Novel catalytic processes in the chemical processing of coal

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The peculiarities of the application of catalysts to chemical transformations of the organic components of coal are discussed. Data concerning the new catalytic processes of coal pyrolysis, gasification, and liquefaction being developed at the Institute of the Chemistry of Natural Organic Raw Materials (Siberian Branch of the RAS) are summarized.

Key words: coal, pyrolysis, gasification, liquefaction; catalysts.

The ratio between the amounts of the various types of fossil fuel used differs significantly from the ratio between the amounts of their explored reserves. In fact, natural gas accounts for 23 % of the total amount of fuel being presently consumed, whereas its portion of the total oil, gas, and coal resources is equal to 3 %. Consumption of oil amounts to 44 %, and that of coal and lignite is 33 %, while their stores comprise 14 and 83 % of the world resources of fossil fuel, respectively. In view of the probable exhaustion of oil and natural gas deposits in the near future, the search for alternative methods for preparing organic compounds for chemistry and energetics is an urgent problem. Over the past 20 years, chemical processing of coal into ecologically safe synthetic fuels and organic chemical products has been studied intensively in many industrially developed countries.

In the evaluation of the long-term prospects of the development of works in the field of the coal chemistry in the Russian Federation the following factors should be taken into account: the dramatic decrease in oil production; the continuing decrease in coke production; the rich reserves of cheap coal in the eastern regions of the country (~17 % of the world coal resources); and the creation of more and more stringent requirements for environmental protection, which stimulates the production of coal-based synthetic fuels that are more ecologically safe than the starting coal.

The main drawbacks of the known technologies for the chemical processing of coal are, as a rule, relatively low productivity (compared with that in petrochemical processes) and drastic technological conditions (high temperatures and pressures). Catalytic processes that make it possible to produce a wide variety of fuels and chemicals from coal are being more and more widely used as more efficient and ecologically safe new-generation technologies for coal processing (Fig. 1).

The following problems arise in accomplishing catalytic transformations of coal:

— the achievement of a developed surface for the contact of coal with the catalyst and overcoming the diffusion restrictions;

— changes in the structure, physical state, and chemical composition of coal during the catalytic transformation;

— the presence of impurities in the coal that deactivate the catalyst;

— the difficulty of isolating the catalyst from the reaction mixture so it can be recycled in the process.

A variety of investigations have been devoted to these problems. In recent years, the results of these investigations have been summarized in a series of reviews and monographs and have also been discussed at two symposia on the problems of catalysis in coal chemistry.[1–3]

The present review considers new possibilities of using catalytic processes in the chemical processing of coal exemplified by works that have been carried out at the Institute of the Chemistry of Natural Organic Raw Materials (ICNORM) of the Siberian Branch of the RAS.

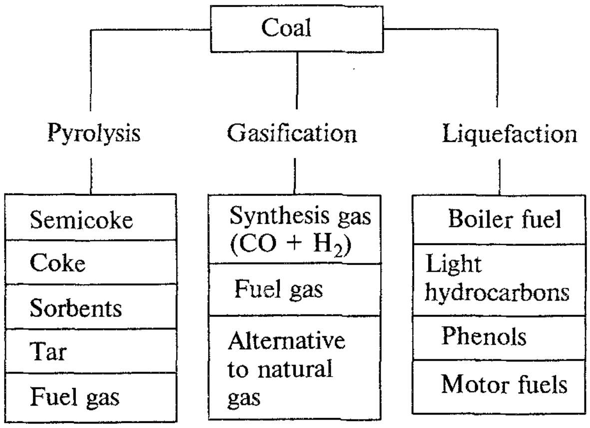

Fig. 1. Catalytic processes in coal processing.

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The basic methods for accomplishing the catalytic transformations of coal

The use of catalysts in the processing of solid organic raw materials differs in some ways from their use in gas-phase and liquid-phase processes of petroleum refining and petrochemistry. The main principles and technological methods for accomplishing catalytic processes in the chemistry of solid organic raw materials have not yet been well developed, though certain progress has been achieved. Various techniques that enable the efficient contact of a catalyst with a solid raw material have been suggested and their practical implementations are being developed.[4–6]

Two main groups of methods used for accomplishing catalytic transformation of coal may be distinguished. One of them includes catalytic transformations at "coal surface—solid catalyst", "coal surface—dissolved catalyst", "coal surface—molten catalyst", and "coal surface—catalyst in the gas phase" interfaces.

