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HYDROGENATION of COAL TAR in the PRESENCE of FERRIFEROUS CATALYSTS in the ENVIRONMENT of MINE METHANE

Abstract: Studying of process of pyrolysis of coal tar fraction with a temperature of boiling up to 523 K was carried out at presence of iron-containing catalysts, and also at presence of the donor forming component – naphthalene. Catalysts were the iron disulfide FeS_2 obtained by modifying of the enriched oxide of iron Fe_2O_3 by heat treatment with sulfur in the environment of hydrogen and the composite catalyst $\text{Fe}_2\text{O}_3/\text{CS}$ – iron oxide on the carbon carrier. As the hydrogenate environment the mine methane was used as its content in mine gas fluctuates from 1 to 98 %. Use of mine methane as the reducing environment allows utilize mine methane and by that resolves environment protection problems. Use of mine methane instead of hydrogen allows to except a number of the additional stages connected with hydrogen obtaining and to reduce the price of pyrolysis process. Additive of a donor-forming component (naphthalene) into a paste-former at a hydrogenation of coal tar increases the content of hydro-derivatives of naphthalene which are an active donor of hydrogen. At thermal destruction of the dephenolized fraction with boiling temperature before 523 K in the presence of hydrogen donor – naphthalene and the $\text{Fe}_2\text{O}_3/\text{CS}$ catalyst the content of hydro-derivative of naphthalene – tetrahydronaphthalene increases up to 18.42 %, which is an active donor of hydrogen. Synthesis of the composite catalyst was carried out by impregnation of a coal sorbent by iron pentacarbonyl $\text{Fe}(\text{CO})_5$ with the subsequent oxidation of the last to iron oxide Fe_2O_3 . It testifies to high activity of the $\text{Fe}_2\text{O}_3/\text{CS}$ catalyst obtained by us which during pyrolysis changes to Fe_3O_4 and activates H-donor abilities of the dephenolized fraction with boiling temperature up to 523 K and accelerates destruction process.

Key words: hydrogenation, coal tar, catalyst, mine methane, coal tar fraction.

Introduction. Perspective methods of conversion of coal, heavy oils and oil residues in motor and boiler fuel are methods of thermal destruction: coking, pyrolysis, hydrogenation. A by-product of production of Sary-Arka Spetskoks» (SAS) LP is coal tar which amounts are measured by tens of thousands of tons per year. Pitch on structure differs from pitch of coke-chemical productions and can't be processed on technology of conversion of coal tar with receipt of the corresponding commodity products [1-6]. Production of specialcoke of Sary-Arka Spetskoks LP is performed according to the scheme of devolatilization of coal in devices with an internal supply of heat in which receipt of semi-coke is followed by a high exit of the liquid products not subject to impact of high temperatures and, therefore, corresponding on quality to pitches of devolatilization of coal [7-10].

The purpose of work is studying of process of a hydrogenation of coal tar of Sary-Arka Spetskoks LLP in the presence of catalysts on the basis of waste of Arselor Mitall iron and steel works in the environment of mine methane.

Studying of process of pyrolysis of fraction of coal tar with boiling point to 523 K was carried out in the presence of iron containing catalysts: FeS_2 received by modifying of the enriched oxide of iron (Fe_2O_3) heat treatment with sulfur in the environment of hydrogen and the composite catalyst received by us – iron oxide

on the carbon carrier ($\text{Fe}_2\text{O}_3/\text{CS}$) and at presence the donor of the forming component (naphthalene). The called catalytic systems on the basis of iron allow to exclude labor-consuming and technically a difficult to achieve stage of allocation (regeneration of the catalyst from a slurry remaining balance of process) and are ecologically more preferable. Besides, use instead of hydrogen of mine methane allows to exclude a number of the additional stages connected with receipt of hydrogen and to reduce the price of process of thermal destruction of fraction of coal tar. On the basis of pyrolysis of fraction of pitch various methods of receipt of valuable chemical goods, and also synthetic liquid, in particular motor fuels by hydrogenation of fraction of pitch are developed. Therefore interest in a research and complex conversion of fraction to 523 K of coal tar, in the presence of various ferriferous catalysts has practical and theoretical value.

As the hydrogenant environment mine methane as his content in mine gas fluctuates from 1 to 98 % is taken. In this regard mine methane can be considered as the most perspective source of alternative motor fuel already now.

