Elaboration of Preparation Methods of Sulphonic-Acid Carbon Materials from Petrochemical Production Wastes

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Abstract

An alternative method of joint disposal of acid tars (high-sulphur petrochemical waste) with wood-chemical industry and agriculture wastes, at which additional neutralization or trapping of sulphur acid decomposition products is not required, was investigated. At thermal treatment of a mixture of acid tar (a mixture of sulphuric acid and heavy oil fractions), template (high-ash biomass) and binder (furfurol, form-aldehyde or resorcinol), sulphated carbon materials applicable as catalysts for a broad range of acid-catalyzed processes were obtained. The impact of synthetic methods for materials on acid and textural characteristics of materials was explored using BET, TGA, XPA, XPS methods and IR spectroscopy. Optimal conditions for the preparation of carbon materials with developed specific surface (up to 168 m^2/g) and a high concentration of sulpho groups (up to 4.55 mass % SO$_3$H) were found. The addition of a template allows increasing calcination temperature (from 225 to 275 °C) that is required to achieve high specific surfaces, without a decrease in acidities (sulpho groups concentration) final samples. Testing of catalytic properties of the carbon materials obtained in modelling of a catalytic process for esterification of enanthic acid with methanol was performed..

Key words: acid tars, acid tars disposal, sulphated carbon materials, high-ash biomass

INTRODUCTION

The sulphuric-acid purification method that is accompanied by significant product losses and the formation of hard-to-recycle large-capacity wastes that are acid tars is widespread in chemical processes of the production of commercial oil products [1]. In Russia, the amount of pond acid tars (PAT) accumulated in ponds totals over a million tons. Up to 70 % of unreacted sulphuric acid, naphthene, aromatic hydrocarbons and other organic substances is contained in PAT. Processing/disposal technologies of PAT [2–4] have small economic efficiency. The major problem at processing of acid tars is availability of sulphuric acid that begins to evaporate and decompose at processing temper-

atures of over 300 °C. This leads not only to corrosion of equipment but also to the need of trapping of sulphurous gases.

This work develops an alternative disposal method of PAT that is to use acid tars without purifying from left over sulphuric acid as a precursor for the preparation of sulphated carbon materials (SCM) in one step. In some industrial processes (synthesis of biodiesel fuel [8, 9], biomass processing [10, 11], alkylation of aromatic compounds [12] *etc.*), SCM are regarded as an inexpensive heterogeneous acid catalyst [6, 7] that allows excluding homogeneous mineral acids from catalytic processes. The major synthesis methods of SCM consist in the preparation of the carbonized precursor followed by its sulphonation (for example, [8] – sulphonation of

carbonized sugars and biomasses) or in a simultaneous stage of carbonization and sulphonation of the original precursor. The disadvantage of this method is inertness of the sulphonatable precursor and, consequently, a low concentration of surface sulpho groups in the final SCM. At simultaneous sulphonation−carbonization of polyaromatic compounds (naphthalene *etc.*) [13, 14] one managed to reach the highest concentrations of sulpho groups for sulphonic-acid carbon materials, however, textural characteristics were relatively low (1−2 m^2/g). The synthesis of SCM from acid tars is convenient to conduct by the second method, since PAT contain significant amounts (>60 mass %) of polyaromatic compounds (asphaltenes *etc.*).

It was earlier demonstrated that the use of copolymerization processes of asphaltenes and resins present in acid tars, similarly to preparation processes of petroleum-polymeric and phenol-formaldehyde resins for the preparation of SCM from acid tars was possible [5]. This allowed obtaining a compact material and bind large amounts of sulphuric acid in a carbon-containing matrix.

In this work, with the purpose of increasing textural characteristics of materials, the introduction of various binding and template additives (high-ash biomaterials) that are large-capacity agriculture and forestry wastes was studied at the synthesis stage of SCM. The effect of conditions of SCM synthesis on acidity (concentration of surface sulpho groups) and textural characteristics of the final materials was studied in the course of the work.

EXPERIMENTAL

Preparation of models of acid tars

A model of acid tar (MAT) was obtained by dissolving in melted bitumen (BN 70/30; content of aromatic compounds >60 %) in heavy oil fraction (Tatneft JSC, Tatarstan, Russia) at a temperature of 80 °C. Afterwards, sulphuric acid (98 %, 50 mass %) was added with stirring to the resulting mixture of MAT and heated at a temperature of 80 °C for 5 h. The mass content of sulphuric acid in the final mixture

(s-MAT) was no less than 40 %. The composition of MAT approximately corresponded to that of a typical high-sulphur PAT.

