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Thermocatalytic Conversion of Petroleum Paraffin in the Presence of Tungsten Carbide Powders

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Abstract. Russia occupies the third place in the world in terms of stocks of heavy oil raw materials. The development of deposits of light and medium oils makes it inevitable to involve heavy, as well as residual, petroleum raw materials in processing to meet the growing demand for petroleum products. Increase of the depth of oil processing possible in various ways, one of which is the use of new efficient catalysts, resistant to corrosion, poisoning and coking. Tungsten carbide, meeting these requirements, is a promising starting compound for the production of cracking catalysts for heavy oil feedstocks. The influence of tungsten carbide and its calcination temperature on the composition and yield of oil paraffin cracking products on the resulting catalysts was studied to investigate its catalytic activity, the optimum treatment temperature of tungsten carbide was determined. The high catalytic activity of a WC sample calcined at 420°C is shown. Using the physicochemical methods of investigation, the properties of tungsten carbide samples, as well as the composition and properties of the paraffin cracking products in the presence of the catalysts obtained, were studied.

INTRODUCTION

At present, only about 40% of the total volume of refined oil in Russia (289 million tons in 2014) is converted to motor fuel (gasoline and diesel fuel), and the rest is mazut of various grades (30%) and heavy oil residues (tar, fuel oil, vacuum gas oil). For comparison in Western countries and the USA 69 to 73% of oil is processed into motor fuel, and the depth of its processing reaches 95%. Thus, the urgency of deepening the processing of oil is increasing.

The main processes for the processing of heavy oil residues are catalytic and thermal cracking, visbreaking and hydrocracking, which, in addition to processing heavy fuel oil and utilizing heavy refined products, make it possible to obtain commodity products-gasoline and diesel fuel. The main obstacles to the widespread introduction of these processes in domestic enterprises are their large energy intensity, as well as high cost.

The main direction of development of processes of deepening of oil and oil fractions processing along with technical solutions is the development of new catalytic systems. To catalysts a number of requirements are shown - an acceptable yield of light fractions, resistance to sulfur-containing compounds, high thermal stability.

Carbides of transition metals, in view of the high mechanical strength and thermal stability, the possibility of changing electronic properties, volume and surface, due to the presence of stoichiometric and nonstoichiometric phases, appear to be promising catalysts of many processes [1, 2].

A number of catalytic studies discuss the reactivity of WC, which can be increased by the preliminary activation of oxygen on its surface [3]. For example, it was shown in [4] that pulsed oxidation of tungsten carbides, titanium and molybdenum leads to an increase in the catalytic activity of carbides and the selectivity of toluene formation in

the n-heptane reforming process. The authors previously studied the activity of tungsten carbide and the effect of surface oxygen-containing structures on the conversion of tar [5]. The aim of this work is to investigate the thermocatalytic transformations of alkanes of normal structure in the presence of initial and calcined tungsten carbide.

Thus, tungsten carbide is a promising material for the production of heavy-cracking catalysts, not only because of its thermal, chemical and mechanical stability, but also due to the possibility of its modification to enhance the activity and selectivity in this process.

EXPERIMENTAL SECTION

As a raw material for the experiments, the oil paraffin P-1 (GOST 23683-89) was used. Commercial powder of tungsten carbide of grade “C” with an average size of 4–9 μm (STP 00196144-0712-2004, JSC “Kirovgrad hard alloy plant”), which was calcined at $T = 320\text{--}520^\circ\text{C}$, was used as catalysts.

Thermal and catalytic cracking processes were carried out in 12 cm^3 stainless steel autoclaves in batch mode under argon atmosphere under the following conditions: temperature 410–450°C, duration 1–2 hours, mass of petroleum paraffin 5 g, catalyst content 0.8 wt. %.

