Mixed oxide Zn-Fe with magnetic properties as a catalytic system for the aquathermolysis of heavy oil

A Lakhova¹, R Zakieva¹, A Valieva¹, Ed Vasiliev¹, N Bashkirtseva¹, S Petrov¹,²

¹Kazan National Research Technological University, Russia
²Kazan Federal University, Kazan, Russia

E-mail: Gulich9696@mail.ru

Abstract. This article investigates the catalytic and magnetic abilities of mixed Zn-Fe oxides during aquathermolysis of heavy highly viscous oil. These systems influenced both the composition of the oil transformed during aquermolysis and its viscosity, moreover, the oil transformed using a Zn-Fe-MO sample (1:1) has a more flatter viscosity-temperature dependence. During magnetic manipulations, it was proved that a mixed Zn-Fe oxide with a ratio of Zn²⁺/Fe³⁺ = 2 cations in the synthesis of layered double hydroxide precursors shows better magnetization (the degree of extraction from the reaction was 91 wt %) and it can be removed from the reaction mixture.

1. Introduction

At the present stage of development, conditioned hydrocarbon resources differ from heavy high-viscosity oils and natural bitumen by a large number of light boiling light hydrocarbons [1]. Due to the high viscosity of unconventional oils, their production is complicated. To convert heavy oil into a conditioned hydrocarbon feedstock, it is necessary to transform its main components - high molecular weight naphthenoaromatic and heteroatomic compounds, resins and asphaltenes, avoiding the appearance of gaseous hydrocarbons and carbonaceous substances [2].

In recent years, interest in metastable aqueous fluids is gaining momentum. The transition of water to a metastable state occurs in a closed volume when it reaches a temperature of 350°C and a pressure of 15 MPa [3,4], while the interface between the liquid and vapor disappears, the new state of water is characterized by low viscosity and high diffusivity. In addition, water is transformed from a polar liquid into a practically non-polar medium. The dissociation constant for water in a metastable state is about 3 orders of magnitude higher than for ordinary water. Accordingly, in addition to the metastable state of water with excellent dissolving properties of organic compounds, it has particularly high concentrations of H⁺ and OH⁻ than water under ordinary conditions. Thus, dense high-temperature water is an effective means of acid-catalyzed reactions of organic compounds without the addition of acid.

In a metastable state, water contributes to an increase in the yield of middle distillates and a decrease in coke formation, which was confirmed in a number of works [5–7]. In [8], the conclusion was confirmed that aromatization and dealkylation of substituents and aromatic fragments of molecules occur, leading to the formation of gaseous products, a hexane-soluble fraction, and coke during the conversion of
asphaltenes in supercritical water [9-15]. The maximum yield of gases and liquid products was observed at a temperature of less than 390°C, which is caused by a large number of unstable aliphatic bonds S-S, S-C and C-O in shales.

Metastable water is a suitable medium for reactions with heterogeneous catalysts, since high diffusion activity promotes mass transfer, and a high dissolving ability prevents coke formation and catalyst poisoning [16]. During the conversion of asphaltite in supercritical water at 400°C and 30 MPa in the absence of metals and with the addition of Al and Zn chips, the yield of volatile and liquid products was 10.3 and 46%, respectively [17].

Recently, catalytic systems based on oxides of mixed phase composition have been of increasing interest. This is primarily due to the simplicity of production, a wide range of cations, which makes it possible to control catalytic activity [18], and the presence of a “memory effect” allows one to obtain catalytic systems with a controlled highly developed surface [19].

In [20], the catalytic activity of Zn-Fe layered double hydroxides was investigated. It was found that a pH close to the alkaline medium increases the catalytic activity of Zn-Fe layered double hydroxide [21]. When calcining Zn-Fe layered double hydroxides, Zn-Fe mixed metal oxides are formed, which exhibit high catalytic activity [22] due to the ability of the matrix of layered double hydroxides to accommodate metal elements distributed homogeneously at the atomic level [23]. In [24], it was found that such nanostructures possess ferromagnetic properties [25]. The magnetic properties of magnetic particles can be greatly modified by a simple change in particle size.

The use of magnetic particles can greatly simplify the separation of spent catalyst from produced crude oil, which is an undoubted advantage of using such systems. Thus, in the studies [26], magnetic separation of the iron Fischer-Tropsch solid catalyst was used, after which the catalyst separated from the suspension was sent for recycling to the Fischer-Tropsch synthesis reactor.