Synthesis of sulphated carbon materials from models of PAT

To obtain SCM a mixture of s-MAT (or MAT) was mixed with binder (furfurol, formaldehyde or resorcin) in a ratio of acid tar/binder = 1 : 10 g/mmol and carefully stirred until the formation of a homogenous mass. Afterwards, the resulting mass was heated with stirring up to 150 °C for 10 min, the polymerization reaction occurred, and a solid loose product was formed (s-MAT-c (MAT-c)). Next, the sample was washed with hydrochloric acid (1 M), distilled water and calcined in a current of inert gas (N$_2$) at temperatures of 200−300 °C for 2 h with the formation of s-MAT-cx (MAT-cx) samples, where x is calcination temperature.

In case of using templates and additional pore-forming agents, appropriate additives were introduced at the stage of mixing MAT with binder. A ratio of acid tar/template is 2 : 1 by mass. Rice husks (Krasnodar Territory), sapropel (Bitter Lake, Omsk Region), low-moor and high-moor peat (Vasyugan Swamp, Tomsk Region), ground miscanthus (Institute of Cytology and Genetics, SB RAS), thiolignin (Baikal Pulp and Paper Mill, Irkutsk Region), hydrolysis lignin (Arkhangelsk Pulp and Paper Mill, Arkhangelsk Region) were studied as templates. Ash contents of the samples (mass %) are given in Table 1.

In case of using metal powders (Zn, Fe or Al) the additive content was 5 mass % from the mass of s-MAT.

Physicochemical research methods

Measurements of the specific surface area of the samples were performed in the dynamic variant, according to the multipoint BET method at adsorption of Ar (Sorbi N. 4.1, META JSC).

Thermogravimetric analysis (TGA) of the samples was conducted on a NETZSCH STA 449C-Jupiter device. TGA curves were recorded in a range from 25 to 1000 °C. Heating was performed either in air flow or an inert gas

TABLE 1

Effect of templates on the specific surface of the SCM sample (s-MAT-c300)

Template (additive) to a mixture of MAT[1]	Template ash, mass %	S_{sp}, m²/g	Template (additive) to a mixture of MAT[1]	Template ash, mass %	S_{sp}, m²/g
Initial MAT[2]	0.1−0.3	−	Miscanthus	3.3	5
Without templates	0.1−0.3	4	Thiolignin	2.8	6
Rice husks	19.5	36	Hydrolysis lignin	1.9	7
Sapropel	64.3	168	Zinc	−	140
High-moor peat	6.0	6	Iron	−	20
Valley peat	29.0	156	Aluminium	−	15

[1]The samples were obtained by heating (150 °C) a mixture of s-MAT−furfurol−template followed by calcining at 300 °C.

[2]Initial mixture of bitumen/heavy oil without sulphuric acid additives, templates, and calcining..

atmosphere (He) at a gas rate of 15 cm³/min and heating rate of 10 °C/min. For analysis, 20 mg of samples was loaded into corundum crucible; calcined alumina was used as a comparison template.

Elemental analysis CHNS was carried out using a VARIO EL CUBE (Elementar Analysensysteme GmbH, Germany) elemental analyzer equipped with a detector on heat conductivity. Analysis allowed carrying out determinations in a sample of carbon, hydrogen, sulphur and nitrogen in a concentration range from 0.01 to 100 % during sample combustion in a current of oxygen at a temperature of 1170 °C (analysis time of 10 min). The sample was analyzed no less than 3 times followed by averaging the data obtained.

Diffraction images of samples were obtained using an ARL X'TRA diffractometer with a wave length of 1.54184 Å, scanning on points using CuK_α radiation. A scan interval is 10−90° (2θ scale), scan step of 0.05°, signal accumulation time at the point of 5 s.

IR spectra were recorded using a Vertex 70v Bruker spectrometer equipped with a (Specac Ltd., UK) special diamond cell was used for shooting opaque samples in the embodiment of frustrated total internal reflection (FTIR) was used. A liquid nitrogen cooled HgCdTe detector was used when shooting. Spectra were recorded in a range from 5000 to 370 cm⁻¹ with a resolution of 4 cm⁻¹. The number of scans in all cases was equal to 128. The resulting spectra were corrected subject to the average refractive index (n = 1.5) on the software attached.

