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Application of metal – carbon catalysts in conversions of lower aliphatic alcohols †

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Abstract. Various carbon materials including carbon nanotubes and graphitised nanofibres used as supports in heterogeneous catalysis are considered. The methods for modification of catalysts and the results obtained as applied to three important processes of organic synthesis, *viz*., conversions of methanol into methyl formate, of ethanol into acetaldehyde and of isopropyl alcohol into acetone, are analysed. The bibliography includes 117 references.

I. Introduction

Design of syntheses of various classes of organic compounds from non-oil raw materials is one of the major trends in the progress in chemical industry. The use of the so-called one-carbon compounds, such as carbon monoxide, carbon dioxide, methanol and methane, in organic synthesis is becoming increasingly topical. The production of essential organic compounds from coal is a reasonable alternative to their manufacture from oil and natural gas.

In 2000, the world production of methanol amounted to 39 752 000 tons;[1] in the first quarter of 2004, methanol production in Russia was 798 000 tons. Methanol is used as starting material in the synthesis of many chemical compounds, *e.g*., formaldehyde, acetic acid, ethylene glycol, *etc*. Synthesis of methyl formate, an important intermediate in many processes of the industrial organic synthesis, is yet another promising route of methanol conversion. The greater part of methyl formate (its annual world production amounts to ~160 000 tons)[2] is utilised for the manufacture of formic acid,[3,4] which is used as a preservative in agriculture. Methyl formate is also processed into formamides[5] and *N*-formylmorpholine; it is used as a solvent for fats, fatty acids, acetylcellulose and as an insecticide.[6] Besides, it can be used in the production of high-purity carbon monoxide, dimethyl carbonate, diphosgene and methyl glycolate[7] and employed instead of synthesis gas in carbonylation and alkoxycarbonylation of alkenes.

Traditionally, methyl formate is prepared by carbonylation of methanol in the presence of alkali metal alcoxides.[2,8] However, purification of starting materials demands considerable investment and is efficient only in the case of large-scale production. However, methyl formate conversion products are mostly utilised in low-tonnage chemistry; therefore, establishing small-scale plants in close promixity of potential consumers is currently rather topical. Dehydrogenation of methanol,[9] which does not require the use of high pressures and is rather insensitive to impurities present in the feed stock, is underway on a large scale. Ethanol, yet another industrial intermediate for organic synthesis, has recently become very popular. There are environmentally safe technologies for its production from organic wastes and biomass which are based on the use of microbial enzymes.[10] At present, the world production of ethanol amounts to 40 milliard litres per year and, according to prognoses, will increase in future.[11] Catalytic dehydrogenation of ethanol into acetaldehyde, a valuable intermediate in the synthesis of a broad range of compounds, is one of directions of ethanol processing. This method has a number of advantages, *e.g*., lack of toxic waste products, relatively mild reaction conditions and production of hydrogen in addition to acetaldehyde, which can further be utilised in other processes.

Isopropyl alcohol, another representative of low-molecular-mass alcohols, is used in production of acetone without formation of side products.

As is known, organisation of a profitable chemical production is only possible with highly active and highly selective catalysts. A search for novel supports, which have a great influence on the structure and properties of catalysts, is an essential step in the development of efficient catalytic systems. The use of novel carbon materials with fibrous-tubular structure and carbon – carbon composites holds great promise.

This review deals with various aspects of the development of efficient low-percentage (with respect to a metal) metal – carbon catalysts, including the methods used for their preparation, modification and activation and choice of optimum conditions for dehydrogenation of lower aliphatic alcohols ($C_1 - C_3$) leading to the corresponding ester, aldehyde and ketone.

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II. Carbon materials and their application in heterogeneous catalysis

1. Preparation and properties of various carbon materials

Carbon materials have long been used in heterogeneous catalysis as both catalysts themselves and supports for active components. These materials possess a number of valuable properties, *e.g.*, controlled specific surface and adsorption capacity, high thermal and chemical stability, high mechanical strength, long service life, *etc.*[12] In 1998, about 70 industrial chemical catalytical processes were run on carbon supports.[13]

At present, a vast array of novel carbon materials [14] [carbon fibres,[15–17] graphite intercalates, fullerenes, carbyne-like compounds (carbolites), nanocarbon structures, pyrocarbons, carbon–carbon composites, *etc.*] are employed along with traditional carbon supports (activated carbons, graphite and soot).[13, 14, 17, 18] These novel materials differ from the traditional supports in low content of mineral admixtures, which is especially important for the preparation of catalytic systems. Their advantages include high resistance to acidic and basic media and high temperatures, controllable porosity. The production technologies of many novel carbon materials enable the preparation of diverse forms, *e.g.,* granules, tissues, honeycomb structures, *etc.*, which significantly facilitates the design and optimisation of reaction units employed in production of many valuable components of organic synthesis. The use of carbon supports allows regeneration of active components of catalysts, which is especially important if the active component is a precious metal.[13, 15] However, the range of commercial porous carbon materials as candidate supports for catalysts is rather narrow. Commercial catalysts are still manufactured on the basis of activated carbons prepared from coal or vegetal stuff.

a. Activated carbons

Activated carbons (AC) are prepared by pyrolysis of carbon-containing materials, *e.g.*, wood, peat, coal and petroleum products. These materials possess a well-developed porous structure, but their microporous structure is not always optimum for the support of catalysts. Besides, the shape and size of activated carbon granules do not always meet the requirements of catalytic processes. Other disadvantages include high content of mineral impurities and sulfur as well as low mechanical strength.[17] Modern catalytic techniques demand carbon materials with large controllable pores and a definite combination of specific properties. These properties are manifested by a novel type of supports based on synthetic carbon–carbon composite materials.[17]

b. Carbon–carbon composite materials

Technical carbon is used as a starting material in the synthesis of porous carbon–carbon composites, which combine the advantages of activated carbons and graphite. Several methods for their preparation are known. For instance, technical carbon is mixed with a hydrocarbon binder; the resulting mass is compacted or granulated to obtain grains of definite shapes. The grains are then subject to thermal treatment in an inert or reducing medium, which results in carbonisation of the hydrocarbon component and formation of porous carbon, which binds technical carbon globules.[17] An alternative approach, which was developed at the Institute of Catalysis of the Siberian Branch of the Russian Academy of Sciences, consists of several successive steps. The first of them includes preparation of matrices, which represent granules of sperical or more complicated shape, from technical carbon. This is followed by compaction of the matrices and deposition of carbon formed by pyrolysis of gaseous hydrocarbons.[19–21] The porous carbon material thus prepared represents a globular system the primary morphological units of technical carbon in which are bound by pyrolytic carbon. Meso- and macroporous composites with low specific surfaces ($2-10\ m^2\ g^{-1}$) are formed in this step. The next step includes their activation by partial selective gasification. The texture and other characteristics of porous materials are controlled by varying the nature and properties of technical carbon, degree of compaction of the matrix by pyrocarbon, degree of scorching of the composite mass in the course of its activation, the nature of the gasifying agent and activation conditions.[22, 23] It is this approach that has been used in the preparation of a novel class of porous carbon–carbon composite materials for adsorption and catalysis, known under the name 'sibunit'.

The porous structures of such materials contain macro-, meso- and micropores. The volumes and sizes of meso- and macropores are controlled by varying the sizes of primary technical carbon globules, their reciprocal positions and the ratio of technical and pyrolytic carbons. The sizes of micropores and fine mesopores can be increased by steaming and oxygen treatment, which does not influence essentially the sizes of large pores.[24] Some characteristics of sibunit and activated carbons are given in Table 1.

