Prospective principles of catalyst utilization using supercritical fluid media

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Abstract. An overview of prospective principles of catalyst utilization using supercritical fluid media is presented. The processes in which these working media act as solvents and extractants, reagents and reaction media are considered. At the same time, we are talking about both heterogeneous catalysts and catalytic complexes dissolved in the water runoff of industrial enterprises. Using the LD-145 catalyst as an example, we studied the possibility of extending its service life instead of recycling, due to a change in the physical and chemical principles of its regeneration. We are talking about replacing the high-temperature process of vapor-air oxidation of catalyst-deactivating compounds with a supercritical fluid extraction process. At the same time, the extractant used is not widespread carbon dioxide, but propane/butane mixture, the use of which makes the process significantly more efficient. This is because a number of binary systems "deactivating compound – extractant" change the type of phase behavior from V-VI to I-II when changing carbon dioxide to propane/butane mixture. Thus, these systems, for example, involving naphthalene, phenol and some other substances in the supercritical fluid state fall outside the binodal of the binary system into the region of unlimited miscibility of components, which significantly increases the kinetics of the catalyst regeneration.

1. Introduction
Spent catalysts with extremely low active metal content are often buried rather than recycled. This may be quite large-scale in terms of the volume and size of the required areas of the relevant territories and unsafe for the environment and the ecology as a whole. For example, the disposal of about 100,000 tons of waste from one of the largest petrochemical enterprises in the Russian Federation, which includes largely spent catalysts, and formed between 1973 and 1982, covers an area of 10 hectares.

Nevertheless, in most cases, catalysts, that are not susceptible to regeneration and have passed into the status of catalytic waste have a sufficiently high content of active metal and, therefore, there is an economically justified need for their recycling in order to extract expensive chemical elements.

Traditional methods of utilization and, firstly, liquid extraction, are characterized by high-energy consumption and the need to solve problems associated with the use of toxic solvents. Little or no toxic sub- and supercritical fluid media in one form or another (reagent, reaction medium, extractant, anti-solvent), as in the processes of synthesis [1-2] and regeneration [1-14] with their participation, are considered as a promising alternative.
In particular, in [15], as a result of a comparative analysis of the efficiency of the processes of leaching cobalt from a spent cobalt-molybdenum hydrotreating catalyst (4% Co; 17% Mo, a surface area of 175 m²/g, pore volume 0.5 cm³/g), it was found that the use of an aqueous-ammonia solution in the supercritical fluid state as a "solvent" is the most effective and cost-effective. A certain convention of the concept of "solvent" in this case is that during the leaching process, this medium simultaneously performs the functions of a reaction medium, a reagent, and an extractant.

It should be remembered that leaching is the process of extracting one or more components from solid-phase raw materials (ore, concentrate, production waste) using an aqueous solution of alkali, acid or other reagent. In this case, leaching is accompanied by a chemical reaction, as a result of which the extracted component passes from a form that is insoluble in water to a soluble one. At the end of the leaching process, the solvent phase (liquid in the traditional version) is separated from the solid phase in one way or another.

The leaching process is a relatively slow process. Therefore, numerous attempts are being made to intensify it by grinding the solid phase, performing the process at high pressures, applying electric fields, thermal and ultrasonic effects, as well as using vibrations, pulsations, etc.

In an aqueous-ammonia solution based on a cobalt ion, an octahedral hexamincobalt ion \((\text{Co}[\text{NH}_3]_6)^{3+}\) is easily formed [16], thus realizing the above-mentioned trajectory of the target component conversion from an insoluble in water state to a soluble one:

\[
\text{Co} + 6\text{NH}_4^+ + \frac{3}{4} \text{O}_2 = (\text{Co}[\text{NH}_3]_6)^{3+} + \frac{3}{2} \text{H}_2\text{O} + 3\text{H}^+.
\]

