Russian Chemical Bulletin, International Edition, Vol. 54, No. 10, pp. 2247—2258, October, 2005

Reviews

Rhenium alkoxides

P. A. Shcheglov★ *and D. V. Drobot*

M. V. Lomonosov Moscow State Academy of Fine Chemical Technology,
86 prosp. Vernadskogo, 119571 Moscow, Russian Federation.
E-mail: P.Shcheglov@mtu-net.ru; P.Shcheglov@mail.ru; dvdrobot@mail.ru

The data on synthesis of individual and heterometallic alkoxide and oxoalkoxide derivatives of rhenium are summarized. Their structures are considered, characteristic features and peculiarities of the structures are analyzed. Data on the thermal decomposition of rhenium alkoxides and its application for the preparation of rhenium-based metallic and oxide materials are given.

Key words: rhenium, alkoxides, oxoalkoxides, synthesis, structure, thermal decomposition, materials.

Introduction

The principal application of rhenium is the production of structural alloys with various refractory metals (in particular, with molybdenum, tungsten, niobium, and tantalum), which possess unique mechanical characteristics and stability against high temperatures and corrosive media. They have been recognized as the materials of choice for the manufacture of jet-propulsion engines, gas turbines, and critical parts in the precision mechanical engineering, nuclear engineering, aircraft industry, and high-vacuum, electric, and electronic technology. Catalysis is one more important application of rhenium and its compounds.[1—3]

Traditional methods for the production of rhenium alloys with other refractory metals (powder metallurgy and electron-beam, induction, and electric-arc melting) suffer from considerable drawbacks. The most critical are high process temperatures (>2000 °C) and specific energy expenditures, impossibility of controlling the sample microstructure, and the difficulty of homogeneous introduction of doping components.[4] The substantial difference between the saturated vapor pressure above rhenium oxides and other refractory metal oxides and incongruent sublimation of lower rhenium oxides hamper the production of specimens with a required set of properties (microstructure, high degree of phase and chemical homogeneity) in the production of oxide materials by the traditional solid-phase synthesis. This determines the topicality of the research aimed at development of new synthetic routes to rhenium-containing metallic and oxide materials. One approach to the manufacture of materials with a specified set of properties is the alkoxide method, which involves hydrolytic or thermal decomposition of metal alkoxide derivatives and related oxoalkoxide derivatives.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 10, pp. 2177—2188, October, 2005.

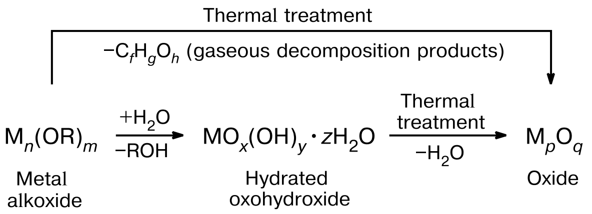
The development of the preparation methods for rhenium-containing materials (alloys with refractory metals, rhenium-based addition alloys, simple and complex oxides, *etc.*) implies the solution of the following problems: (1) search for and development of methods for the synthesis of new rhenium alkoxide and oxoalkoxide derivatives, including heterometallic ones; (2) study of their physicochemical properties including the structure in the solid state and thermal decomposition processes; (3) determination of the chemical and phase compositions of the products of thermal decomposition of rhenium alkoxide and oxoalkoxide derivatives under various conditions and the search for rational applications of the materials produced in this way.

This paper summarizes the results of studies considering the above-outlined problems.

Foundations of alkoxide method

The sol—gel method is based on the solubility of metal alkoxides in organic solvents and their ability to undergo hydrolysis; the thermolysis method is underlain by their low thermal stability (most compounds of this type decompose at 100—300 °C) (Scheme 1). The sublimation and evaporation of alkoxide derivatives have been used to produce materials by the chemical vapor deposition (CVD) technique.

Scheme 1



Depending on the nature of the metals and the composition of the gas medium (reducing, oxidative, inert), thermolysis may give metals or oxides of the metal in various oxidation states. Decomposition of appropriate compounds containing several metals may furnish materials with a complex composition and a high degree of homogeneity.

Metal alkoxides have been tested in the industrial practice for the production of ferroelectrics and related materials, dielectrics, solid electrolytes, heat-resistant materials, high-temperature superconductors, protective coatings, films with specific optical and electrophysical properties, and catalysts.[5—10] As applied to materials based on rhenium, this line of research started to develop only in the 1990s.

Synthesis of rhenium alkoxides

The first data on the synthesis of an individual rhenium alkoxide dates back to 1937.[11] Most of individual alkoxides of this metal have been synthesized and described much later.[12—31] Despite the significance of the rhenium-based materials for the modern engineering and industry and good prospects of rhenium alkoxides for the production of materials with a complex composition, it was not until the mid-1990 that data on its heterometallic derivatives were reported. These compounds have not been studied systematically as yet.

Let us consider the known methods for the preparation of rhenium alkoxides.

Ligand substitution is a general method for the preparation of alkoxides of various metals, which is also applicable to rhenium derivatives. According to this method, the initial metal compounds (amide, halide, and oxohalide complexes, or compounds with more complex composition) react with alkoxylating reagents. The following individual rhenium alkoxides have been synthesized using these reagents:[11—17,20] $Re(OEt)_3$, $Re_3(OPr^i)_9$, $Re_3(OCH_2Bu^t)_9$, $Re_2(OMe)_{10}$, $Re(OMe)_6$, $Re_2O_3(OMe)_6$, $ReO(OBu^t)_4$, $ReO_3(OMe)$, and $ReO_3(OBu^t)$.

Since metal alkoxides are highly sensitive to moisture, the syntheses are conducted without ingress of water vapor and the reactants and solvents are dehydrated prior to use.

The ethoxide $Re(OEt)_3$ is synthesized[11] by the reaction of a solution of $ReCl_3$ in ether with an ethanol solution of NaOEt.

$$ReCl_3 + 3\ NaOEt \longrightarrow Re(OEt)_3 + 3\ NaCl$$

The compounds $Re_3(OPr^i)_9$ and $Re_3(OCH_2Bu^t)_9$ are prepared[12—14] by the reaction of $Re_3(\mu\text{-}Cl)_3Cl_6(THF)_3$ with NaOR in THF (yield 31—74%).

$$Re_3(\mu\text{-}Cl)_3Cl_6(THF)_3 + 9\ NaOR \longrightarrow$$
$$\longrightarrow Re_3(OR)_9 + 9\ NaCl + 3\ THF$$

The alkoxide $Re_2(OMe)_{10}$ [15] is synthesized by the reaction of ReF_6 with $Si(OMe)_4$ in MeCN, which gives fluoroalkoxides $ReF_{6-x}(OMe)_x$, followed by the reaction of the fluoroalkoxides with $Mg(OMe)_2 \cdot 2MeOH$ in THF (yield 60%).

The compound $Re(OMe)_6$ [16] is prepared in 80% yield by the reaction of ReF_6 with excess $Si(OMe)_4$.

$$ReF_6 + 6\ Si(OMe)_4 \longrightarrow Re(OMe)_6 + 6\ SiF(OMe)_3$$

The reaction of $ReOCl_4$ with MeOH in diethyl ether in the presence of Et_3N affords $Re_2O_3(OMe)_6$ [17] (yield 74%).

$$2\ ReOCl_4 + 8\ MeOH + 8\ Et_3N \longrightarrow$$
$$\longrightarrow Re_2O_3(OMe)_6 + 8\ [HNEt_3]Cl + Me_2O$$

In another method, $Re_2O_3(OMe)_6$ was isolated in 46% yield[18,19] from the electrolyte formed upon the anodic dissolution of rhenium metal in MeOH.