XPS spectra were recorded on a Vacuum Generators Escalab High Pressure electron spectrometer (Great Britain) using non-monochromatic MgK_α radiation (hv = 1253.6 eV, 150 W).

Catalytic activity testing of SCM in the esterification reaction of enanthic acid

The esterification reaction of enanthic acid ($C_6H_{13}COOH$, Fluka, 99 %) with absolute methanol (CH_3OH, Fluka, 99.9 %) was used as a model test of catalytic activities of the resulting samples. In a conical flask equipped with a reflux condenser, 2.7 mL of methanol, 3 mL of enanthic acid (2 : 1 mol/mol) and 0.5 g of the catalyst was loaded. The reaction was carried out at a temperature of 80 °C with stirring (500 rpm); it was stopped in 2 h, the catalyst was filtered of and conversion of the starting substrate was determined, according to on titration of an aliquot (0.1 mL) of the reaction mixture with a 10 % NaOH solution.

RESULTS AND DISCUSSION

Effect of templates and binders on textural characteristics of CSM

To increase textural characteristics of CSM the introduction of various binding and templatic additives that are large-capacity agriculture and forest chemical industry wastes was studied. It was suggested that templates of vegetable origin would allow reaching high textural characteristics, since the preparation of highly porous

and high-surface sorbents (rice husks [15], sapropel [16]) from them was probable at relatively low treatment temperatures. This technique is an inexpensive analog of the hard template method used in the preparative synthesis of spatially organized materials [17].

It was preliminarily demonstrated that one managed to increase textural characteristics of materials when using copolymerizing binders. Thus, the largest specific surface was reached in case of furfurol. Samples of mixtures of s-MAT [5], s-MAT−furfurol, s-MAT−resorcinol, s-MAT−formaldehyde (or formalin 33 %) heated to 150 °C and then calcined at 300 °C had S_{sp} equal to ≤1, 4, 2, 2 m^2/g, respectively. Thermolysis regions of the C−sulpho group (180−350 °C), as well as of decomposition aliphatic fragments bound with graphene units (400−600 °C) are registered during thermogravimetric analysis (30−1000 °C in a current of helium) of samples of carbonized-sulphatized MAT. In case of TGA analysis of a sample of s-MAT-c300 obtained when heating a mixture of MAT and furfurol without sulphuric acid, the mass loss in the temperature region of 180−350 °C is substantially a lower in comparison with a sample of s-MAT-c300. It is noteworthy that polymerization and carbonisation of MAT in the presence sulphuric acid proceeded more deeply with the formation of a greater part of graphene units. Completely carbonized blocks are thermally more stable in the helium flow (residue mass in case of thermolysis of s-MAT-c300 significantly exceeded the residue mass for MAT-c300 (55 and 35 %)).

TABLE 2

Specific surface values of SCM-template (additive) samples at various calcination temperatures (T_{calc})

Template (additive) to a mixture of s-MAT	S_{sp}, m^2/g T_{calc}, °C		
	225	250	300
Sapropel	−	5	168
Valley peat	−	42	156
Sapropel−Zn	31	67	−
Valley peat−Zn	47	75	−

Note. Dash indicates not determined.

The templates used and textural parameters reached with their help when calcining samples up to 300 °C are given in Table 1. As it turned out, sapropel, low-moor peat found themselves among the most promising templates. As it turned out, sapropel, low-moor peat found themselves among the most promising templates. It is interesting to note that among templates, more high-ash ones, *i. e.*, less valuable from the viewpoint of industrial processing, turned up to be more promising for the preparation of high surface area. Partial deashing and material structuring with the formation of a porous structure occurred during heating. The heating temperature of 300 °C is already sufficient for the development of high specific surface and was selected as the limit, as it is close to the boiling point of sulphuric acid.