The catalysts were analyzed by the following analytical methods: X-ray phase analysis (XRD); thermo-programmed oxidation (TPO); X-ray photoelectron spectroscopy (XPS); infrared (IR) spectroscopy; Scanning electron microscopy combined with X-ray energy-dispersive spectroscopy (SEM, EMF). Gas chromatography (GC) was used to study the composition of raw materials and products of its thermocatalytic transformation; chromatography-mass spectrometry (GC-MS); differential scanning calorimetry—thermogravimetry (DSC-TGA).

RESULTS AND DISCUSSION

Using the TPO method the temperature of oxidation of the initial tungsten carbide starting at 600°C (Fig. 1), therefore, at the selected calcination temperatures of 320, 420 and 520°C, tungsten carbide particles can not be completely oxidized to WO_3 . According to the data obtained, WC is in a hexagonal modification, as evidenced by characteristic reflexes at 31.5°, 35.6° and 48.3° (Fig. 1b). Calcination of tungsten carbide in air does not lead to the formation of new phases possessing a long-range order, sufficient for the appearance of new reflexes in the diffraction pattern and their detection within the sensitivity of the XRD method.

Micrographs of tungsten carbide are shown in Fig. 2. WC particles have a spherical shape, calcination does not change the shape or size of the particles. The data obtained on the combined with SEM energy dispersive X-ray spectrometer show that the initial WC contains 8.31 wt. % oxygen on the surface, and the sample calcined at 420°C—15.04 wt. %. At the same time, a wide band of stretching vibrations –W–O–W–O– in the range of 600–1000 cm^{-1} is observed on the IR spectra of WO_3 and WC*520, while in WC*420 there is only an unclearly expressed arm in this region, absent in the initial carbide and WC*320.

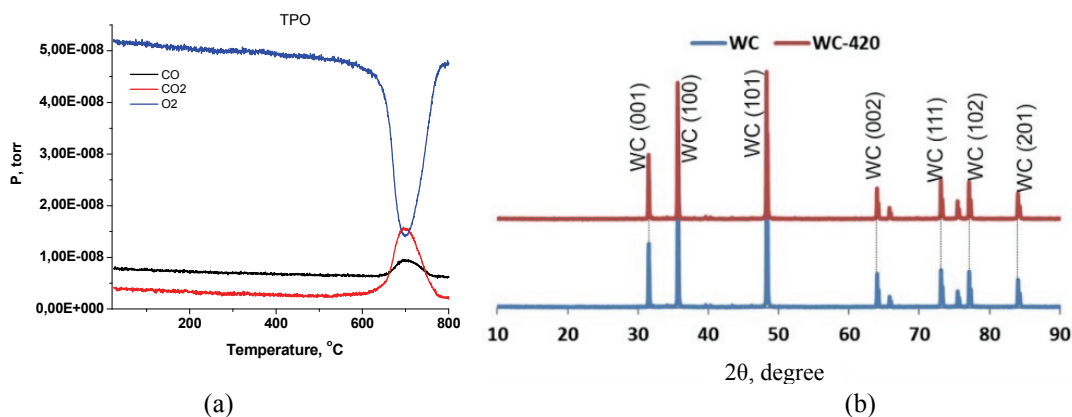


FIGURE 1. TPO of the initial WC(a) and XRD diffractograms of initial and calcined WC(b)