Table 1. Some properties of porous carbon materials of the sibunit and activated carbon type.[17]

Parameter	Sibunits	Activated carbons
Specific surface area /$m^2\ g^{-1}$	2–800	600–1800
Total pore volume /$cm^3\ g^{-1}$	0.2–1.2	0.2–1.2
Micropore volume /$cm^3\ g^{-1}$	0.01–0.15	0.2–0.6
Mesopore volume /$cm^3\ g^{-1}$	0.2–0.8	0.1–0.3
Macropore volume /$cm^3\ g^{-1}$	0.1–0.7	0.1–1.0
Mean pore radius /nm	4–200	from <1.5 to >100
Ash content (mass %)	<1	>3
Crush strength /kg cm^{-2}	40–200	5–60

The technology of sibunit synthesis allows directed modification of its textural characteristics in the whole range required for the solution of specific problems of catalysis and adsorption.[25] Other advantages of these composites include reproducibility of their porous structure, high chemical purity, high mechanical strength, high activity and long operating life of catalysts based on them. These materials manifest high thermal stability; their chemical stability in oxidative media is much higher than that of activated carbons prepared from plants and coal.

Traditional carbon supports and sorbents are available only in the form of tablets, spherical granules or grains with diameter not exceeding 3–5 mm. At the same time, in some chemical processes the most efficient supports for catalysts have intricate geometrical shapes, *e.g.*, rings, straw, petals, microassemblies and honeycomb structures.[26] The use of sibunit as a support makes it possible to solve this problem.

c. Carbon fibre materials

A great number of recent publications and patents are devoted to carbon materials with fibrous-tubular structure. Carbon fibrous materials (*e.g.*, fibres, cords, felts, fabrics, yarns, cotton wool) are usually prepared by pyrolysis of polymeric fibres and fibrous articles with subsequent high-temperature treatment. After preliminary activation, these materials can be used as sorbents, ion-exchangers and supports for catalysts.[27–29] Activated fibrous carbon materials not only possess large specific surface and high porosity, but also manifest high thermal and chemical stability. Modern technologies allow preparation of materials of various shapes, which significantly extends the possibilities of hardware implementation of technological processes.

Polyvinylchloride fibres, phenolic polymers, polyvinyl alcohol, polyacrylonitrile, hydrated cellulose, *etc.* are used as raw materials for the preparation of carbon fibres. Their properties including chemical stability depend largely on the choice of the starting polymer, conditions for its carbonisation and thermal treatment (activation) as well as by different additives.[30] For example, carbon fibres prepared from hydrated cellulose manifest

Table 2. Characteristics of carbon fibresprepared from polyacrylonitrile.[30]

Parameter	Fibre	
	carbonised	graphitised
Density /g cm^{-3}	1.3–1.65	1.3–1.9
Specific surface area /m^2 g^{-1}	0.3–1000	0.15–3.0
Temperature coefficient of linear expansion, $10^6\,\alpha$ /K^{-1}	4	2
Specific heat capacity /kJ m^{-1} K^{-1}	0.66	0.66
Thermal conductivity coefficient /W m^{-1} K^{-1}	0.837–20.934	83.74–125.6
Electric resistance, $10^5\,\rho$ /Œ m	0.4–70	0.003–0.6
Sublimation temperature /°C	–	3600
Hygroscopicity (%)	0.1–10	1
Tensile strength /MPa	350–700	1200–3100
Modulus of elasticity /GPa	30–200	300–700

higher chemical stability than fibres prepared from polyacrylonitrile (PAN) under identical conditions. The main characteristics of carbon fibres prepared from PAN are listed in Table 2.[30]

Carbon fibres based on hydrated cellulose are prepared in several steps:[31] (1) processing of raw materials (fibres, fabrics or felts) to make them more resistant to oxygen; (2) drying at 25–150 °C to remove water, carbon oxides and carbonyl compounds from the surface of fibres; (3) heating and partial oxidation at 200–300 °C; (4) high-temperature treatment of fibres (depending on the temperature regime, this step results in carbonisation or graphitisation of fibres); (5) activation and dressing of the fibre surface.

The first step consists of removal of bound water. Dehydration in the second step yields fragments containing carbonyl groups and C=C bonds. The third step includes thermal cleavage of the C–C and C–O bonds, which yields H_2O and gaseous decomposition products (CO_2, CO, *etc*.). Carbonisation, which occurs in the fourth step, begins at 375–450 °C and is complete at 1200 °C. In the course of gasification, all atoms of the organic polymer (with the exception of carbon) are eliminated from carbon fibres which acquire a ribbon-like structure. Graphitisation requires higher temperatures and is complete at 2200–2800 °C. This step includes final thermolysis of the polymer and accumulation of aromatic fragments and is accompanied by an increase in the ordering of ribbon-like structures, elasticity modulus and electroconductivity of carbon fibres. And, finally, the fifth (activation) step is carried out in the presence of an oxidising agent (*e.g*., atmospheric oxygen, water steam, carbon dioxide) for 30–60 min at 600–900 °C to increase the specific surface of carbon fibres.

The activation of carbon fibres and carbon–carbon composites (sibunits), is accompanied by burnout of their amorphous components and formation of microporous structures.[32] Further oxidation results in partial burnout of more ordered structures and formation of macropores. The chemical activity of carbon fibres depends on their structure, which is largely determined by conditions employed in this step and, to a lesser degree, by the nature of the starting polymer.[30] At present, about 90% of all carbon fibres based on polymers are used for the production of composite materials.[33] Carbon fibres are also used as components in heat-insulating materials and in medicine.[34, 35]

d. Carbon nanofibres and nanotubes

Carbon nanofibres (CNF) formed upon decomposition of gaseous hydrocarbons on the surface of metal components of catalysts are becoming increasingly popular nowadays. The process of their preparation begins with the formation of hydrogen-containing carbon deposits on the surface of metal particles. These deposits are dissolved in the metal and diffuse through it to form a thin graphite layer on the opposite side of the metal particles.[16] The catalysts used for the preparation of CNF usually contain iron, cobalt, nickel, chromium, vanadium, molybdenum or their alloys. The ability to dissolve carbon and/or to form carbides is the major requirement for such catalysts. This reaction is carried out at 700–1200 K; methane, CO, synthesis gas, acetylene and ethylene are used as the starting materials.[16, 36]

Considerable attention is given to elucidation of mechanisms of formation and morphological characteristics of carbon nanofibres.[37] It was established[38] that carbon fibres prepared from a mixture of carbon oxides with methane on a nickel catalyst consist of single fibres with a diameter 2000–3000 nm which contain nickel microinclusions. These experiments were carried out in the temperature range 500–650 °C; the ratios of the reactants varied from 0.5 to 2.0 ($CO_2:CH_4$) and from 0.5 to 3.5 ($CO:CH_4$). The length of the fibres exceeded their diameters by several orders of magnitude and depended on the contact time of the catalyst with the reaction mixture. According to the suggested scheme,[38] the formation of carbon fibres proceeded *via* a metastable carbide-like nickel–carbon complex. In the case of a CO_2–CH_4 mixture, this complex is formed as a result of methane dissociation, whereas in the case of a CO–CH_4 mixture, its formation was due to dissociation of methane and disproportionation of carbon monoxide.

The regularities of formation of carbon with fibrous-tubular structure by disproportionation of CO were studied.[39] This reaction occurred in three successive steps. The first step included formation of catalytically active phases, which are represented by carbides with various compositions. In the second step, superficial carbon was formed as a result of disproportionation of CO on catalytically active surfaces. And, finally, the third step consisted of bulk spatial transformation of superficial carbon in a fibrous-tubular structure containing catalyst microinclusions.

The structure of carbon fibres strongly depends on the conditions of synthesis.[37] Morphological characteristics of carbon fibres are determined by the chemical nature of the catalyst and conditions for their preparation. Besides, the sizes of nanofibres depend linearly on the sizes of the catalyst particles.

A classification of fibrous-tubular carbon-containing nanomaterials according to their structures and properties has been suggested.[15] These materials are divided into carbon nanotubes (CNT) and graphitised nanofibres. The main difference between them is the lack of hollow cavities in the latter. The diameter of graphitised nanofibres is larger than that of nanotubes and can reach 500 nm. Nanotubes in turn are subdivided into two main categories, *viz*., single-wall and multi-wall nanotubes. Ideal single-wall carbon nanotubes are made of a perfect graphene sheet rolled up into a cylinder and closed by two caps. Their internal diameter varies from 0.4 to 2.5 nm, while their length varies from several microns to several millimetres. Multi-wall nanotubes can be regarded as a set of coaxial single-wall tubes of increasing diameters.[15] The number of walls in a multi-wall nanotube varies from two to several tens, and the distance between the walls of two neighbouring tubes is equal to 0.34 nm. Depending on the arrangement of the layers, graphitised nanofibres are subdivided into three main types, *viz*., platelet, ribbon-like and herringbone structures.

