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Metal complex catalysis in the chemistry of solid organic raw material

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ABSTRACT. **The applications of metal complexes in processes involving the conversion of solid organic raw material is examined. Data are presented on the use of metal complex catalysts for the preparation of organic compounds, synthetic fuels, and cellulose and its derivatives from coal and plant biomass.**

The bibliography includes 81 references.

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I. Introduction

The principal sources of natural raw materials are petroleum, natural gas, coal, oil shale, and plant biomass. At the present time the world production of petroleum and natural gas approaches the maximum possible amount and in the near future will begin to fall. In order to overcome the deficiency of petroleum raw material, it is planned in the industrially developed countries to manufacture synthetic hydrocarbon fuels from coal, the available amount of which greatly exceeds that of petroleum and gas. Almost all the most important petrochemical products can be obtained by the chemical processing of coal. Two aspects of the preparation of synthetic fuels and chemical products from coal are most promising: liquefaction and gasification. The liquid and gaseous products formed thereby are subjected to further conversion into motor fuels and valuable organic substances.

Plant biomass is a continuously renewed source of organic raw material. Photosynthesis generates annually about 200 billion tons of biomass on our planet, which greatly exceeds the world production of mineral organic fuels. Chemical wood conversion processes have as a rule two principal aims: the isolation of individual components of wood (for example, cellulose) or the depolymerisation of wood with formation of lower-molecular weight products (for example, sugars and furfural). Not only the entire set of compounds which are nowadays synthesised from petroleum but also a whole series of unique products, for example biologically active substances, can be obtained from primary products of plant origin. The preparation of synthetic liquid and gaseous fuels from the plant biomass is promising.

The majority of the methods for the chemical conversion of coal and biomass used at present are less efficient than petrochemical processes. The solid organic raw material is less susceptible to conversion into low-molecular-weight products than petroleum and requires more severe reaction conditions. In order to intensify the coal and biomass conversion processes, catalysts developed initially for the conversion of liquid and gaseous organic raw material are being used on an increasing scale.[1,2] However, the possibilities of traditional catalysis in this field are limited by the difficulty of ensuring a sufficiently close contact between the solid raw material and the catalysts. It is therefore useful to use liquid catalytic systems capable of penetrating into the pores of the solid organic reactant. Many reactions occurring in the chemical conversion of coal and plant biomass include, together with heterolytic stages, also homolytic stages. In order to accelerate the latter, one can use a wide range of metal complex catalysts or bifunctional catalytic systems in solution. There exist fairly numerous examples of the effective employment of metal complex catalysts for the acceleration and increase in the selectivity of the synthesis of organic compounds from coal and wood and also for the improvement of processes leading to the formation of synthetic fuels. The introduction of metal complexes into the pores of the organic raw material or their fixation on the surface is also used on an increasingly wide scale to effect energochemical solid fuel conversion processes (gasification, pyrolysis, liquefaction). Metal complexes are frequently used in this connection as precursors of highly dispersed particles formed at elevated temperatures.

This review deals with certain aspects of the application of metal complex catalysts in the chemistry of solid organic raw material and an attempt is made to give a systematic account of the experimental data obtained during the last 5–8 years in this non-traditional field of catalysis.

II. Characteristics of the catalytic reactions of solid organic raw material

The use of catalysts to convert solid organic raw material has a number of features distinguishing it from the traditional conversion reactions of liquid and gaseous products.[3] In the technological application of catalytic solid fuel conversion processes, it is essential to take into account the characteristic features of the composition and structure of the fuel.

1. Composition and reactivity of different types of coal and wood

According to generally accepted ideas, the organic mass of coal consists of condensed aromatic nuclei linked via aliphatic side groups, which include carbon, hydrogen, oxygen, sulphur, and nitrogen atoms.[4,5] Oxygen-containing groups promote the formation

of bonds between organic and inorganic components of coal. Such groups are present in phenols, alcohols, ethers, carboxylic acids, and carbonyl compounds. The structure of the vitrinite component of coal, whose amorphous macromolecular lattice consists of a series of stable cluster units or aggregates linked by relatively weak bridges made up of aliphatic carbon atoms or by ether bridges as well as weak hydrogen or donor–acceptor bonds, has been studied in greatest detail.