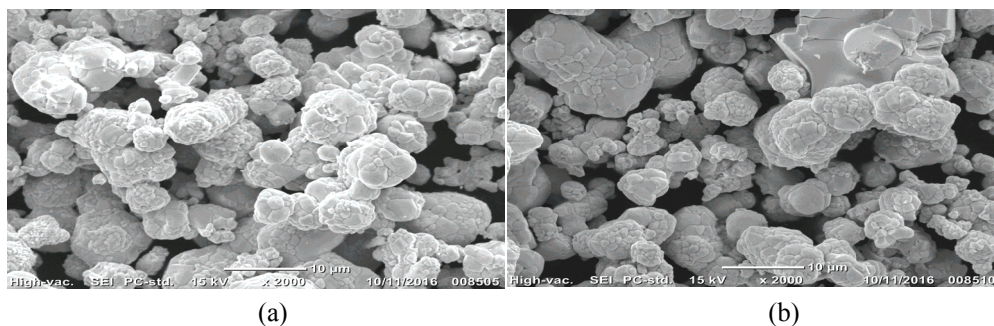


FIGURE 2. Micrographs of initial (a) and calcined (b) tungsten carbide

Figure 3a shows the photoelectron spectra of the W4f region measured for WC (a) and WC*420 (b) samples, both initial and after surface etching by argon ions for 15 minutes. From the analysis of the presented spectra, it can be concluded that the surface of the samples contains tungsten carbide (WC)— $E_b = 31.6$ eV and oxide (WO_3)— $E_b = 35.9 \pm 0.1$ eV, and the initial surfaces of the samples differ from each other by the ratio of these forms. On the surface of the oxidized WC*420 sample, the oxide form of tungsten is significantly larger. The etching of the surface by argon ions results in the partial removal of the oxidized layer from the sample surface. In order to more accurately determine the ratio of the carbide and oxide forms of tungsten, the XPS-Peak program decomposed the peaks of the W4f region into separate spectral components (carbide and oxide in two states). The results of this decomposition, as well as the ratio of the carbide and oxide forms of tungsten on the initial surface of the measured samples are shown in Fig. 3b. The states of tungsten with other degrees of oxidation are not observed.

Summarizing the obtained data, it is shown that: the particles consist of tungsten carbide of hexagonal modification, contain oxygen on the surface, as the calcination temperature increases, the amount of oxygen on the surface of the sample increases, oxygen-containing structures do not give a diffraction pattern when studying samples by X-ray diffraction (which is characteristic for structures that do not possess sufficient long-range order in connection with the small size or high defectiveness, which can be interpreted by the islet character of their distribution on the surface of the formation), W^{6+} , W^0 and $-W-O-W-O-$ bonds are found on the particle surface. After calcination, the content of W^{6+} increases. Thus, taking into account all the established facts about the structure of tungsten carbide, a hypothetical scheme (Fig. 4) was constructed for the structure of the WC particle, which reflects a spherical particle, in the surface layer of which there are island structures of two types: 1) tungsten trioxide, 2) nonstoichiometric oxygen-containing tungsten structures in oxygen environment $W_xC_yO_z$.

Samples of cracked products of the initial petroleum wax at various temperatures and duration of the experiment were investigated by the XMS method. Based on the results obtained, yields of light fractions and conversion rates were calculated (Table 1).

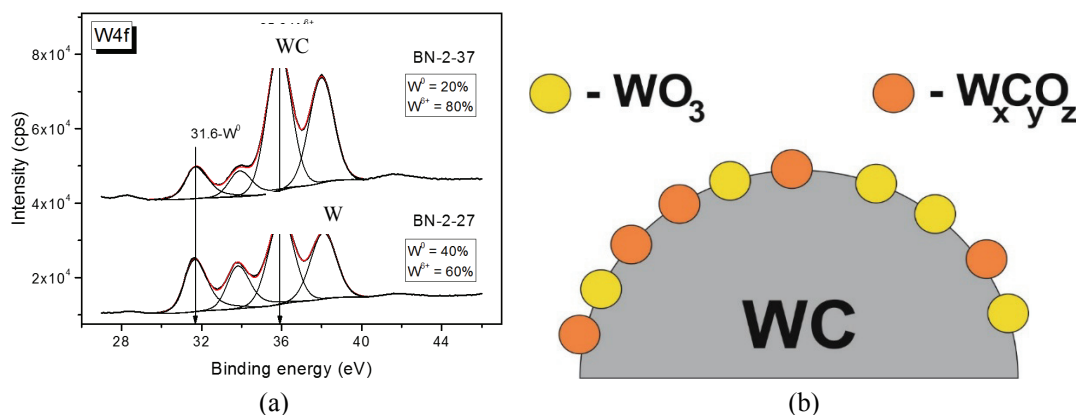


FIGURE 3. Photoelectron spectra of the W4f level of the initial WC (down curve) and WC*420 (upper curve) samples after being decomposed into separate spectral components (a). Hypothetical scheme of WC (b)