The USA and Japan are the major manufacturers of fibrous-tubular carbon nanomaterials and, to a lesser extent, Europe and Korea. These materials are used, along with traditional fibres based on polymers (polyacrylonitrile, viscose, *etc*.), in the production of composite materials.[37] Nanofibres and nanotubes are also employed in the production of electrodes,[40] they proved to be efficient adsorbents and hydrogen storages.[16, 37]

2. Oxidative modification of carbon supports

As is known,[13] carbon does not virtually interact with active components of metal–carbon catalysts. Fixation of a precursor of the active component on the carbon surface is an important step in the preparation of supported catalysts. This is achieved, in

particular, by oxidation of the carbon surface. In the oxidative treatment, surface functional groups (acidic, basic or neutral) are formed.[41] Acidic groups include carboxylic, anhydride and lactone groups; weakly acidic and neutral groups are represented by phenolic, carbonyl, quinone and ester groups, while pyrone and chromene are regarded as the main basic groups. The determination of the amount, thermal stability and nature of surface oxygen-containing groups is carried out by temperature-programmed desorption (TPD).[41] These groups are destroyed during TPD to yield carbon dioxide from carboxylic, anhydride and lactone groups and carbon monoxide from phenolic, carbonyl, quinone and pyrone groups. The structures of surface oxygen-containing groups and gaseous decomposition products formed in the TPD as well as the decomposition temperatures have been studied.[42] The interaction of free active centres of the carbon surface with oxygen is usually accompanied by conversions of one kind of oxygen-containing groups into another.

The possibility of incorporation of oxygen into carbon supports is determined by their structural features. The boundaries of the basal planes of the graphite structure contain carbon atoms with unsaturated valences. High concentration of unpaired electrons in these regions has a strong impact on the chemisorption. Graphite weakly chemisorbs oxygen, because the boundary zone in graphite crystallites is small in comparison with the basal plane. At the same time, microcrystalline carbon materials, such as activated carbons, have less ordered structures and a much larger boundary zone, which favours oxygen chemisorption.[13] In contrast to graphite, the basal planes of activated carbon crystallites contain multiple defects, which play the role of chemisorption sites for the oxidant.[43] And, finally, activated carbons are highly porous and possess large specific surfaces; consequently, the number of potential active sites for the oxidant chemisorption is large enough.

It is noteworthy that the susceptibility of carbon materials to oxidation and, as a consequence, the number of oxygen-containing surface groups formed upon chemisorption of the oxidant depend on the degree of their graphitisation. Interactions of carbon materials with oxidants also depend on oxidation conditions, *e.g.*, reaction temperature. Treatment of carbon materials with oxygen may result in physical (reversible) and chemical (irreversible) adsorption of the oxidant gas. The former takes place at low temperatures, but the role of chemisorption increases with an increase in temperature. Chemisorbed oxygen molecules dissociate into atoms, which interact with surface carbon to form superficial complexes.[44]

Oxygen-containing complexes can be formed on the carbon surface upon interaction not only with oxygen, but also with many other gaseous oxidants, *e.g.*, ozone, nitrogen oxides or carbon dioxide.[13, 30, 45] Nitric acid, sodium hypochlorite, potassium permanganate and hydrogen peroxide can be used as liquid oxidants. Electrochemical oxidation of carbon materials is also possible.[30]

Impregnation of a carbon support and ion exchange with a solution containing a precursor of the active component are the most popular approaches to prepare the catalysts. The mode of interaction of metal salts with supports strongly depends on the nature and number of functional groups formed on the support surface under the action of the oxidant.[13] The major portion of the metal is applied onto the carbon surface, if the maximum surface of the support is chemically accessible, *i.e.*, if the largest electrostatic forces arise between the positively charged surface and negatively charged anions of a salt of the active component precursor, or, *vice versa*, between the negatively charged surface and the salt cations.[46, 47] Thus the adsorption capacity of granular activated carbon with respect to copper ions increases upon modification with citric acid due to introduction of carboxyl groups.[45]

The nature of the solvent used for impregnation is a factor determining the distribution of a metal (*e.g.*, platinum) on the surface of carbon supports.[48] Since carbon materials are, as a rule, hydrophobic, they possess very low affinity for polar solvents and high affinity for non-polar solvents.[13] Accordingly, impregnation of granular activated carbon with a solution of a platinum salt in acetone results in more uniform distribution of the salt over the surface of grains of the support than in the case of aqueous solutions.[48] The presence of oxygen-containing groups on the surface of carbon materials decreases their hydrophobicity, *i.e.*, increases the hydrophilicity, and favours impregnation of the support with aqueous solutions.[49]

The effects of surface groups on the dispersity and sintering of metal – carbon catalysts were studied.[50, 51] Preliminary modification of the surface significantly affects the interaction of the active phase with the support in the formation of a catalyst and the dispersity of the metal. The latter can be controlled by thermal and chemical modification of the porous structure of the support ensuring the formation of surface oxygen-containing groups.[41] Thus oxidative treatment of activated carbon favours more uniform distribution of nickel over the support granules in a nickel – carbon catalyst. Probably, this is due to more intense diffusion of nickel into pores of the support. Preliminary oxidative treatment of carbon supports also has a beneficial effect on the stability of catalysts. Presumably,[30] the oxidation favours the formation of acid ion-exchange groups that form chelates with metal-containing compounds, which prevents the migration of the metal over the carbon surface. The surface oxygen-containing groups play the role of binding sites for the active metal component on the carbon surface.[49] The strongest 'anchoring' effect is manifested by weakly acid and neutral oxygen-containing groups, probably, due to stability of such groups at temperatures used for pretreatment of catalysts, whereas the acid groups decompose with liberation of carbon dioxide.

The ever-increasing number of publications devoted to effects of oxygen-containing surface groups on the properties of carbon supports and ultimately on the properties of catalysts prepared points to high prospects of this line of research.

3. Metal – carbon systems in catalysis

Catalytic systems based on activated carbons compete favourably with catalysts based on oxide supports. Thus the activities of In- and Sn-doped palladium catalysts supported on activated carbons that are used for denitrification of water are comparable with those on metal oxides.[52] Catalysts with activated carbon as a support are used for methanol conversion into synthesis gas.[53] In the presence of copper – chromium catalysts, the degree of methanol conversion exceeds 90%, and side products including methane are formed in only trace amounts.

Despite the relatively high cost of commercial fibrous carbon materials, they are becoming more popular as supports for active components of heterogeneous catalysts.[54, 55] The use of catalysts supported onto fibrous carbon nanomaterials in hydrogenation, hydroformylation, decomposition and oxidation of methanol is documented.[14, 15, 37, 56] Catalysts supported onto carbon fibres doped with Co, Ni, Cr and Mn were tested in various conversion reactions of secondary alcohols.[57, 58] Owing to well-developed porous structure and high thermal stability, novel fibrous carbon materials can be used as catalysts in oxidative dehydrogenation of organic compounds, in particular, of cumene.[59, 60] Comparative studies have shown that the yield of styrene on carbon nanotubes is 1.5 times higher than on graphite.[60] It is noteworthy that no loss of CNT due to carbon oxidation took place, which was the case with soot as a catalyst.

Ruthenium catalysts on CNT and oxide supports (MgO, Al_2O_3, TiO_2) accelerate decomposition of NH_3 with the formation of CO-free hydrogen.[61] The highest activity was observed for Ru/CNT, which is explained by high degree of dispersity of its active component and chemical purity of the support. These conclusions were confirmed by the results of TPD studies and high-resolution tunneling microscopy.

A nickel catalyst supported on carbon nanotubes manifested much higher activity in the hydrogenation of benzene than an analogous catalyst on γ-Al_2O_3.[62] This was attributed to higher

dispersity of the active component on CNT and weaker interaction of Ni with the support. Ni/CNT manifested higher thermal stability than Ni/γ-Al_2O_3, since the unique porous structure of CNT prevents agglomeration of Ni particles.