The compound $ReO(OBu^t)_4$ [17] is formed in 84% yield upon the reaction of $ReOCl_4$ (a solution in diethyl ether) with $LiOBu^t$ (a solution in petroleum ether).

$$ReOCl_4 + 4\ LiOBu^t \longrightarrow ReO(OBu^t)_4 + 4\ LiCl$$

The compounds $ReO_3(OMe)$ and $ReO_3(OBu^t)$[20] are prepared by the reaction of ReO_3Cl or $ReO_3(OSiMe_3)$ (a solution in hexane) with $Me_3Si(OR)$. The yield is 74—87%.

$$ReO_3Cl + Me_3Si(OR) \longrightarrow ReO_3(OR) + Me_3SiCl$$

$$ReO_3(OSiMe_3) + Me_3Si(OR) \longrightarrow$$
$$\longrightarrow ReO_3(OR) + (Me_3Si)_2O$$

The synthesis of $ReO_3(OBu^t)$[21] was accomplished by the reaction of Re_2O_7 with Bu^tOH or $(Bu^t)_2O$ (yield 90%).

The compounds $Re_4O_{6-y}(OMe)_{12+y}$ can be prepared in several ways. For example, the complex $Re_4O_6(OMe)_{12}$ [18,19] crystallizes upon the reaction of Re_2O_7 with MeOH and on storage of solutions of $Re_2O_3(OMe)_6$ (yield >90%). Crystallization from the electrolyte formed upon anodic dissolution of rhenium metal in MeOH affords the $Re_4O_{6-y}(OMe)_{12+y}$ crystals with variable composition ($0 < y < 4$), depending on the conditions, in a yield of >70% based on Re.[18,19,22—25]

The complex $Re_4O_6(OPr^i)_{10}$ [23,24,26] crystallizes from the electrolyte produced upon anodic dissolution of rhenium metal in Pr^iOH (yield 33% based on Re).

The alkoxide $ReMoO_2(OMe)_7$ [23,27] was isolated from the electrolyte with Re : Mo = 1 : 1, obtained by anodic dissolution of rhenium metal in MeOH in the presence of $[MoO(OMe)_4]_2$ (yield 62% based on Mo).

Crystallization from the electrolyte formed upon anodic dissolution of rhenium metal in MeOH in the presence of $[MoO(OMe)_4]_2$ gave $Re_{4-x}Mo_xO_{6-y}(OMe)_{12+y}$ samples[18,19,23—25,28] ($0.10 \le x \le 2.82$, $y_{max} = 0.14$) in 22—70% yield based on Re. Crystals with $y = 0$ are formed in 60—92% yield based on Re[18,19] on refluxing Re_2O_7 with a solution of $[MoO(OMe)_4]_2$ in toluene.

The complexes $Re_{4-x}W_xO_{6-y}(OMe)_{12+y}$ [18,19,23] crystallize from a solution obtained by anodic dissolution of rhenium metal in MeOH in the presence of $[WO(OMe)_4]_2$; they are also formed when Re_2O_7 is refluxed with a toluene solution of $[WO(OMe)_4]_2$. The latter method provides more compositionally homogeneous specimens. The specimens with $x < 1$ and with $x \approx 2$ have been prepared in a yield of up to 96% based on Re.

The compounds $Nb_{4-x}Ta_xO_2(OMe)_{14}(ReO_4)_2$ and $Nb_{2-x'}Ta_{x'}(OMe)_8(ReO_4)_2$ [23,24,29—31] were formed in 30—93% yield based on Re by the reaction of Re_2O_7 with a solution of $Nb_2(OMe)_{10}$ and/or $Ta_2(OMe)_{10}$ in toluene ($0 \le x \le 4$; $0 \le x' \le 2$).

Ligand substitution processes are often complicated by the formation of relatively stable intermediate compounds, in particular, complexes containing different ligands. For example, ReF_6 reacts with $Si(OMe)_4$ to give a mixture of compounds $ReF_{6-x}(OMe)_x$, which can be converted into $Re_2(OMe)_{10}$ on treatment with $Mg(OMe)_2 \cdot 2MeOH$.[15]

The substantial drawbacks of these methods include the large number of steps, laboriousness, and the need to use complicated equipment. Most of these do not comply with the condition of versatility or process flexibility. Moreover, the preparation of the starting compounds often represents a separate problem. Therefore, many of the above-mentioned methods are applicable only under laboratory conditions.

These drawbacks determine the topicality of the development of new synthetic routes not only to individual rhenium alkoxides but also to compounds containing more than one metal. We participated in the development of two approaches to the preparation of alkoxides, namely, reactions using rhenium(VII) oxide and the electrochemical method.

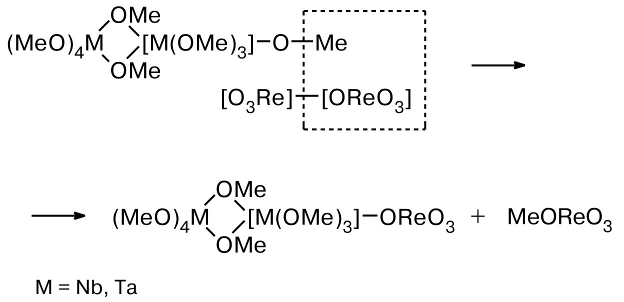
The first method involves the reactions of Re_2O_7 with alcohols, ethers, or metal alkoxides. The reaction of Re_2O_7 with alcohols or ethers was first used to prepare the individual alkoxide $ReO_3(OBu^t)$.[21] A number of studies[18,19,23,24,29—31] in which we participated have demonstrated that the reaction of Re_2O_7 with metal alkoxides (Mo, W, Nb, Ta) is an efficient way for the synthesis of heterometallic alkoxides. Thus, trimetallic rhenium-containing compounds were obtained for the first time.

An essential feature of the reactions of Re_2O_7 with alkoxides or alcohols is the formation of unstable rhenium(VII) alkoxides. Rhenium in the higher oxidation state exhibits oxidizing properties with respect to the alkoxy group, being thus reduced to a lower oxidation state (predominantly, +6). The methods based on this reaction can be subdivided into two groups: (1) processes in which the reduction of rhenium(VII) affords the target products, the alkoxides of rhenium in lower oxidation states; (2) processes in which rhenium reduction is undesirable.

The syntheses of $Re_4O_6(OMe)_{12}$, $Re_{4-x}Mo_xO_{6-y}(OMe)_{12+y}$, and $Re_{4-x}W_xO_{6-y}(OMe)_{12+y}$ can be cited as examples of the former type of processes. An individual rhenium complex was isolated from the solution obtained upon the reaction of Re_2O_7 with MeOH. The reaction of Re_2O_7 with a solution of $[MoO(OMe)_4]_2$ or $[WO(OMe)_4]_2$ in toluene affords the corresponding bimetallic complexes with variable composition.[18,19]

In the synthesis of $Nb_{4-x}Ta_xO_2(OMe)_{14}(ReO_4)_2$ and $Nb_{2-x}Ta_x(OMe)_8(ReO_4)_2$, rhenium reduction is a side reaction. When Re_2O_7 reacts with $Nb_2(OMe)_{10}$ and/or $Ta_2(OMe)_{10}$, the corresponding bi- and trimetallic derivatives are formed through the addition of rhenium as perrhenate (*i.e.*, without a change in the oxidation state) to the niobium/tantalum alkoxides. However, decomposition of the intermediate rhenium(VII) methoxide arising at an early step according to the putative mechanism shown in Scheme 2 results in the subsequent reduction of rhenium.

Scheme 2



The rate of rhenium reduction can be decreased and the yield of target products can be increased by using special thermal conditions of the process according to which the initial step of the reaction is carried out at a relatively low temperature.[24,29—31]

One more approach to the synthesis of rhenium alkoxides is based on electrochemistry (Table 1). This method consists of anodic dissolution of metals in required alcohols. A large number of alkoxides of various metals have been prepared by electrochemical synthesis (Sc, Ga, Y, La, Ln, Si, Ti, Ge, Zr, Hf, Nb, Ta, Mo, W, Fe, Co, Ni, *etc*.).[1,32,33] This method is not free from drawbacks, the most important being the use of rather high voltage (≤250 V) due to the low conductivity of the alcohol medium and low current yields (<50%) observed in some cases due to side processes. However, this technique is most convenient from the standpoint of industrial implementation.