Overall, natural types of coal have a much more complex chemical composition than petroleums. The molecular groups forming part of coal are to a large extent linked to one another by chemical bonds. The aim of the chemical processing of coals is their depolymerisation with formation of low-molecular-weight products which would have a homogeneous composition. The conversion of coal into individual organic compounds to which the chemist is more accustomed is achieved by heat treatment and treatment with various reagents. This entails in the first place the rupture of weakest aliphatic chains linking the condensed aromatic structures and donor–acceptor bonds.

Wood biomass consists mainly of cellulose (40–50%), lignin (16–33%), and hemicelluloses (15–30%). The remaining small fraction consists of extractable substances and inorganic components.[6] The most valuable substance in wood, namely cellulose, is a linear polysaccharide made up of $C_6H_{10}O_5$ units linked by 1–4 glycosidic bridges. Hemicelluloses are polysaccharides with shorter chains made up of $C_5H_8O_4$ units. Lignin is less reactive than cellulose and hemicelluloses. Among all the components of wood, it is closest in its composition and properties to brown coal. The aromatic structures of lignin are believed to include combination of phenylpropane structural units linked by ether or carbon–carbon bonds.

The characteristics of the structure and reactivity of the components of coal and biomass must be taken into account in selecting the optimum procedures for the introduction of catalysts into the solid organic raw material.

2. Applications of metal complex catalysis

It is useful to distinguish the following aspects of the use of metal complexes to effect the catalytic conversions of solid organic raw material: catalysis by soluble metal complexes introduced into the pores of the organic substance; catalysis by metal complexes fixed on the surface of the solid reactant; catalysis by highly dispersed particles or clusters formed on decomposition of the metal complexes introduced into the raw material or fixed on its surface.

The possible applications of metal complexes in solution are limited by the threshold of their thermal stability (in most cases 150–200 °C). The mechanism of the catalytic conversion can include a stage in which the metal complex is adsorbed on the reactive sections of the surface of a solid organic raw material. Catalytic reactions can also take place in solutions where metal complexes accelerate the reactions of the products of the thermal fragmentation of coal or of the components of the biomass.

If the catalyst accelerates the conversion of liquid or gaseous substituents of the reaction mixture without interacting at the same time with the solid raw material, an atypical pathway can be achieved in the catalytic process. Catalytic reactions of this type are an example of mediated catalysis, which is being used on an increasingly wide scale in the conversion reactions of coal and plant raw material.

The closest contact between the raw material and the catalyst can be achieved by binding catalytically active metal complexes to the surface reactive groups of coal and wood such as phenolic, acid, aldehyde, and lactone groups. They all enter into the composition of cellulose, lignin, and other components of wood, which leads to extensive possibilities for a uniform distribution of catalytically active compounds in the solid raw material.

The methods for the chemical fixation of metal complexes on the surfaces of oxide and polymeric carriers have been thoroughly developed.[7–9] There are also data concerning the fixation of various transition metal compounds on cellulose materials. Thus cations can be arranged in the following sequence in terms of their ability to be sorbed by cellulose: $Cd^{2+} > Zn^{2+} > Cu^{2+}$.[10] The maximum sorption capacity of the Cd^{2+} cations is due to their high polarisability. In an acid medium, the exchange adsorption of cations increases as a consequence of their being bound to the COOH and SO_3H groups. A reactive oxygen-containing group (e.g. an acid or phenolic group) can be obtained at high concentrations also on the surfaces of different types of coal as a result of special activating treatment.

The metal complexes introduced into the raw material are not only themselves catalysts of the various reactions of coal and the biomass but can also be converted into other catalytically active compounds as a result of thermal and chemical influences. Thus thermally unstable compounds can afford oxide or metallic particles on heating in air or in an inert atmosphere. Hydroxide or oxide compounds can be obtained by treatment with alkali. As an example of the formation of metallic clusters in the cellulose structure, one may refer to a study[11] in which zerovalent metal atoms were introduced into cellulose by dissolving the latter in a copper-ammonia solution which was then extracted by an aqueous solution of alkali. Next, the cellulose, containing up to 16% of Cu^{2+} atoms, was reduced with sodium dithionate or hydrazine; this resulted in the formation of zerovalent copper atoms linked to the cellulose matrix by coordinate bonds. The subsequent treatment of the copper-containing cellulose with solutions containing metal cations with lower electrochemical potentials ($PtCl_2$, $PdCl_2$, H_2PtCl_6) makes it possible to achieve a partial replacement of copper by the atoms of another metal.