Carbon nanofibres can be used as supports for a nickel catalyst applied for the decomposition of ethylene to produce CO-free hydrogen.[63] The maximum yield of hydrogen on Ni/CNF is 2.5 times higher than on Ni/SiO_2.

A comparison of iron–copper catalysts supported onto carbon nanofibres, activated carbon and γ-Al_2O_3 revealed [64] that the degree of ethylene hydrogenation on Fe–Cu/CNF exceeded that on Fe–Cu/activated carbon and Fe–Cu/γ-Al_2O_3 more than fourfold. The size of particles of the active component in the Fe–Cu/CNF catalyst was 12–16 nm, whereas that in Fe–Cu/activated carbon and Fe–Cu/γ-Al_2O_3 catalytic systems varied from 6–10 to 2–8 nm, respectively. These results are consistent with the concept [63] according to which it is the porous structure and chemical composition of the support rather than the dispersity of the active component that play the crucial role in the activity of catalysts. It was suggested [64] that the surface layer of carbon fibres in bimetallic catalytic systems can be enriched with one of elements of the active component giving rise to strong metal–support interactions. Such an interaction is hardly possible for a carbon support with a less ordered structures.

Copper-containing catalysts supported onto carbon fibres were used in the dehydrogenation of cyclohexanol.[65] The yield of the target product at 350 °C was 93%. The dehydrogenation of isopropyl alcohol on this catalyst gave acetone (yield 95%–96% with 100% selectivity). The same system modified with Ti, TiO_2 and TiC was used for catalytic purification of hydrogen and decomposition of H_2S. The use of titanium as an additive resulted in virtually complete dissociation of hydrogen sulfide into hydrogen and sulfur.

Studies on denitrification in water using Pd–Cu-catalysts supported onto activated carbon cloth (ACC), Al_2O_3 and SnO_2 revealed [66] that Pd–Cu/ACC manifested 2.7–3 times higher activity than Pd–Cu/Al_2O_3 or Pd–Cu/SnO_2. The rate of denitrification on Pd–Cu/ACC was 33 mmol (g Cat)$^{-1}$ h^{-1} (Cat is catalyst), whereas that on Pd–Cu/Al_2O_3 and Pd–Cu/SnO_2 did not exceed 12 and 15 mmol (g Cat)$^{-1}$ h^{-1}, respectively.

A comparative study of Co–Mo-containing catalysts supported onto nanoporous carbon (NC) and traditional supports, *e.g.*, activated carbon and Al_2O_3, has been studied [67] in hydrodesulfurisation of dibenzothiophene and 4,6-dimethyldibenzothiophene. The overall activities of the catalysts increased in the following order: Co–Mo/Al_2O_3 < Co–Mo/activated carbon < Co–Mo/NC. The mesoporous structure of NC and its large surface area favoured higher dispersity of the catalyst. The metal loading lowered the surface area of activated carbon, but did not virtually affected the other supports.

A whole family of sibunit-based palladium catalysts have been developed. These include catalysts for hydrogenation of aromatic nitro compounds and vegetable oils, hydrorefining of terephthalic acid from *p*-carboxybenzaldehyde, hydrogenation and disproportionation of colophony, *etc.*[24,68] Sibunit is also used for the preparation of sulfide Ni–Mo-catalysts, which are used for hydrorefining [69] and hydrodemetallisation,[70] and of rhenium catalysts for dehydrogenation of cyclohexane [71] and isopropyl alcohol,[72] hydrogenation of ethyl acetate [73] and some other organic reactions.[74]

III. Conversions of lower alcohols on metal–carbon catalysts

1. Synthesis of methyl formate by dehydrogenation of methanol

In-depth thermodynamic studies of dehydrogenation of methanol into methyl formate (MF) [75] with consideration of side reactions (*e.g.*, dissociation of methanol into carbon monoxide and hydrogen; decarbonylation of methyl formate; dehydration and steam conversion of methanol), revealed that the equilibrium constants of side reactions significantly exceed that of dehydrogenation of methanol so that the equilibrium concentration of MF in the reaction products is low. Thus, synthesis of methyl formate by this method is expedient only if highly selective catalysts are available. The properties of these catalysts determine the optimum temperature of the process. The concentration of methyl formate in the equilibrium mixture increases with an increase in temperature, but this is accompanied by increase in its decomposition rate. High concentrations of methanol and/or methyl formate suppress the decomposition of MF.[76] High temperature (240 °C) and properly selected partial pressure of methanol allows virtrually complete prevention of MF decomposition.

The degree of methanol conversion can also be increased by removal of hydrogen from the reaction zone using advanced membrane technologies.[76,77] Membranes of palladium–ruthenium alloys can be used to this end. However, they undergo deactivation by CO formed in a side reaction, *viz.*, decomposition of methyl formate. This problem was successfully overcome through the use of a specially designed reactor [76] where the membrane was not deactivated even at high (~20%) concentrations of CO in the gas mixture, whereas the permeability of this membrane with respect to hydrogen significantly decreased after passage of hydrogen containing admixture of CO in the absence of the catalytic mixture.

Copper-containing catalysts are especially active in the dehydrogenation of methanol.[78] The key role in this process is ascribed to the interaction of the support with components of the catalytic system. In metal–carbon catalysts, the lack of strong interaction of the active component with the support facilitates the reduction of the metal on the surface.[79,80] For this reason, a series of well-known carbon materials that have not previously been employed in the process under consideration were tested as potential supports for copper catalysts.

The following supports were used:[81–84] (1) activated carbon AC_1 prepared from peat; (2) activated carbon AC_2 prepared from coconut shells (grain diameter 1.7–3.35 mm, moisture content 2.80 mass %, ash content 0.60 mass %, packed density 0.510 g cm^{-3}, abrasion resistance 95%–99%, pH 7.5); (3) fibrous-tubular carbons (FTC) prepared by decomposition of gaseous hydrocarbons on an iron catalyst with subsequent removal of iron with a large excess of 37% hydrochloric acid, washing off chloride ions and drying at room temperature for 24 h and at 105 °C for 3 h (the size of graphite crystallites was 53 Å, density 3.862 g cm^{-3}); (4) non-woven carbon material (NCM) prepared from hydrated cellulose fibres (total pore volume > 0.8 cm^3 g^{-1}, surface density 120 g m^{-2}, carbon content > 99 mass %, layer thickness > 0.8 mm); (5) woven carbon material (WCM) prepared from PAN fibres (carbon content 98%–99%, abrasion resistance 700–800 N); (6) sibunit P-232 obtained by deposition of pyrocarbon on a technical carbon support with subsequent activation (total pore volume with respect to H_2O 0.57 cm^3 g^{-1}, apparent density 0.597 g cm^{-3}).

Catalysts containing 5 mass % of copper were prepared by impregnation of the aforementioned supports with a solution of a copper salt (nitrate, acetate or tetraammine nitrate) with subsequent drying at 100 °C and reduction of samples in a hydrogen flow at 400 °C.

Analysis of the reaction mixture in a flow-through reactor at a volumetric flow rate of methanol of 3.0 h^{-1} and temperature of 200–400 °C revealed [84,85] that it was only Cu/sibunit that provided a sufficiently high degree of methanol conversion in the given temperature range. Presumably, the formation of catalytic sites on carbon supports requires higher concentrations of the metal than on oxide supports.[86] The highest degree of methanol conversion (63.3%) was observed at 350 °C; however, this parameter decreased with further increase in temperature. On other catalysts, the degree of methanol conversion was 12%.[87,88]

In addition to methyl formate, the liquid phase contained non-consumed methanol and water present in the alcohol. The gas

phase contained hydrogen and carbon monoxide. At temperatures above 250 °C, CO_2 was found in the gas phase, whereas at 300 °C methane was additionally formed. The highest selectivity of MF formation (88.9% at 200 °C) was observed on Cu/AC_2; however, the activity of this catalyst was low. Moreover, its selectivity dropped with an increase in temperature. At temperatures above 300 °C, the highest selectivity was manifested by Cu/WCM.

The reduction of catalytic activity at elevated temperatures can be caused by several factors.