An opportunity to use of additional pore-forming additives was tested. The use of zinc,
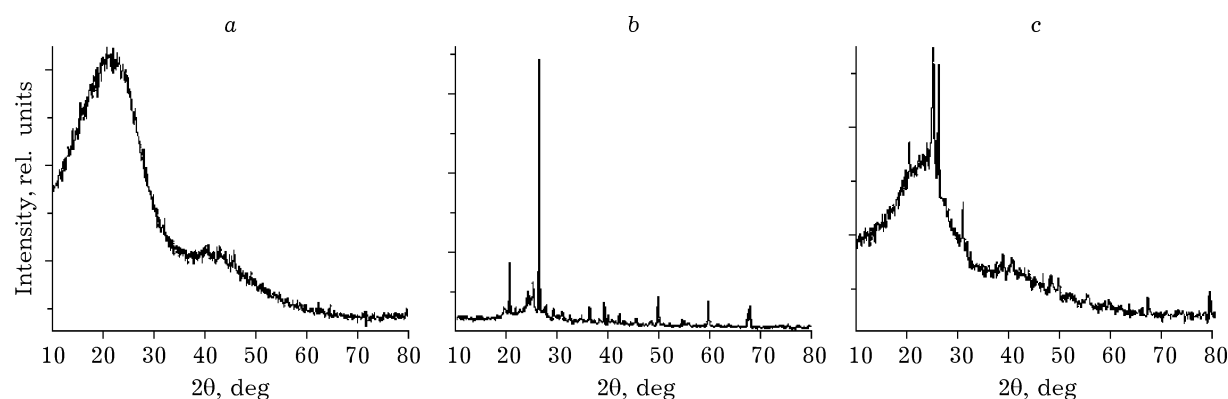

Fig. 1. Diffractograms of s-MAT-c300 samples with various templates: *a* − without template, *b* − sapropel, *c* − valley peat.

its salts and other metals was repeatedly tested during the synthesis of carbon materials with high textural characteristics of wastes of plant origin (for example, [18], the thermolysis and carbonization of sawdust). When using Zn one managed to achieve a significant increase in the textural characteristics of the materials, such as carbonization-sulphonation of mixtures of s-MAT−furfurol (see Table 1) and mixtures of s-MAT−template−furfurol (Table 2).

The SCM obtained were studied by various physical research methods. Diffractograms of the resulting s-MAT-c300 samples with various templates are given in Fig. 1. Depending on the template used the appearance of various phases of the ash component not removed at the washing stage was observed in diffractograms.

Broad reflexes corresponding to highly disordered reflexes 002 and 004 of graphite (significantly higher temperatures are required for the formation of a more ordered structure). Narrow peaks that can be referred to the structure of α-quartz were observed in diffractograms in case of using valley peat and sapropel, and reflexes relating to aluminosilicates (albite, muscovite, leucite) and hematite were identified in case of the SCM−sapropel sample.

Effect of calcination temperature on textural characteristics of SCM

The synthesis temperature of samples significantly affects specific surface values. To obtain high surface higher calcination temperature are required, on the other hand, the cleavage of sulpho groups from the carbon material surface occurs at high temperature (over 200 °C). Thus, maximum decreasing the thermal treatment temperature at preserving the specific surface is crucial.

The most promising templates contributing to developing high specific surface were selected from data of Table 1, and the effect of the temperature of heating the sample on the specific surface values of the final material was carried out. As can be seen from the data obtained a decrease in the calcination temperature lead to a rapid decline in the specific surface of the prepared samples. Nevertheless, an additional metal additive in case of triple sys-

tems s-MAT-c−valley peat−Zn and s-MAT-c−sapropel−Zn allowed decreasing a drop in textural characteristics of samples.

State of sulphur in samples and effect of the calcination temperature on the concentration of acid groups