The first data on the application of this method to rhenium derivatives were published only recently.[22,27] This method was used to prepare the following compounds: $Re_4O_6(OMe)_{12}$, $Re_4O_2(OMe)_{16}$, $Re_4O_{6-y}(OMe)_{12+y}$, $Re_4O_6(OPr^i)_{10}$, $ReMoO_2(OMe)_7$, $Re_{4-x}Mo_xO_{6-y}(OMe)_{12+y}$, and $Re_{4-x}W_xO_{6-y}(OMe)_{12+y}$.[18,19,22,24—28] In the synthesis of rhenium alkoxides, lithium chloride is used as a conductive additive. The process is carried out in water-cooled cell equipped with a reflux condenser at an electrolyte temperature of 15—50 °C. Crystallization from the electrolyte obtained by anodic dissolution of rhenium in alcohols affords individual Re compounds. Bimetallic derivatives were prepared by the successive anodic dissolution of two metals or by dissolution of rhenium in an alcohol solution containing the second metal alkoxide.

Table 1. Synthesis of rhenium alkoxides by electrochemical method

Product	Anode	Cathode	Electrolyte composition	U/V	I/A	j_a /A cm^{-2}	t/h	Yield (%)	Refs
$Re_4O_2(OMe)_{16}$	Re	Pt	MeOH, LiCl	31.4—110	0.16—0.12	0.1—0.2	36—38	91—96 (based on Re)	22, 24, 25
$Re_4O_{6-y}(OMe)_{12+y}$ (y = 0.55)	Re	Stainless steel	MeOH, LiCl	110	~1	0.56	8—36	70—90 (based on Re)	18
$Re_4O_6(OPr^i)_{10}$	Re	The same	Pr^{i}OH, LiCl	250	0.025	0.025	20.5	33 (based on Re), 48 (current)	26
$ReMoO_2(OMe)_7$	Re	Pt	MeOH, LiCl, $[MoO(OMe)_4]_2$	110	—	>0.8	10	62 (based on Mo)	27
$Re_{4-x}Mo_xO_{6-y}(OMe)_{12+y}$ ($x \le 1$)	Re	Pt	MeOH, LiCl, $[MoO(OMe)_4]_2$	29.5—60	0.18	0.07—0.10	8—16	22—70 (based on Re)	19, 28
$Re_{4-x}W_xO_{6-y}(OMe)_{12+y}$ ($x < 1$)	Re	Pt	MeOH, LiCl, $[WO(OMe)_4]_2$	30—60	—	0.07—0.10	—	70 (based on Re)	19
$Re_4O_6(OMe)_{12}$	Re	Pt	MeOH, LiCl	25	0.055	0.01—0.02	8	93 (based on Re), 79 (current)	24, 25
$Re_{4-x}Mo_xO_{6-y}(OMe)_{12}$ (x = 0.10, 2.82)	Mo, Re	Pt	MeOH, LiCl	22—28	0.01—0.045	0.01—0.04	28—116	74—90 (based on the metal), 60—63 (current)	24, 25

Note. U is voltage, I is current, j_a is current density, t is electrolysis duration. For the first six compounds, the process was conducted in an undivided cell and for the other two compounds, in a divided cell.

The cathodic reduction of rhenium compounds taking place simultaneously with the anodic dissolution of the metal is an important process influencing the composition and properties of the products formed in the electrosynthesis. The role of this process is dictated by the fact that the anodic dissolution of rhenium first gives Re^{VI} derivatives, which are reduced at the cathode to Re^{V} derivatives, and the ratio of these forms in the electrolyte determines the composition of the crystallization product. When electrolysis was carried out in methanol, by varying the process conditions, it was possible to obtain structurally related complexes $Re_4O_6(OMe)_{12}$, $Re_4O_2(OMe)_{16}$, and $Re_4O_{6-y}(OMe)_{12+y}$.[18,22,24,25] The formation of the rhenium(v) compound, $Re_4O_2(OMe)_{16}$, is facilitated by conducting the process in an undivided cell and by an increase in the cathodic current density. The variation of the electrochemical parameters of the process carried out in an undivided cell also allowed the researchers to obtain crystals with variable composition, namely, Re^{V} and Re^{VI} derivative, $Re_4O_{6-y}(OMe)_{12+y}$. The electrolysis in a divided cell (*i.e.*, under conditions suppressing the cathodic reduction of rhenium derivatives) gave the rhenium(vi) complex $Re_4O_6(OMe)_{12}$.

An important factor affecting the properties of mono- and heterometallic alkoxides is their association and condensation through the formation of bridging alkoxy or oxo ligands, respectively.

In particular, this is the mechanism of the formation of tetranuclear derivatives in the reactions involving Re_2O_7 and in electrochemical processes. The major reaction in this case is association of binuclear complexes existing in the solution; for rhenium(vi) derivatives, this should be represented as follows:

$$2\,Re_2O_3(OMe)_6 \longrightarrow Re_4O_6(OMe)_{12}.$$

The association and condensation involving rhenium(v) derivatives results in tetranuclear species $Re_4O_{6-y}(OMe)_{12+y}$ containing rhenium simultaneously in different oxidation states (+6 and +5). This type of process ensures the formation of compounds with isomorphous replacement of atoms having similar properties. When binuclear complexes of rhenium and other metals (for example, $[MoO(OMe)_4]_2$, $ReMoO_2(OMe)_7$, and $[WO(OMe)_4]_2$) are simultaneously present in a solution in different ratios, compounds $Re_{4-x}Mo_xO_{6-y}(OMe)_{12+y}$ and $Re_{4-x}W_xO_{6-y}(OMe)_{12+y}$ containing both metals are formed. The central fragment of the complexes $Nb_{4-x}Ta_xO_2(OMe)_{14}(ReO_4)_2$ composed of four niobium/tantalum atoms is formed upon condensation of the starting binuclear niobium/tantalum derivatives due to the formation of oxo bridges.

An important aspect of practical application is that the methods developed for the synthesis of bi- and trimetallic alkoxides allow one to obtain specimens with a pre-specified ratio of two metals. This opens up the way for deliberate action on the composition and properties of materials.

Structure of rhenium alkoxides

The structure of rhenium alkoxides is shown in Fig. 1.

The structure of rhenium(iii) derivatives $Re_3(OPr^i)_9$ and $Re_3(OCH_2Bu^t)_9$ is based on triangular Re_3 fragments with rhenium—rhenium bonds:[12–14] the Re atoms are located at the vertices of a regular triangle and are alternately bound by three alkoxo bridges (three Re=Re bonds).

The structure of binuclear rhenium compounds $Re_2(OMe)_{10}$, $Re_2O_3(OMe)_6$, and $ReMoO_2(OMe)_7$ is based on two metal-and-oxygen octahedra linked by sharing edges or faces. For $Re_2(OMe)_{10}$,[15] these are two ReO_6 octahedra with a common edge and the Re=Re bond, while in the case of $Re_2O_3(OMe)_6$,[17] the same two octahedra share a face (Re—Re bond). In the latter case, the structure contains two terminal and one bridging oxo ligand.

The structure of $ReMoO_2(OMe)_7$ [23,27] is composed of two distorted MO_6 octahedra (M = Re or Mo) with a common face and terminal oxo ligands (M—M bond). The distribution of the atoms of two metals among the crystal positions is random and partially ordered, the populations being 0.71(1) Re + 0.29(1) Mo and 0.29(1) Re + 0.73(1) Mo.