First, agglomeration of metal particles on the surface of the support can occur as a result of their migration or sintering.[89] Sintering is possible even in the preparation and pretreatment of the catalyst. The migration of active component (metal) particles over the surface of the support and the formation of large agglomerates can be explained by thermodynamic instability of smaller particles.

Second, deactivation can be caused by fouling of the surfaces of the active component and the support itself by carbon deposits of different origin.[89]

It was shown that virtually no changes in specific surface of copper-containing catalysts occurred following methanol dehydrogenation in the temperature range from 200 to 400 °C. This confirms the assumption that the reduction of activity results from sintering of active component particles. Specific surface of a specimen based on sibunit somewhat increased after several runs. Probably, sintering of copper is accompanied by its partial removal from the granulated support with a flow of the reaction mixture. This is rationalised as the virtual lack of interaction between the active component and the carbon support.[13]

Data from X-ray photoelectron spectroscopy (XPES) suggest that, after reduction, the active component of the catalyst 5% Cu/sibunit is predominantly localised on the surface of the granulated support. Its content in the dead catalyst is markedly reduced suggesting that the copper particles migrate over the surface of sibunit granules rather than in their interior in the course of methanol conversion. Analysis of powdered grains of the dead catalyst revealed that the amount of copper particles inside pores of sibunit is much smaller than in the surface layer.[85] It may thus be concluded that the preparation and preactivation procedures favour the formation of catalysts of the shell type, and the decrease in the catalyst activity can be attributed to the migration of copper particles over the surface of the support.

As mentioned above, Cu/sibunit is the most efficient catalyst for dehydrogenation of methanol into MF, the yield of MF being 28.4% at 275 °C and 45% methanol conversion. However, low thermal stability is a serious drawback of sibunit-based catalysts. Their activity drops drastically at temperatures above 275 °C.

The oxidative modification of the carbon support described above, which decreases its hydrophobicity and provides a more uniform distribution of the active component, is one of the ways to increase stability of supported catalyst[49] To this end, sibunit was oxidised by treatment with 10% and 20% H_2O_2 or HNO_3, or by passing air at 400 – 500 °C (Refs 85 and 90). Copper was applied onto the modified support washed with distilled water and dried at 100 °C. Copper-containing catalysts usually manifest much higher selectivity and thermal stability on such supports. The highest yield of MF (36.8% at 325 °C) was obtained in the presence of sibunit pretreated with 20% HNO_3. This specimen contained 2.8% of oxygen incorporated upon oxidation. The maximum yields of MF on catalysts based on supports premodified with 20% H_2O_2 or air at 500 °C were 32.9% at 300 °C or 29.7% at 275 °C, respectively. It is noteworthy that the maximum yield of MF after liquid-phase oxidation of sibunit was achieved at higher temperatures than on non-modified specimens.[91, 92]

Introduction of high-melting modifying agents (promoters) might be an alternative approach to increase the catalyst stability. It was supposed[85, 90] that the use of zinc oxide to this end would favour retention of the optimum dispersity of copper in the catalyst 5% Cu/sibunit and ensure stronger interaction between the active component and the carbon support. However, the addition of 0.25 mass % – 3.75 mass % of zinc oxide significantly decreased the selectivity together with the obvious increase in the thermal stability of the catalyst.

The ability to selectively accelerate the target reactions is yet another important feature of modifying additives. Considering that rhenium-containing catalysts possess good dehydrogenating properties,[71, 93] copper- and rhenium-containing mono- and bimetallic sibunit catalysts were tested in methanol decomposition at 200 – 400 °C.[83]

Synthesis of methyl formate from methanol on copper-containing oxide catalysts is accompanied by decomposition of MF into carbon monoxide and hydrogen or into carbon dioxide and methane.[77, 94] Decarbonylation of MF[75, 95] and steam conversion of carbon monoxide[96] and methanol[97, 98] also took place under these conditions. The selectivity of MF formation at high degrees of conversion rapidly decreased as a result of decomposition of MF. The kinetics and mechanism of MF conversion on copper-containing oxide catalysts were studied in detail.[77, 94, 99, 100]

In the presence of monometallic copper- and rhenium-containing sibunit catalysts, methanol conversion into MF increased at first with an increase in temperature from 200 to 250 °C and then decreased gradually. With an increase in the rhenium concentration from 1% to 2%, the selectivity of the reaction at 250 °C increased from 33.3% to 42.9%. The same increase in the content of copper on a monometallic catalyst increased the selectivity from 46.5% to 59.1%. However, the decomposition of MF on 1% Cu/sibunit proceeded much faster than on 1% Re/sibunit. For instance, the yield of methanol at 200 °C on the former was three times larger than on the latter. It is noteworthy that the ratio $CO : H_2$ is equal to 1 : 1 on 1% Re/sibunit, which corresponded to the stoichiometry of MF decomposition, while that for the copper-sibunit catalyst was equal to 2 : 1. This suggests that the selectivity of MF formation changed oppositely to methanol

Table 3. Effect of rhenium additives to copper-sibunit catalysts on the conversion of methanol and selectivity of formation of methyl formate (pressure 0.1 MPa, volumetric flow rate 7.5 h^{-1}).[83]

Parameter	Addition of Re (mass %)								
	2% Cu/sibunit					4% Cu/sibunit			
	0	0.25	0.5	1.0	2.0	0	0.25	0.5	1.0
Total conversion (%) at									
200 °C	1.6	1.5	1.4	1.3	1.1	1.3	1.5	2.7	2.3
250 °C	4.3	4.1	3.7	3.5	3.4	2.2	5.8	5.2	4.7
300 °C	5.9	6.2	6.4	6.9	7.1	3.1	8.7	8.4	8.6
Selectivity (%) at									
200 °C	69.0	66.4	62.5	60.0	59.2	65.8	63.5	62.3	53.5
250 °C	59.1	52.5	49.9	42.4	35.1	55.6	52.6	52.5	44.3
300 °C	42.1	36.0	28.4	17.1	12.5	20.0	28.2	25.5	20.8

conversion. At high degrees of conversion, the selectivity of formation of the target product decreased rapidly as a result of decomposition of MF into CO_2 and CH_4.

The dehydrogenation activity of bimetallic Cu–Re/sibunit catalysts containing 2% and 4% of copper changed insignificantly with an increase in temperature from 200 to 300 °C (Table 3).[83] The addition of 0.25%–1% rhenium to 4% Cu/sibunit resulted in a threefold increase in the total conversion of methanol at 300 °C with a slight increase in selectivity. A catalyst containing 4% of Cu and 0.25% of Re on sibunit manifested the highest dehydrogenation activity. Such a noticeable increase in the catalyst activity implies that sintering of copper at high temperatures proceeds more strongly in the absence of this additive. The addition of 0.25% rhenium to 4% Cu/sibunit increased not only its activity and selectivity, but also its stability.[83]

Thus, modification with rhenium provides an efficient copper-sibunit catalyst for dehydrogenation of methanol into methyl formate.

2. Synthesis of acetaldehyde by dehydrogenation of ethanol

Copper-containing catalysts are most active in dehydrogenation of alcohols.[12,101] As a rule, copper is supported onto silica gel.[102] It was suggested that acetaldehyde is formed on the surface of metallic copper, since the UV spectrum of Cu/SiO_2 contains a single peak at 560 nm, which is assigned to Cu^0 (Ref. 103). Activated carbon, which is basic by nature, also catalyses the dehydrogenation of ethanol.[104] On oxidised carbons, ethanol undergoes dehydrogenation and dehydration, the latter yielding diethyl ether and ethylene. Dehydration usually occurs on surface Brønsted acid centres and increases with an increase in the total surface acidity. However, oxidation of carbon promotes acetaldehyde formation, since dehydrogenation is catalysed by Lewis acid centres. Most probably, the dehydrogenation takes place on both basic and acidic surface centres, not necessarily simultaneously on both types of centres. In addition, the increase in the intensity of formation of acetaldehyde with an increase in specific surface suggests that the dehydrogenation is catalysed not only by external, but also by some internal surface groups.[104]

The main drawback of copper-containing catalysts is their short service life. In connection with the problem of enhancement of stability of catalysts for ethanol dehydrogenation, studies into properties of various supports, their interactions with active components of catalytic systems and choice of modifying agents and pretreatment conditions become of special importance.

