The use of supercritical solvents in crude oil fraction conversion

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Abstract. Nowadays, the production of liquid fuel faces such problems as the matching of the final product with the world standards. To solve these problems, the development of novel technologies and highly effective catalysts for crude oil processing and hydrotreatment is of great interest. In the current work, we provide the combined methodology for the conversion of sulfur-containing oil fractions and heavy hydrocarbons based on the application of supercritical solvent and polymer stabilized oxide catalysts. The mixture of propanol-2 and n-hexane in the supercritical state was used as a solvent in this work. It was found that such combination allows the effective C-C and C-S bond breaking. In this paper we describe the studies on the influence of solvent composition and catalyst on the conversion of two widely used oil model compounds (anthracene and dibenzothiophene).

1. Introduction

Crude oil is a complex mixture of highly hydrophobous hydrocarbons including heavy condensed compounds and heteroatomic substances. Oil is mainly consisted of carbon and hydrogen, but some other elements, such as oxygen, nitrogen, sulfur, fluorine, and metals can also present. The main approach of crude oil processing is the rectification which allows kerosene, gasoil and diesel fuels to be obtained. Other methods include cracking, pyrolysis, hydrodemetallization, hydrodesulfurization, hydrodeoxygenation etc.

Catalytic hydroprocessing of oil fractions is a widely used technology for oil treatment which is applied for the improvement of oil fraction quality. Nowadays, there are two main methods used for the hydroprocessing of oil fractions: catalytic hydrotreatment and catalytic hydrocracking. Hydrotreatment process is focused on the removal of heteroatoms such as sulfur, nitrogen, oxygen and metals. Catalytic hydrocracking is focused on the decrease in the boiling temperature of oil fractions [1, 2]. Currently, the intensive studies aimed at the decrease of hydrotreatment cost are performed. These studies include the development of novel catalysts for the process and the search for the process conditions.

The first approach used for the reducing of oil hydroprocessing cost is the catalyst development. Nowadays, the Co-Mo or Ni-Mo sulfided catalysts are used for hydrotreatment. In hydrocracking, in turn, zeolites are widely applied. In spite of high activity, these catalysts are characterized by the fast deactivation due to the coke formation. The use of the oxide-based catalysts is a prospective method for the improvement of hydroprocessing effectiveness. The oxide-based catalyst activity in the hydrocracking and hydrodesulfurization processes directly depends on the dispersion of the active phase and the presence of hydroxyl groups on the catalyst surface [3]. The high dispersion of the active phase can be obtained by using of specific methods for the catalyst synthesis. One of such methods is the metal...
deposition on the supports in the medium of supercritical fluids. The studies on the application of catalysts obtained by the supercritical synthesis in the hydrotreatment processes showed that the high surface area, presence of hydroxyl groups, and unique morphology (high dispersion, uniform distribution, small particle size etc.) leads to the increase in the effectiveness of oil hydroconversion. Such catalysts provide both high degree of desulfurization and high selectivity in the hydrocracking [4–6]. Besides, the oxide-based catalysts showed high activity without the preliminary sulfurization [5].

Another approach for the improvement of hydrotreatment processes is the use of supercritical solvents for hydrocracking and hydrodesulfurization. Such solvents allow the process conditions (mainly temperature) to be reduced and also can decrease the mass-transfer limitations. Supercritical water (SCW) is the mostly wide used solvent for hydprocessing of oil fractions. SCW has a oxidative ability which makes it prospective in the hydrodesulfurization and allows the heteroatoms to be fully removed [7-9]. Hydrocracking in SCW is characterized by a high conversion degree and a high yield of gasoline fractions due to the hydrothermal destruction of heavy hydrocarbons. Besides, water in the supercritical state can serve as a hydrogen atom donor that makes it possible to perform the process in the inert atmosphere [10-13]. Other solvents which can be used as hydrogen donors are tetralin [14], hexane, and dodecane [15]. The researchers note that the use of supercritical solvents leads to the decrease in the viscosity and density of the oil hydprocessing product and prevent the coke formation of the catalyst surface which enhances its stability [14].