Experimental Part. Experiments on pyrolysis of the dephenolized fraction with a temperature of boiling up to 523 K were made in the stationary autoclave (volume of 0,08 l). The dephenolized fraction was placed into the autoclave, added the calculated quan-

tity of above-called catalysts and the donor-forming component (naphthalene). The fraction with a temperature of boiling up to 523 K has been acquired by method of direct distillation of initial coal tar. As a rule, the low-boiling (boiling away to 573 K) fractions of pitches were subjected to dephenolizing. For studying of a possibility of extraction of phenols directly from fraction with a temperature of boiling up to 523 K we have carried out work on extraction of phenols from this fraction with use of extractant on the basis of water solutions of technical ethanol with concentration of 70 %. For this purpose has been taken fraction of pitch with a temperature of boiling up to 523 K with extractant – ethanol solution – in the ratio 1:1. After agitation within 1 hour we fill in in the burette for division into a long time (24 hours). According to gas chromatography-mass spectroscopy the initial fraction with a temperature of boiling up to 523 K contains 53% of total phenols, and after extraction of 70 % alcohol solution – 8,7 %.

The autoclave was closed, blown mine methane and gave the excessive (initial) pressure of gas of methane to 3,0 MPas, heated at a temperature of 698 K within 60 minutes.

After chilling of the autoclave to room temperature gas was collected in a gas pipette for the analysis. Content of the autoclave was diluted with benzene and filtered. Separated from a firm remaining balance liquid products by means of the glass filter, washed out benzene, dried in case of 378 K and analyzed structure of a firm remaining balance by method of the X-ray phase analysis (RFA). X-ray phase analysis of a firm remaining balance carried out on the DRONE-2.0 installation by method of powders with use of Fe-radiation with Ni, or MnO the filter in from 2 to 37 V. Intensity range of diffraction maxima estimated by an analytical method in a tetragonal singoniya.

In the analysis of component structure of main products of pyrolysis of the dephenolized fraction with a temperature of boiling up to 523 K the method of the gas chromatography-mass spectroscopy (CMS) on the Agilent 7890 (USA) device with a mass spectrometer of 5975 inert XL and a gas-liquid chromatography on the device of Kristallyuks was used 4000 (Russia) [11]. Sample preparation of this fraction was carried out as follows: 1 g dissolved in 20 ml of acetone and dried up sodium sulfate, 1 ml of solution diluted up to 10 ml and added 10 mcl the internal standard o- picoline and fluoranthene with concentration of 40 g/l. Concentration of standards in pitch constituted 8 g/kg.

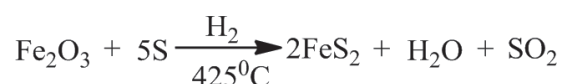
Chromatography conditions: column: DB-5, 30 m of X 0,25 mm of X 0,5 microns; gas: helium, 0,8 ml/min.;

thermostat: 323 K - 4 min., 323- 473K - 283 K/min, 283-573 K - 293K/min, 573K - 4 min.; evaporator: 523K. Identification of substances carried out on the mass and spectral NIST98 database.

It is known that as catalytically active materials in processes of deep conversion of heavy hydrocarbonic raw materials it is possible to use the cheap and available waste of metallurgical production and boiler slags containing iron, titanium, nickel [12-17]. Such catalytically active materials are used in processes of an conversion coal up to full deterioration. As initial material for the catalyst of a thermal conversion of heavy hydrocarbonic raw materials we used waste of sheet-rolling production of JSC Arselor Mittal Temirtau. According to primary analysis the product contains 89,7 % of hematite (Fe₂O₃). Besides, at structure there is a chloride of iron III valent and at insignificant quantities chlorides of manganese and chrome.

The initial product for the purpose of removal of chlorides was subjected to heat treatment at a temperature of 973K. According to the X-ray-phase analysis (DRON-2,0) content of the basic constituting - oxide of iron III increased to 98,5 %, the possibility of determination of other phases is below a device sensitivity limit.

The enriched product for increase in activity was modified heat treatment with sulfur in the environment of hydrogen:



For this purpose have placed in the stationary autoclave 10 g of the enriched oxide of iron, 6,5 g of sulfur, have filled with hydrogen up to 5,0 MPa and heated at a temperature 698 K within 3 hours.

The X-ray phase analysis of a sample carried out on the diffractometer the Drone – 2.0 with use of FeK₂ – radiations ($\lambda = 1,9373 \text{ \AA}$), Mn – the filter, in the range of 100 – 900 (2 θ), with a speed of rotation of the counter of 2 hails/min. For roentgenogram interpretation the databank JCPDS was used. The received product according to the X-ray phase analysis represents iron sulfide (FeS₂ – pyrites), and also phases are found: $\frac{1}{2} (\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O})$ - lepidocrocite (γ – FeOOH); S – sulfur; FeSO₄ · 4H₂O; FeFe₂(SO₄)₄ · 14H₂O.