The structure of tetranuclear rhenium methoxy derivatives $Re_4O_{6-y}(OMe)_{12+y}$ and related bimetallic complexes is based on planar Re_4 fragment. The structure of $Re_4O_{6-y}(OMe)_{12+y}$ [18,19,22] is characterized by the ReO_6 ocrahedra sharing edges and faces; the rhenium atoms occupy the vertices of a nearly regular quadrangle and are bound alternately by oxo bridges and double alkoxy bridges. No metal—metal bonds are present. When $y = 0$, one terminal oxo ligand per rhenium atom is present, while for $y = 4$, the structure does not contain terminal oxo ligands. For $0 < y < 4$, these occur in the statistic disorder with alternative methoxy groups (*i.e.*, the crystals are built by joint packing of molecules containing different numbers of oxo and alkoxy groups).

The structure of $Re_{4-x}Mo_xO_{6-y}(OMe)_{12+y}$ [18,19] is similar to that of $Re_4O_{6-y}(OMe)_{12+y}$. Some rhenium atoms are replaced by molybdenum atoms in the isomorphous manner. The distribution of the metal atoms of two sorts among the positions is random and partially ordered (from 0.83(2) Re + 0.17(1) Mo to 0.98(2) Re + 0.02(2) Mo for the crystal with $x = 0.4$). The structure of the derivative $Re_{4-x}W_xO_{6-y}(OMe)_{12+y}$ [18,19] is similar to that of $Re_{4-x}Mo_xO_{6-y}(OMe)_{12+y}$.

In the case of the isopropoxide $Re_4O_6(OPr^i)_{10}$, the metal—oxygen core of the structure is constructed

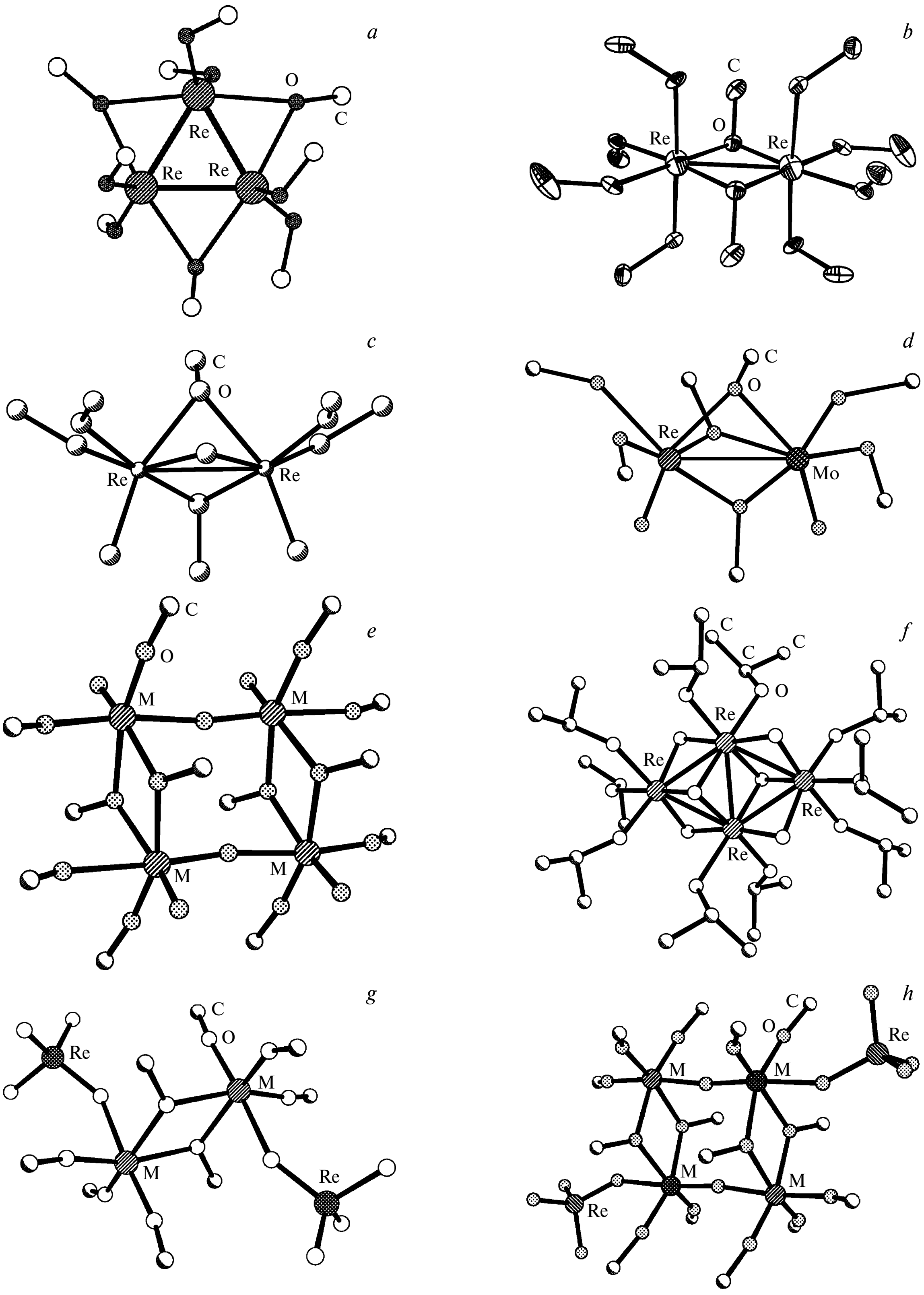


Fig. 1. Structure of rhenium alkoxides: $Re_3(OR)_9$ (R = Pr^i, CH_2Bu^t) (*a*); $Re_2(OMe)_{10}$ (*b*); $Re_2O_3(OMe)_6$ (*c*); $ReMoO_2(OMe)_7$ (*d*); $Re_4O_6(OMe)_{12}$ (M = Re), $Re_{4-x}Mo_xO_6(OMe)_{12}$ (M = Re, Mo), $Re_{4-x}W_xO_6(OMe)_{12}$ (M = Re, W) (*e*); $Re_4O_6(OPr^i)_{10}$ (*f*); $Nb_2(OMe)_8(ReO_4)_2$ (M = Nb), $Ta_2(OMe)_8(ReO_4)_2$ (M = Ta), $Nb_{2-x'}Ta_{x'}(OMe)_8(ReO_4)_2$ (M = Nb, Ta) (*g*); $Nb_4O_2(OMe)_{14}(ReO_4)_2$ (M = Nb), $Ta_4O_2(OMe)_{14}(ReO_4)_2$ (M = Ta), $Nb_{4-x}Ta_xO_2(OMe)_{14}(ReO_4)_2$ (M = Nb, Ta) (*h*).

according to the $Ti_4(OMe)_{16}$ pattern: the planar Re_4 fragment is an almost regular rhombus, and the oxo ligands function as bidentate or tridentate bridges. The structure of $Re_4O_6(OPr^i)_{10}$ [23,24,26] contains four ReO_6 octahedra connected by common edges and five Re—Re bonds with a higher order. The metal atoms are located in one plane and are connected by two μ_3- and four μ_2-oxo bridges.

Bi- and trimetallic derivatives of rhenium, niobium, and tantalum exist as two structures containing perrhenate groups. One is based on $M_2(OMe)_{10}$ (M = Nb or Ta) and the other, on fragments consisting of four metal atoms. In the complex $Nb_{4-x}Ta_xO_2(OMe)_{14}(ReO_4)_2$,[23,24,29—31] four niobium (or tantalum) atoms form a fragment resembling the structure of $Re_4O_{6-y}(OMe)_{12+y}$. This can be conceived as resulting from condensation of two $Nb_2(OMe)_{10}$ or $Ta_2(OMe)_{10}$ molecules through the formation of two oxo bridges and replacement of two alkoxy groups by perrhenate groups in the *trans*-position to the oxo bridges. Trimetallic complexes are formed due to isomorphous replacement of niobium atoms by tantalum. The distribution of the metal atoms of two sorts among the positions is statistic, partially ordered (for the crystal with $x = 2$, the populations of the position connected to the ReO_4 group are (0.70±0.05) Nb + (0.30±0.05) Ta; for the other position, (0.29±0.05) Nb + (0.71±0.05) Ta). The complex $Nb_{2-x'}Ta_{x'}(OMe)_8(ReO_4)_2$ [23,24,29—31] has two $Nb(Ta)O_6$ octahedra that share an edge. This compound can be represented as the product of replacement of two axial alkoxy groups in the $Nb_2(OMe)_{10}$ or $Ta_2(OMe)_{10}$ molecules by perrhenate groups. Trimetallic complexes are formed upon isomorphpous replacement of niobium by tantalum. The metal atoms of two sorts are statistically distributed among the positions.