2. Materials and methods

2.1. Catalyst synthesis

The synthesis of catalysts was carried out in stainless steel high-pressure reactor Parr-4307 (Parr Instrument, USA) according to the procedure described elsewhere [16–18]. 1 g of the support, milled to a particle size of <70 µm, treated with acetone and dried at 70±2 °C, was placed in the reactor, and a solution of the corresponding precursor in 15 mL of water was added. The precursor amount was calculated for 1-10 wt. % of the metal by weight of the support. 0.1 g of sodium bicarbonate was used as a mineralizer. The reactor was sealed and purged three times with nitrogen to remove air. The reaction mixture was heated to a temperature (200 °C) in a nitrogen atmosphere at a pressure of 6 MPa. The final pressure after heating was 7.8 MPa. The catalyst synthesis process took 15 minutes under operating conditions. After the end of synthesis, the catalyst was filtered, washed with 10-20 mL of distilled water and dried at 70±2 °C. The catalysts were reduced in a hydrogen flow at a temperature of 300 °C.

As a support, hypercrosslinked polystyrene non-functionalized MN-270 (Purolite Inc., Great Britain) was used. Nickel nitrate (Ni(NO₃)₂·6H₂O, c.g., Reachim, Russia), cobalt nitrate (Co(NO₃)₂·6H₂O, c.g., Reachim, Russia), iron nitrate (Fe(NO₃)₃·9H₂O, c.g., Reachim, Russia), ruthenium hydroxochloride (RuOHCl₂·2H₂O, c.g., Aurat, Russia) were used as precursors of the active phase.

2.2. Hydroprocessing procedure and liquid phase analysis

The experiments were performed in a six-cell Parr Series 5000 Multiple Reactor System (Parr Instrument, USA). 1 g of the model compound (anthracene, dibenzothiophene) was dissolved in 30 ml of solvent. The solvent composition varied from 0 to 50 vol. % propanol-2 in n-hexane. The reactor was sealed and purged three times with nitrogen to remove air. Then the nitrogen pressure was set to 3.0 MPa, and the reactor was heated to 270 °C. After reaching the reaction temperature, the pressure increased to 7.5-9.5 MPa, depending on the composition of the solvent. Experiments were performed with varying process time (from 10 min to 3 h) to maintain phase equilibrium.

The liquid phase was analyzed by GCMS using gas chromatograph GC-2010 and mass-spectrometer GCMS-QP2010S (SHIMADZU, Japan) equipped with chromatographic column HP-1MS with 30 m length, 0.25 mm diameter and 0.25 µm film thickness. The column temperature program was set as follows: initial temperature 120 °C was maintained for 5 min then the column was heated up to 250 °C with the rate of 5 °C/min and maintained at 250 °C for 5 min. Helium (volumetric velocity of 20.8 cm³/s,
the pressure of 253.5 kPa) was used as a gas-carrier. The injector temperature was 280 °C, ion source temperature was 260 °C; interface temperature – 280 °C.

3. Results and discussions
First, the influence of solvent composition on the hydroprocessing of oil model compound was studied. The supercritical solvent consisted of n-hexane which has relatively low critical point ($T_c = 234 ^\circ C, P_c = 3.03$ MPa), and propanol-2 with the critical temperature close to that for n-hexane ($T_c = 235.6 ^\circ C, P_c = 5.37$ MPa). Propanol concentration in n-hexane was varied from 0 to 50 vol. %. Figure 1 presents the influence of solvent composition on the rate of anthracene and dibenzothiophene conversion.

