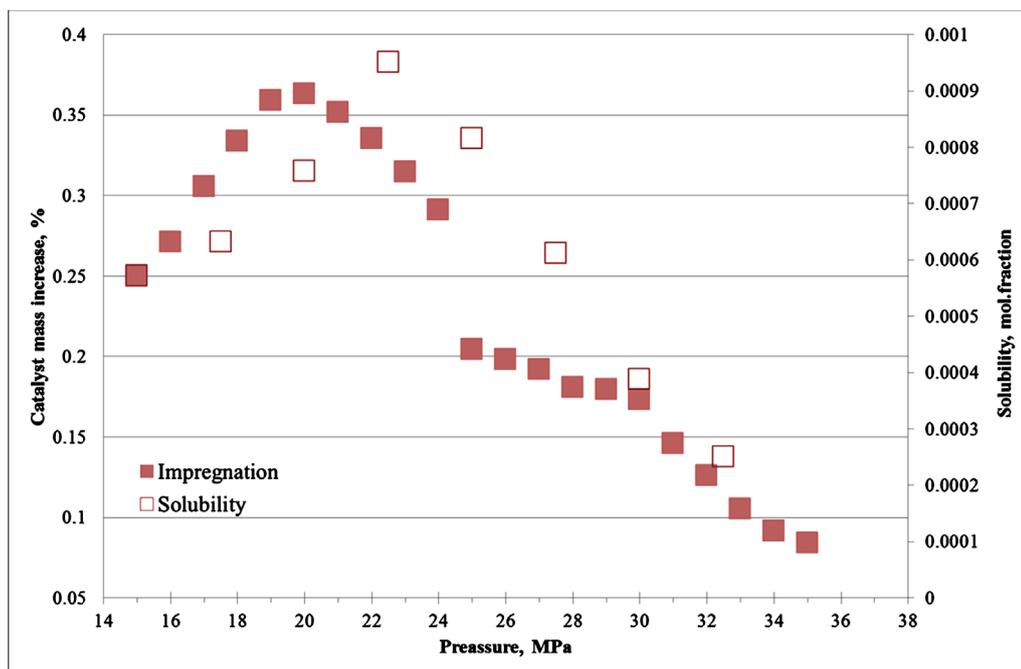
Figure 5. Increase in mass of the catalyst carrier as a result of implementation SC-CO_2-impregnation-process. Comparison to nature of impregnation material solubility change in supercritical carbon dioxide at a temperature $T = 318.15°K$.
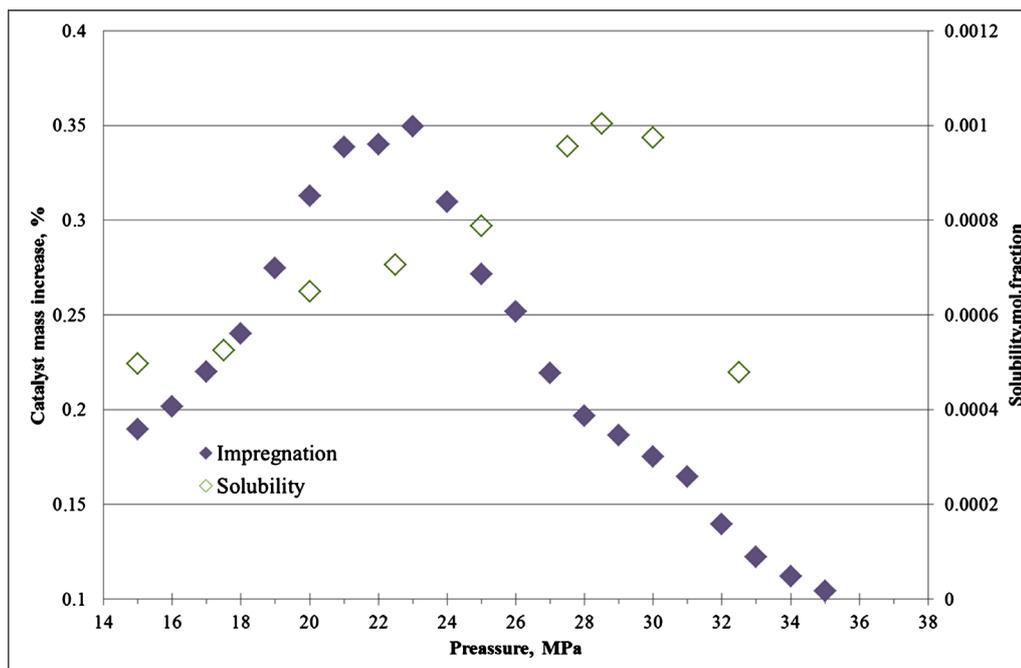
Figure 6. Increase in mass of the catalyst carrier as a result of implementation SC-CO_2-impregnation-process. Comparison to nature of impregnation material solubility change in supercritical carbon dioxide at a temperature $T = 328.15°K$.