The structure of rhenium oxoalkoxides is determined by the following features, which are common to transition metal alkoxides.

(1) Typical feature of the alkoxy and oxo ligands is the ability to form bonds with two or more metal atoms. This fact, together with the tendency of the central atom for increasing the coordination number and for completing the environment to an octahedron results in most of the compounds under consideration being associated or condensed to contain more than one metal atom in the structure.

(2) As the size of the hydrocarbon radical increases, the above trend is counteracted by the opposite trend for decreasing the coordination number and the degree of association (entropy factor). This feature is illustrated by the difference between the structures of related compounds $ReO_3(OMe)$ and $ReO_3(OBu^t)$: a polymeric structure with bridging methoxy ligands has been proposed for the former,[20] while the latter is monomeric.[20,21]

(3) Most of compounds under consideration contain oxo ligands apart from the alkoxide groups in the metal coordination sphere. These ligands are formed, in particular, upon hydrolysis induced by traces of water, elimination of the ether, and oxygen oxidation of alkoxides of metal in a lower oxidation state (*e.g.*, those formed upon cathodic reduction of the products resulting from the anodic dissolution of the metal during the electrochemical synthesis).

Table 2. Characteristic of the metal—metal bonds in alkoxide derivatives

Compound	r(M—M)/Å	Bond order	Refs
$Re_4O_{6-y}(OMe)_{12+y}$	3.45, 3.65	—*	18, 19, 22, 23
$Re_2O_3(OMe)_6$	2.559(1)	1	17
$ReMoO_2(OMe)_7$	2.658(2)	1	27
$Re_4O_6(OPr^i)_{10}$	2.5204(7)—2.5501(5)	>1	23, 24, 26
$Re_2(OMe)_{10}$	2.5319(7)	2	15
$Re_3(OPr^i)_9$	2.36	2	12, 13
$Re_3(OCH_2Bu^t)_9$	2.365(1)—2.372(1)	2	14

* No bond.

(4) Association or condensation of metal complexes in lower oxidation states may give metal—metal bonds (Table 2). The structural criterion for the formation of these bonds is that the metal—metal distance is comparable with or shorter than that in the structure of the corresponding metals,[34] or shorter than twice the effective metallic radius, which is 2.76 Å for Re: $r(M—M) \leq \leq 2r_m(M)$.

The compound $Re_4O_6(OPr^i)_{10}$ is of interest as regards the metal—metal bonds. In this structure, the Re—Re distances, equal to 2.5204(7)—2.5501(5) Å, are comparable with the length of a localized Re—Re bond with a higher order (see Table 2). Since two Re atoms in this complex occur in +5 oxidation state and the other two atoms, in +6 oxidation state, there are six electrons available for their binding to each other. Clusters similar to $Re_4O_6(OPr^i)_{10}$ with five virtually equal metal—metal distances have been found previously[35—37] only in a system with ten electrons (*i.e.*, two electrons per every short metal—metal distance), namely, in the oxide phase $Ba_{1.14}Mo_8O_{16}$, in which $r(Mo—Mo) = 2.578(1)—2.616(1)$ Å. A decrease in the number of electrons involved in the formation of metal—metal bonds entails distortion, resulting in a pronounced elongation of two symmetrically equivalent sides of the rhombus.[38] In the $W_4(OEt)_{16}$ molecule with eight electrons, the elongated side of the rhombus is 2.936(2) Å, the shorter side is 2.646(2) Å, and the diagonal is 2.763(1) Å.[39,40] A system with four electrons, for example, $Mo_4O_8(OPr^i)_4(Py)_4$, contains only two localized metal—metal bonds.[41]

(5) Oxo and alkoxo ligands serve as effective π-donors; this results in an increase in the M=O and M—O(R) bond order in the case of terminal ligands. The length of the single σ-bond can be estimated from the sum of the

Table 3. Parameters of the rhenium—oxygen bonds in alkoxides (distances (r) and angles (ω))

Compound	r(M—OR$_{\text{term}}$) /Å	ω(M—O—R) /deg	r(M—μ_2-OR) /Å	ω(M—μ_2-O—R) /deg	r(M—O$_{\text{term}}$)	r(M—μ-O)	Refs
					Å		
$Re_4O_6(OMe)_{12}$	1.883(7)— —1.936(7)	124.4(6)— —129.8(6)	2.046(6)— —2.189(7)	119.0(5)— —121.6(6)	1.665(8)— —1.682(7)	1.876(6)— —1.905(5) (μ_2)	18
$Re_2O_3(OMe)_6$	1.867(12)— —1.903(11)	128.5(13)— —131.3(10)	2.094(11)— —2.139(10)	124.7(11)— —126.4(10)	1.690(11), 1.703(12)	1.916(13), 1.917(13) (μ_2)	17
$Re_2(OMe)_{10}$	1.943(4)— —1.907(4)	125.6(4)— —124.9(4)	2.036(4)	—	—	—	15
$Re_4O_6(OPr^i)_{10}$	1.950(5)— —2.148(6)	—	—	—	—	1.866(6)— —1.999(5) (μ_2), 2.018(5)— 2.073(5) (μ_3)	24, 26

corresponding covalent radii.[42] The r_c(Re) + r_c(O) value is ~2.06 Å. This value resembles more closely those typical of bridging OR groups and is much greater than the observed M—O bond lengths for terminal OR groups (Table 3). An exception to this rule is $Re_4O_6(OPr^i)_{10}$, in which the M—O bonds are elongated, evidently, due to electron density redistribution between the metal—metal and metal—oxygen bonds.[24,26] The order of the corresponding bonds between the metal and terminal OR groups in transition metal alkoxides varies from 1 to 2.[42,43]

The increase in the M—O(R) bond order entails an increase in the M—O—C bond angles. The following model has been proposed to account for this phenomenon.[43,44] Without π-bonding, the oxygen atom can be described by the sp^3 state, and upon the formation of a double bond, this is the sp^2 state; in the former case, the bond angle is expected to be about 109°28´, while in the latter case, it should approach 120°. Despite the obviously conditional character of this model as applied to M—O(R) multiple bonds, it interprets qualitatively the observed great M—O—C angles for terminal alkoxy groups (see Table 3). Since the size of the M—O—C angle is markedly affected by steric (nonelectronic) factors, an unambiguous relationship between the bond angles and the bond order (length) does not always hold.

