Heterogenous catalysts based on Fe-pillared clays for catalytic aquathermolysis processes of heavy oil

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Abstract. Aquathermolysis process is one of the key technologies of reducing the viscosity and exploitation of huge deposits of heavy crude oil. That process combines thermal and catalytical effects in the presence of water. There are a lot of types of catalysts used in aquathermolysis process, such as water and oil soluble, heterogeneous catalysts and minerals. One of the type of heterogeneous catalysts are pillared clays that used in catalytic, sorption and separation processes. Pillared clays (PILC) are the class of two-dimensional micro-mesoporous materials that have a high specific surface area, constant porosity, developed texture and active compounds in the structure, i.e. combine both the carrier and the catalyst. In this study the physico-chemical properties of Fe-pillared clays and its application in the “reconnaissance” heavy oil catalytic aquathermolysis experiments of has been investigated.

1. Introduction

The catalytic aquathermolysis process becomes more significant research area for investigation of heavy crude oil upgrading since the end of last century.

Among well-known recovery techniques, thermal recovery by catalytic aquathermolysis process is the simple and effective method for heavy oil upgrading. The aquathermolysis has various advantages like 1) reduction of viscosity, 2) desulfurization, and 3) hydrogenation of heavy oils. Also the important benefit of aquathermolysis process is in situ viscosity reduction [1].

In general the catalysts used for aquathermolysis process are mineral, watersoluble, oil soluble, and dispersed catalysts. The viscosity reduction with these types of catalysts is in the order of mineral <water-soluble catalyst<oil-soluble catalyst<dispersed catalyst. Also during aquathermolysis, the saturates and aromatics increase while the amount of asphaltene and resin decreases.

There are a lot of investigation about reducing of heavy crude oil viscosity with modified hematite nanoparticles [2, 3], iron organic and non organic salts [4], iron catalyst and hydrogen donors [5], catalysis by keggin heteropoly acid salt [6], iron oxide and iron hydroxide ultradispersed colloidal particles [7], iron(III) tris(acetylacetonate) [8], amphiphilic metallic chelate catalyst-aromatic sulfonic iron [9], oil soluble catalytic solution (organic-metallic compounds of Mo, Fe, Co, Ni) [10], and mineral compounds with and without catalysts [11-13]. When the mineral is used with the metals, this mineral acts as support for
metals providing a more effective catalyst [14]. The use of different hydrogen donors on aquathermolysis also improves the quality of the heavy crude oil [15].

Investigation of mineral compounds modified by metal particles is interesting field in catalytical processes.

Pillared interlayered clays (PILC) are microporous materials synthesized by intercalation of oligonuclear complexes of different types metal cations into layered aluminosilicates interlayered spaces with following calcinations [16]. Large surface area, high pore volume and presence of catalytic active substrates make PILCs a promising material in heterogeneous catalysis. Moreover, varying the complex composition and metal type allow to adapt pillared systems for various catalytic processes.

Majority of domestic and overseas papers traditionally focus on synthesis of pillared aluminosilicates by method based on alkaline hydrolysis of metal salts with varying of initial reagents and process conditions [17]. In this case depending on process conditions in the pillaring solution various hydroxocations with different number of metal nuclears (charge and size) can be present. This circumstance doesn't allow obtaining catalyst with stable properties. It's worth to notice several works related to optimization of pillared clay obtaining methods including manipulations with parent aluminosilicates, polyhydroxocations, intercalation and pillaring conditions [18].

The particular research works describing hydrothermal synthesis of polyhydroxocations [19, 20] and research works [21, 22] where complex organic cations used as a pillaring agent should be noticed.

2. Objects and methodology

The precursor of layered compounds for PILC catalyst synthesis was bentonite clay with montmorillonite content about 95 wt. %.

Fe-PILC catalyst has been prepared by multi-stage saturation of 1% smectite suspension by iron acetate solution in ratio with 5 mmol of Fe to 1 g of clay. After preparation the samples was calcined in oxidation and reduction conditions at 450 °C during 4 h.

Chemical analysis of catalyst samples was determined with a universal XRF spectrometer SUR RENOM-FV.

X-ray diffraction (XRD) patterns of the samples were recorded by D2 Phaser diffractometer (Bruker Axs GmbH) with a CuKα radiation. Diffraction patterns were carried out by DIFFRAC.SUITE package software.

The textural properties of the samples were determined by nitrogen adsorption-desorption at 77 K by Quantochrome NOVA 2200e analyzer after degassing of samples at 378 K during 3 h. Specific surface area values were calculated by the Brunauer–Emmett–Teller (S_BET). The t-plot method was used to determine external surface area (S_{external}) and the micropore volume (V_{micropore}). The Barrett-Joyner-Halenda (BJH) method was applied to determine the mesopore volume (V_{mesopore}) and mesopore volume distribution as a pore size function.
Mössbauer spectra were recorded by MS1104EM spectrometer N40-12 with Co$^{57}$ source in the Ro matrix transmission geometry and NaJ crystal scintillation counter detector. Spectrometer speed scale calibration was carried out by α-Fe spectra at the room temperature.

Scanning electron microscopy (SEM) microphotographs were obtained with powdered samples on a Carl Zeiss Merlin microscope operating at an accelerating voltage of 5 kV and a probe current of 300 pA for minimal exposure on the sample.

Transmission electron microscopy (TEM) microphotographs were collected on a Hitachi HT 7700 Exalens microscope operating at an accelerating voltage of 100 kV.

