Catalytic properties of the thermoactivated schungite rock

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A high catalytic activity of the thermoactivated schungite rock was demonstrated for reactions of CO oxidation, neutralization of CO + NO_x mixtures (model exhaust gas), oxidation of *o*-xylene, and oxidative dehydrogenation of ethylbenzene to styrene.

Key words: schungite rocks, thermoactivation, catalytic activity, carbon monoxide, ethylbenzene.

One of the promising routes to simplify preparation, reduce the cost of catalyst manufacture, and decrease the level of technogenic contamination during their production and utilization is the replacement of synthetic catalytic systems by naturally occuring, usually multicomponent, materials.

Schungite rocks of Karelia represent a poorly studied (with respect to the catalytic properties) and rare in composition natural material formed mainly by quartz and schungite carbon. Carbonates (calcite, siderite, dolomite), laminated aluminosilicates (kaolinite, hydromica), and iron sulfides and hydroxides (pyrite, goethite, hydrogoethite) are present in the rocks as minor components.

According to the available data, the schungite rock (SR) manifests catalytic activity in the dehydration of alcohols[1] (acid-base type reactions) and decomposition of hydrogen peroxide[2] and oxidation of CO [3] (redox type reactions).

The purpose of this work is to study the catalytic activity of the thermoactivated SR in reactions of oxidation of CO, neutralization of model exhaust gases (CO + NO_x mixtures), oxidation of *o*-xylene, and oxidative dehydrogenation of ethylbenzene.

Experimental

Samples of the SR from the Zazhoginskoe deposit with a carbon content of ~30 wt.% and a grain size of 1.0—2.5 mm were studied. The SR samples without thermal treatment manifested no measurable activity in the reactions chosen for the study.

The SR were thermally activated at 500 °C. This temperature was chosen from the results of thermogravimetric analyses of the SR in air, which showed that near 500 °C the thermogram has an exotherm corresponding to a rapid loss in weight due to carbon burn-off.[4] The same temperature was used for SR activation in a hydrogen atmosphere.

Thermooxidative and thermoreductive activations of the samples were carried out in a flow of air (3 or 6 h) or hydrogen (6 h), respectively. The thermooxidative-reductive activation was performed by the successive treatments in a flow of air and hydrogen (6 h each). The activated SR exhibited catalytic activity in all reactions studied. An increase in the activation procedure beyond 6 h did not affect the activity.

Except for carbon, the content of the main chemical components in the samples recalculated to oxides was determined at the Analytical Certification Testing Center of the All-Russia Institute of Mineral Resources using chemical and elemental analyses.[5]

The specific surface area of the samples (S_{sp}) was measured by the Brunauer—Emmett—Teller method using the thermal desorption of argon adsorbed at a low temperature.[6] The pore volume (V_p) was determined by mercury porosimetry.[7]

To prepare Pt catalysts, H_2PtCl_6 was used. The successive treatments of the samples impregnated with an acid were carried out in a flow of air and then hydrogen. The catalysts containing 0.1 and 0.4 wt.% Pt on SR were studied.

The catalytic activity has been studied by methods described earlier.[8,9] The oxidation of CO on the SR was studied in a flow-type unit. The volume of the SR samples was 1 cm^3, the flow rate was 900 h^{-1}, and the reaction mixture contained 5—6% CO and 94—96% air. The compositions of the reaction mixture and reaction products were examined by GC on an LKhM-72 chromatograph (katharometer as the detector, helium as the carrier gas, columns were packed with molecular sieves 5 Å to determine CO and with Polysorb to determine CO_2).

The reaction of neutralization of CO + NO_x mixtures (model exhaust gas) was also studied in a flow-type unit with a flow rate of 2000 h^{-1}. The reaction products were analyzed by chromatography on a column packed with Polysorb.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1555—1560, August, 2004.

