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Composition of aquathermolysis catalysts forming in situ from oil-soluble catalyst precursor mixtures

Sergey A. Sitnov[a,*], Irek I. Mukhamatdinov[a], Alexey V. Vakhin[a], Anna G. Ivanova[b], Elena V. Voronina[b]

[a] Institute of Geology and Petroleum Technologies, Kazan (Volga Region) Federal University (KFU), 18 Kremlyovskaya St., P.O.Box: 420008, Kazan, Russia
[b] Institute of Physics, Kazan (Volga Region) Federal University (KFU), 18 Kremlyovskaya St., P.O.Box: 420008, Kazan, Russia

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ABSTRACT

Increasing efficiency of thermal recovery methods of heavy oil through injection of destructive hydrogenation catalysts precursors is a relevant task. In this paper the composition and properties of the active binary catalysts, which formed from a mixture of oil-soluble iron-, nickel- and copper-based precursors have been studied by XRD, Mössbauer spectroscopy, SEM, EDX-mapping methods. Moreover, the efficiency of a mixture of the corresponding metals in reducing the content of heavy components (SARA) of heavy crude oil from Ashal'cha field (Republic of Tatarstan) have been investigated. Mössbauer spectroscopy and EDX-mapping detected the formation of not only spinel ferrites MFe_2O_4 (where M = Ni or Cu), but also individual oxides. Moreover, in case of nickel-based catalyst three phases are formed: magnetite $FeO{\cdot}Fe_2O_3$, spinel ferrite $NiFe_2O_4$ and superparamagnetic finely dispersed phase of iron oxides (and probably nickel oxides). According to XRD results, the oxides formed in the first stage transform into nonstoichiometric spinel ferrites $Cu_{0.86}Fe_{2.14}O_4$ and $Ni_{1.43}Fe_{1.7}O_4$ under hydrothermal influences. It is related with the thermodynamically beneficial processes of conversion of this specific phase composition. Based on the SARA and elemental analysis of the initial and converted oil, it was found that catalytic aquathermolysis decreases the content of asphaltenes and resins (about 45%) in the presence of catalyst nanoparticles, which indicates an improvement in the quality of the heavy oil.

1. Introduction

The global demand of society for the energy is rising every day. At the same time, the structure of oil reserves changes as well. The heavy hydrocarbon resources represent a significant share of the total oil world reserves. This explains a magnificent interest and concentration of petroleum industry on unconventional and hard-to-recover hydrocarbons, particularly on heavy oils. The main restriction in their recovery is an abnormally high viscosity due to tremendous amount of resins and asphaltenes in heavy crude oil composition. However, there is a vast amount of researches focused on developing heavy oil recovery. Injection of various heat carriers into the reservoirs decreases the viscosity of heavy oil in situ and hence, provides their production. In case of steam injection, the temperature of carrier may attain 350–400°C, while the reservoir may be heated up to 200–250°C and higher. Obviously, in such temperatures, the chemical conversion of heavy oil components is possible. (Katritzky et al., 1990; Savel'ev et al., 2007; Gafurov et al., 2018).

The conduction of chemical conversions during steam treatment processes of heavy oil is justified by gas evolvement. Ruzin and Ursegov (2005) observed the hydrogen sulfide content in the products of oil from Usinskoe reservoir, developing by steam injection methods. The interesting results have been obtained while studying the influences of water phase condition on CO_2 yield. The catalytic activity of water steam, which increased the CO_2 yield by four times in contrast with a water in liquid state, was observed.

Thus, aquathermolysis is an in situ upgrading technique of high viscous heavy hydrocarbons. The aquathermolysis has a common principle with internal combustion, low temperature oxidation and other methods – injection of various reagents into the heated reservoirs (Weissman and Kessler, 1996). Yet, heavy crude oil cools down after the production in downstream conditions and the viscosity rises again. Consequently, the refinery of such crude oil becomes difficult due to the high content of resins and asphaltenes. It is generally accepted that steam treatment influences chemical conversion of asphaltenes. Many studies have been focusing on introducing catalysts for in-situ destructive hydrogenation of resins and asphaltenes (Muraza and Galadima, 2015; Petrov et al., 2017; Kayukova et al., 2018). The

* Corresponding author.
E-mail address: sers11@mail.ru (S.A. Sitnov).

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