The search for the best support for a catalyst of acetaldehyde synthesis was carried out by performing conversion of ethanol on supports devoid of an active component, *viz*., galumin (calcium alimunium cement), silica gel and sibunit.[105–107] On galumin, which contains alumina, in addition to acetaldehyde, C_4 compounds (butan-1-ol, diethyl ether and ethyl methyl ketone) were identified in liquid products; these are formed on acid centres. Dehydration with formation of large amount of ethylene was the main reaction on silica gel over the whole range of temperatures studied (200–500 °C). Acetaldehyde and, at temperatures above 250°C, diethyl ether formed in insignificant amounts. No ethanol decomposition took place on sibunit at temperatures below 250 °C. At higher temperatures, CO, CO_2 and H_2 were formed in trace amounts. At temperatures above 400 °C, the reaction products contained acetaldehyde. On sibunit, the conversion of ethanol was as low as 2% at 500 °C, whereas on oxide supports (galumin and silica gel) it reached 80% and 70%, respectively. Among copper-containing catalysts based on these supports, the Cu/sibunit system manifested the highest activity in the dehydrogenation: the yield of acetaldehyde was 43% at 400 °C. Due to lower selectivities of systems based on the oxide supports, the yields of acetaldehyde were by 11%–13% lower.

Thus, side reactions accompanying acetaldehyde synthesis from ethanol are much less pronounced on sibunit than on the oxide supports.

It was shown[91,92] that ethanol conversion on copper-sibunit catalysts increases with an increase in the copper concentration from 0.3 mass % to 10 mass %. This is accompanied by a decrease in the selectivity of acetaldehyde synthesis and by formation of side products, *viz*., buta-1,3-diene, ethyl acetate, butan-1-ol and acetone. The increase in the copper content in the catalyst from 3 to 5 mass % decreases the selectivity by 22%. The maximum yield of acetaldehyde (54%) was obtained on 3% Cu/sibunit. At the copper content of 5%, the yield of acetaldehyde decreased to 43%, but it did not change with a further increase in the copper content. Presumably, these catalysts are of the shell type where copper is predominantly localised in the surface layer, which makes the porous cavity of sibunits inaccessible for the reaction. This is corroborated by a decrease in the specific surfaces of catalysts with an increase in the copper content. Higher copper content in the surface layer of 5% Cu/sibunit (2.9 at %) in comparison with 3% Cu/sibunit (2.2 at %) was confirmed by XPES.

The temperature-dependent changes in the compositions of ethanol conversion products on the most efficient catalyst (3% Cu/sibunit) are given in Table 4.

By selecting conditions of pretreatment of a copper-sibunit catalyst (3% Cu/sibunit), one can significantly increase the yield of the target product.[101] The catalyst calcined in argon and subsequently reduced in hydrogen at 400 °C afforded the highest yield of acetaldehyde (69.2%) at 375 °C. Preliminary calcination has a great impact on the selectivity of the process. An increase in the calcination temperature from 200 to 400 °C increases the selectivity of acetaldehyde formation. Reduction of the catalyst with hydrogen increases the conversion of ethanol and the yield of acetaldehyde (by 10%–14%). The difference between the yields of acetaldehyde in the presence of non-reduced and reduced catalysts can be explained by different states of copper on the surface of the support. XPES studies showed that 64% of copper atoms in the reduced sample are in the Cu^0 or in the Cu^+ state, while the rest 36% are in the Cu^{2+} state. The corresponding values

Table 4. Composition of ethanol conversion products on a 3% Cu/sibunit catalyst at different temperatures.[101]

T/°C	Product content (mol.%) (see [a])														
	E	AA	Et	DEE	H_2O	EA	EMK	BT	Ac	C_2H_4	H_2	CO	CO_2	CH_4	BD
200	–	3.68	77.01	–	16.21	–	–	–	–	–	3.10	–	0.01	–	–
250	–	11.67	58.14	–	14.48	0.31	0.09	–	–	0.03	15.27	–	0.01	–	–
300	–	18.97	34.83	0.16	12.89	0.54	0.25	0.09	tr.	0.09	30.52	–	0.04	–	1.62
350	–	23.05	16.07	0.14	11.38	0.51	0.32	0.06	0.12	0.08	43.01	0.07	0.08	0.06	5.05
400	tr.	27.86	12.05	0.16	12.11	0.26	0.32	0.04	0.20	0.05	42.08	0.21	0.06	0.16	4.44
450	0.02	13.65	56.95	–	15.70	0.16	–	0.18	0.10	0.05	12.30	0.25	0.04	0.21	0.39
500	0.10	8.74	61.63	–	15.49	0.05	–	–	–	0.09	12.16	0.63	0.06	0.57	0.62

[a] E is ethane; AA is acetaldehyde; Et is ethanol; DEE is diethyl ether; EA is ethyl acetate; EMK is ethyl methyl ketone; BT is butan-1-ol; Ac is acetone; BD is buta-1,3-diene; tr. is traces.

for a calcined non-reduced sample are 51% and 49%, respectively; the copper ions exist, most probably, only in Cu^+ and Cu^{2+} states. Presumably, higher concentration of Cu^{2+} in the calcined sample is the reason for inferior reaction parameters in the presence of non-reduced catalysts.

Stability is an extremely important characteristics of catalysts, especially of those intended for industrial use. However, the activity of 3% Cu/sibunit is lost dramatically at temperatures above 400 °C. According to XPES data, under the action of the reaction medium, copper passes into a Cu^{2+} state, which is less active as regards ethanol conversion, in the temperature range 200 – 500 °C. The period of stable active operation of the catalyst under conditions ensuring the maximum yield of the target product (375 °C, volumetric flow rate 0.3 h^{-1}) is 30 h after which its activity decreases.[108] Analysis of the XPE spectrum of the dead catalyst revealed an insignificant increase in Cu^{2+} content in comparison with the initial specimen. This suggests that the decrease in the catalytic activity of Cu/sibunit during its continuous operation is due to agglomeration of copper particles.

The agglomeration of copper particles into larger crystallites can be prevented and enhancement of the interaction of copper with the support surface can be reached if the catalyst is supplemented with magnesium oxide and chromium oxide. Magnesium oxide is known to decrease both the activity and the selectivity of Cu/sibunit catalysts, while chromium oxide causes significant increase in their activity at temperatures above 400 °C. However, a twofold (in comparison with the non-modified catalyst) increase in the degree of ethanol conversion was accompanied by a decrease in its selectivity. The best results were obtained at the copper : chromium oxide ratio 20 : 1 (the yield of acetaldehyde was 63.3% at 375 °C). Moreover, the addition of chromium oxide prolonged the operation life of the catalyst. Under conditions ensuring the maximum yield of acetaldehyde, the system can steady operate for at least 80 h.

Thus, the use of a carbon-containing material (sibunit) as a support allowed the development of an efficient catalyst for acetaldehyde synthesis. The parameters of this process can be improved through optimisation of conditions for pretreatment of copper – sibunit catalysts. Their stability can be increased by promotion with chromium oxide. The yield of acetaldehyde attained markedly exceeds the yields on the known industrial catalysts.[101]

3. Synthesis of acetone from isopropyl alcohol

Isopropyl alcohol undergoes easy (in comparison with other aliphatic alcohols) dehydrogenation to give acetone and dehydration to give propene.

Traditional copper-containing catalysts for dehydrogenation of alcohols into aldehydes usually contain significant amounts of a metal. Thus the commercial catalyst SNM-1 ($CuO - ZnO - Al_2O_3$) manufactured in Russia contains 64% of CuO. A 30% rhenium catalyst on activated carbon manifests high dehydrogenating properties, but rapidly loses its activity.