III. Synthesis of organic compounds from coal and biomass

The total number of wood conversion products known at the present time exceeds 2500. These are sugars, ethyl alcohol, furfural, laevoglucosan, xylitol, polyhydric alcohols, phenolic derivatives, organic acids, paraffinic hydrocarbons, biologically active compounds, and other products. Many of them are formed in processes involving the hydrolysis, oxidation, and pyrolysis of the solid organic raw material.

The chemicals obtained from coal and plant biomass may in time replace many of the products of petrochemical synthesis.

1. Hydrolysis of cellulose-containing products

The hydrolysis of cellulose-containing products, used to obtain sugars and furfural, includes a multiplicity of a wide variety of reactions, most of which have a heterolytic mechanism. The traditional catalysts of hydrolytic reactions are acids and bases. In order to obtain furfural, it is essential to ensure that pentosans are hydrolysed and the resulting pentoses are dehydrated.

Transition metal compounds can be used as catalysts of the dehydration of pentoses to furfural.[12] Some of them, for example, chromium salts, are 10–15 times more active than sulphuric acid. The combined use of inorganic acids together with metal compounds in many cases both accelerates the formation of furfural and increases its yield.

The catalytic activity of metal complex catalysts can be explained by the formation of metal–sugar complexes, which weakens the intermolecular bonds in pentosans as a consequence of the polarising action of the cation.[12] The catalytic activity of metal complexes increases with increase in the charge on the metal cation, i.e. with increase in its polarising activity. The nature of the ligands is also quite important because metal complexes can undergo partial hydrolysis under the reaction conditions. Anions can then give rise to the corresponding acids, which are capable in turn of influencing the rate of cleavage of polysaccharides and of the dehydration of monosaccharides.

By means of catalysis, it is possible to direct the conversion of the plant raw material via new pathways. Thus in the treatment of aspen wood in a stream of steam at 200–400 °C in the presence of certain transition metal compounds (for example, iron compounds), it has been possible to obtain laevoglucosenone in up to 5 wt.% yield relative to the initial raw material.[13] This compound is promising for the synthesis of valuable substances used in perfumery, medicine, and the food industry.

2. Oxidation and pyrolysis of solid organic raw material

When metal complexes are introduced into a solid organic raw material, the metal cations are frequently bound to the functional groups forming part of the composition of the solid fuel. The same metal ion forming part of the composition of humates can increase the resistance of the substrate to degradation, while in combination with phenoxide ions it can promote the decomposition processes. This leads to the appearance of the possibility of regulating thermochemical conversion reactions of coal and biomass by the selective introduction of metal-catalyst cations into the functional groups of the solid raw material.

There exist examples of the effect of transition metal compounds introduced into coal on the catalytic conversion of the latter into aliphatic polycarboxylic acids.[14] The introduction of iron, manganese, and copper ions as well as metal tungstates and molybdates accelerates the oxidation of wood lignin by hydrogen peroxide which proceeds in an acid medium with decomposition of aromatic rings and the formation of oxalic, malonic, acetic, and formic acids.[15] The oxidation of lignin is accelerated by the potassium hexacyanoferrate(III)/hexacyanoferrate(II) catalytic system; the catalytic effect depends on the potential of the oxidation-reduction system.[17,18]

The catalytic effect of copper chloride was manifested by an increase in the rate of the oxidative ammonolysis of lignin in an aqueous medium or methanol at 127 °C.[16]

Certain metal complex catalysts make it possible to increase the yield of the volatile organic compounds formed in the pyrolysis of wood. Thus the introduction of manganese chloride into wood from deciduous trees increases the yield of laevoglucosan in steam pyrolysis to 10–13.4 wt.% relative to the weight of the absolutely dry wood.[19]

3. Reactions of compounds originating from coal and wood

Organic substances of plant and coal origin have found extensive applications in the national economy. Catalytic processes have been used recently on an increasing scale for their conversion. Some of the most important monosaccharide conversion products are furfural and its derivatives.