To the second group of methods belong catalytic transformations of coal which occur according to the mechanism of mediated catalysis by the transfer of the catalyst (Cat) action through the reaction medium:

Cat → components of the reaction medium →
→ coal → transformation products.

A combined scheme involving contributions from both direct and mediated catalytic effects to the transformation of coal is often realized in coal processing. In the case of direct catalysis, the final products (liquid, gaseous, and solid) result from catalytic reactions at the "coal surface—catalyst" interface. The pathway of mediated catalysis involves stages of catalytic transformations of liquid or gaseous components of the reaction medium. The latter are either formed from coal through chemical reactions or introduced as reagents.

At this time a variety of methods for using catalysts in coal processing have been suggested. The majority of them are depicted in Fig. 2. The greatest contact area is achieved when the catalyst is introduced into the coal by chemical bonding with surface reactive groups (for example, —COOH or —CHO), by insertion into the coal structure with the formation of intercalation compounds, or by using dissolved, molten, or volatile catalytic systems.

The use of mediated catalysis considerably facilitates the technology of catalytic processes. In this case, a high efficiency process can be achieved by using mechanical mixtures of pulverized or dispersed catalyst and coal as well as steady-state or fluidized beds of traditional petroleum refining catalysts.

Information on novel catalytic processes of coal transformation developed over the last 5—10 years is presented in the subsequent sections.

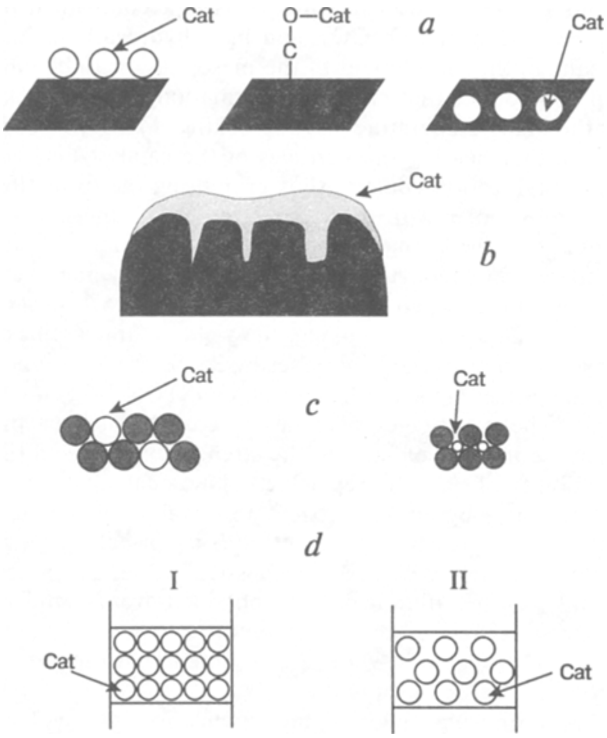


Fig. 2. Ways of using catalysts (Cat) in coal transformations: catalysts introduced into the coal by application or chemical bonding (*a*); dissolved or molten catalysts (*b*); a mechanical mixture of powdered or dispersed catalyst and coal (*c*); traditional heterogeneous catalysts in the processing of petroleum raw materials (*d*): I — in a fixed (coal paste) bed; II — in a fluidized (coal dust or paste) bed.

Catalytic pyrolysis

In order to improve the technology for producing metallurgical coke and to widen the raw material base for the coke industry, catalytic methods of coking have been proposed.[7–9] In the production of metallurgical coke two principle stages can be distinguished. The first of these involves the formation of a plastic mass (mesophase) by heating the batch at 350—400 °C. A further increase in the temperature results initially in the hardening of the mesophase followed by crystallization of coke, which is completed at 1000—1200 °C.