According to [17-19], the mechanism of this reaction under conditions close to atmospheric conditions is as follows: at the initial moment, because of oxygen adsorption by the catalytic surface, an intermediate compound \(\text{Co...O}\) (2) is formed at the location of cobalt, which subsequently reacts with ammonia ions (3). And, finally, the amine-cobalt ion \((\text{Co}[\text{NH}_3]_6)^{2+}\) is oxidized to examinable ion \((\text{Co}[\text{NH}_3]_6)^{3+}\) (4):

\[
\text{Co} + \frac{3}{4} \text{O}_2 + \text{H}^+ + e^- = \text{Co...O} + \frac{1}{2} \text{H}_2\text{O},
\]

\[
\text{Co...O} + 6 \text{NH}_4^+ = (\text{Co}[\text{NH}_3]_6)^{2+} + \text{H}_2\text{O} + 4\text{H}^+,
\]

\[
(\text{Co}[\text{NH}_3]_6)^{2+} = (\text{Co}[\text{NH}_3]_6)^{3+} + e^-.
\]

It is noted that there is a combination of rapidity and irreversibility of the discussed surface reaction (activation energy is 12.54 kcal/mol) on the one hand, and the existence of such a limiting factor as the level of oxygen mass transfer to the liquid-solid interface on the other. As a result, it is concluded that the reaction is diffusion-controlled.

Considering that the reaction medium in the supercritical fluid (SCF) state is characterized by a significantly higher diffusivity than that in the case of liquid-phase media, a logical assumption is made in [15] about the preference for the implementation of the cobalt leaching process in an aqueous-ammonia solution in the SCF state. In this case, the prerequisites for the fact that the kinetics of the process will largely be determined by the speed of the chemical reaction are supplemented by such a concomitant factor as a possible increase in the solubility of oxygen in the reaction medium. As a consequence of these two main reasons, the transition of cobalt from an insoluble in water state to a soluble state and its direct dissolution in an aqueous-ammonia solvent in a supercritical fluid state should be faster than it is in a liquid-phase medium. As a result, it can be said that there are prerequisites for reducing the duration of the process, increasing the degree of extraction and reducing the consumption of the solvent.

The efficiency of the cobalt leaching process from the spent hydrotreating catalyst was estimated using the indicator [15]:

\[
e = 1 - (\Delta\text{Co}/\text{Co}),
\]

where: \(\text{Co}\) – cobalt content in the non-leached catalyst, % wt.; \(\Delta\text{Co}\) – cobalt content in the leached catalyst, % wt.
The conditions for implementing the process of leaching cobalt from a spent hydrotreatment catalyst are presented as follows [15]: 1 – \( P << P_{cr}, T << T_{cr}; \) 2 – \( P > P_{cr}, T << T_{cr}; \) 3 – \( P > P_{cr}, T < T_{cr}; \) 4 – \( P > R_{cr}, T > T_{cr}. \) The process implemented in supercritical fluid conditions exceeds the efficiency of processes implemented in conditions 1, 2 and 3 by an average of 6.8 %, 4.0 % and 14.2 %, respectively. The authors of the study [15] state the fact of reducing the required amount of solvent during the leaching process under SCF conditions.

The principles based on the formation of organometallic complexes that are soluble in supercritical fluid media were used in [20-21] to solve the problem of utilization of rhodium-platinum and palladium catalysts. In [20], the mechanism of utilization of the so-called "automotive" catalyst (Toyota Central R&D Labs.,Inc.,Japan) containing rhodium and platinum involves the formation of organometallic complexes based on a complex-forming chelating ligand of the "Cyanex 302" brand [bis(2,2,4-trimethylpentyl) monothyophosphinic acid] and the implementation of a supercritical fluid CO\(_2\) extraction process.

Based on the results of the study, we can draw a clear conclusion: rhodium and platinum can be successfully extracted and, in particular, a result close to 100% can be achieved within 10 minutes in the framework of the SC-CO\(_2\) extraction process implemented at \( T=333\) K and \( P=20 \) MPa.

The same approach was used in [21] to solve the problem of waste palladium catalyst utilization. In this case, in contrast to the previous one, a comparative analysis of the efficiency of the extraction process was performed for three different complexing ligands: acetylacetone (AA), tri-n-butylphosphate/nitric acid complex (TBP/HNO\(_3\)/H\(_2\)O) and [bis(2,2,4-trimethylpentyl) monothyophosphoric acid] ("Cyanex 302"). Successful and close to 100% extraction of palladium from the utilized catalyst was possible only if the complexing ligand "Cyanex 302" was used. The result was achieved within 10 minutes in the SC-CO\(_2\) extraction process implemented in the temperature range \( T=313-353\) K and the pressure range \( P = 8-20 \) MPa.