Zirconium complexes fixed on a polymeric carrier are effective catalysts of the preparation of furfural by the dehydration of a 2–5% solution of pentoses.[20] The use of the vanadyl-porphyrin complex as the catalyst makes it possible to raise the yield of 5-hydroxymethylfurfural in the conversion of an aqueous solution of sucrose at 90–100 °C.[21] The zirconyl chloride catalyst has also been used to obtain hydroxymethylfurfural from sugars and glucose.[21] In the presence of the titanium sulphate catalyst on a polymeric carrier, the degree of conversion of xylose into furfural reaches 87%.[22] There are data concerning the use of titanium-porphyrin complexes immobilised in a polymer gel in the dehydration of xylose.[23]

It has been suggested that metal chlorides be used as catalysts in the processing of cellulose-containing waste.[24] This makes it possible to hydrolyse part of the cellulose to glucose under mild conditions and the remainder can be converted into wood charcoal.

The reactions of reactive compounds obtained from plant raw material, such as xylitol (a pentahydric alcohol), laevoglucosan (containing a strained anhydride ring and three reactive OH groups), and dioxanorbornene (containing an anhydride ring and a carbon–carbon multiple bond) are also catalysed by dissolved and heterogenised metal complexes.

Valuable products of small-scale chemistry are also obtained in the catalytic processing of extractable substances. The use of catalysts leads to new possibilities for the synthesis of pyrethroids, pheromones, fungicides, and other biologically active substances from the volatile monoterpenoids present in turpentine and also in the essential oils obtained from the bark and green matter of conifers.

An important aspect of the synthesis of organic products from solid organic raw material is the catalytic processing of the mixture of carbon monoxide and hydrogen formed on gasification of coal or biomass. In the presence of heterogeneous Fischer–Tropsch catalysts, mainly complex hydrocarbon mixtures are formed.[25]

The use of metal complex catalysts makes it possible to carry out many reactions leading to the synthesis of individual organic compounds, based on the reaction of CO with molecular hydrogen and other substrates—methanol, formaldehyde, alkenes, dienes, acetylenes, and allyl and chloro-substituted compounds.

The problems of metal complex catalysis in the processing of synthesis gas have been examined in detail in a monograph.[26] Catalysts of a new type used in this field, namely transition metal carbonyl clusters deposited on oxide supports, ensure the formation of individual hydrocarbons (in particular C_2–C_4 alkenes) with a high selectivity at moderate temperatures. When iron and iron-cobalt clusters deposited on silica gel are used, the selectivity in the formation of ethylene or propene reaches 90%.[27]

IV. Preparation of cellulose from wood

1. Delignification of wood in order to obtain cellulose

The delignification of wood is a process involving the removal of lignin from the lignocellulose material by treatment with chemical reagents.[28] The delignification of wood is used to obtain celluloses, which are widely used in industry, especially in the manufacture of paper and chemical fibres.

The results obtained indicate the occurrence of heterolytic and radical reactions in the delignification process. This made it possible to achieve a more specific approach to the selection of catalysts from this process. Catalysts of the oxidation-reduction type based on anthraquinone and its derivatives have been investigated in greatest detail in this process.[29]

There has been a growth of interest recently in the application of metal complex catalysts for the intensification of the preparation of cellulose. Cobalt, manganese, copper, iron, and chromium complexes with organic ligands are used as catalysts in order to replace scarce anthraquinone.[30] The study of the reactions of compounds modelling lignin showed that cobalt and iron complexes with *meso*-tetra-*p*-sulphophenylporphyrin groups promote to a greater extent the acceleration of the dissociation of the β-ether linkages and increase the yield of guaiacol to a greater extent than does anthraquinone.[30] The degree of delignification of wood in the sulphate and sulphite methods of preparation of cellulose increases after the introduction into the solution of 0.005–0.025% of molybdenum in the form of molybdenum-containing compounds.[31]

New methods for the oxidative delignification of plant raw material in a medium containing sodium hydroxide or sodium carbonate are being developed: the oxygen-alkaline or oxygen-soda delignification.[29] They are based on the ability of wood lignin to be converted by oxidants into soluble compounds with rupture of lignocarbohydrate linkages. The cheapest and ecologically cleanest reagent for the oxidation of lignin is molecular oxygen. The oxidation of organic compounds by molecular oxygen constitutes a thoroughly investigated field of catalysis. The selection of catalysts for the process presents no difficulties.[32] Here it is important to protect cellulose from degradation. This requires the development of rational methods for the introduction of catalysts into the wood raw material, the use of inhibitors preventing the oxidation of cellulose, and the selection of optimum process conditions.