Modification of metal catalysts used for the conversion of isopropyl alcohol can be achieved by replacement of activated carbons by sibunit.[72] In a series of monometallic 1% Cu-, Re-, Ni- and Pd/sibunit catalysts, the highest activity was manifested by 1% Re/sibunit (Table 5). At 250 °C, the yield of acetone on this catalyst was commensurate with that obtained on 30% rhenium/activated carbon at 195 °C.[108]

On bimetallic catalysts containing 1% Re and Cu, Re and Ni or Re and Pd, the degree of conversion of isopropyl alcohol into acetone markedly exceeds that on monometallic 1% Cu/sibunit, Ni/sibunit and Pd/sibunit catalysts. Thus the introduction of rhenium to a palladium-containing catalyst increases its activity 35-fold and its stability, nearly twofold. Bimetallic catalysts retain their activities and high selectivity (77% – 90%) even after 6 – 9 h of operation.

The obvious advantage of bimetallic catalysts over monometallic ones is that rhenium favours the reduction of the second metal (Cu, Ni or Pd). In the alcohol dehydrogenation, the activities of the above-mentioned bimetallic catalysts increase in the following order: Re – Cu < Re – Ni < Re – Pd.

Table 5. Dehydrogenation of isopropyl alcohol on mono- and bimetallic catalysts supported onto sibunite (volumetric flow rate 1.1 h^{-1}, reaction in a flow of hydrogen).[72]

Metal content	Reaction conditions		Degree of alcohol conversion (%)		Selectivity of acetone formation (%)
	T /°C	time /h	total	into acetone	
1% Re	200	1	34.2	26.5	77.0
	250	2	66.6	54.7	82.0
1% Re + 1% Cu	200	1	27.7	21.0	75.8
	250	2	61.7	49.0	79.4
1% Cu	200	1	20.5	15.3	74.6
	250	2	52.5	43.7	83.2
1% Re + 1% Ni	200	1	61.5	53.0	86.0
	250	2	79.7	64.0	80.3
1% Ni	200	1	15.1	12.1	80.1
	250	2	43.1	33.3	77.3
1% Re + 1% Pd	200	1	76.1	55.5	82.7
	250	2	93.0	77.2	83.0
1% Pd	200	1	1.6	1.6	100.0

No rhenium crystalline phase could be detected by X-ray phase analysis in a bimetallic catalyst containing 2% Re and 2% Ni on sibunit, which suggests a highly dispersed state of rhenium. The data listed in Table 6 illustrate the effects of added rhenium on the activity of 2% Cu/sibunit in the conversion of isopropyl alcohol at 200 – 270 °C.[109] Liquid products formed on a monometallic (*i.e.*, containing no rhenium) catalyst contain acetone and water (along with the non-consumed alcohol), while the gas phase contains propene and hydrogen. At 200 °C, the dehydrogenation and dehydration occur in parallel. Thirty minutes after the beginning of the reaction, the total conversion of the alcohol on 2% Cu/sibunit is ~15.3%, while the ratio of yields of acetone and water is 3.3. With an increase in temperature from 200 to 270 °C, the dehydrogenating activity of the monometallic catalyst increases 3.2-fold. The selectivity of acetone formation increases from 76.6% to 86.7%. If after 2 h-operation of 2% Cu/sibunit at 270 °C the temperature is decreased to 200 °C, the initial dehydrogenating activity of the catalyst is recovered virtually completely.

Rhenium, which has a high melting temperature (3170 °C), is not subject to recrystallisation in the course of the catalytic process; therefore its addition can increase the stability of catalytic systems.[85] As can be seen from Table 6, the addition of 0.25% rhenium improves the dehydrogenating properties of 2% Cu/sibunit in the conversion of isopropyl alcohol. The lack of a strong metal – support interaction on a carbon support facilitates the reduction of the metal on the catalyst surface, which takes place even at 200 °C.[109]

Glow discharge plasma treatment in oxygen is a way to control properties of copper and copper-rhenium catalysts.[110] The effect of plasma treatment was assessed by measuring the degree of conversion of isopropyl alcohol into acetone in the temperature range 177 – 327 °C. The catalysts were processed in the following regimes: (1) hydrogen treatment; (2) hydrogen treatment with subsequent catalysis and repeated hydrogen treatment; (3) plasma treatment with subsequent hydrogen treatment; (4) plasma treatment; (5) plasma treatment with subsequent catalysis and final hydrogen treatment.

The yield of acetone after treatment of a copper-sibunit catalyst in regime (3) decreased, while that of Cu – Re/sibunit increased. Manifold increase in the activity was observed after treatment of the catalyst in regime (5). In order to elucidate the reasons for the change in activity of the catalyst depending on the

Table 6. Conversions of isopropyl alcohol on 2% Cu/sibunit catalysts containing different concentrations of rhenium (flow systems, atmospheric pressure, reaction in H_2 flow, volumetric flow rate 1.0 h^{-1}, reaction time 30 min).[109]

Re content (%)	T/°C	Composition of liquid phase (%)			Conversion (%)			Selectivity (%)	
		acetone	H_2O	alcohol	total	into acetone	into H_2O	acetone	H_2O
0	200	11.6	1.1	87.3	15.3	11.7	3.6	76.6	23.4
	235	28.6	1.8	69.6	33.8	28.1	5.7	83.1	16.9
	250	33.6	1.7	64.7	38.4	33.0	5.4	86.0	14.0
	270	37.7	1.8	60.5	42.7	37.0	5.7	86.7	13.3
0.25	200	18.2	1.0	80.8	21.5	18.3	3.2	85.0	15.0
	235	39.2	1.7	59.1	43.9	38.6	5.3	87.8	12.2
	250	45.1	2.4	52.5	51.1	43.6	7.5	85.4	14.6
	270	56.4	2.8	40.8	62.4	53.8	8.6	86.3	13.7
0.5	200	23.9	2.0	75.1	29.4	23.1	6.3	78.6	21.4
	235	46.8	2.4	50.8	52.6	45.2	7.4	85.9	14.1
	250	49.7	2.2	48.1	54.8	47.9	6.9	87.4	12.6
	270	57.3	2.4	40.3	62.6	55.2	7.4	88.1	11.9
1.0	200	23.0	2.6	74.4	30.4	22.3	8.1	73.3	26.7
	235	37.3	3.6	59.1	46.1	35.2	10.9	76.0	24.0
	250	45.1	3.6	51.3	51.5	39.5	12.0	76.0	24.0
	270	53.6	4.1	42.3	62.0	49.8	12.2	80.3	19.7
2.0	200	35.1	3.1	61.8	43.3	33.9	9.4	78.3	21.7
	235	51.0	7.2	41.8	64.8	44.5	20.3	68.7	31.3
	250	59.2	8.9	31.9	71.8	50.0	24.2	67.5	32.3
	270	65.4	9.7	24.9	80.1	54.2	25.9	67.6	32.4

Table 7. Activation energies and preexponential factors for dehydrogenation of isopropyl alcohol on 2% Cu/sibunit catalysts containing different amounts of rhenium before and after plasma treatment in regime (4) (see the text).[110]

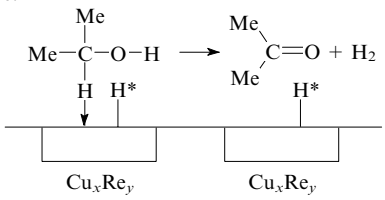
Re content (%)	Before treatment		After treatment	
	E_a/kJ mol^{-1}	$\ln A_0$	E_a/kJ mol^{-1}	$\ln A_0$
0	38.7	14.1	–	–
0.25	34.9	12.3	38.7	14.1
0.5	48.4	16.5	13.4	9.2
1.0	51.7	16.3	38.1	13.4
2.0	57.5	17.7	46.5	16.2

mode of treatment were elucidated by studying the temperature dependences of the yield of acetone (Y) at low degrees of conversion in the Arrhenius coordinates ($\ln Y$ *vs.* T^{-1}). As can be seen from Table 7, the values of activation energies (E_a) and the preexponential coefficients (A_0) for the dehydrogenation of isopropyl alcohol on 2% Cu/sibunit and 2% Cu + 0.25% Re/sibunit are very similar. Much higher E_a values (48.4, 51.7 and 57.5 kJ mol^{-1}, respectively) were obtained for samples with a higher rhenium content (0.5%, 1.0% and 2.0%).