In [1], the solubility of palladium chloride complexes with organic ligands in supercritical carbon dioxide (\( T=308.15-328.15 \) K, \( P=10-32 \) MPa) was studied. We are talking about benzonitrile, styrene and cyclohexene complexes of palladium chloride. The palladium catalyst synthesized on the basis of a benzonitrile complex showed encouraging results. The efficiency of the impregnation process used in this case indirectly indicates the potential efficiency of the SCF extraction process in the context of the problem of utilization of the discussed catalyst.

In [7], the fact of extraction of the active metal of a deactivated sample of the hydrodesulfurization catalyst DN-3531 during its regeneration using a mixture of SC-CO\(_2\)+DMSO (dimethylsulfoxide) was revealed. Additional research, the results of which are presented in [22], allowed us to establish the following. The active metal, nickel oxide, does not dissolve in pure SC-CO\(_2\), whereas under the conditions of the SCF regeneration process with carbon dioxide modified with dimethyl sulfoxide, nickel oxide dissolves in DMSO and forms a complex compound \([\text{Ni(DMSO)}]^{2+}\), which in turn dissolves in SC-CO\(_2\). This explains the entrainment of the active metal that occurs in this case. The authors of [22] quite reasonably believe that the result obtained in this study is interesting from the point of view of utilization of the discussed catalyst.

In 2006, the South Korean company "Samnam Petrochemical Co., Ltd." put into operation an industrial plant for the SCWO processing of 36 tons per day of terephthalic acid production wastewater, containing benzoic acid, \( p \)-tolyl aldehyde, toluylic acid, 4-carboxybenzaldehyde, 4-hydroxymethyl benzoic acid, as well as cobalt and magnesium acetates used in the preparation of the corresponding catalyst. Within 10 minutes, 99.9% oxidation of organic compounds occurs. Simultaneously with the oxidation process, more than 90% of cobalt and magnesium precipitate as their oxides and in the form of particles up to 3 mm in size [23].

A similar task and approach are implemented in [24]. In this case, we are talking about a molybdenum complex that accelerates the reaction of propylene epoxidation in a multi-tonnage industrial process carried out in PJSC Nizhnekamskneftekhim. The above-mentioned catalytic complex, after washing the reaction product, is concentrated in the washing water, which until now has only been subjected to thermal neutralization, and as a result, high-cost molybdenum salts are lost,
being distributed in the flue gases and the corresponding melt. Therefore, up to 45 tons of molybdenum is lost annually at an average cost of 1.8 million rubles per ton. The following components of this water flow are also lost: ethylbenzene (2.5% by weight), acetophenone (1% by weight), methylphenylcarbinol (6.5% by weight), phenol (2.5% by weight) and propylene glycol (12% by weight). It is clear that in this case the economic costs are compounded by the environmental problems that arise.

Initially, the oxidation of water runoff under supercritical fluid conditions (SCW) was implemented using hydrogen peroxide as an oxidizer. However, at the stage of the feasibility study of the process implementation in industry, hydrogen peroxide turned out to be unnecessarily expensive. For this reason, the authors of [24] decided to implement the oxidation stage using a flow unit and air oxygen as an oxidizer. The SCWO process is implemented under conditions of an excess of air oxygen in the range of 100-400%, at temperatures of 673-873 K and a pressure of 22.5 MPa.

The implementation of the oxidation process in SCF conditions has significant advantages over the widespread thermal neutralization by reducing the amount of emissions into the atmosphere, improving the quality of neutralization and the possibility of recycling the neutralized water. With the appropriate composition of water runoff, it is possible to use the heat of the exothermic reaction for internal production needs. In addition, perhaps, it is no less important for the problem, that the inorganic part of the water body containing the molybdenum complex simply precipitates in SCF conditions and can be easily extracted. The concentration of molybdenum in the inorganic residue was performed using a high-frequency induction plasma unit.

The listed methods and special cases of utilization of catalysts using SCF media form an opinion about the sufficient perfection and capabilities of the essentially new approach, which, as noted above, has already proven itself [1-14] as a successful method in the task of regeneration of heterogeneous catalysts. Taking into account the volume of spent catalysts, and understanding the lack of perfection of traditional high-temperature methods of regeneration of heterogeneous catalysts in existing production facilities, an attempt was made to SCF regenerative utilization of some catalysts that fell into the category of spent. In this case, a higher or lower probability of restoring the catalytic capabilities of a valuable element of chemical technology can be combined, for example, with the formation of recommendations for limiting the permissible number of high-temperature steam-air regenerations for the operated catalysts and the subsequent use of approaches implemented in milder thermodynamic conditions. A selective hydrogenation catalyst of the LD-145 brand was used as a sample of the catalyst that fell into the category of spent ones at PJSC Nizhnekamskneftekhim.