An example of the use of metal complex catalysts in the oxygen-alkaline delignification may be provided by the increase by a factor of 2–3 of the rate of delignification of wood in the presence of catalytic amounts of transition metal complexes of *o*-phenanthroline (0.1–0.3% of the mass of the absolutely dry wood). Such complexes are formed as a result of the interaction of *o*-phenanthroline with the variable-valence metals present in the reaction mixture.[33]

The catalytic activity of transition metal ions can change during the oxygen-alkaline delignification process as a consequence of the change in the composition of the reaction mixture. For this reason, the introduction of $MnCl_2$ in the initial stage accelerates the degradation of wood polysaccharides. On the other hand if manganese chloride is introduced in a subsequent stage, the yield of cellulose rises (by 0.8–4.1%) and the quality of its fibres improves.[34]

In the presence of hexacyanoferrate(II) ions and additives preventing the degradation of cellulose (alcohol, amines, ethers), the yield of cellulose as the product of the oxygen delignification of lignocellulose raw material in an aqueous medium at 65 °C and pH 10–14 increases.[35] Certain catalysts, for example, tungsten and molybdenum oxyanions, promote the delignification of wood by hydrogen peroxide. This process can be achieved under comparatively mild conditions. Thus the delignification of firwood chips in the presence of tungstic acid (2% of the weight of the absolutely dry wood) takes place at 95 °C.[36]

There are instances of the effective application of metal complex catalysts in the bleaching of cellulose, although their role is not always ultimately clear. The selectivity of the delignification of cellulose in acid–alkaline bleaching increases in the presence of molybdenum and tungsten complexes introduced in an amount of 0.001% of the weight of the fibre.[37] The maximum effect is obtained when these catalysts are used together with stabilisers such as urotropine, triethanolamine, and trisodium phosphate.

The Co^{2+} complex of a Schiff base (*N,N'*-bis-salicylidene-ethylenediamine) accelerates the delignification and bleaching of beechwood,[38] the efficiency of its action increasing with decrease in the basicity of the medium. In oxygen-alkaline bleaching, the high-molecular-weight component of lignin undergoes oxidative degradation to fragments which are soluble in the bleaching solution. An amount of the catalyst such that the cobalt content is 0.1% of the weight of the lignin is optimal. Bis(3-salicylideneaminopropyl)-amine cobalt is the most stable under the conditions of the oxygen-alkaline delignification of wood.[39]

The compounds of certain transition metals (for example, titanium and vanadium) accelerate the peroxide delignification and bleaching of lignocellulose materials, preventing at the same time the oxidative degradation of the cellulose component of the plant raw material.[40] In the presence of tungsten, molybdenum, and chromium ions, the quality of the cellulose obtained improves.[41]

Catalysts can exert a positive effect also on non-oxygen cellulose bleaching processes. Thus, in the catalysis by Cu^{2+} ions (0.1–0.3%) of the hypochlorite bleaching of natron cellulose, the activation energy for the reactions occurring diminishes.[42]

2. Preparation of cellulose derivatives

Catalytic processes are being applied on an increasing scale in the chemical modification of cellulose in order to synthesise a wide variety of its derivatives. The conversion into ethyl groups and other reactions of the OH groups of cellulose are achieved and graft copolymers are obtained with participation of catalysts of the acid–base type and metal complex systems.

The $Fe^{2+}-H_2O_2$ oxidation-reduction system in which Fe^{2+} ions are bound to the COOH groups of cellulose initiates the grafting to cellulose of various monomers—vinyl acetate, methyl-5-vinyl-tetrazole, and dimethyl(carboxymethyl) ammoniaethyl methacrylate bromide.[43,44] The mechanism of the formation of graft polymers using the $Fe^{2+}-H_2O_2$ system postulates the oxidation in the first stage of Fe^{2+} ions to Fe^{3+} by hydrogen peroxide.[45] The Fe^{3+} ions promote the development of oxidation processes in cellulose, a decrease in the degree of its polymerisation, a decrease in the number of COOH groups, and an appreciable accumulation of carbonyl groups. The bulk of the graft polymer is formed in the subsequent stage initiated by the $Fe^{2+}-H_2O_2-$reductant system. The carbonyl groups of cellulose, formed in the initial stage of the process, can play the role of the reductant. The additional introduction of reductants (for example, hydroxylamine or hydrazine) makes it possible to eliminate the development of degradative processes in the first stage of the copolymerisation.