Due to electrostatic, ionic and other interactions, the presence of water in reaction systems significantly complicates the control of the degree of monodispersion of nanoparticles. And, as can be seen from the examples, it is possible to control the processes of nucleation and growth of nanoparticles by adding additional stabilizing substances and using two-phase systems [17].

In this work, several goals were set:

- determination of the possibility of using mixed oxides as catalytic systems for the aquathermolysis process of heavy high-viscosity oil;

- identification of the relationship between the ratio of Zn²⁺ and Fe³⁺ cations in the synthesis of complex oxides and their magnetic properties.

2. Methodology

2.1. Materials and synthesis

The synthesis of the initial layered double hydroxides containing cations of divalent and trivalent metals of various nature was carried out by the coprecipitation method described in detail in [27]. For this purpose, mixtures of aqueous solutions of zinc and iron nitrates with a molar ratio of $M^{2+}/M^{3+} = 1-2$ were prepared. The resulting solutions were added dropwise to 100 ml of distilled water. During the synthesis, a constant pH 10 was maintained by adding a NaOH solution (3 M). The synthesis temperature was 70°C. To control the pH, an electrode with an integrated temperature sensor (Mettler Toledo) was used. After adding the entire salt solution, the suspension was stirred for 24 hours at the
synthesis temperature. This hydroxide was washed with distilled water until a neutral pH of the wash water was obtained, filtered and dried for 4 hours at 110°C. The hydrotalcites synthesized in this way contained carbonate anions between brucite-like layers, which subsequently facilitated the transition to the oxide phase. The oxide phase was formed by calcining Zn-Fe hydrotalcites at 500°C in an oven for 5 hours.

2.2. Analysis

Microphotographs of the synthesized catalyst systems were obtained with a Hitachi TM 1000 microscope.

Hydrothermal systems are formed under the conditions of steam-thermal methods for the extraction of super-viscous oils. A distinctive and main feature of hydrothermal systems in reservoir conditions is a closed volume, where at high temperatures above 200°C in an environment of water vapor there is an increased pressure. During this process, a change in the concentrations of the starting reagents and the qualitative composition of the final products leads to a constant change in the mechanisms of the proceeding reactions until an equilibrium state appears, which corresponds to the establishment of a constant pressure in the system. Changing any of the system parameters entails a series of successive transformations until the moment of equilibrium. Under these conditions, accelerated reactions are achieved with an increase in the yield of the liquid product and maintaining a hydrogen balance between the initial super-viscous oil and the final conversion products. The high degree of conversion under hydrothermal conditions of viscous oils and natural bitumen is predetermined by the high content of thermally unstable (~ 180°C) heteroatomic compounds and supramolecular structures in their composition, unlike conditional oils, which include thermally stable (above 350°C) n-alkane hydrocarbons.

The experiment on the catalytic conversion of super-viscous oils in a hydrothermal system at high pressure and temperature in isothermal mode is shown in Figure 1. The experiments in the reactor, which are a tubular reactor withstand a pressure of 200 cm, withstand a working pressure of 250 bar at a temperature of 400°C, are equipped with a manometer, three-zone thermocouple, connected to the recorded medium, fine adjustment ventilation for the removal of gaseous products. The ratio of oil to water was 3:1. Time of heating to the desired temperature was ~ 40 minutes, then at the given temperature experiment lasted for ~ 20 minutes. Studies have been conducted to identify the patterns of changes in the composition and rheological properties of highly viscous heavy oil extracted from carbon deposits of Bashkir tier.

Rheological researches were conducted on a rheometer HaakeRheoStress 6000 with the use of a measuring cell of the cone-plane type with a diameter of 35 mm and a corner of a cone 2° and shear rate ranging from 0.0009906 to 800 s⁻¹, under temperatures ranging from 10 to 80°C. The Dynamic viscosity \( \eta \), in MPa·s was calculated by the measured shear stress and shear rate.

To study the bulk composition of the liquid products, asphaltenes were preliminarily precipitated with a 40-fold excess of petroleum ether (boiling point 40–70°C); then, the group of saturated hydrocarbons and two groups of resins, benzene extractable (BR) and alcohol–benzene extractable (ABR) resins, were isolated by liquid adsorption chromatography.

The residual content of the catalytic system in the oil after removing it with a magnet was determined by filtration. 100 g of sample were weighed and diluted with four times the amount of solvent (gasoline). The mixture was thoroughly mixed and filtered through a prepared heated and weighed filter. The beaker and filter were washed with solvent until the solvent was completely clear and colorless. Then the filter
was dried in a thermostat at a temperature of 105-110ºC and weighed. The percentage of catalytic particles removed was calculated.