In the works carried out at the ICNORM, the effect of pyrite-containing catalysts (FeS_2 or FeS_2 deposited onto coke dust and lignite semicoke) on the coking process has been studied. It was found that a pyrite-containing catalyst increases the amount of the mesophase and influences the chemical composition of the liquid products by affecting the redistribution of the hydrogen and oxygen during coking. The catalyst accelerates the destruction of the oxygen-containing components of the reaction mixture. This is accompanied by the evolution of CO, CO_2, and light hydrocarbons and results in the enrichment of the mesophase with chemical compounds that ensure the formation of strong coke at the high-temperature stage of coking. Moreover, during further heating the particles of the catalyst may act as crystallization centers, thus promoting the formation of strong coke with a higher content of fine-grained structures. The strength characteristics of laboratory cokes prepared with catalytic additives are noticeably improved. For example, when pyrite deposited onto coke dust is used as the catalyst of coking, the yield of large grains of coke (40 mm in size) increases by 25 % (as determined by the procedure according to the GOST 9521-72 standard). The advantages of catalytic coking, such as the increase in the yield and in the strength of coke and the possibility of partially replacing coking coals that are in short supply by cheaper coals, are certainly of practical interest. At present, the scientific basis of coking technology, which will make it possible to enhance the quality of metallurgical coke obtained from standard coking batches as well as to produce standard quality coke from batches with high contents of low-grade coals, are being developed.

A promising field of the application of catalytic pyrolysis is the production of anodic materials of enhanced quality. Some data on the properties of laboratory anodes prepared with the use of organic (OA) and inorganic (IA) catalytic additives are summarized in Table 1. The advantages of these anodes include an increase in their mechanical strength (by 10 %), a decrease in porosity, an increase in density, a decrease in the specific electric resistance, and improvement of the fracture indices and oxidizability as well as a decrease in the amount of benzo[*a*]pyrene evolved into the atmosphere during the process.

The scientific basis for an efficient technology for the thermal processing of coal and wood wastes in apparatus with fluidized beds of catalysts yielding valuable carbon-containing products has been developed at the ICNORM. A physicochemical investigation of the oxidative pyrolysis of lignite in a fluidized bed with the IK-12-70 Al—Cu—Cr-containing catalyst and a number of low-cost iron-containing catalysts based on ore materials (Martin, boiler, and electrosmelting slags, *etc.*) has been carried out. It was found that when an air—coal dust mixture is blown through a fluidized bed of heated catalyst particles, volatile compounds are evolved from the coal. These are exothermically oxidized on the surface of the catalyst particles and thus provide autothermal conditions for the pyrolysis. The intensity of heat evolution in the fluidized bed of an oxidation catalyst is one to two orders of magnitude higher than in the case of an inert material (Fig. 3).

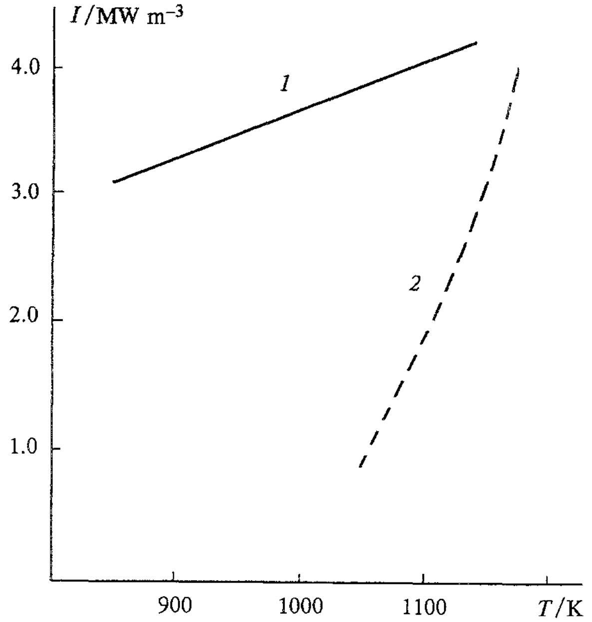


Fig. 3. Intensity (*I*) of heat evolution in a fluidized bed of a catalyst of oxidation (*1*) and of an inert material, chamotte (*2*) at various temperatures.