To determine the chemical composition of the surface of samples and element valences the XPS method was used. In SCM samples, sulphur was present in two forms: thiophene (S^{2-}) is rigidly bound in the material frame and is not removed at its calcining, as well as sulphate (S^{6+}) that was formed at carbonization/sulphonation of the material. Calcining SCM samples at the temperatures of 300 °C and higher led to complete elimination of sulpho groups, which was detected in XPS spectra. Spectra of S2p for SCM (s-MAT) samples before and after (s-MAT-c300) calcining at 300 °C are given in Fig. 2. As can be seen from the spectrum of s-MAT, two signals relating to different states of sulphur are observed. The peak with a value of the bond S2$p_{3/2}$ energy of 163.3 eV relates to the sulphur that is found in the composition of thiophene residues, and the S2$p_{3/2}$ signal with a value of the bond energy equal to 168.5 eV relates to sulphur in the form of sulpho groups [19]. Thus, the difference between sulphur content according to data of elemental analysis for s-MAT and s-MAT-
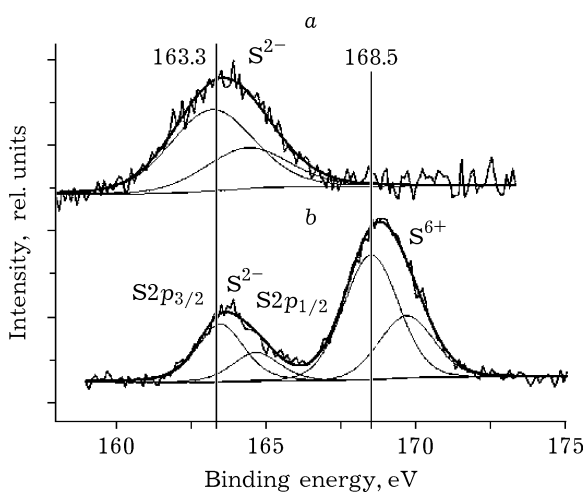

Fig. 2. Spectra of S2p for s-MAT-c300 (*a*) and s-MAT (*b*) samples.

TABLE 3

Atomic ratios between elements on the surface of SCM samples

Samples (templates)	S_{total}/C	S^{6+}/S^{2-}	O/C
s-MAT-c200	0.033	1.93	0.146
s-MAT-c300	0.009	0	0.208
s-MAT-c200 (valley peat)	0.037	2.24	0.151
s-MAT-c300 (valley peat)	0.011	0	0.210

c300 can be used for assessment of the concentration of sulpho groups in samples.

At synthesis of SCM with template, sulphur content in samples turns out to be significantly higher (up to 3 times) than for SCM prepared without using templates. Herewith, sulphur in samples was mainly present as sulpho groups ($S^{6+}/S^{2-} = 2.24$ for s-MAT-c200 sample (valley peat)).

This is presumably due to the fact that sulphuric acid present in the initial mixture is bound to both polyaromatic fragments of SCM and template particles. Atomic ratios of elements on the surface of SCM before and after calcining are given in Table 3. As can be seen from experimental data, calcining the SCM sample at 300 °C leads to the loss of sulpho groups on the surface and to an increase in the oxidation degree of the surface of carbon materials.

The elimination of sulpho groups at varying the calcination temperature was investigated in more details using infrared spectroscopy FTIR (Fig. 3). Infrared spectra were registered for s-MAT-cx and s-MAT-cx−valley peat samples calcined at various temperatures (200−300 °C, with an interval of 25 °C). When increasing the calcination temperature of samples the intensity of the bands in the region of 1040, 1165 и 2900 cm^{-1} (characteristic frequencies for SO$_3$H groups [20]) consistently decreased. The most significant change in IR spectra of s-MAT-cx (see Fig. 3, *a*) and s-MAT-cx−valley peat samples (see Fig. 3, *b*) occurred in a temperature range of 225−250 and 250−275 °C, respectively. Thus, the introduction of template led to better binding of sulpho groups in the SCM sample, which allowed achieving a greater stability during calcining.