When cellulose is treated with an alcohol–benzene solution of $KMnO_4$, Mn^{3+} complexes, bound strongly to cellulose, are produced.[46] The formation of C–O–Mn linkages weakens the carbon–oxygen bond, which leads to the appearance of unpaired electrons on the carbon atoms in the 1-, 2-, and 3-positions in the anhydroglucose unit of cellulose. The free radicals arising as a result of the presence of an unpaired electron on the C(2) and C(3) atoms are capable of initiating the grafting of various compounds at the C(1) atom—they initiate the block copolymerisation of these compounds.

Ce^{4+} ions catalyse the grafting to cellulose of acrylonitrile, styrene, vinyl fluoride, vinylidene fluoride, methyl methacrylate, ethyl

acrylate, acrylamide, and the styrene–methyl methacrylate mixture.[47–49] Methyl methacrylate is grafted to cellulose in the presence of vanadium(V) acetyl-acetonate.[50] The use of the V^{5+}–cellulose xanthate oxidation-reduction system makes it possible to achieve a continuous method for the preparation of modified viscose fibre containing simultaneously quaternary ammonium and carboxy-groups.[51]

There are data[52] concerning the preparation of graft copolymers of cellulose with acrylic acid and the grafting of 4-vinylpyridine to cellulose in the presence of Co^{3+} ions. In order to obtain cellulose derivatives with a grafted lactone, polymerisation catalysts, especially tetramethyltitanium, are used.[53] Oxycellulose with a high content of carboxy- and carbonyl groups has been obtained by the catalytic oxidation of cellulose in the presence of $RuCl_3$.[54] In an acid medium, the reaction takes place at a higher rate even at 20 °C without appreciable degradation of cellulose.

V. Preparation of synthetic fuels

1. Liquefaction of coal

The heterogeneous catalysts for the liquefaction of coal have now been investigated in greatest detail.[55] However, there are also fairly numerous examples of the effective employment of homogeneous metal complex catalytic systems for this purpose.

Two main aspects of the use of dissolved catalytic systems in carrying out such processes have been established. One of them is associated with the search for low-temperature dissolved catalysts. The other is based on the application of solutions of catalytically active compounds as precursors of catalysts formed as a consequence of the decomposition of the initial substances at temperatures above the threshold of their thermal stability. It is noteworthy that it is not always possible to draw a clear-cut boundary between these versions owing to the insufficient information about the state of the catalyst employed.

It has been suggested that dissolved rhodium complexes with phosphine or amine ligands [for example, $RhCl(PPh_3)_3$ and $Rh_2(HCOO)_2(bipy)Cl_2$] as well as catalytic systems consisting of rhodium salts and added triphenylphosphine be used for the hydrogenation of coal under mild conditions.[56] Dissolved catalytic systems, obtained by the reaction of $FeCl_3$ and $Ni(COOH)_2$ with organoaluminium compounds and treated with H_2, exhibit a high activity in coal hydrogenation processes.[57]

At 400 °C and a hydrogen pressure of 13.5 MPa, the degree of conversion of brown coal in the presence of the above catalysts is 90%. At an elevated temperature and pressure, a high degree of liquefaction of coal is attained in the presence of organocobalt complexes soluble in the reaction mixture.[58]

Cheap iron catalysts for the hydrogenation of coal are of greatest interest from the practical standpoint. The influence of the composition of iron compounds and of the methods for their introduction into coal on the liquid product formation processes has been investigated. The iron cations introduced into coal by ion exchange are not inferior in their catalytic activity to industrial aluminocobalt–molybdenum catalysts of the hydrogenation of brown coal.[59]

The reaction of coal with iron salts under the conditions of the synthesis of ferrocene affords iron compounds resistant to the action of acids and alkalis.[60] NMR and IR spectroscopic data, comparison of model substances, and analysis of literature data have made it possible to conclude that, on interaction with coal, iron forms π-complexes of the type of ferrocene.

There are data showing that the degree of conversion of brown coal at 450 °C increases in the presence of the ferrocene complex of iron and iron pentacarbonyl, acetate, acetylacetonate, and chloride.[61] The iron pentacarbonyl complex $Fe(CO)_5$ exhibits the highest activity.[62] Being liquid at the usual temperature, it mixes readily with organic solvents, penetrates deeply into the coal pores, and decomposes at 300 °C with formation of highly dispersed metallic iron. The catalytic effect of iron pentacarbonyl and also of molybdenum and tungsten carbonyls intensifies when they are used together with elemental sulphur. Under these conditions, highly dispersed particles of the metal sulphides are formed in the course of the reaction. They are more active in the liquefaction of coal than the metals themselves.