The limits for stable thermal processing of the lignite from the Kansk-Achinsk field into upgraded solid fuels

Table 1. The properties of laboratory anodes prepared with the addition of catalysts

Additive (proportion (%))	Strength /kg cm^{-2}	Specific electric resistance /Ohm mm^2 m^{-1}	Density /g cm^{-3}	Porosity (%)	Destructibility*	Collapsibility*	Oxidizability*
		Coal-tar pitch as the binder					
—	312.8	73.2	1.41	30.1	32.8	9.6	23.2
OA (0.025)	326.2	72.8	1.42	30.2	27.4	8.2	19.2
IA (0.025)	344.9	69.9	1.49	28.4	31.6	8.8	22.8
		Petroleum pitch as the binder					
—	257.3	78.3	1.38	29.4	46.4	8.7	37.7
OA (0.009)	324.4	70.5	1.48	27.2	39.6	7.9	31.7
IA (0.006)	295.2	72.4	1.43	29.3	38.3	6.6	31.7

Note. The data were obtained in collaboration with M. Yu. Ugai, M. L. Shchipko, V. K. Frizorger, and S. I. Sharanda. * In mg cm^2 h^{-1}.

(of the thermocoal type) and semicoke[10—12] have been established, and the parameters for producing carbon-containing materials possessing high porosities based on them have been chosen. Under the thermal shock conditions occurring in this process, a developed system of macro- and mesopores is formed owing to excessive pressure inside coal particles, which arises due to the evolution of volatile substances. Micropores are predominantly formed during the interaction of the pyrolized solid material with water vapor and CO_2, which follows the thermal shock. Optimization of the stages of the pyrolysis of the coal from the Kansk-Achinsk fields and of the activation of the resulting semicoke made it possible to produce porous materials with a surface of 800—900 $m^2\ g^{-1}$ and a sorption capacity with respect to iodine of 60—70.[13,14]

The technology for the oxidative pyrolysis of coal has been developed at the technological pilot plant of the ICNORM with a productivity of 200 kg of coal per hour. The main parameters of the pyrolysis of the Kansk-Achinsk coal in a fluidized bed of the IK-12-70 catalyst and an inert material (chamotte) are listed in Table 2. As follows from these data, the intensity of the pyrolysis increases 3—10-fold, depending on the conditions chosen, as the inert material (chamotte) of the fluidized bed is replaced by the IK-12-70 catalyst. Losses of heat to the surroundings also sharply decrease, which considerably improves the heat balance of the process. Wear-resistant catalysts were chosen (Fig. 4).

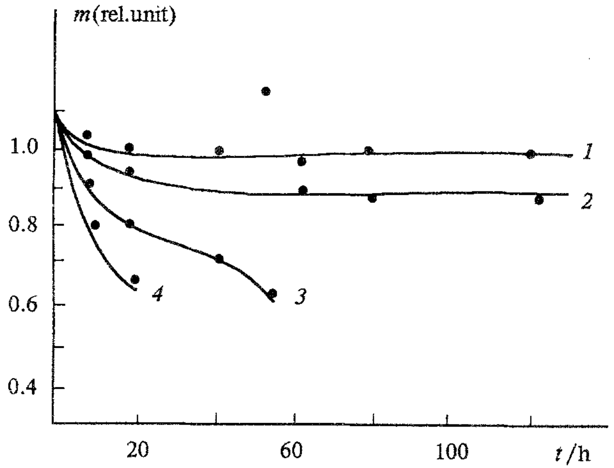


Fig. 4. The dependence of the loss of mass (*m*) of catalysts due to attrition in a fluidized bed on the operation time: IK-12-70 (*1*); Martin slag (*2*); boiler slag (*3*); chamotte (*4*).

In general, the process of the autothermal catalytic pyrolysis of coal has the following advantages:

— high productivity per unit volume of the apparatus owing to the short-time residence of the coal dust particles in the reaction zone;

— a severalfold decrease in metal consumption as a result of the decrease in the amount of equipment and the absence of recirculating mass flows in the technological cycle;

— the possibility of widening the range of products by varying the parameters of the process without changing the design of the plant;

— enhanced ecological security resulting from the absence of tar formation and the decrease in the volume of waste gases and in the concentration of harmful compounds therein.