Table 1. Content of the main chemical components in the starting and thermoactivated SR samples

Sample	Composition (wt.%)								
	C	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	K_2O	TiO_2
Starting SR	31.00	54.50	4.62	2.04	1.50	0.66	0.02	1.15	0.22
SR thermoactivated in an air flow at 500 °C	10.08	74.63	5.76	1.58	0.77	0.71	0.90	2.43	0.28

An SR sample 2 cm^3 in volume was used for *o*-xylene oxidation, the *o*-xylene concentration in vapor being 0.1 mol cm^{-3}, and the flow rate of an *o*-xylene—air reaction mixture was 1800 h^{-1}.

Oxidative dehydrogenation of ethylbenzene was studied in a flow-type reactor of a KL-1 design (Special Design Bureau of the N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences). The concentration of ethylbenzene in a mixture with air or (for comparison) nitrogen was 0.1 mol cm^{-3}, the volume of the SR sample being 2 cm^3, and the flow rate of the reaction mixture was 1060 h^{-1}. The reaction products were analyzed on columns packed with Polysorb.

IR spectroscopic analysis was performed on a Specord M-80 spectrophotometer. Samples of the SR were compacted into pellets with KBr. The spectra were recorded in air at 20 °C.

Results and Discussion

Influence of thermoactivation on the composition and texture of the samples. The changes in the content of the main chemical components due to the thermooxidative activation of the SR sample are shown in Table 1.

The carbon content in the samples upon their activation in an air flow decreases due to partial burn-off from 31 to 10 wt.%, and the content of silica and alumina, as well as that of several other oxides, increases. According to the published data,[10,11] iron oxides predominate (1.5—2 wt.%) among the transition metal oxides occurring in the rock.

According to X-ray diffraction data, the main phases in the starting rock and in the sample subjected to thermooxidative activation are low-temperature quartz and schungite carbon. The latter is a carbonaceous substance represented by an amorphous to X-rays phase.

Mineralogical and X-ray computational microtomographic (XCMT) analyses showed that in the starting rock the siliceous matrix is uniformly saturated with finely dispersed schungite carbon. After the thermooxidative treatment, the fraction of the carbonaceous component decreases and the component migrates to enrich the external peripheral zone of pellets and zones of internal breaks.

A similar surface enrichment is also observed in the peripheral zone of grains of the iron-containing mineral phase (minerals of the goethite group: goethite, hydrogoethite).[12,13] Thus, the concentrations of carbon and the iron-containing phase on the surface of the thermoactivated SR are higher than their average content in the rock.

Table 2. Influence of thermooxidative activation on the parameters of the SR texture: specific surface (S_{sp}), pore volume (V_p), and average pore radius (*r*)

Sample	$S_{sp}/m^2 g^{-1}$	$V_p/cm^3 g^{-1}$	*r*/nm
Starting SR	9.0	0.025	13
SR thermoactivated in an air flow for 6 h at 500 °C	12.0	0.192	211
SR thermoactivated in air for 8 h at 411 °C*	28.0	0.289	596
SR thermoactivated in air for 1 h at 528 °C*	29.3	0.175	106

* According to the data in Ref. 4.

Following the thermooxidative activation, the specific surface and total pore volume (Table 2) increase by 1.3 and 8 times, respectively. This is caused by the development of the porous structure when a portion of carbon was "burnt off." The S_{sp} values correspond to usual values for catalysts based on individual and mixed oxides of transition metals, including iron oxides.

Varying the conditions of oxidative activation, one can control the average content of carbon in the samples, the content of carbon and the iron-containing phase on the surface, and the characteristics of the texture (see Table 2). As shown by the study of benzene vapor adsorption, this activation renders the samples microporous.[12]

The IR spectra of the starting SR and the sample subjected to thermooxidative activation are shown in Fig. 1. The spectrum of the starting sample (see Fig. 1, curve *1*) contains several bands at 1200—400 cm^{-1} attributed to stretching vibrations of Si—O. The high-frequency region exhibits a broad band at 3500 cm^{-1} caused by the presence of water of hydroxyl groups linked with the surface by a hydrogen bond. The thermooxidative treatment of the SR (see Fig. 1, curve *2*) increases the intensity of the bands due to the partial removal of carbon and improves their resolution, which usually indicates a decrease in the degree of imperfection of the lattice.[9]

The spectra of the SR after thermoreductive and thermooxidative-reductive activations are presented in