(6) M—O bond length is substantially smaller for the terminal oxo ligand than for a terminal alkoxy group. For example, in $Re_4O_6(OMe)_{12}$, these values are 1.665(8)—1.682(7) and 1.883(7)—1.936(7) Å, respectively.[18] The M—(μ_2-O) and M—(μ_3-O) bond lengths for oxo ligands are usually somewhat shorter than the distances to the alkoxy groups (exceptions to this rule are due to the strong *trans*-effect involved). In particular, the Re—(μ_2-O) bond lengths in $Re_4O_6(OMe)_{12}$ are 1.876(6)—1.905(5) and 2.046(6)—2.189(7) Å for the oxo and MeO ligands, respectively.[18]

(7) In most structures incorporating metal atoms connected by μ_2-OR groups (in particular, those containing the [M_2O_2] ring), the M—O—M angle ranges from 107 to 112°; the M—O—C angles for bridging alkoxy groups are ~120—130°, and the valence state of oxygen can be conventionally described as sp^2. Due to the formation of the M—M bond, the M—O—M angle markedly decreases. For example, in the $Re_4O_6(OMe)_{12}$ molecule containing no Re—Re bond, the Re—O—Re angles at the bridging MeO groups are 108.5(3)—110.8(3)°;[18] in the case of $Re_2O_3(OMe)_6$, containing a single Re—Re bond, these angles are 74.4(3) and 74.7(3)°.[17]

(8) In octahedral complexes, one can observe a substantial *trans*-effect, which is most pronounced in transition metal complexes containing multiple metal—ligand bonds.[45—47] In the complexes in question, this is manifested in the fact that shortening of the M—O bond induces elongation of the bond in the *trans*-position. This effect brings about the following structural feature. If the *trans*-position relative to the terminal oxo ligand is occupied by a bridging OR ligand, then the longer M—(μ-OR) bond of the asymmetric bridge is located in this position. For example, in the $Re_4O_6(OMe)_{12}$ structure, the M—(μ-OR) bond lengths in the *trans*-position to the terminal oxo ligands amount to 2.140(6)—2.189(7) Å, while those in the *trans*-position to the terminal OMe groups are 2.046(6)—2.074(6) Å.[18]

(9) Isomorphous replacement of atoms with similar properties affords crystalline complexes with variable composition in which the ratio of the two metals can be varied over a broad range.

For example, the replacement of rhenium by molybdenum or tungsten gives rise to rhenium-based tetranuclear complexes $Re_{4-x}Mo_xO_{6-y}(OMe)_{12+y}$ ($0 \le x \le 2.82$) and $Re_{4-x}W_xO_{6-y}(OMe)_{12+y}$ ($0 \le x \le 2$).[18,19,24,28] Since tetranuclear structure is not encountered for individual molybdenum or tungsten derivatives, in this case, the isomorphous replacement of rhenium by these metals is possible only in a limited range of compositions.

In the case of $Nb_{4-x}Ta_xO_2(OMe)_{14}(ReO_4)_2$ and $Nb_{2-x'}Ta_{x'}(OMe)_8(ReO_4)_2$, the Nb : Ta ratio susceptible for isomorphous replacement of niobium by tantalum is boundless. The bimetallic niobium/rhenium ($x = 0, x' = 0$) and tantalum/rhenium complexes ($x = 4, x' = 2$) as well as trimetallic complexes with a variable composition ($0 < x < 4, 0 < x' < 2$)[23,24,29,30] have been prepared.

An interesting feature of isomorphous replacement in the complex $Nb_{4-x}Ta_xO_2(OMe)_{14}(ReO_4)_2$ is the fact that, due to the differences in the environment of symmetrically independent crystallographic positions, the replacement of niobium atoms by tantalum is nonuniform: the position connected to the perrhenate group is occupied predominantly by niobium atoms, while the other, by tantalum atoms.[23,24,30] For a crystal with Nb : Ta = 1 : 1, the populations of the former position are 70% Nb + 30% Ta; this position is characterized by enhanced π-interaction with oxygen atoms, which is manifested in the pronounced shortening of the M—(μ_2-O) bond; therefore, it is thermodynamically favorable for the lighter Nb atom. For the heavier Ta atom, the second position characterized by predominant σ-bonding to oxygen (with elongated M—(μ_2-O) bond) is thermodynamically more favorable. The populations of this position are 30% Nb + 70% Ta. This specific feature of replacement is responsible for the nonmonotonic pattern of variation of the crystal properties (in particular, thermal stability) upon the change in the composition.

Applications of rhenium alkoxides

Studies of the thermal properties of rhenium alkoxides have shown that they decompose at relatively low temperatures (100—300 °C) yielding either oxide or metal phases, depending on the process conditions (Scheme 3, Table 4).[23—25,29]

Decomposition of individual rhenium alkoxides $Re_4O_6(OPr^i)_{10}$, $Re_4O_2(OMe)_{16}$, $Re_{4-x}O_{6-y}(OMe)_{12+y}$, and $Re_4O_6(OMe)_{12}$ in air or in an inert atmosphere affords rhenium oxides, ReO_3 or monoclinic ReO_2, as highly dispersed powders with an average particle size of less than 30—50 nm; similar decomposition of the bimetallic derivatives $Re_{4-x}Mo_xO_{6-y}(OMe)_{12+y}$ and $Re_{4-x}W_xO_{6-y}(OMe)_{12+y}$ yields single-phase specimens of rhenium/molybdenum $(Re,Mo)O_2$ or rhenium/tungsten $(Re,W)O_3$ solid solutions. By decomposition of bi- and trimetallic rhenium, niobium, and tantalum derivatives, complex oxide phases of the Re—Ta(Nb)—O systems based on a block type structure derived from L-Ta_2O_5 were prepared for the first time (the traditional synthesis of these phases is impossible).

Decomposition of alkoxide in a hydrogen atmosphere allows one to prepare nano-sized powders of rhenium metal (from individual derivatives) or rhenium alloys (from the bimetallic complexes $Re_{4-x}Mo_xO_{6-y}(OMe)_{12+y}$, and $Re_{4-x}W_xO_{6-y}(OMe)_{12+y}$).

Rhenium alkoxides proved to be promising starting materials for the development of catalysts by insertion into a zeolite matrix. In particular, mono- and bimetallic rhenium alkoxides $Re_2O_3(OMe)_6$ and $ReMoO_2(OMe)_7$ have been used to prepare new-generation catalysts by insertion of these compounds into a NaY zeolite matrix followed by their thermal decomposition. A substantial

Scheme 3

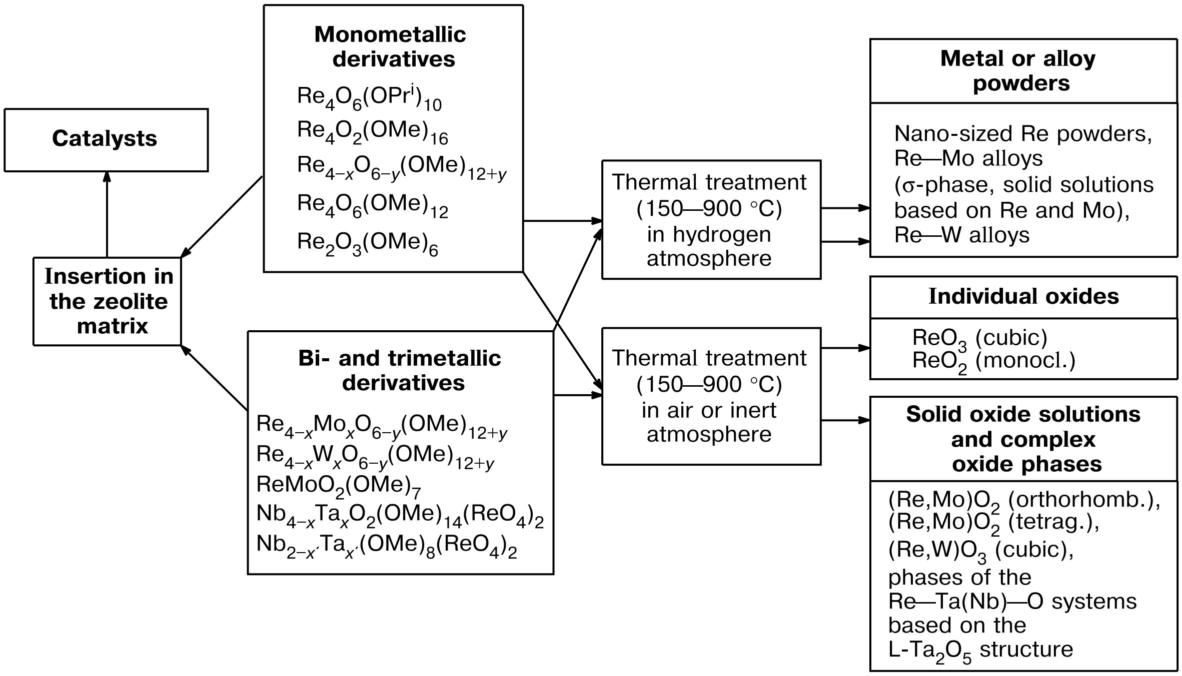


Table 4. Examples of the synthesis of metallic and oxide materials based on rhenium