Table 2. The main characteristics of autothermal pyrolysis of the Kansk-Achinsk coal[11]

Characteristic	Run			
	1	*2*	*3*	*4*
The material of the bed	Chamotte	The IK-12-70 catalyst		
Purpose	Control	Production of the thermocoal	Production of sorbents	Semicoke of the ETKh type
The intensity of the process /t.h.f. $(m^2\ h)^{-1}$	0.63	6.9	4.3	1.6
Productivity of the plant (kg of coal per hour)	62.1	163.3	103.6	37.8
The temperature of the bed/°C	850	610	670	770
Intensity of heat evolution /MWt m^{-3}	2.0	2.3	2.5	2.8
Items of the thermal balance (%)				
Physical heat of the products	16.8	4.2	6.1	11.5
Heat content of gases	22.8	0.1	3.4	20.3
Heat content of the residual solid fuel	49.8	94.8	85.2	64.4
Losses to the surroundings	10.2	0.9	1.6	4.3

Note: t.h.f. is a ton of a hypothetical fuel.

The solid products of the pyrolysis of coals from the Kansk-Achinsk basin can be widely used as upgraded energy fuel, briquetted household fuel, reducing agents for ferrous and nonferrous metallurgy, components in the production of metallurgical coke, and carbon sorbents.

Catalytic gasification

The procedures for gasification of coal developed at this time have the following drawbacks: relatively low yields of the gas per unit volume of the gasifier, drastic temperature conditions, and difficulties associated with the control of the composition of the gaseous products. The use of catalysts for coal gasification allows these characteristics to be improved.

However, the use of catalysts may cause new technological problems and raise the price of gasification. Development of simple and reliable methods for introducing the catalyst into the reactor and for its extraction for recirculation in the process should be noted as the main problems that still require technological solutions. A procedure for catalytic gasification of dust-like coal in the fluidized bed of an oxidation catalyst is being developed at the ICNORM.[15,16] The use of a fluidized bed solves the problem of how to introduce and withdraw the catalyst. Available and cheap boiler and metallurgical slags, which may be used in the process until they have been completely worn out mechanically, have been suggested as catalytically active materials for a fluidized bed. The procedure for the gas-vapor gasification of Kansk-Achinsk coal under reduced pressure was tested at a pilot plant with a circulating fluidized bed having a productivity of up to 100 kg of coal per hour.

Catalytic gasification has been accomplished by two methods (Table 3). One of them involves partial gasification of boiler and Martin slags in a fluidized fixed bed leading to 40—70 % conversion of the coal. During this process gasification of the most reactive portion of the fuel occurs, and the solid residue is a porous material with good sorption properties. The other process that has been carried out involves complete gasification of Kansk-Achinsk coal in a circulating fluidized bed. The complete conversion of the solid fuel into gaseous fuel is achieved by recirculation of the entrainment in the oxidizing zone of the gas generator. In this case, the intensity of the process, equal to 2.3 t $(m^2 h)^{-1}$ at 950 °C, is very high (see Table 3) and exceeds similar characteristics of the known procedures for noncatalytic gasification in fluidized beds and concurrent flows, 0.9 t $(m^2 h)^{-1}$.

Catalytic liquefaction

The main drawbacks of the known procedures for catalytic liquefaction of coal result from the low productivity of the processes, the use of high hydrogen pressures, the necessity to isolate the catalyst so it can be recirculated in the process, and, finally, from the large amounts of harmful polycyclic compounds in the products of liquefaction. Some of the technological problems can be solved by choosing cheap catalysts based on ore materials. The application of these catalysts makes it possible to exclude the labor-consuming procedure of the isolation of the catalyst from the slag residue, which is difficult to accomplish and which is necessary, for example, for the isolation of molybdenum in the process developed at the Institute of Combustible Fossils. In addition, the replacement of synthesis gas by hydrogen makes it possible to exclude several additional steps associated with the preparation of hydrogen (purification of the synthesis gas, conversion of CO, isolation of H_2) and to lower the price of the liquefaction of coal.