![Figure 1. Influence of solvent composition on oil compound conversion rate](image1)

It is well seen, that an increase in the content of propanol-2 in the solvent composition leads to an increase in the conversion rate for both anthracene and dibenzothiophene. However, the highest conversion rate was observed in the presence of 40 vol. % propanol-2 (50 and 60% respectively for 3 hours). These results can be explained by the acceleration of the cracking reaction of C-C and C-S bonds due to an increase in the concentration of the H-atom donor. Moreover, both studied compounds showed the close reaction rates that is probably due to the close reaction ways consisting of the C-C or C-S bond breaking. The main product in both cases was benzene. Small amounts of toluene and cresol were also obtained during anthracene conversion. However, the yield of aromatic hydrocarbons did not exceed 40% in the case of anthracene and 50% in the case of dibenzothiophene (see figure 2).

![Figure 2. Influence of solvent composition on benzene yield](image2)
After the choice of the optimal solvent composition (40 vol. % of propanol-2, 60 vol. % of n-hexane),

the choice of the most effective catalyst was carried out. Mono- and bimetallic catalyst testing was
carried out according to the method described in Section 2.2. It was found that the presence of a catalyst
significantly increased the degree of substrate conversion compared to the non-catalytic process. At the
same time, the yield of hydrocarbons also increased (table 1).

Table 1. Catalyst influence on the anthracene and dibenzothiophene conversion T = 270 °C, P_{in} = 3.0
MPa, C_{0} = 33.3 g/L, catalyst mass = 0.1 g).

| Catalyst          | Relative rate at 50% conversion, mol/L·min | Benzene yield, wt. % |
|-------------------|------------------------------------------|----------------------|
|                   | Anthracene | Dibenzothiophene | Anthracene | Dibenzothiophene |
| Non-catalytic     | 0.0005     | 0.0006           | 38         | 50                |
| 10%-Ni-MN-270     | 0.0010     | 0.0013           | 87         | 91                |
| 10%-Co-MN-270     | 0.0008     | 0.0010           | 82         | 84                |
| 10%-Fe-MN-270     | 0.0006     | 0.0008           | 68         | 71                |
| 1%-Ru-10%-Ni-MN-270 | 0.0012   | 0.0016           | 92         | 95                |
| 1%-Ru-10%-Co-MN-270 | 0.0009   | 0.0011           | 86         | 88                |
| 1%-Ru-10%-Fe-MN-270 | 0.0008   | 0.0009           | 74         | 78                |

It was found that the nickel-containing sample has the highest activity among monometallic catalysts.
In the presence of 10%-Ni-MN-270 over 90% of conversion of model compounds of oil fractions was
observed for 3 hours.

As in the non-catalytic process, the main product of the processing of anthracene and
dibenzothiophene was benzene (yield up to 90%). At the same time, no benzene horologes were
identified in the reaction mixture.

Promotion of catalysts by ruthenium leads to an increase in catalytic activity. The highest yield of
hydrocarbons for all the studied substrates was obtained while using a ruthenium-nickel catalyst, which
provides full conversion of the initial reagents within 120 and 150 minutes for dibenzothiophene and
anthracene, respectively. It is noteworthy that the addition of ruthenium to the catalyst causes the
hydrogenation of benzene. A negligible cyclohexane amount (up to 2 wt. %) was observed in the
presence of bimetallic catalysts.

4. Conclusion
In the current work, the choice of supercritical solvent composition and catalyst for the hydproprocessing
of model compounds of crude oil fractions was carried out. It was found that the solvent consisted of 40
vol. % of propanol-2 and 60 vol. % of n-hexane in the supercritical state showed the maximum degree
of conversion as well as the maximum yield of benzene in the cracking of anthracene and desulfurization
of dibenzothiophene. Based on the data obtained, it was proposed that the reactions mainly proceed
through the C-C or C-S bond breaking. 1%-Ru-10%-Ni-MN-270 synthesized by the hydrothermal
deposition provides 100% conversion of the initial substrates within 120 and 150 minutes for
dibenzothiophene and anthracene, respectively. The benzene yield was found to be over 90 wt. % in the
presence of Ru-Ni-containing catalyst. Thus, the approach developed in this work allows effectively
conversion of oil fractions to be reached. Moreover, the use of supercritical solvent makes it possible to
decrease significantly the reaction temperature of the hydproprocessing of oil fractions.

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