From the economic standpoint, it is preferable to use the $CO + H_2O$ mixture for the liquefaction of coal instead of the expensive H_2. This process can be accelerated by the oxyanions of certain transition metals.[63] In the course of the liquefaction of coal at 400 °C, the complexes of tungsten, molybdenum, chromium, and manganese in the highest oxidation states are reduced, forming compounds insoluble in water, which makes it possible to remove the catalytically active metal from the solution. It has been suggested that metal-carboxylic acids are formed in the presence of CO and then decompose to the metal hydride and CO_2. Metal hydrides reduce coal or react with H_2O, liberating H_2.

2. Liquefaction of the plant biomass

The high content of oxygen in the plant biomass makes it irrational to use H_2 in the liquefaction processes, since a large amount of it is consumed on the removal of oxygen in the form of H_2O. Nevertheless, there are examples of the use of heterogeneous and homogeneous catalysts in processes involving the hydrogenation of wood and its principal components by molecular hydrogen. Thus, in the presence of dissolved catalytic systems based on iron, molybdenum, cobalt, and copper compounds, the degree of conversion of cellulose reaches 93% at temperatures in the range 250–350 °C and an initial H_2 pressure of 5 MPa.[64] Mainly water-soluble organic compounds and gaseous products, among which CO and CO_2 predominate, are formed. Competing reactions involving the hydrolysis, pyrolysis, and hydrogenation of cellulose take place simultaneously. Pyrolysis predominates at 250 °C, hydrogenation begins to prevail on raising the temperature to 300 °C, and dehydrogenation and charring of the cellulose predominate at 350 °C. The best hydrogenation catalysts at all temperatures are molybdates. The minimum consumption of H_2 is achieved when chloride catalysts—$CuCl_2$ and $FeCl_3$—are used.

In the presence of solvents with H-donor properties, the wood raw material is liquefied without the participation of H_2. The use of compounds such as $CoCl_3$ and $CuCl_3$ as dissolved catalysts makes it possible to convert cellulose into products soluble in aqueous or aqueous-organic media.[65]

Catalytic biomass liquefaction processes in an aqueous medium on treatment with carbon monoxide and synthesis gas have been vigorously investigated in recent years. The use of CO, which is cheaper than hydrogen, makes it possible to trap the oxygen of the biomass in the form of CO_2. The catalytic effect when carbon monoxide is used as the reductant is achieved as a result of the formation of metal formates, which act as reductants. The virtually complete conversion of wood in water (up to 99% relative to the dry ash-free mass) can be attained by impregnating it with

$Fe(NO_3)_3.3H_2O$ or $Co(NO_3)_3.6H_2O$ solutions and by subsequent treatment at 350–420 °C under a pressure of synthesis gas of 10.5–36.4 MPa.[66] The yield of the liquid products is 75%. Nickel compounds can also serve as catalysts. Thus, when $NiCO_3$ is added to a suspension of wood filings in water, the degree of conversion of wood increases by a factor of 3.[67]

3. Thermochemical reactions of solid fuels

In the high-temperature catalytic pyrolysis and gasification of coal and biomass, metal complexes were used in the stage involving the formation of catalytically active surface compounds or highly dispersed particles of the active component.

The influence of catalysts on the yield and porous structure of wood charcoal in the pyrolysis of wood and its components has been investigated. The use of metal chlorides with acid properties, for example, $TiCl_4$, $CrCl_3$, and $FeCl_3$, increases the rate of pyrolysis of hemicelluloses and cellulose by a factor of 10, reduces the wood degradation temperature by 100–150 °C, and increases the yield of the charcoal by a factor of 1.5.[68,69] It has been suggested that catalysts of this type accelerate the dehydration reaction. The compounds formed, containing aldehyde groups, condense to high-molecular-weight substances, which lead ultimately to an increased yield of wood charcoal.