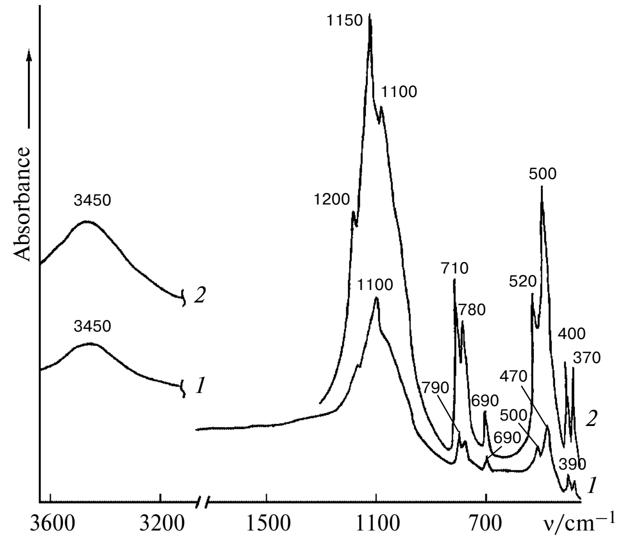

Fig. 1. IR spectra of the starting SR (*1*) and SR thermoactivated for 6 h at 500 °C in an air flow (*2*).

Fig. 2. Unlike the thermooxidative treatment, the thermoreductive treatment does not virtually change the shape of the spectrum in a region of stretching Si—O vibrations (see Fig. 2, curve *1*) but increases the intensity of the band at 3450—3500 cm^{-1} and induces the appearance of a band at 1630—1640 cm^{-1} (*cf.* curve *1* in Fig. 1) corresponding to bending vibrations of H—O—H. This indicates the formation of water, probably, due to the partial reduction of metal oxides, which are present in the SR as impurities.

The thermooxidative-reductive activation (see Fig. 2, curve *2*) increases the intensities of all bands compared to those in spectrum *1* following to partial removal of carbon. In this case, the intensities of the bands at 3500 and 1640 cm^{-1}, indicating, as assumed above, the presence of water, increase as a result of the reduction of foreign metal oxides.

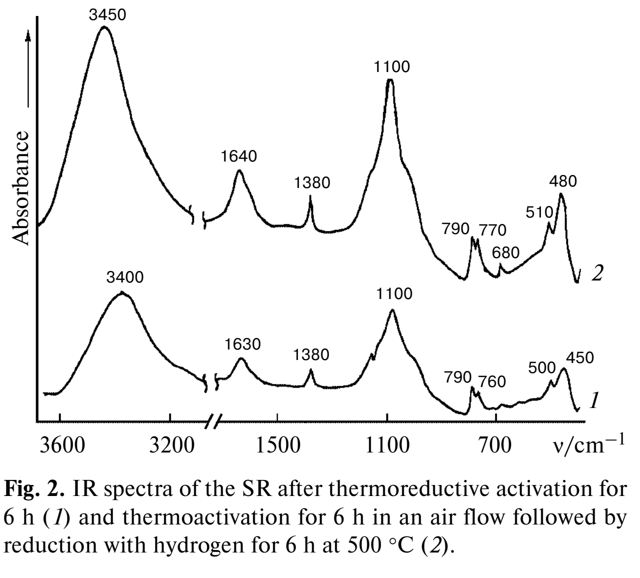

Fig. 2. IR spectra of the SR after thermoreductive activation for 6 h (*1*) and thermoactivation for 6 h in an air flow followed by reduction with hydrogen for 6 h at 500 °C (*2*).

Thus, the thermooxidative activation of the SR favors a decrease in the carbon content and an increase in the content of other components. Moreover, it heals imperfections in the crystal structure renders the samples microporous with an increase in S_{sp}, and enriches the near-surface grain layers in carbon and the iron-containing mineral phase. For the thermoreductive activation of the SR, the main effect is the partial reduction of foreign metal oxides. For the thermooxidative-reductive activation, the effects caused by the thermooxidative and thermoreductive treatments are combined.