The object of the study was ultra-viscous oil from Ashalchinskoye oilfield (Volga-Ural basin, Republic of Tatarstan, Russia) with 0.965 g/cm$^3$ of density. Ashalchinskoye oilfield is one of the experimental objects for testing and optimization of high-viscosity oil extraction technologies located in the territory of the Republic of Tatarstan [23].

The aquathermolysis process experiments were conducted in a 0.25 L autoclave for 2 h at 250 °C at the vapor pressure 3 MPa. The mass ratio was 4:1 for oil:water and 200:1 for oil:catalyst into the catalytic system.

3. Results and Discussions

Saturation of smectite clay by iron pillaring solution led to iron content increasing in 10 times according to the chemical analysis. In the Tab. 1 the chemical composition of the smectite clay sample and the Fe-PILC sample is presented.

| Sample                                      | Chemical composition (wt.%) |
|---------------------------------------------|-----------------------------|
|                                            | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | MgO | CaO | Na$_2$O |
| Smectite                                    | 61,3    | 18,5        | 4,1         | 2,2 | 0,9 | 1,9    |
| Fe-PILC after calcination in the oxidation conditions | 39,1    | 12,5        | 42,8        | 1,5 | -   | -      |

The textural properties of Fe-PILC samples are given in Table 2. Calcination of Fe-PILC samples in oxidation and reduction air conditions lead to the differences in surface areas and pore sizes. Chemical reduction of iron-containing clusters in the Fe-PILC lead to decrease the specific surface and micropore disappearance.

| Sample                                               | $S_{BET}$, m$^2$/g | $V_{mesopore}$, cm$^3$/g | $V_{micropore}$, cm$^3$/g | $D_{average}$, nm |
|------------------------------------------------------|--------------------|--------------------------|---------------------------|------------------|
| Fe-PILC after calcination in the oxidation conditions | 320                | 0.21                     | 0.04                      | 2,77             |
| Fe-PILC after calcination in the reduction conditions | 134                | 0.26                     | –                         | 7,96             |

X-ray diffraction results for Fe-pillared clay are shown the presence of the first basal spacing (d$_{001}$) of 2,1 nm that confirms successful intercalation iron compounds between aluminosilicate layers. After calcination the basal spacing has decreased to 1,9 nm due to
remove organic ligands and water. Calcination in the reduction conditions leads to partial interlayer spaces collapse and to basal spacing displacement to 1 nm. The most possibly reason explain this behavior connected with decrease of particle sizes iron oxidic form to lower degrees of oxidation form in reducing process.

SEM and TEM images of clay and Fe-PILC samples before and after calcination were shown on Fig. 1.

**Fig 1.** SEM (left) and TEM (right) images of Fe-PILC samples:
- \(a,d\) – smectite; \(b,e\) – Fe-PILC after calcination in the oxidation conditions;
- \(c,f\) – Fe-PILC after calcination in the reduction conditions
According to SEM images \((a,b,c)\) the smectite clay sample has morphology with an extended silicate plates packed to tactoids. After pillaring processes the aggregate size decreases and it packed as house of cards. This effect is more expressed for calcined in the reduction conditions sample. On the TEM images \((d,e,f)\) aluminosilicate plates are observed. For smectite sample \((d)\) aluminosilicate plate has no any dark inclusions that appear in the Fe-PILC after calcination in the oxidation conditions and clearly marked for the sample calcined in the reduction conditions. That includes has a rounded shape and size about 10-20 nm. According TEM images with elemental mapping showed on fig. 2 the small size particles located inside and on the aluminosilicate sheets consist Fe.

![TEM images of Fe-PILC sample after calcination in reduction conditions](image)

**Fig 2.** TEM images of Fe-PILC sample after calcination in reduction conditions

Mössbauer spectroscopy data of Fe-PILC samples show the presence of superparamagnetic iron and magnetite-like oxides forms particles separately distributed into clay structure and bounded with clay aluminosilicate matrix.

The aquathermolysis process results using different catalysts are given in the table 3.

### Table 3. Results of catalytic aquathermolysis experiments

| Reaction mixture                          | Density (g/cm³ at 20 °C) | Boiling point (b.p.) (°C) | Dynamic viscosity (Pa·s at 20 °C) | Fraction output (wt.%) | Tars and asphaltenes content (wt.%) | Sulfur content (wt.%) |
|------------------------------------------|--------------------------|--------------------------|-----------------------------------|------------------------|-----------------------------------|----------------------|
| Initial oil                              | 0.9650                   | 170                      | 2.68                              | 1.00                   | 12.00                             | 34.4                 | 4.70                 |
| Oil with water                           | 0.9541                   | 130                      | 2.91                              | 2.70                   | 37.90                             | 31.6                 | 4.22                 |
| Oil with water and Fe-PILC after calcination in oxidation conditions | 0.9578                   | 100                      | 2.61                              | 2.63                   | 15.37                             | 30.6                 | 4.16                 |
| Oil with water and Fe-PILC after calcination in reduction conditions | 0.9437                   | 80                       | 1.23                              | 5.00                   | 20.55                             | 20.6                 | 3.56                 |
4. Conclusions

Fe-pillared clays contain nano-clusters of iron oxides in different oxidation degrees which separately located in their structure. The results for aquathermolysis processes showed that viscosity, density, sulfur and tar-asphaltene content had been decreased and content of light oil fraction had been increased. Thus, Fe-pillared clay can be promising catalyst in the aquathermolysis process.

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