TABLE 1. Conversion, light fractions yields in the presence of WC at various temperature and process time parameters

Catalyst	Temperature, °C	420		430		440	
	Process time, h	1.5	2	1.5	2	1	1.5
Without catalyst	Yield of light fractions (up to 350°C), wt. %	43.0	46.4	51.3	71.7	27.4	76.9
	Conversion, %	50.3	50.3	63.6	83.5	31.8	91.2
WC	Yield of light fractions (up to 350°C), wt. %	52.8	69.9	63.6	76.1	73.3	76.6
	Conversion, %	63.3	77.7	73.6	88.4	84	91.5
WC*420	Yield of light fractions (up to 350°C), wt. %	–	68.4	60.3	71.8	48.9	72.7
	Conversion, %	–	77.3	77.7	87.0	56.2	83
WC*520	Yield of light fractions (up to 350°C), wt. %	–	43.9	55.7	76.4	34.8	76.6
	Conversion, %	–	50.4	62.5	81.0	40.7	85.2
WO ₃	Yield of light fractions (up to 350°C), wt. %	–	40.7	53.6	–	35.2	77.2
	Conversion, %	–	46.4	65.4	–	41.8	89.9

The initial WC has a high activity in the process of thermocatalytic transformations of petroleum paraffin. So in all combinations of time and duration of the process, an increase in the conversion of the initial paraffin by 47.7, 27.4, 13.0, 10.1 and 4.9 wt. % is observed for $T = 440^\circ\text{C}$ and $\tau = 1$ h, $T = 420^\circ\text{C}$ and $\tau = 2$ h, $T = 420^\circ\text{C}$ and $\tau = 1$ h, $T = 430^\circ\text{C}$ and $\tau = 1.5$ h, $T = 430^\circ\text{C}$ and $\tau = 2$ h respectively, compared with experiments without additives. The growth in the yield of light fractions in this series is 45.9, 23.5, 9.8, 12.3 and 4.4 wt. %, respectively. Calcination of carbide at a temperature of 320°C does not affect the composition of its products in comparison with the initial WC.

The presence of WC*420 leads to an increase in the conversion rate relative to the control experiments with the parameters: $T = 420^\circ\text{C}$ and $\tau = 2$ h, $T = 440^\circ\text{C}$ and $\tau = 1$ h, $T = 430^\circ\text{C}$ and $\tau = 1.5$ h at 27.0, 22.7, 14.1 wt. %, respectively. The increase in the yield of light fractions under such process conditions is 22.0, 21.5, 9.0 wt. %, respectively. However, only at $T = 430^\circ\text{C}$ and $\tau = 1.5$ h, the activity of WC*420 is higher than that of the initial WC and the increase in the conversion of the initial petroleum wax is 4 wt. %.

Samples WC*520 and WO₃ have the lowest activity when added to petroleum paraffin, in their presence the increase in conversion of the initial petroleum paraffin observed at only 440°C and the duration of the experiment for 1 hour is 7.2 and 10.6 wt. % respectively.

CONCLUSION

The initial WC sample, whose surface contains predominantly $\text{W}_x\text{C}_y\text{O}_z$, has a high activity in the process of thermocatalytic transformations of petroleum paraffin. An increase in the WO₃ content on WC*420 surface leads to an increase in activity in the process of thermocatalytic petroleum paraffin conversions at $T = 430^\circ\text{C}$, $\tau = 1.5$ hours. WC samples containing the maximum amount of WO₃ have the lowest activity in the process of thermocatalytic transformations of petroleum paraffin.

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