Oxidation of CO, neutralization of CO + NO$_x$ mixtures, and oxidation of *o*-xylene. The main catalysts for exhaust gas neutralization are known to be multicomponent systems based on noble metals (Pd, Pt, Rh). Intensive search for alternative catalysts using, in particular, transition metal oxides, is under study.

The influence of the thermoactivation method on the catalytic activity of SR, as characterized by the temperature dependence of the CO conversion (α), is shown in Fig. 3. Curve *1* indicates a low activity of the SR after the thermoreductive activation for 6 h: the CO conversion at 400 °C is ~20%. The thermooxidative activation for 3 or 6 h makes it possible to achieve the 100% conversion of CO at temperatures about 500 and 400 °C, respectively. The thermooxidative-reductive activation increases the activity of the SR more strongly: the 100% conversion is achieved at 370—380 °C (see Fig. 3, curve *4*).

The increase in the catalytic activity due to the thermooxidative activation of the SR can be explained by an increase in the accessibility of active sites for reactants:

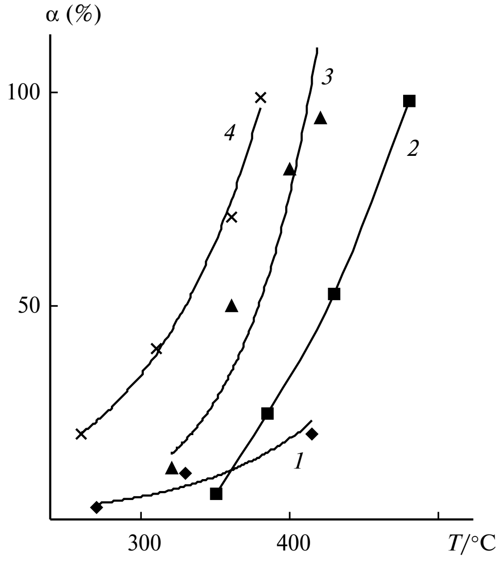

Fig. 3. Temperature dependences of the CO conversion (α) for the samples thermoactivated by different methods: thermoreductive activation for 6 h (*1*), thermooxidative activation for 3 (*2*) and 6 h (*3*), and thermooxidative-reductive activation (*4*).

these sites are oxides of foreign transition metals. This occurs due to the elimination of a portion of carbon, which screens these sites, and diffusion of iron ions and other impurity ions (for the iron-containing mineral phase, this was confirmed by mineralogical and XCMT analyses) into the near-surface grain layers. The subsequent thermoreductive treatment can further increase the activity due to the partial reduction of the oxide sites on the rock surface, which is confirmed by IR spectroscopic data.

The published data indicate that the SR can be used (without activation) as a support for oxide catalysts active in CO oxidation.[3,14] In this work, we studied the activity of the SR-supported platinum catalysts (0.1 and 0.4 wt.% Pt) in CO oxidation. Platinum was incorporated in both the starting SR and the SR subjected to the thermooxidative activation for 3 and 6 h. After impregnation of the support with H_2PtCl_6, the catalysts were reduced by hydrogen or calcined in air.

The data in Fig. 4 show that after reduction with hydrogen the activity of the catalysts supported on the starting rock (curve *1*) is lower than that on the sample thermoactivated in air (curve *2*). The catalyst activity increases when H_2PtCl_6 was introduced on the starting rock followed by the calcination of the catalyst at 500 °C in air (curve *3*). In this case, the catalyst is formed under the conditions of simultaneously occurring processes of thermooxidative activation of the support and decomposition of H_2PtCl_6. The SR-supported catalysts are less active than the conventional catalytic system 0.1 wt.% Pt/Al_2O_3 (curve *4*). However, taking into account a substantially higher S_{sp} value for Al_2O_3 (80 $m^2 g^{-1}$) compared to that of the SR (9—12 $m^2 g^{-1}$), one can conclude that the specific catalytic activity of the 0.1 wt.% Pt/SR system is rather high, which is evidently explained by a contribution from the activity of the support.