Starting complexes	Decomposition conditions	Products		Refs
		Phase composition	Particle size/nm	
$Re_4O_{6-y}(OMe)_{12+y}$	150—400 °C, in air	Cubic ReO_3	<30	23—25
$Re_4O_{6-y}(OMe)_{12+y}$	120—400 °C, in a vacuum	Monoclinic ReO_2 phase	<50	23—25
$Re_4O_6(OPr^i)_{10}$	400 °C, in air	ReO_3	—	23, 24
$ReMoO_2(OMe)_7$	250 °C, 2 h, in air; then 800 °C, 3 h, in H_2	Re—Mo alloy (σ-phase)	$(3-5) \cdot 10^3$	23
$ReMoO_2(OMe)_7$	400 °C, 1 h, in H_2	Re—Mo alloy (σ-phase)	10—50; $5 \cdot 10^4$*	23
$Re_{3.90}Mo_{0.10}O_6(OMe)_{12}$	500 °C, 1 h, in H_2	Re—Mo alloy (Re-based solid solution with the HCP structure)	<50	24, 25
$Re_{1.18}Mo_{2.82}O_6(OMe)_{12}$	500 °C, 1 h, in H_2	Re—Mo alloy (Mo-based solid solution with the BCC structure)	<50	24, 25
$Re_{4-x}W_xO_{6-y}(OMe)_{12+y}$	200—240 °C, in air	$(Re,W)O_3$ phase with the ReO_3 type structure	>10	23
$Nb_4O_2(OMe)_{14}(ReO_4)_2$	900 °C, heating 10 °C min^{-1}, in nitrogen	$Re_2Nb_4O_{12\pm\delta}$ phase with the $L\text{-}Ta_2O_5$ structure	—	23, 24, 29
$Ta_4O_2(OMe)_{14}(ReO_4)_2$	900 °C, heating 10 °C min^{-1}, in nitrogen	$Re_2Ta_4O_{12\pm\delta}$ phase with the $L\text{-}Ta_2O_5$ structure	—	23, 24, 29
$Nb_{4-x}Ta_xO_2(OMe)_{14}(ReO_4)_2$	160—170 °C, 3.6—8.3 h, in a vacuum	$Re_2(Nb_{4-x}Ta_x)O_{12\pm\delta}$ phase with the $L\text{-}Ta_2O_5$ structure	—	24
$Ta_4O_2(OMe)_{14}(ReO_4)_2$	900 °C, heating 10 °C min^{-1}, in air	Rhenium-doped (2 at.%) $L\text{-}Ta_2O_5$ phase	—	23, 24, 29
$Nb_2(OMe)_8(ReO_4)_2$	900 °C, heating 10 °C min^{-1}, in nitrogen	$Re_2Nb_2O_{12\pm\delta}$ phase with the $L\text{-}Ta_2O_5$ structure	—	24, 29

* Aggregates.

advantage of this approach is the possibility of preserving the high-dispersed state *via* stabilization of clusters, including those containing two different metals, in the zeolite cavities. Decomposition of the alkoxides inserted in the matrix affords metal or oxide nanoclusters whose mobility is restricted inside the pores. In the case of bimetallic systems, it is possible to obtain, directly in the pores, highly dispersed particles uniform not only in their size but also in their composition, which is pre-specified by the ratio of the metals in the initial compound. A study of the catalytic properties of the materials obtained by this method showed a substantial positive synergistic effect for the product of insertion of the bimetallic complex compared with the materials based on individual rhenium and molybdenum compounds.[48]

The above-described processes of thermal decomposition underlie the alkoxide method of the production of rhenium-based materials and allow one to produce materials with reproducible set of specified properties. The main features of these processes are as follows.

First, low decomposition temperature of these compounds allows the preparation of finely dispersed (in particular, with a particle size of several nm) oxide or metallic materials. During thermal treatment, particles are enlarged; this provides the possibility of controlling the product microstructure by varying the conditions and of obtaining specimens with a particle size from several nanometers to several micrometers.

Second, in the case of bi- and trimetallic systems, using the alkoxide method, one can retain the specified composition (metal ratio) and the high degree of homogeneity throughout the whole process. By decomposition of bi- and trimetallic complexes with the metal ratio varying over a broad range, one can produce materials with a pre-specified composition.

Third, the low decomposition temperatures of alkoxides in combination with a high degree of chemical homogeneity markedly reduces the temperature and duration of the production of oxide and metallic materials. Specifically, this approach essentially decreases the energy consumption in particular stages of the synthesis of refractory metal-based alloys compared to traditional methods. Single-phase rhenium-based alloys can be obtained at a temperature more than 2000 °C lower than the rhenium melting point.

Conclusion

The traditional method for alkoxide synthesis is based on ligand substitution reactions. This method was used to prepare individual rhenium alkoxides. Alternative synthetic routes include reactions of rhenium(VII) oxide with alcohols and alkoxides of other metals and anodic dissolution of metals in alcohols. These methods made it possible to synthesize both known and new monometallic rhenium alkoxides and also to synthesize for the first time bi- and trimetallic rhenium, molybdenum, tungsten, niobium, and tantalum complexes. The isomorphous replacement of metals in bi- and trimetallic derivatives opens up the way to the alkoxide derivatives with variable composition, in which the ratio of the metals can be varied over a broad range.

An important structural feature of alkoxides and oxoalkoxides is the presence of alkoxy and oxo bridges, which ensure the formation of polynuclear (in particular, heterometallic) compounds.

Alkoxides possess low thermal stability. Their decomposition at temperatures above 100—300 °C leads, depending on the conditions, to individual oxides, solid solutions, complex oxide phases, and metal and alloy powders. The variation of temperature conditions of the decomposition allows one to produce both nano-sized and coarsely crystalline materials. Decomposition of heterometallic compounds with variable composition affords materials with a high degree of homogeneity and a prespecified atomic ratio of two metals.

Development of synthetic routes to and studies of the properties of rhenium alkoxides demonstrates the good prospects of the application of these compounds for the production of oxide and metallic materials based on rhenium.

The authors are grateful to V. G. Kessler and G. A. Seisenbaeva for collaboration.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 03-03-32750).

