Installation for the implementation of the supercritical fluid extraction regeneration of nickel-molybdenum catalyst

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Abstract. The process of supercritical fluid extraction recovery of the catalyst at pressures of 10, 20 MPa and temperatures of 343, 373, 433, 473 K with pure supercritical carbon dioxide on the original device has been implemented. An increase in pressure and temperature has a positive effect on the catalyst regeneration process. With increasing pressure increases the density of CO₂, and, consequently, its dissolving ability. With increasing temperature, the pressure of saturated vapors of compaction products increases and, as a result, their concentration in CO₂ increases. In order to increase the efficiency of the supercritical CO₂-extraction process for the regeneration of catalyst samples, carbon dioxide modification with various additives (chloroform, dimethylsulfoxide, acetone, ethanol, and non-polar inert with respect to the catalyst composition hexane) was used. Modification of supercritical carbon dioxide with ethanol and hexane at a temperature of 473 K and a pressure of 20 MPa led to an increase in the mass loss of catalyst samples by 12 and 14%, respectively, which indicate the removal of deactivating substances during regeneration by the method of supercritical fluid extraction.

1. Introduction
Catalysis is one of the most important areas of chemistry and chemical technology. The direction of high technology and high-tech. It is not by chance that the main volume of highly effective catalysts in our country is purchased in foreign countries. The high efficiency of catalysts, and especially those formed using rare metals, is combined with the same high cost. In practice, as a rule, deactivation of catalysts is accompanied by a regeneration procedure, which allows to significantly increase their service life. However, the existing methods of regeneration, as their physico-chemical base, have oxidation and burning of catalyst-deactivating compounds, carried out, as a rule, at temperatures of 450 – 600 °C. The energy consumption of these processes is combined with another significant negative factor, such as a change in the structure of the catalyst carrier, and sometimes its sintering, determined primarily by high temperatures. As a result, in this case, the catalysts can withstand only 2-3 regeneration cycles, and then follows the disposal of such an expensive product [1].

The catalyst LD-145 is used at PJSC Ninekamskneftekhim in the process of selective hydrogenation to purify pyrolysis gasoline from aromatic hydrocarbons, which is carried out in two stages. The first stage proceeds on the palladium catalyst LD-265 [2], which involves the complete removal of unstable components of pyrolysis gasoline (diolefins, alk enyl aromatics, styrene compounds) and the partial removal of olefins. In the second stage, the C₆-C₈ aromatic fraction is
cleaned of olefins together with hydrodesulfurization on nickel-molybdenum (LD-145) and cobalt-molybdenum (HR-406) catalysts.

In addition to the reactions of selective hydrogenation, adverse reactions occur: such as polycondensation, thermal and catalytic polymerization of unstable compounds, which results in the formation of coke deposits on the active surface of the catalysts, significantly reducing the activity and regeneration period of the catalyst.

At the chemical industry, traditional oxidative regeneration is used to remove coke compounds, consisting of controlled burning coke with gas mixtures containing oxidizing agents (oxygen) and proceeding at catalysis temperatures and above. However, this regeneration is multistage, time consuming and energy consuming [3].

Therefore, in recent times, searches are being conducted for new ways of regeneration, which are realized in non-aggressive, inert environments with minimal energy consumption. One of the alternative ways of regeneration is the use of the supercritical fluid extraction process (SCFE), which seems preferable due to the combination of the unique properties of supercritical fluid (SCF) media: extremely low viscosity, high penetrating and dissolving ability. Despite the fact that a rather wide range of substances is used as supercritical extracting, supercritical carbon dioxide (SC-CO$_2$) is the most demanded and popular. This is due to its convenient critical parameters, inertia, fire and explosion safety, as well as environmental friendliness of the product and the production as a whole [4].