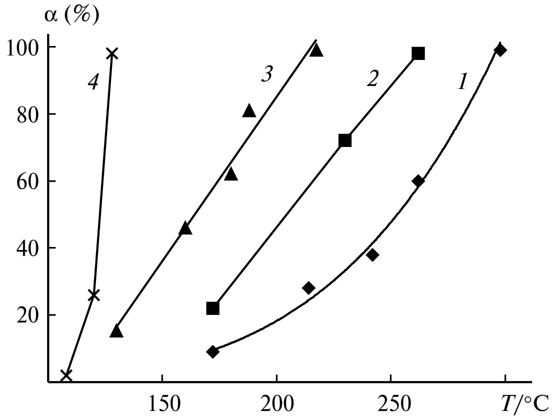

Fig. 4. Temperature dependences of the CO conversion (α) for the catalysts 0.1 wt.% Pt/SR: the catalyst on the starting SR reduced by hydrogen (*1*), the catalyst on the SR after thermooxidative activation for 3 h reduced by hydrogen (*2*), the catalyst on the starting SR calcined in air for 6 h at 500 °C (*3*), and the catalyst 0.1 wt.% Pt/Al_2O_3 (*4*).

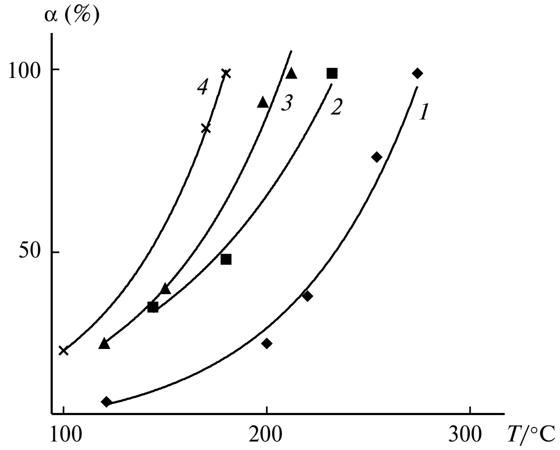

Fig. 5. Temperature dependences of the CO conversion (α) for the catalysts 0.4 wt.% Pt/SR: the catalyst on the starting SR reduced by hydrogen (*1*), the catalyst on the SR after thermooxidative activation for 3 h reduced by hydrogen (*2*), the catalyst on the starting SR calcined in air for 6 h at 500 °C (*3*), and the catalyst on the SR after thermooxidative activation for 6 h reduced by hydrogen (*4*).

The catalysts with a high Pt content are more active (*cf.* Figs 4 and 5). The thermoactivation conditions and the method of SR treatment exert the same effects on the activities of the catalysts with Pt concentrations of 0.1 and 0.4 wt.% in this reaction.

The catalysts supported on the starting rock and reduced by hydrogen (see Figs 4 and 5, curves *1*) are least active. The thermooxidative activation of the SR increases the activities of the supported catalysts, and the 6-h activation has a stronger effect than the 3-h treatment (see Fig. 5, curves *2* and *4*).

The platinum catalysts supported on the starting SR and calcined in air (see Figs 4 and 5, curves *3*) are more active than the hydrogen-reduced catalysts supported on the rock thermoactivated for 3 h in air. This confirms that the activation of the support and decomposition of H_2PtCl_6 can occur simultaneously. However, the highest activity is shown by the samples supported on the SR after its thermooxidative activation for 6 h and reduced by hydrogen (100% conversion of CO is achieved at 170—200 °C; *cf.* curves *3* and *4* in Fig. 5).

The fact that the specific features of the thermoactivation of the SR and the SR-supported Pt catalyst have the same effect on the activity of the latter indicates a substantial contribution of the activity of the support to the activity of the supported catalyst.

The 0.4 wt.% Pt/SR catalyst was tested to stability. The temperature of the catalyst was increased to a level providing the maximum (100%) conversion of CO, then the reactor was cooled, hereafter the activity was measured in a regime in which temperature was reduced to room temperature. Then the reactor was heated again to the temperature corresponding to the full conversion of CO. The experiment was carried out for 3 days, and the complete reproducibility of CO conversion persisted within this time, indicating a stable operation of the catalyst.