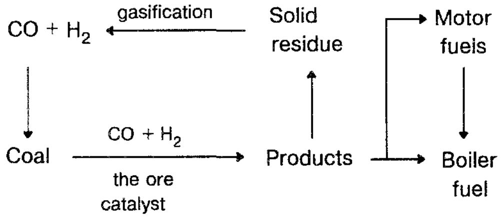
The investigations carried out at the ICNORM (in collaboration with a number of institutes of the RAS) confirmed that the use of iron-containing ore catalysts (pyrite, pyrrhotite, or magnetite) for the liquefaction of the Kansk-Achinsk coals in proton-donating solvents should be expedient.[17] The efficiency of their catalytic action is comparable with that of the synthetic cobalt-

Table 3. Characteristics of partial (method 1) and complete (method 2) catalytic gasification in a fluidized bed of the catalyst yielding solid sorbents and fuel gas[16]

Characteristic	Method 1	Method 2*
T/°C	850—950	850—950
Composition of the gas (%, v/v):		
H_2	7.2—12.6	6.2—10.1
CO	6.7—11.6	5.6—10.1
CH_4	0.4—2.0	0.4—2.0
Hydrocarbons	—	—
CO_2	12.6—16.7	14.3—17.1
N_2	62.5—67.3	64.1—69.1
O_2	0.1—0.5	0.1—1.0
Extent of coal conversion (%)	40—80	≤90
Intensity of the process/t $(m^2 h)^{-1}$	0.6—1.0	1.1—2.3

* A circulating fluidized bed.

molybdenum-aluminum catalyst, since hydrogenation of coal in a proton-donating solvent occurs according to a mechanism of mediated catalysis. The liquefaction of coal occurs due to the transfer of hydrogen atoms from a molecule of an organic solvent (for example, tetralin, which is dehydrogenated to give naphthalene). The role of the catalyst is predominantly that it regenerates the H-donating properties of the solvent (in particular, by hydrogenating naphthalene to form tetralin). Cooperative efforts by researchers of ICNORM and the Institute of the Chemistry of Solid Fuel and Mineral Raw Materials of the Siberian Branch of the RAS found that the mechanochemical activation of iron-containing ore catalysts mixed with elemental sulfur in water has a substantial effect on the hydrogenation of Kansk-Achinsk coals.[18] With an activated catalyst (hematite, magnetite, pyrrhotite, or pyrite) the extent of coal conversion at 430 °C and p_{H_2} = 12 MPa increases 2—4-fold. It has also been shown that in the presence of iron-containing ore catalysts the extent of coal conversion decreases only slightly when hydrogen is replaced by synthesis gas (Fig. 5). This allows one to suggest a rather simple scheme of the catalytic liquefaction of coal with synthesis gas:



After separation of liquid fuels, the remaining solid residue is subjected to gasification to give synthesis gas which is again used for liquefaction of coal. The presence of the ore catalyst in the solid residue intensifies gasification.

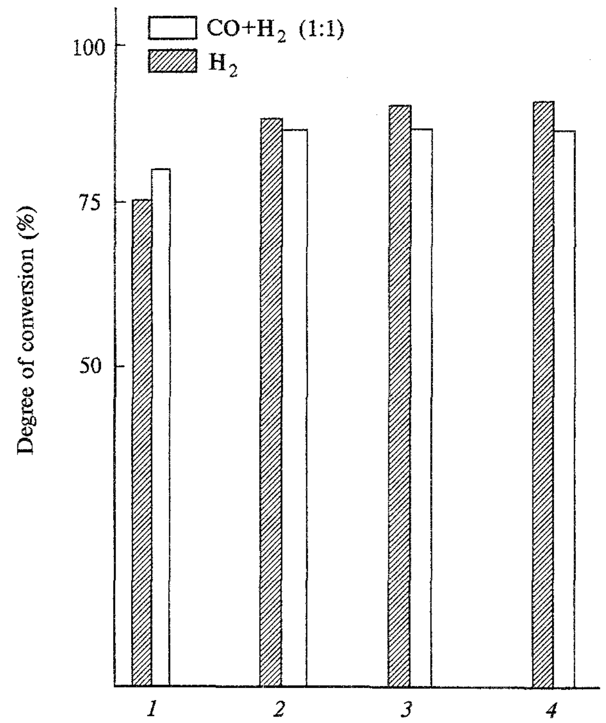


Fig. 5. Data[19] on liquefaction of Kansk-Achinsk coals in an autoclave in tetralin at 430 °C and $p^0_{H_2}$ = 5 MPa without a catalyst (*1*), with hematite (*2*), pyrite (*3*), and Al—Co—Mo catalyst (*4*).