Testing of the catalytic activity

The esterification reaction of enanthic acid (C$_6$H$_{13}$COOH) with absolute methanol (CH$_3$OH) was used as a catalytic test for characterizing the activity of a series of the materials obtained (s-MAT-cx−valley peat−Zn, where $x =$ 200, 225, 250, 275 and 300 °C, Fig. 4) in acid-catalyzed processes. This reaction is reversible; therefore, the use of absolute alcohol (excess) and carboxylic acid without water is crucial. The reaction without catalysts (in the autocatalytic mode) almost did not proceed under similar conditions (conversion <2 %).
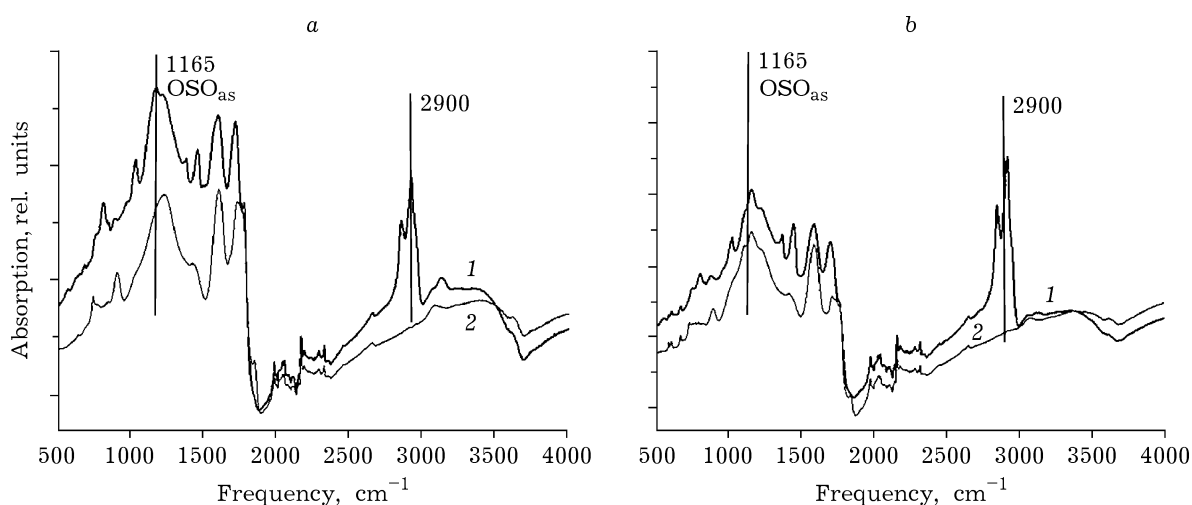

Fig. 3. Infrared spectra FTIR of s-MAT-cx (*a*) and s-MAT-cx−valley peat (*b*) samples calcined at various temperatures (°C): *a* − 225 (*1*) and 250 (*2*); *b* − 250 (*1*) and 275 (*2*).
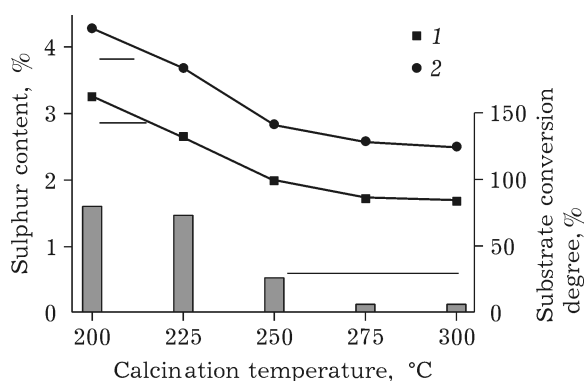
Fig. 4. Sulphur content in s-MAT-cx and catalytic activities of s-MAT-cx−valley peat−Zn samples in the esterification reaction of enanthic acid *vs* the calcination temperature and template. Samples: *1* − without template, *2* − template is valley peat−Zn.

Samples with the calcination temperature not exceeding 225 °C turned out to be most active. When increasing the calcination temperature, the concentration of surface SO_3H groups and the catalytic activity turned out to be significantly lower. Based on the catalytic data obtained, the activity of s-MAT-cx samples significantly depends on the concentration of sulpho groups in the sample (from 4.55 mass % SO_3OH for s-MAT-c200 up to 0 mass % S for s-MAT-c300) and to lesser extent from the specific surface. The residual activity of samples after calcining at high temperatures is due to both autocatalysis and residual carboxylic centres on the surface of carbon materials.

CONCLUSION

It was demonstrated during the work that the introduction of high-ash templates contributes to structuring carbon carriers synthesized by carbonization of acid tars and additional binding of sulphuric acid in the form of surface sulpho groups, which significantly increases acidity of the resulting materials. Based on the data obtained from analysis of SCM samples by IR spectroscopy, XPS and TGA, a range of treatment temperatures was established, at which as both stabilization and cleavage of sulpho groups from the surface of SCM are ob-

served. A combo template demonstrating relatively high specific surface area (60−80 m^2/g) at low treatment temperatures (225−250 °C) at preserving a high sulphur content in the form of sulpho groups (up to 4.55 mass % SO_3OH) was defined. The comparative assessment of SCM acid properties using a model of the catalytic esterification reaction of enanthic acid with methane was carried out, from which one can see that SCM samples with the calcination temperature up to 250 °C demonstrate high catalytic activities.

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