The neutralization of the model exhaust gas was studied for the SR samples subjected to the thermooxidative-reductive activation. Model mixtures of the exhaust gas of two compositions were studied: (*A*) 3% CO, 3.5% NO, 11% O_2, and 82.5% N_2 (relatively low concentrations of toxicants and oxygen excess) and (*B*) 16.7% CO, 21.8% NO, 23% O_2, and 59.2% N_2 (a high concentration of toxicants at a restricted oxygen content).

The temperature dependences of the catalytic activity of the thermoactivated SR related to CO oxidation and NO_x reduction are presented in Fig. 6. Mixture *A* showed much higher activities: the conversions of CO and NO_x reach 55—50% at temperatures of 200—250 °C, and for mixture *B* the activity was in the region of 35—30% at ~300 °C.

For both mixtures, the CO conversion exceeds the conversion of NO_x. The lower activity of the SR in mixture *B* is caused by NO_x excess, which prevents the efficient occurrence of the reaction

$$2\,NO + 2\,CO \longrightarrow N_2 + 2\,CO_2,$$

and by an oxygen deficiency for the oxidation of carbon monoxide in the reaction

$$2\,CO + O_2 \longrightarrow 2\,CO_2.$$

It should be noted that the temperature at which the 50% conversion of CO is achieved in gaseous mixture *A* is much lower (~200 °C) than that for CO oxidation in the absence of NO_x (~400 °C; see Fig. 3) on the same samples of the activated SR.

The deep oxidation of *o*-xylene on the SR subjected to the thermooxidative activation for 6 h begins to occur with a noticeable rate at temperatures higher than 350 °C, and at 450 °C the conversion achieves almost 100% (see below). No products of partial oxidation were observed.

T/°C	206	259	299	356	408	450
α (%)	0	1	3	12.7	83.2	99.4

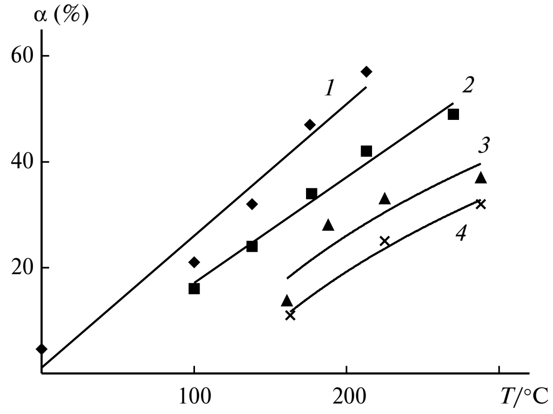

Fig. 6. Temperature dependences of the conversion (α) of CO (*1*, *3*) and NO_x (*2*, *4*) on the SR in mixtures *A* (*1*, *2*) and *B* (*3*, *4*).

Oxidative dehydrogenation of ethylbenzene to styrene. It is known that the industrial synthesis of styrene is mainly performed by the dehydrogenation of ethylbenzene at 550—650 °C using Fe_2O_3-based catalysts containing K_2CO_3 and Ce and Mo oxides. Similar catalysts of the recent generations also contain V, W, Li, Mg, Ca, Ti, Zr, Ni, and Co oxides. To decrease the partial pressure, ethylbenzene is diluted with water vapor[15] in a ratio of 1 : (10—15). The catalysts are regenerated with oxygen, which removes carbonaceous deposits from the surface.

In the presence of air, ethylbenzene is reversibly adsorbed on the SR subjected to the thermooxidative activation for 6 h at 100—110 °C. This adsorption process decreases with the temperature increase and ceases completely at 200 °C. Beginning from 160 °C, styrene appears in the reaction products. At temperatures higher than 200 °C, some amount of benzaldehyde is formed along with styrene, and traces of light hydrocarbons are present.

The temperature dependences of the overall conversion of ethylbenzene in the presence of air oxygen (oxidative dehydrogenation) and in a nitrogen flow (dehydrogenation) and the change in the selectivity of styrene formation (*S*) for oxidative dehydrogenation are presented in Fig. 7.