Treatment of the catalyst 2% Cu + 0.25% Re/sibunit in regime (4) slightly increases its activity, which can be attributed to the larger number of active centres rather than to structural changes, as can be evidenced from a significant increase in $\ln A_0$ with a small change in E_a. A decrease in the activation energy of the reaction on 2% Cu + 0.5% Re/sibunit under identical conditions is due to the substantial changes in the structures of the active centres. However, the effect of this factor is compensated by a significant decrease in the number of these active centres (factor A_0); therefore, the yield of acetone on this catalyst is only slightly higher than on 2% Cu + 0.25% Re/sibunit processed in a similar regime. The increase in the yield of acetone on 2% Cu + 1% Re/sibunit can be explained exclusively by a decrease of the activation energy, since the value of A_0 after treatment in regime (4) decreased. On 2% Cu + 2% Re/sibunit, the changes in the E_a and $\ln A_0$ are insignificant.

Treatment in regimes (1–5) has different effects on the activitiesy of copper and copper–rhenium catalysts on sibunit. This suggests that active centres of copper–rhenium catalysts based on sibunit represent bimetallic clusters Cu_xRe_y with Cu–Re bonds. Presumably, the active centre of the catalyst contains a hydrogen atom, since the highest activity was manifested after plasma treatment followed by a series of catalytic runs and final hydrogen treatment (regime 5). If plasma treatment was not followed by hydrogen treatment, the activity changed only insignificantly and showed a tendency to decrease, apparently due to partial removal of hydrogen from the active centres.

Apparently, the role of rhenium atoms in the active centres consists, first, of stabilisation of the structure of these centres.[72, 108] This follows from the fact that copper–rhenium catalysts maintain their activity on sibunit for longer periods of time than catalysts containing no rhenium. Second, the interaction of Re atoms with Cu atoms results in positive polarisation of the latter, which favours the displacement of an electron from the carbon atom of the CH group of isopropyl alcohol first to the copper atom and then to the hydrogen atom in the active centre. This, in turn, favours the interaction of the hydrogen atom in the active centre with a positively polarised hydrogen atom of the hydroxy group. It is noteworthy that the work function of electron is equal to 5.0 eV for rhenium and 4.4 eV for copper. Hence, the dehydrogenation process can schematically be presented as follows:



Ab initio quantum-chemical calculations (GAUSSIAN-98) confirmed the suggested structure of the active centre.[111] The lower activity of 2% Cu + 2% Re/sibunit as compared with that

Table 8. Conversion of isopropyl alcohol in samples obtained by passage of volcanic gas through sibunit.[116]

Gas temperature /°C	Total metal content (mass %)	Reaction conditions			Yield of liquid products (%)	Degree of alcohol conversion (%)	
		T/°C	time /min	volumetric flow rate /h^{-1}		total	into acetone
339	0.056	400	30	3.14	98.0	23.0	21.1
		400	60	0.98	96.7	22.4	19.4
		400	90	2.20	96.6	18.7	15.6
610	0.025	400	30	2.20	89.0	33.0	23.0
		400	60	3.14	97.6	23.9	22.0
		450	90	3.14	91.1	49.6	42.1
		450	120	3.14	100	40.3	40.3
		500	30	3.14	84.6	47.3	33.0
		450	60	3.14	100	12.0	11.9
610	3.13	400	30	3.14	100	20.0	20.0
		450	60	3.14	96.7	38.6	37.7
See [a]	see [a]	400	30	3.41	97.7	10.3	5.3

[a] The original sample non-treated with the volcanic gas.

of 2% Cu + 0.5% Re/sibunit is probably due to formation, in the former case, of rhenium structures outside the active centres.

Thus, 2% copper/sibunit catalysts containing 0.25% – 0.5% of rhenium selectively dehydrogenate isopropyl alcohol into acetone. Glow discharge plasma treatment of Cu/sibunit catalysts in oxygen decreases the yield of acetone, while similar treatment of Cu – Re catalysts increases it. The activity of catalysts can be increased manifold by plasmochemical treatment followed by a series of catalytic conversions of isopropyl alcohol and, finally, reduction with hydrogen.

4. Catalytic properties of natural volcanic rock from the Isle of Iturup

High concentrations of compounds containing rhenium, copper and other metals were found in the gases leaking from fumaroles (small holes and clefts through which eruptive gas emerges from the Earth's interior) of the volcano Kudryavy (the Isle of Iturup in the Kuriles).[112 – 114] Volcanic rock represents a solid silicate mass with ingrained sulfide sublimate crystals of pyrite (FeS_2), galenite (PbS) and rhenium sulfide (ReS_2). Sulfide sublimates form small (as a rule, less than 40 μm) isolated excretions on the boundaries of volcanic rock grains and in the pores of other minerals. Volcanic rock contains the following metals (mass %): Re (0.005), Cu (0.005), Ag (0.0002), Zn (0.070), Cd (0.040), Ga (0.0015), In (0.020), Tl (0.0004), Co (0.0005), Ni (0.003), Ge (0.001), Sn (0.030), Pb (0.020), As (0.010), Sb (0.005), Bi (0.030), V (0.015), Mo (0.004). Rock samples manifest high dehydrogenating activity, although the content of metal sulfides (including rhenium sulfide) is an order of magnitude lower than in ordinary dehydrogenation catalysts.[115]

Synthetic samples prepared by passage of volcanic gas through quartz tubes filled with a support for 14 – 17-days manifested catalytic activity in the dehydrogenation and dehydration of isopropyl alcohol. The samples were prepared on zeolite, alumina and sibunit. On zeolite and on γ-Al_2O_3, the dehydration of isopropyl alcohol was complete at 400 °C and at 300 °C, respectively; no dehydrogenation was observed on these catalysts. On sibunit non-treated with volcanic gases, both dehydrogenation and dehydration took place at 400°C, the total degree of isopropyl alcohol conversion being ~10%. The catalytic properties of sibunit samples are summarised in Table 8. The major contribution to the dehydrogenating activity of volcanic rock samples and artificial samples is made by magnesium, molybdenum and rhenium sulfides.

Rhenium and other rare elements of volcanic gas are best adsorbed on zeolite. A method for isolation of rhenium from zeolite is developed, which can be useful for the design of novel efficient catalysts for different organic chemical and petrochemical processes.[74, 115 – 117]

IV. Conclusion

The data presented above suggest high potential of modern carbon materials having globular and fibrous-tubular structure and carbon – carbon composite materials (*e.g.*, sibunit) as supports for catalysts. The use of metal-containing catalysts based on sibunit significantly increases the efficiency of formation of methyl formate, acetaldehyde and acetone by dehydrogenation of the corresponding aliphatic alcohols. Catalysts have been developed that enable significant increase in the yields of target products despite the lower (by an order of magnitude) content of copper in comparison with commercial copper-containing oxide catalysts used for dehydrogenation of alcohols. Rhenium-sibunit catalysts manifest high activity in the dehydrogenation of isopropyl alcohol. Bimetallic catalysts Re – Pd, Re – Ni and Re – Cu on sibunit are much more stable than monometallic systems. Substitution of sibunit for the activated carbon as a support makes it possible to reduce rhenium content from 30% to 1% – 2% without any loss of catalytic activity in the dehydrogenation of isopropyl alcohol. The activity of the catalyst can also be increased using glow discharge plasma treatment in oxygen. The excretions from the volcano Kudryavy (Isle of Iturup, Archipelago Kurile Islands) contain oxides of Si, Al, Fe, *etc.*, and some metal sulfides (including Re and Cu sulfides) and manifests dehydrating and dehydrogenating properties in the conversion of isopropyl alcohol. Synthetic samples prepared by condensation of high-temperature volcanic gases on sibunit manifest only dehydrogenating activity. The excretions from the volcano Kudryavy can be regarded as a source of rhenium (in the form of ReS_2) for novel efficient catalysts.

Development of novel metal-containing catalysts for dehydrogenation of aliphatic alcohols in which sibunit is used as a support instead of metal oxides is a basis for the design of efficient catalytic procedures for the synthesis of valuable organic intermediates alternative to the existing techniques. Taking into account the growing tendency towards a departure from the use of crude oil, the use of lower aliphatic alcohols as a raw material seems to be a promising trend in chemical industry.

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