The construction of theoretical models of crystals of mixed oxides based on the results of the analysis was carried out using the Avogadro program.

![Figure 1. Thermodynamic experimental conditions with Zn-Fe-MO (1:1) (1) and Zn-Fe-MO (2:1) (2).](image)

### 3. Results and Discussions

In order to understand the structure of mixed oxide structures with different values of the Zn$^{2+}$/ Fe$^{3+}$ ratios, Avogadro program constructed elementary lattices, the parameters of which are well studied [18] and are presented in Table 1. The compounds obtained are represented by cubic syngony, space group Fd3m, spinel type structure. The structures are shown in Figure 2.

| Cationic composition | Lattice parameter, Å | Unit cell volume, V |
|----------------------|----------------------|---------------------|
| Zn-Fe-MO (1:1)       | 8.357                | 583.648             |
| Zn-Fe-MO (2:1)       | 8.391                | 590.801             |

The ideal spinel shown in Figure 2a is eight “molecules” of ZnFe$_2$O$_4$. Relatively large oxygen ions form a face-centered cubic lattice. In such a tightly packed cubic structure, there are two types voids (places): tetrahedral and octahedral, the environment of which consists of four and six oxygen ions, respectively. For every 32 oxygen atoms in a tight packing, there are 32 octahedral and 64 tetrahedral voids, but in the spinel space group there are equivalent positions for only 8 atoms with tetrahedral and 16 atoms
with octahedral coordination. That is, Zn atoms are in tetrahedral positions, and Fe atoms are in octahedral positions.

There are more zinc atoms in the synthesized oxides than is required in spinel, thus creating an inverse structure, which, according to [28,29], leads to large magnetization values (more than 50 emu/g) arising from the non-compensation of the antiferromagnetic B-sublattice, which is known to be completely filled in normal configuration. Thus, the structure will have the form \((\text{Zn}_{1-x}\text{Fe}_x) [\text{Zn}_x\text{Fe}_{2-x}]\text{O}_4\).

**Figure 2.** Unit cells a) \(\text{ZnFe}_2\text{O}_4\) spinel; b) \(\text{Zn-Fe-MO (1: 1)}\); c) \(\text{Zn-Fe-MO (2: 1)}\).

Microphotographs of samples obtained thanks to optical microscopy are presented in Figure 3. The sizes of aggregates vary between 9.8–10 nm. The mixed oxide phases are represented by spherical particles.

**Figure 3.** Microphotographs of a) \(\text{Zn-Fe-MO (1: 1)}\); b) \(\text{Zn-Fe-MO (2: 1)}\).

The catalytic conversion of super-viscous oil under hydrothermal conditions in the presence of ZnFe with a developed specific surface leads to the formation of low-boiling fractions of hydrocarbons boiling up to 200°C, shown in Figure 4. An increase in oil content occurs in the component composition of the converted oil. For the physical adsorption of asphalt-resinous oil substances on the surface of ZnFe complex oxides under hydrothermal conditions, a low temperature of 350°C and a pressure above 100 bar are favorable. With an increase in pressure in the first experiment to 140 bar, the oil content in the converted oil increases. It can be concluded that pressure has a greater effect on the rate of catalytic conversion reactions under hydrothermal conditions. High pressure in the hydrothermal system creates favorable conditions for adsorption on the surface of complex oxides of asphalt-resinous substances of
oil. With increasing temperature, the laws of chemical adsorption come first, where the adsorbed monomolecular layer, consisting of resins and thermally stable oil asphaltenes, enters into chemical interaction with complex ZnFe surfaces with the formation of chemical bonds on the interface. It can be assumed that the formation of boiling compounds and saturated hydrocarbons is due to the destruction of asphalt-resinous substances. The increase in the content of the low boiling fraction NK-200°C, together with an increase in the amount of hydrocarbons, is a consequence of the catalytic activity of ZnFe complex oxides.

**Figure 4.** SARA analysis of the initial (1) and converted oil during experiments with Zn-Fe-MO (1:1) and Zn-Fe-MO (2:1).

The transformed oil under hydrothermal conditions in the presence of ZnFe complex oxides is characterized by a reduced viscosity in the Newtonian flow region, shown in Figure 5, compared with the original oil. The dynamic viscosity of oil at low temperatures up to 15°C is due to intermolecular interactions of high molecular weight polar and heteroatomic compounds of resin molecules and asphaltenes, capable of forming aggregative combinations.