References

1. R. H. Tuffias, R. B. Kaplan, and M. A. Appel, Proc. Int. Symp. "*Rhenium and Rhenium Alloys*" *(Orlando, Florida (USA), 10—13 February, 1997)*, Ed. B. D. Bryskin, Publ. TMS, 275.
2. R. W. Broomfield, D. A. Ford, H. K. Bhangu, M. C. Thomas, D. J. Frasier, P. S. Burkholder, K. Harris, G. L. Erickson, and J. B. Wahl, *Proc. Int. Symp. "Rhenium and Rhenium Alloys" (Orlando, Florida (USA), 10—13 February, 1997)*, Ed. B. D. Bryskin, Publ. TMS, 731.
3. M. A. Ryashentseva and Kh. M. Minachev, *Renii i ego soedineniya v geterogennom katalize* [*Rhenium and its Compounds in Heterogeneous Catalysis*], Nauka, Moscow, 1983, 248 pp. (in Russian).
4. *Tugoplavkie metally i splavy* [*Refractory Metals and Alloys*], Eds G. S. Burkhanov and Yu. V. Efimov, Metallurgiya, Moscow, 1986, 352 pp. (in Russian).
5. N. Ya. Turova, E. P. Turevskaya, V. G. Kessler, and M. I. Yanovskaya, *The Chemistry of Metal Alkoxides*, Kluwer Acad. Publ., Boston—Dordrecht—London, 2002, 568 pp.
6. N. Ya. Turova and M. I. Yanovskaya, *Izv. Akad. Nauk SSSR. Neorgan. Materialy*, 1983, **19**, 693 [*Inorg. Mater.*, 1983, **19** (Engl. Transl.)].
7. E. P. Turevskaya, M. I. Yanovskaya, and N. Ya. Turova, *Neorgan. Materialy*, 2000, **36**, 330 [*Inorg. Mater.*, 2000, **36**, 260 (Engl. Transl.)].
8. *Sol-Gel Technology for Thin Films, Fibers, Preforms, Electronics, and Specialty Shapes*, Ed. L. C. Klein, Noyes Publ., Park Ridge, New Jersey (USA), 1988, 407 pp.
9. Yu. M. Rodionov, E. M. Slyusarenko, and V. V. Lunin, *Usp. Khim.*, 1996, **65**, 865 [*Russ. Chem. Rev.*, 1996, **65**, 797 (Engl. Transl.)].
10. M. Veith, *J. Chem. Soc., Dalton Trans.*, 2002, 2405.
11. J. G. F. Druce, *J. Chem. Soc.*, 1937, 1407.
12. D. M. Hoffman, D. Lappas, and D. A. Wierda, *J. Am. Chem. Soc.*, 1989, **111**, 1531.
13. D. M. Hoffman, D. Lappas, and D. A. Wierda, *J. Am. Chem. Soc.*, 1993, **115**, 10538.
14. W.-W. Zhuang, B. E. Truitt, and D. M. Hoffman, *Inorg. Chem.*, 1997, **36**, 3330.
15. J. C. Bryan, D. R. Wheeler, D. L. Clark, J. C. Huffman, and A. P. Sattelberger, *J. Am. Chem. Soc.*, 1991, **113**, 3184.
16. E. Jacob, *Angew. Chem.*, 1982, **94**, 146.
17. P. G. Edwards, G. Wilkinson, M. B. Hursthouse, and K. M. Abdul Malik, *J. Chem. Soc., Dalton Trans.*, 1980, 2467.
18. G. A. Seisenbaeva, A. V. Shevelkov, J. Tegenfeldt, L. Kloo, D. V. Drobot, and V. G. Kessler, *J. Chem. Soc., Dalton Trans.*, 2001, 2762.
19. G. A. Seisenbaeva, V. G. Kessler, and A. V. Shevelkov, *J. Sol-Gel Sci. Technol.*, 2001, **19**, 285.
20. P. Edwards and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1984, 2695.
21. C. Ringel and G. Boden, *Z. Anorg. Allg. Chem.*, 1972, **393**, 65.
22. V. G. Kessler, A. V. Shevel´kov, G. V. Khvorykh, G. A. Seisenbaeva, N. Ya. Turova, and D. V. Drobot, *Zh. Neorgan. Khim.*, 1995, **40**, 1477 [*Russ. J. Inorg. Chem.*, 1995, **40** (Engl. Transl.)].
23. D. V. Drobot, P. A. Shcheglov, G. A. Seisenbaeva, and V. G. Kessler, *Izv. Vuzov. Tsvetnaya metallurgiya* [*Higher School Bull. Nonferrous Metallurgy*], 2002, **6**, 32 (in Russian).
24. P. A. Shcheglov, Ph.D. Thesis, Moscow Institute of Fine Chemical Technology, Moscow, 2002, 198 pp. (in Russian).
25. P. A. Shcheglov, D. V. Drobot, Yu. V. Syrov, and A. S. Mal´tseva, *Neorgan Materialy*, 2004, **40**, 220 [*Inorg. Mater.*, 2004, **40**, 176 (Engl. Transl.)].
26. P. A. Shcheglov, G. A. Seisenbaeva, D. V. Drobot, and V. G. Kessler, *Inorg. Chem. Commun.*, 2001, **4**, 227.
27. V. G. Kessler, G. A. Seisenbaeva, A. V. Shevelkov, and G. V. Khvorykh, *J. Chem. Soc., Chem. Commun.*, 1995, 1779.
28. G. A. Seisenbaeva, A. V. Shevel´kov, V. G. Kessler, N. N. Belanishvili, and D. V. Drobot, *Zh. Neorgan. Khim.*, 1999, **44**, 383 [*Russ. J. Inorg. Chem.*, 1999, **44**, 332 (Engl. Transl.)].
29. P. A. Shcheglov, D. V. Drobot, G. A. Seisenbaeva, S. Gohil, and V. G. Kessler, *Chem. Mater.*, 2002, **14**, 2378.
30. P. A. Shcheglov, G. A. Seisenbaeva, S. Gohil, D. V. Drobot, and V. G. Kessler, *Polyhedron*, 2002, **21**, 2317.
31. Pat. RF 2227788; *Byul. Izobret.*, 2004, 12 (in Russian).
32. V. A. Shreider, E. P. Turevskaya, N. I. Kozlova, and N. Ya. Turova, *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1981, 1687 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1981, **30** (Engl. Transl.)].

33. V. A. Shreider, E. P. Turevskaya, N. I. Koslova, and N. Ya. Turova, *Inorg. Chim. Acta*, 1981, **53**, L73.
34. F. A. Cotton and R. A. Walton, *Multiple Bonds Between Metal Atoms*, J. Wiley and Sons, New York—Chichester, 1982, 466 pp.
35. R. E. McCarley, T. R. Ryan, and C. C. Torardi, *Am. Chem. Soc., Symp. Ser.*, 1981, **155**, 41.
36. R. E. McCarley, *Am. Chem. Soc., Symp. Ser.*, 1983, **211**, 273.
37. C. C. Torardi and R. E. McCarley, *J. Solid State Chem.*, 1981, **37**, 393.
38. F. A. Cotton and A. Fang, *J. Am. Chem. Soc.*, 1982, **104**, 113.
39. M. H. Chisholm, J. C. Huffman, and J. Leonelli, *J. Chem. Soc., Chem. Commun.*, 1981, 270.
40. M. H. Chisholm, J. C. Huffman, C. C. Kirkpatrick, J. Leonelli, and K. Folting, *J. Am. Chem. Soc.*, 1981, **103**, 6093.
41. M. H. Chisholm, K. Folting, J. C. Huffman, and C. C. Kirkpatrick, *Inorg. Chem.*, 1984, **23**, 1021.
42. M. H. Chisholm, *Polyhedron*, 1983, **2**, 681.
43. A. A. Pinkerton, D. Schwarzenbach, L. G. Hubert-Pfalzgraf, and J. G. Riess, *Inorg. Chem.*, 1976, **15**, 1196.
44. D. Bradley, *Usp. Khim.*, 1978, **47**, 638 [*Russ. Chem. Rev.*, 1978, **47** (Engl. Transl.)].
45. E. M. Shustorovich, *Zh. Struktur. Khim.*, 1974, **15**, 977 [*J. Struct. Chem. (USSR)*, 1974, **15** (Engl. Transl.)].
46. E. M. Shustorovich, M. A. Porai-Koshits, and Yu. A. Buslaev, *Coord. Chem. Rev.*, 1975, **17**, 1.
47. E. M. Shustorovich and Yu. A. Buslaev, *Koordinats. Khim.*, 1975, **1**, 740 [*Sov. J. Coord. Chem.*, 1975, **1** (Engl. Transl.)].
48. A. L. Kustov, V. G. Kessler, B. V. Romanovsky, G. A. Seisenbaeva, D. V. Drobot, and P. A. Shcheglov, *J. Mol. Catal. A*, 2004, **216**, 101.

Received January 14, 2005;
in revised form June 15, 2005