2. Experimental part
In the SCF extraction process, a propane/butane mixture was used as an extractant, including 45.8% by weight of propane and 54.2% by weight of butane (the critical parameters of propane, butane, and propane/butane mixture according to [25-26] are characterized by the following values: propane: \( T_{\text{CR}} = 369.82 \, \text{K} \) (96.67 °C), \( P_{\text{CR}} = 4.247 \, \text{MPa} \); butane: \( T_{\text{CR}} = 425 \, \text{K} \) (151.85 °C), \( P_{\text{CR}} = 3.797 \, \text{MPa} \); propane/butane mixture: \( T_{\text{CR}} = 394.25 \, \text{K} \) (121.1 °C), \( P_{\text{CR}} = 4.3 \, \text{MPa} \).

Figure 1 shows the scheme of the SCF extraction unit. According to the regeneration procedure, the extractor (3) is filled with the spent catalyst. After filling the extractor, its shell (4) is heated. After reaching the set temperature in the extractor, the extractant is fed into it, preheated to the same temperature using a heat exchanger (11). The required pressure of the propane/butane mixture is generated by a liquid pump (2) and maintained by a backpressure regulator (9).
The required flow rate of the extractant is set. Extractant, passing through the extractor, dissolves the deactivating compounds on the surface of the catalyst. Finally, the solution of these deactivating compounds in the extractant is fed to the separator (6), in which the extractant is restored for recycling and the compounds extracted from the catalytic surface (extract) are isolated.

3. Results and discussions

Regeneration of the LD-145 catalyst using a supercritical propane/butane mixture was performed at \( t=140^\circ\text{C} \) and \( P=10 \text{ MPa} \). Figure 2 shows the kinetics of extraction regeneration of the studied catalyst.

Thermal analysis methods were used to assess the degree of extraction of catalyst deactivating compounds (Fig. 3).

The maximum rate of mass loss on the DTG curve in the region of 600-875 °C without the imposed exothermic effect is explained by the removal of residual degraded (aromatic) fragments.

The activity of the studied catalyst sample was estimated by the conversion of the dibenzothiophene hydrodesulfurization reaction and naphthalene hydrogenation on model raw materials (test conditions: \( t=300 \text{ °C} \), \( P=3 \text{ MPa} \), 1 hour exposure). With low activity of the spent LD-145 catalyst in the methylnaphthalene hydrogenation reaction (10.7% conversion) and no hydrodesulfurization reaction, the regenerated sample is characterized by a significant increase in the conversion of methylnaphthalene (70.9% conversion) and recovery activity in the hydrodesulfurization reaction (conversion 52.3%).

Returning to the problem of choosing the nature of the extractant, it should be noted that the propane/butane mixture, in contrast to the widespread carbon dioxide, makes the process significantly more efficient. This is because a number of binary systems "deactivating compound – extractant"
changes the type of phase behavior from V-VI to I-II when changing carbon dioxide to propane/butane mixture. Thus, these systems involving, for example, naphthalene, phenol, and some others [27] in the supercritical fluid state fall outside the binodal of the binary system into the region of unlimited miscibility of components, which significantly increases the kinetics of the catalyst regeneration.

Thus, the test results indicate a significant increase in the catalytic activity of catalyst samples that have undergone SCF regeneration by the extraction method. It seems that the early replacement of the gas- and steam-air method of catalyst regeneration used in practice with the SCF extraction method may provide an opportunity to extend the service life of the catalyst, instead of its early disposal.

4. Conclusion
The analysis of methods for recycling spent catalysts using working media in a supercritical fluid state is presented.

On the example of the LD-145 selective hydrogenation catalyst with the existing "spent" status, the possibility of a significant improvement in its characteristics due to the replacement of the physico-chemical principles of regeneration is shown. We are talking about replacing the process of high-temperature steam-air oxidative regeneration, which was previously used in the commercial operation of the catalyst, with SCF extraction using a propane/butane mixture as an extractant.

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