Definite information about the processes occurring in the catalytic pyrolysis of wood is provided by the study of the thermal reactions of metal-containing celluloses.[70] The active role of molybdenum ions in the condensation reactions of partly degraded cellulose fragments is indicated by the results obtained when molybdenum-containing cellulose hydrate is exposed to high temperatures. During the pyrolysis of the iron-containing cellulose, the carboxylate ions are initially decarboxylated with the simultaneous reduction of Fe^{2+} cations to the metal. In the next stage, highly dispersed iron inclusions are oxidised to Fe_2O_3, which is accompanied by a significant loss of organic mass.

Catalytic pyrolysis can be used to obtain metal-containing carbon sorbents. During the pyrolysis of wood impregnated with iron, cobalt, nickel, and copper compounds, sorbents are formed with a porous carbon structure in which metallic particles are inserted.[71] On thermal decomposition of monocarboxycellulose substituted by Fe^{3+} cations, highly dispersed oxides seemingly retaining the lattice of the initial fibre, are formed.[72]

The conversion of the solid carbonaceous raw material into gaseous products of different composition takes place when it is subjected to a heat treatment in oxygen, water vapour, carbon dioxide, or hydrogen. The effect of certain catalysts makes it possible to accelerate the gasification process or to reduce its temperature while retaining a higher rate and, what is no less important, to regulate the composition of the gas formed.

In order to introduce catalysts into wood charcoal, the reactive groups of wood were subjected to ion exchange for metal compounds, after which the modified wood was subjected to pyrolysis.[73] The catalysts for the gasification of wood charcoal by carbon dioxide at 800 °C can be arranged in the following sequence in terms of their activities:

$$Co > Ca > Ni > Mg \sim K \sim Na > Cu.$$

The ion-exchange cobalt catalyst exhibits a very high activity. For example, wood charcoal is fully gasified by CO_2 at 600 °C after only 5 min.

Surface transition metal complexes play an important role in the catalytic gasification of solid fuel. Technical carbon, carbon fibre, and graphite containing titanium, vanadium, and chromium surface compounds of the C–O–M type were used as model objects in one of the studies.[74] The grafting of the transition metal complexes to the surface of the solid material makes it possible to increase by two orders of magnitude the rate of gasification and to lower the temperature and activation energy for the reaction.

In order to investigate the activities of iron catalysts in processes involving the gasification of carbonaceous materials by steam and hydrogen, iron compounds were introduced into a carbon support by impregnating the latter with the corresponding aqueous solutions or by means of ion exchange. It is suggested that in the course of the reaction the surface metal complexes are reduced, forming highly dispersed species which effectively catalyse the gasification process at temperatures above 700 °C.[75]

When two-component catalytic systems, including a transition and an alkali metal, are used for the gasification of carbonaceous materials, synergistic effects are observed. In processes involving the gasification of coal by steam at 700–800 °C, the maximum activity is shown by the $Na[HFe(CO)_4]$ and mixed $Fe(NO_3)_3 + Na_2CO_3$ systems.[76] Sodium hydrotetracarbonylferrate accelerates the gasification of coal by steam at 700 °C by a factor of 4.5.[77] For comparison, we may note that an increase in the rate of the non-catalytic gasification by a factor of 6 requires an increase in temperature from 700 to 1000 °C.

The observed non-additive increase in the activity of the mixed system has been explained by the fact that alkali metals facilitate the stage in which iron oxides are reduced by carbon, which limits the rate of the process as a whole. There are data showing that iron and nickel acetylacetonate complexes behave as process catalysts, while K_2CO_3 increases the surface area of the carbonaceous material in the gasification process.[78]

A specific feature of the gasification of solid fuels is that under the reaction conditions carbon is not only one of the reactants but also serves as the carrier for the catalyst. There are data indicating the formation of intercalation compounds of the metal during heat treatment at elevated temperatures.[79] It has been suggested[80] that metal–carbon inclusion complexes can play the role of catalytic centres in the gasification reactions. At the beginning they are not accessible to the gasifying agent but are involved in the process to the maximum extent for a degree of conversion of carbon up to 80%. The formation of metal–carbon complexes also prevents the vaporisation of the deposited metal compounds during heat treatment; they become active after the burning away of an appreciable proportion of the carbonaceous material. It is entirely possible that the mechanism of the catalytic gasification of the biomass includes as the main stages the interaction of the metal-catalyst cation with the surface phenolic, alcoholic, and acid groups of the organic matrix and the subsequent thermal decomposition of the resulting surface metal complexes.[81]

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