The key problem of the innovation process under discussion is the solubility of catalyst-deactivating compounds in SCF media of a corresponding chemical nature. The three main factors determining the solubility of a substance in a particular solvent include: the nature of the solute and solvent, their state of aggregation and thermodynamic conditions. Two oppositely acting trends determine the nature of the change in the solubility of a substance in a supercritical fluid solvent. On the one hand, an increase in temperature leads to an increase in the saturated vapor pressure of the solute and, as a consequence, its concentration in the solvent phase increases. Therefore, the solubility increases. On the other hand, an increase in temperature (at $p = \text{const}$) leads to a decrease in the density of solvent SCF. And this already determines the decrease in the dissolving capacity of the supercritical fluid medium or the solubility of the substance in the supercritical fluid.

The problem of the solubility of substances in supercritical fluid solvents has been the subject of intensive studies of the last 2-3 decades [5-9], including a search in the direction of developing new experimental methods and techniques for studying this important thermodynamic characteristic [10].

Often, solubility is defined as a property of practical importance. Indeed, sustained high interest in supercritical fluid environments and technologies based on them is not yet supported by the same high growth rates in the number of commercial implementations, and one of the important reasons for this situation, according to many researchers, is the lack of knowledge of the characteristics of phase equilibria, especially for multicomponent systems in supercritical fluid state. The latter quite significantly determine the capabilities of the stages of modeling, optimization and scaling of processes and technologies in general.

This paper is devoted to the study of the possibility of regeneration of the catalyst for selective hydrogenation of LD-145 by the method of supercritical fluid CO$_2$-extraction.

2. Materials and Methods.

Samples of the spent catalyst were obtained as a result of a single selection from the enterprise of PJSC “Nizhnekamskneftekhim” of the BC plant when they are replaced after the working cycle.

The extraction process of regeneration with the use of pure and modified supercritical carbon dioxide as an extracting is implemented on an experimental setup, schematically represented in figure 1 [11].
3. Results and discussion
The kinetics of extraction regeneration of the catalyst LD-145 using SC-CO$_2$ is shown in figure 2 and figure 3, confirms the fundamental possibility and feasibility of using the SCFE process.

**Figure 1.** Scheme of supercritical fluid CO$_2$ extraction installation: 1 - cylinder with CO$_2$; 2, 4 - refrigeration unit; 3 - plunger pump of high pressure brand “Waters P50A”; 5 - capacity for co-solvent; 6 - high pressure plunger pump of the brand “LIQUPUMP 312/1”; 7 - three-way valve; 8, 9 - thermostatically controlled extractor; 10 - meter - temperature controller; 11a, 11b - extract collections; 12 - thermostat; 13, 14 - reducing valves; 15 - gas meter.

**Figure 2.** Kinetics of SCFE of the process of regeneration of the catalyst LD-145 with pure SC-CO$_2$ at $p = 10$ MPa.
The results of the study of the effect of the concentration of co-solvents of different chemical nature on the change in the mass of the catalyst in the process of its regeneration at $T = 473$ K and $p = 20$ MPa are presented in figure 4. Hexane as a co-solvent was more effective than acetone or chloroform. The concentration of co-solvents corresponding to the optimal value, i.e. maximum efficiency of the regeneration process was 2 - 4% of the mass.

Figure 3. Kinetics of SCFE in the process of regeneration of the catalyst LD-145 with pure SC-CO$_2$ at $p = 20$ MPa.

Figure 4. The effect of the concentration of co-solvents of different nature on the change in the mass of the catalyst in the process of SCFE regeneration.

Figure 5 shows the change in the mass of the catalyst during the regeneration process using co-solvents.

Figure 5. Kinetics of SCFE in the process of regeneration of the catalyst LD-145 with modified SC-CO$_2$.
The results of the study of the kinetics of the SC-CO$_2$ extraction process indicate the removal of deactivating compounds from the surface of the spent catalyst. Modification of SC-CO$_2$ contributes to a more complete removal of compaction products and ensures the restoration of catalytic activity.

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