It has been shown that the ore catalysts based on hematite and magnetite may be used for vapor-phase cracking of high-boiling carbon products and petroleum

Table 4. The effect of the ore catalyst (hematite) on hydrogenation of lignite and vapor-phase cracking of high-boiling coal products and petroleum residue[18]

Catalyst	Preliminary treatment	Raw material	Extent of conversion	Yield of liquid products (%)			
				<180 °C	<350 °C	>350 °C	Asphaltenes
	Hydrogenation of the Kansk-Achinsk coal at 430 °C and p_{H_2} = 12 MPa						
None	—	Lignite	28	6.3	38.0	—	2.9
Hematite	None	The same	45	6.5	41.5	—	5.9
	Activated*	» »	92	7.1	66.8	—	7.3
	Vapor-phase cracking of high-boiling coal products at 470 °C and p_{H_2} = 0.25 MPa						
None	—	Fraction >350 °C	3	—	—	—	—
Hematite	None	The same	38	—	36	62	—
	Activated**	» »	74	—	73	26	—
	Vapor-phase cracking of the petroleum residue at 470 °C and p_{H_2} = 0.25 MPa						
None	—	Fraction >350 °C	3	—	—	—	—
Hematite	None	The same	46	—	44	54	—
	Activated*	» »	60	—	58	40	—

* Mechanochemical activation of the catalyst mixed with elemental sulfur in water. ** Mechanochemical activation of the catalyst in water.

residues (Table 4). Mechanochemical activation of the catalyst in water results in a 1.5—2-fold increase in the extent of conversion at 470 °C and $p = 0.2\div0.3$ MPa. The advantages of catalytic vapor-phase cracking are high yields of low-boiling products, low sulfur content in the products, exclusion of the use of hydrogen, and the absence of high pressures. There is also no need to isolate the catalyst and recirculate it.

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Thus, the examples given attest to the high potential of chemical catalysis for solving the problems of the production of synthetic fuels and organic products from fossil coals. The use of catalysts and catalytic processes in coal processing makes it possible to increase the efficiency of coal pyrolysis, gasification, and liquefaction and lays the foundation for a new generation of techniques for the chemical processing of coal, characterized by enhanced efficiency, selectivity, and ecological security. In the case of processing of "heavy" organic raw material, such as coal and lignite, special requirements (compared with those in petroleum processing and petrochemistry) are imposed upon the catalysts used. We believe that the application of cheap disposable catalysts based on ores, such as slags of the metallurgical and energetic industries, ore concentrates, and slimes, is in many cases economically justified and technically possible.

One of the basic problems in this nontraditional field of catalysis is the development of efficient methods for catalytic control of the cleavage of particular chemical bonds in a solid organic matrix and the formation of new bonds. To achieve this, systematic investigations of the kinetics and mechanism of the action of various catalysts in homolytic and heterolytic transformations of natural organic polymers and in the reactions of individual compounds simulating various fragments of the structure of a solid organic substrate need to be carried out.

The concept of direct and mediated catalysis is useful for identifying the mechanism of the thermocatalytic transformations performed. To accelerate the chemical reactions occurring according to a mechanism of direct catalysis, *i.e.*, by the direct action of the catalyst on the chemical bonds in the organic coal matrix, efficient contact between the catalyst and the solid reactant is required. This may be achieved by fixing a metal-complex catalyst at the functional groups (hydroxyl, carboxyl, *etc.*) of the coal. Efficient methods for the immobilization of metal-complex catalysts on oxide and polymeric organic supports are well known.[20,21] However, the application of these methods to natural polymeric materials, such as coal, has not been sufficiently investigated. Systematic investigations of the state of metal-complex catalysts on a coal matrix and their transformations into other compounds during thermal catalytic reactions of the solid substrate are necessary.

The investigation of the mechanism of mediated catalysis in the transformation of solid organic stock, associated with the transfer of the catalytic action to the solid substrate through the medium, is of particular interest. In this case, traditional heterogeneous catalysts, for example, deposited catalysts, are efficient. The oxidative pyrolysis of lignite in a fluidized bed of a catalyst, coking of clinkering coal, and hydrogenation of coal in proton-donating solvents considered in this review are subjects for further investigation of the mechanism of the action of heterogeneous catalysts under the conditions of mediated catalysis.

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