Synthesis of the composite catalyst was carried out by impregnation of a coal sorbent a pentacarbonyl of Fe(CO)₅ iron with the subsequent oxidation of the last to Fe₂O₃ iron oxide. For this purpose have placed in the 50 ml autoclave 5 g of the received crushed sorbent, 1 g of a pentacarbonyl of iron, heated at 473 K

within 30 minutes, then have oxidized the pentacarbonyl of iron applied on active coal to oxide according to the scheme:



After oxidation the amount of oxide of the iron applied on a sorbent – 0.4g by Fe_2O_3 (8 % of the mass of a sorbent) is determined by a weight difference. Formation of hematite on a surface of a sorbent is confirmed with data of the X-ray phase analysis. The received product according to the X-ray analysis represents oxide of iron (Fe_2O_3).

Results and Discussion. The carbon substrate as which use active coals differs from other used substrates in polydisperse porous structure of the active phase providing more uniform distribution on granule volume that promotes increase in activity of the catalyst [18-21]. Catalysts on carbon substrates are characterized by the spherical shape of granules providing the increased mechanical durability, a possibility of a variation of parameters of porous structure, structure of a mineral part and the size of granules in the course of receiving. Besides, the catalyst on the coal substrate can be easily utilized with return of an active phase to process.

Paste was heated in the autoclave at a temperature up to 698 K, gaseous products were removed, and liquid products were analyzed by the CMS method. Individual structure of the dephenolized fraction with a temperature of boiling up to 523 K is provided in tables 1 and 2.

Table 1 – Individual structure of products of pyrolysis of the dephenolized fraction with boiling temperature up to 523 K in presence of FeS_2 catalyst*

Compound No.	Yield time, minute	Name of compound	Content, mass. %
1	4,54	phenol	1,05
2	5,23	2 methylphenol	5,54
3	5,23	4- methylphenol	5,54
4	5,98	2 ethylphenol	3,40
5	6,14	2,4 dimethylphenol	1,92
6	6,28	3- ethylphenol	1,87
7	6,64	tetrahydronaphthalene (tetralin)	1,09
8	6,82	naphthalene	27,10
9	8,25	1 methylnaphthalene	4,50
10	9,31	1 ethylnaphthalene	1,07
11	9,82	2,3 dimethylnaphthalene	1,35

*Experimental conditions: fraction with boiling temperature up to 523 K – 15 g; methane pressure – 3 MPa, FeS_2 catalyst – 0,75 g (5 %); naphthalene – 0,75 g (5 %); paste heating temperature – 698 K, time – 1 hour

Table 2 – Individual structure of products of pyrolysis of the dephenolized fraction with boiling temperature up to 523 K in presence of composite catalyst*

Compound No.	Yield time, minute	Name of compound	Content, mass. %
1	4,53	phenol	0,57
2	5,91	2- ethylphenol	7,74
3	6,06	2,4 dimethylphenol	1,45
4	6,21	3- ethylphenol	0,61
5	6,58	tetrahydronaphthalene (tetralin)	18,42
6	6,88	naphthalene	2,11
7	8,13	1 methylnaphthalene	0,37
8	9,28	1 ethylnaphthalene	0,51
9	9,88	1-2,3 dimethylnaphthalene	0,09
10	10,39	2 ethylnaphthalene	0,11
11	11,82	2 butylnaphthalene	0,54
12	12,69	dihydroanthracene	0,06
13	12,81	octahydroanthracene	0,13
14	13,56	tetrahydroanthracene	0,08

*Experimental conditions: fraction with boiling temperature up to 523 K – 15 g; methane pressure – 3MPa; $\text{Fe}_2\text{O}_3/\text{CS}$ catalyst – 0,75 g (5 %); naphthalene – 0,75 g (5 %); paste heating temperature 698 K, time – 1 hour

Apparently from tables 1 and 2 in case of thermal destruction of the dephenolized fraction with a boiling temperature up to 523 K in the presence of the donor of hydrogen of naphthalene and the $\text{Fe}_2\text{O}_3/\text{CS}$ catalyst content of hydro-derivative naphthalene – tetrahydronaphthalene (18,42 %) which is an active donor of hydrogen increases. The firm product after process of pyrolysis according to X-ray phase analysis represents magnetite. It testifies to high activity of the $\text{Fe}_2\text{O}_3/\text{CS}$ catalyst received by us, which during pyrolysis changes to Fe_3O_4 and activates H-donor capabilities of the dephenolized fraction and accelerates destruction process.