The conversion of ethylbenzene in the presence of oxygen in the 250—360 °C temperature interval increases from 18 to 47%, and the selectivity with respect to styrene increases. The low activity of the SR for ethylbenzene dehydrogenation in a nitrogen flow (see Fig. 7, curve *2*) indicates that styrene is formed, in the presence of oxygen, predominantly *via* oxidative dehydrogenation.

At temperatures higher than 360 °C, the reaction is impeded by the deep oxidation of ethylbenzene and styrene. At 406 °C, the overall conversion of ethylbenzene achieves 89%, and only 28.5% are transformed into styrene.

The overall conversion of ethylbenzene on the SR is the sum of its conversions to styrene and products of deep oxidation. The conversion of ethylbenzene to styrene prevails in a region of moderate temperatures, while the deep oxidation of hydrocarbons predominates at high temperatures.

The conversion and selectivities achieved by the oxidative dehydrogenation of ethylbenzene to styrene on the SR at a relatively low temperature (at 360 °C, the conversion of ethylbenzene is ~50% and the selectivity with respect to styrene is 80%) are quite comparable with the average parameters of the industrial process.[15] This indicates a principal possibility and advisability to develop an SR-based natural low-temperature catalysts for styrene

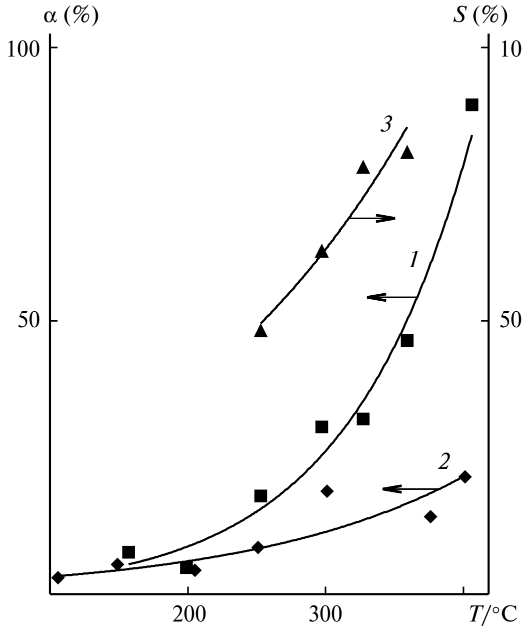

Fig. 7. Temperature dependences of the ethylbenzene conversion (α) in an air flow (*1*) and nitrogen (*2*) and the selectivity of styrene formation (*S*) in an air flow (*3*) on the SR subjected to thermooxidative activation for 6 h.

synthesis appropriate for oxidative dehydrogenation or a combined process.

In addition to metal oxides and noble metals, carbon-containing materials are known to be active catalysts of oxidative dehydrogenation (450—700 °C). In particular, iron oxide supported on active carbon and active carbon itself are such catalysts.[16,17] The temperature of the reaction on carbon is only 350—400 °C. The results obtained show that in this reaction the optimum temperature of catalysis (360 °C) corresponds to that observed on carbon, indicating a possible activity of the carbon component of the SR.

Thus, we demonstrated for the reactions studied that both the carbon component and foreign oxides of the SR can likely be responsible for the catalytic activity. The active surface is formed during the thermoactivation of the SR. Varying the conditions of the this treatment, one can control the carbon content in the rock, the degree of enrichment of the surface with carbon and oxide impurities, the specific surface, and the size and structure of pores. This provides challenges for controlling the properties of SR-based catalytic systems.

Schungite rocks can also be used as supports, for instance, for Pt catalysts, to obtain stable catalytic systems with a high specific activity in CO oxidation. The high mechanical strength and thermal stability of the SR have been established previously.[10,11] All these data confirm the necessity of further studies to develop novel catalysts, including low-temperature (energy-saving) catalysts, using the schungite rock as an active phase or support.

The authors thank G. N. Pirogova (Institute of Physical Chemistry, Russian Academy of Sciences) for assistance in IR spectroscopic analysis and participation in discussion of results of the work.

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Received November 17, 2003;
in revised form May 14, 2004