Experimental unit used for preliminary treatment of the catalyst (regeneration by hydrogen), and for further test of this catalyst for activity and selectivity during cleaning ethane-ethylene fraction from acetylene impurity. The work has been carried out according to the following method which is also described in [9] [16].

The catalyst sample with a capacity of 0.5 cm^3 and particles size of 0.2 - 0.5 mm is loaded into a middle part of the reactor. At the bottom of this reactor a junction of the measuring and regulating thermocouple of temperature regulator has been located. Moreover, for additional heating of the incoming gas stream, a layer of inert carrier (floured quartz glass or porcelain with a particle size 0.2 - 0.5 mm) has been poured over the catalyst bed.

Restoration of the catalyst has been carried out at a temperature near 200˚C in hydrogen stream in process lasting 2 hours. After that, temperature in the reactor decreases to the value chosen for carrying out experiment. Then supply of hydrogen stops and the supply of ethane-ethylene fraction (EEF) of the following composition (volume %): C_1—0.22; C_2 (ethane)—13.11; C_2 (ethylene)—80.99; C_2 (acetylene)—1.05; H_2—4.73 with the demanded volume supply speed starts. Composition of EEF has been defined by the customer of the present study.

The initial ethane-ethylene mixture and the gas mixture after the reactor has been analyzed on a KHROM-4 ("Meta-chrome", Bauman str. 100, Yoshkar-Ola, Russia) chromatograph with a flame ionization detector. Mixture components has been separated at 70˚C and a carrier gas (nitrogen) flow rate 25 cm^3/min on a column 3 m long with a 3 mm inside diameter packed with Al_2O_3 + $NaHCO_3$ (6 wt%), made in our University. The frequency of taking gas mixture samples after the reactor was 1 per hour. If the complete absence of acetylene has been observed at certain reactor temperature and ethane-ethylene mixture flow rate, the volume flow rate has been increased to a value at which the content of acetylene at the exit of the reactor was 1 - 2 ppm. Just this ethane-ethylene mixture volume rate has been used as a characteristic of the activity of the given catalyst at the selected temperature.

Three samples of palladium catalysts with the maximum maintenance of a complex (**Table 2**) in them are selected for research:

- The sample 1 is prepared at T = 318.15˚K and P = 20 MPa (the maintenance of 0.3632%).
- The sample 2 is prepared at T = 323.15˚K and P = for 21 MPa (the maintenance of a complex of 0.3617%).
- The sample 3 is prepared at T = 328.15˚K and P = 23 MPa (the maintenance of a complex of 0.3497%).

Activity of catalysts has been defined according to the method described in works [9] [16] and estimated concerning the content of acetylene in the mixture which passed hydrogenation reaction to the content of acetylene in initial mixture. Selectivity of the catalyst in the presented work has not been established. Hydrogenation is carried out at a temperature of 100˚C.

Results of activity research are presented in **Table 3**. The table shows that at a temperature t = 100˚C activities of catalysts samples prepared by the method described in this work is commensurable with activities of the samples prepared by a traditional method [9] [16].

The reaction of acetylene to ethylene hydrogenation takes place on a catalyst surface, but not in volume of its pores. Even though, high activity of the catalysts prepared in present work reached at a temperature of 100˚C that makes only the middle of the range which is traditionally used in industrial technology (50˚C - 150˚C).

Efficiency of the prepared palladium catalyst samples is indirectly proved by surface area of these samples, presented in **Table 4**. In case when the same mass of active metal precipitates on a carrier surface, quite often

Table 3. Activity of palladium catalysts samples.

Catalyst sample	Initial content of acetylene (peak height, mm)	Final content of acetylene (peak height, mm)	Catalyst activity, %
The sample 1	205	18	91.21
The sample 2	214	19	91.12
The sample 3	209	19	90.09

Table 4. Surface area of the prepared palladic catalyst samples.

The sample	Hinge plate, g	Scale	Height of peak, mm	Width of peak, mm	Area of peak, mm^2	Volume of gas, cm^2	Surface area, m^2/g
Raw Al_2O_3	0.071	64	134	1.8	15436.8	3.201	220.103
The sample 1	0.061	64	126	1.2	9676.8	2.02245	161.796
The sample 2	0.053	64	109	1.2	8371.2	1.74958	161.093
The sample 3	0.059	64	111	1.3	9235.2	1.93016	159.647

obstruction of pores of aluminum oxide takes place and, as a result, the area of its surface significantly decreases. When metal is evenly distributed in all volume of a firm matrix, the surface area of the catalyst decreases not so significantly. From **Table 4** it is visible that the decrease of surface area of the palladium catalyst samples prepared in the present work in comparison with the pure raw aluminum oxide is not so considerable indicating uniform distribution of the precipitated complex in volume of the carrier.

4. Conclusion

Results of the conducted research show efficiency and attractiveness of SC-CO$_2$-impregnation process within a problem of heterogeneous catalysts production which will be even more convincing in relation to the reactions proceeding in volume of pores of a high-porous matrix of the catalyst carrier.

Acknowledgements

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