Conclusions. Thus, for increase in process of efficiency of a hydrogenation the new catalyst FeS_2 , obtained from waste of Arselor Mitall iron and steel works and the composite catalyst received in vitro – iron oxide on the carbon substrate $\text{Fe}_2\text{O}_3/\text{CS}$ was developed and approved. Use of such catalysts leads to cost reduction on regeneration, to reducing harmful emissions in the atmosphere. And additive of the donor forming component (naphthalene) in a paste-forming in case of a hydrogenation of coal tar increases content of hydro-derivatives of naphthalene which is an active donor of hydrogen. The new paste-forming received by us (the dephenolized fraction with a boiling temperature up to 523 K) in the presence of H-donor a component – naphthalene in the course of pyrolysis

is comparable on activity to the traditional donor of hydrogen tetralin.

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ТҮЙІНДЕМЕ

Қайнау температурасы 523 К дейінгі тас көмір шайыр фракциясының тотықтырғыш компоненті (нафталин) мен темірқұрамды катализаторлар: (FeS₂) қаныққан темір оксиді (Fe₂O₃) және бізбен алынған темір оксиді көміртегі тасымалдағыш бетіне енгізілген компонентті катализатор (Fe₂O₃/КТ) қатысында пиролиз үрдісі қарастырылды. Гидрлеу ортасы ретінде шахталы метан алынды, өйткені шахталы газдың құрамында оның мөлшері 1 ден 98 % дейін теңселеді. Шахталы метанның тотықтырғыш ортасы ретінде пайдалануы шахталы метанды кәдеге жаратуға мүмкіндік туғызып, экологиялық мәселелерді шешеді. Сутегі орнына шахталы метанды пайдалану, сутегіні алу және пиролиз үрдісін арзандату сияқты бір қатар қосымша сатыларды жоюға болады. Тас көмір шайырының гидрогенизациясындағы тотықтырғыш компонент (нафталин) қосымшасы мен пастақұрастырғыш белсенді сутегі тотықтырғышы болатын нафталиннің гидро туындыларының құрамын жоғарлатады. Фенол сыздандырылған 523 К дейінгі фракциясының сутегі тотықтырғышы ретінде нафталин және Fe₂O₃/КТ катализатор қатысында термиялық деструкция нәтижесінде белсенді сутегі тотықтырғышы болатын нафталиннің гидро туындысының мөлшері – тетрагидронафталин 18,42 % тең болды. Композитті катализатордың синтезі көмір сорбентін темірпентакарбонилмен Fe(CO)₅ қанықтырып, темір оксидіне Fe₂O₃ дейін тотықтыру арқылы жүргізілді. Бұл алынған катализатордың Fe₂O₃/КТ жоғары белсенділігін көрсетеді, пиролиз кезінде Fe₃O₄ формасына өзгеріп, 523 К дейінгі фенолсыздандырылған фракциясының Н-тотықтырғыш қасиеттерін күшейтіп, деструкция үрдісін жылдамдатады.

Түйінді сөздер: гидрогенизация, тас көмір шайыры, катализатор, шахталы метан, тас көмір шайырының фракциясы.

РЕЗЮМЕ

Изучение процесса пиролиза фракции каменноугольной смолы с температурой кипения до 523 К проводилось в присутствии железосодержащих катализаторов, а также в присутствии доноробразующего компонента – нафталина. Катализаторами служили дисульфид железа FeS₂, полученный модифицированием обогащенного оксида железа (Fe₂O₃) термической обработкой с серой в среде водорода и композитный катализатор Fe₂O₃/УН – оксида железа на углеродном носителе. В качестве гидрирующей среды взят шахтный метан, так как его содержание в шахтном газе колеблется от 1 до 98%. Использование шахтного метана в качестве восстановительной среды позволяет утилизировать шахтный метан и тем самым решает экологические вопросы. Использование вместо водорода шахтного метана, позволят исключить целый ряд дополнительных стадий, связанных с получением водорода и удешевить процесс пиролиза. Добавка доноробразующего компонента (нафталина) в пастообразователь при гидрогенизации каменноугольной смолы увеличивает содержание гидропроизводных нафталина, которые являются активными донорами водорода. При термической деструкции обесфеноленной фракции с температурой кипения до 523 К, в присутствии донора водорода нафталина и катализатора Fe₂O₃/УН увеличивается содержание гидропроизводного нафталина – тетрагидронафталина (18,42%), который является активным донором водорода. Синтез композитного катализатора проводили пропиткой угольного сорбента пентакарбонилем железа Fe(CO)₅ с последующим окислением последнего до оксида железа Fe₂O₃. Это свидетельствует о высокой активности полученного нами катализатора Fe₂O₃/УН, который в ходе пиролиза изменяется до Fe₃O₄ и активируют Н-донорные способности обесфеноленной фракции с температурой кипения до 523 К, и ускоряет процесс деструкции.

Ключевые слова: гидрогенизация, каменноугольная смола, катализатор, шахтный метан, фракция каменноугольной смолы.

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