**Figure 5.** Dynamic viscosity of the initial (1) and converted oil during experiments with Zn-Fe-MO (1:1) (2) and Zn-Fe-MO (2:1) (3).
The main contribution to lowering the viscosity of the Newtonian flow of transformed oil is made by low-boiling components. Throughout the studied temperature range for the converted oil, a decrease in viscosity is observed, the viscosity-temperature dependence becomes less gentle, the dependence of oil viscosity on temperature becomes more pronounced.

As for the magnetic properties, after magnetic manipulations and measurements, the percentage of removed catalytic systems from the converted oil was Zn-Fe-MO (1:1) and Zn-Fe-MO (2:1), respectively, 91% and 67% from placed particles into the reactor.

4. Conclusions

In conclusion, we can say that oxides of a mixed phase composition based on Zn-Fe can be used as catalytic systems for the process of aquathermolysis of heavy oils. This is indicated by their effect on the composition of the converted oils, as well as their effect on viscosity. In addition, such systems are able to be removed from the reaction mixture, which allows controlling the reaction, removing mechanical impurities and reusing such systems. It can also be said that the Zn-Fe-MO (1:1) catalytic system has more acceptable catalytic (has a flatter viscosity-temperature dependence) and magnetic (the degree of removal from the system was 91%) indicators than the same system but with the ratio of $\text{Zn}^{2+}/\text{Fe}^{3+} = 2$ cations in the synthesis of layered double hydroxide precursors.

Acknowledgments

The reported study was funded by RFBR, project number 19-35-90120.

References

[1] Grunis E et al 2014 Georesources 59 28
[2] Hein F 2017 Journal of Petroleum Science Engineering 154 55
[3] Krivtsov E 2013 News of Tomsk Polytechnic University 332 86
[4] Tumanyan B 2015 Russian Chemical Reviews 84 1145
[5] Gai X et al 2016 Fuel Processing Technology 142 315
[6] Kondoh H et al 2016 Fuel Processing Technology 145 96
[7] Sato T et al 2010 The Journal of Supercritical Fluids 55 232
[8] Kozhevnikov I et al 2010 The Journal of Supercritical Fluids 55 217
[9] Khelkhal M A, Eskin A A, Mukhamatdinov I I et al 2019 Energy and Fuels 33 9107
[10] Khelkhal M A, Eskin A A, Sitnov S A, Vakhin A V 2019 Energy and Fuels 33 7678
[11] Vakhin AV, Aliev F A, Kudryashov S I et al 2018 Petrol. Sci. Technol. 36 1829
[12] Vakhin A V, Mukhamatdinov I I, Aliev F A et al 2018 Petrol. Sci. Technol. 36 1850
[13] Mukhamatdinov I I, Khaidarova A R, Zaripova R D et al 2020 Catalysts 10(1) 114
[14] Vakhin A V, Sitnov S A, Mukhamatdinov I I et al 2018 Petrol. Sci. Technol. 36 1857
[15] Khelkhal M A., Eskin A A, Vakhin A V 2019 Energy and Fuels 33 12690
[16] Ates A et al 2014 Applied Catalysis B: Environmental 147 144
[17] Fedyaeva O et al 2014 The Journal of Supercritical Fluids 88 105
[18] Bolongini M 2003 Microporous and Mesoporous Materials 66 77
[19] Qian E Journal of Molecular Catalysis A: Chemical 387 76
[20] Seftel E et al 2008 Microporous and Mesoporous Materials 113 296
[21] Abderrazek K et al 2016 Applied Clay Science 119 229
[22] Tichit D et al 2003 Cattech 7 206
[23] Sideris P et al 2008 Science 321 113
[24] Chayene G et al 2015 Materials Chemistry and Physics 1-7
[25] Arora A et al 2013 Asian Journal of Chemistry 25 7283
[26] Chernavskii P et al 2009 *Oil & Gas Science and Technology* **64** 25
[27] Karpova S et al 2013 *Semiconductor Physics and Technology* **47** 1022
[28] Sagayaraj R et al 2018 *Journal of Materials Science: Materials in Electronics* **29** 2151
[29] Mukhamatdinov I I, Salih I Sh S, Rakhmatullin I Z et al 2020 *Journal of Petroleum Science and Engineering* **186** №106721