Substitution features in the isomorphous replacement series for metal-organic compounds $(Nb_xTa_{1-x})_4O_2(OMe)_{14}(ReO_4)_2$, $x = 0.7$, 0.5, 0.3—Single-source precursors of complex oxides with organized porosity

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ABSTRACT

Trimetallic oxoalkoxide complexes $(Nb_{0.7}Ta_{0.3})_4O_2(OMe)_{14}(ReO_4)_2$ (**I**), $(Nb_{0.3}Ta_{0.7})_4O_2(OMe)_{14}(ReO_4)_2$ (**II**) and $(Nb_{0.5}Ta_{0.5})_4O_2(OMe)_{14}(ReO_4)_2$ (**III**) were obtained by the interaction of rhenium heptoxide (VII) Re_2O_7 with niobium and tantalum alkoxides $M_2(OMe)_{10}$ (M = Nb, Ta) in toluene. The centrosymmetric molecules (**I**)–(**III**) can be considered as a product of condensation of two $M_2(OMe)_9(OReO_3)$ molecules with the formation of two oxo-bridges. The specific feature of the structure is the uneven distribution of metal atoms in the crystallographic positions, where one symmetry-independent position, connected via μ-O with a perrhenate ReO_4^- group, is predominantly occupied by niobium atoms, while the other one connected via alkoxide groups has a higher tantalum content. The distribution of Nb and Ta in the structure is truly even only for compound **III**. The niobium and tantalum content is varied to a different extent for **I** (less) and for **II** (more), which is apparently due to small differences in the sizes of these two cations, resulting in preferences for packing of different molecules in the structures. Thermal decomposition of $(Nb_{1-x}Ta_x)_4O_2(OMe)_{14}(ReO_4)_2$ (x = 0.3, 0.5, 0.7) in air leads to the formation of crystalline species of solid solutions based on tantalum and niobium oxides displaying semi-ordered pores with the size of $100-250$ nm. In the dry nitrogen atmosphere, the decomposition leads to the amorphous complex oxides containing rhenium, niobium and tantalum.

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1. Introduction

Mixed-metal oxoalkoxide complexes are attractive potential precursors of complex oxide and alloy materials [1]. Rhenium metal has found broad application as a component of catalysts for alkylation in the organic synthesis and for industrial cracking processes [2]. The rhenium(VI) oxide, ReO_3, is used as a heterogeneous catalyst in metathesis reactions [3,4]. The biggest limitation of this catalyst is that ReO_3 can easily be reduced to inactive ReO_2 and all attempts to oxidize it to regenerate ReO_3 result in the loss of volatile Re_2O_7. Hence, it is necessary to create conditions, permitting continuous functioning of these catalysts. Earlier we have shown in our work that incorporating ReO_3 into the NaY zeolite matrix can produce nanocomposites, where this oxide is more stable to the reducing conditions [5,6]. Application of niobium and tantalum oxides as matrices in the in situ synthesis of rhenium oxide-based nanocomposites can offer a cost-efficient approach to materials with enhanced stability

to reduction. In the literature, there are recent works on rhenium-based catalysts for the metathesis of olefins CH_3ReO_3/Nb_2O_5 [3,4], which showed high catalytic activity for metathesis of 1-pentene [4]. Mixed oxides of general formula $(Nb_{1-x}Ta_x)_2O_5$ are mainly used as photocatalysts for water decomposition [7,8], catalytic reactions [9], biomaterials [10], nanoporous materials for different applications [10] and materials for optoelectronics [10].

The traditional method of obtaining the multicomponent oxides is usually via standard procedures such as the conventional solid-state reactions between binary oxides. This method was successfully implemented for the preparation of $(Nb_{1-x}Ta_x)_2O_5$ [11], $Bi_3Fe_{0.5}Nb_{1.5}O_9$, [12] and many other refractory materials. Unfortunately, the ceramic method requires heat treatment at rather high temperatures and leads to poorly homogeneous materials consisting of larger particles [13].

There are some alternative methods for obtaining multicomponent Nb or Ta oxides. For instance, mixed oxides $SrNb_2O_6$ and $SrTa_2O_6$ were obtained via thoroughly mixing Nb or Ta hydroxides and commercially purchased strontium hydroxide and prolonged heating at a relatively low temperature (<400 °C). The main limitation of this process is that it is multistep and applies

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the HF acid in the technique applied for the preparation of Nb and Ta hydroxides [14]. Other alternative routes such as sol–gel synthesis based on metal-organic precursors, and the citrate method are often considered. Even the citrate method has such limitations as being a multistep and time-consuming procedure [15]. For instance, $(Nb_{1-x}Ta_x)_2O_5$ solid solutions have been obtained by a neutral templating sol–gel method, using the pentachlorides as metal precursors and a block copolymer as the template. According to this method, it is possible to obtain the mesopours oxide $(NbTa)_2O_5$, which, however, contains chloride impurities [16,17]. The mesoporous mixed oxides based on Nb and Ta or Mo can also be obtained by the thermal decomposition of organic–inorganic precursors with the required ratio of metals in the molecular structure. The syntheses of precursors are complicated and involved several steps, hence providing relatively low yields of the final products [18,19].

Bi- and trimetallic alkoxides complexes can also be used, as precursors of complex oxides that contain required metals at the given ratios. The most generally applied approach in this case is the metal-organic sol–gel synthesis, where nanoparticles of complex oxides (Micelles Templated by Self-Assembly of Ligands, MTSALs [20]) are formed in organic media through the hydrolytic decomposition of precursors. Poor solubility of all the hydroxide components, resulting from hydrolysis in the given media, insures conservation of the stoichiometry. The thermodynamic stability of the target complex oxide phase then enables its formation under milder conditions. The application of a complex precursor in this case facilitates the introduction of proper stoichiometry but is very often not mandatory. Thus, the trimetallic precursors, whose existence was postulated in the alkoxide systems successfully applied for the synthesis of Bi–Sr–Nb perovskite oxide [21] and Ba–Zr–Ti-oxide phases [22,23], were shown in more close studies [24,25] not to be individual compounds, but mixtures of bimetallic species. The application of individual trimetallic precursors appears, in contrast, to be especially attractive in the synthesis of complex oxides via metal-organic chemical vapor deposition and the metal-organic decomposition route, where different thermal stability and volatility of homometallic reactants can be a problem.

Trimetallic complexes based on rhenium, niobium and tantalum of the following formula $(Nb_{0.5}Ta_{0.5})_4O_2(OMe)_{14}(ReO_4)_2$ and $(Nb_{0.5}Ta_{0.5})_2(OMe)_8(ReO_4)_2$ with the Nb:Ta ratio 1:1 have been described earlier in [26]. The synthesis of these complexes was based on the interaction between Re_2O_7 and bimetallic alkoxide of niobium and tantalum, $NbTa(OMe)_{10}$ [27]. It is possible to obtain these compounds due to isomorphous substitution for niobium atoms by tantalum ones, because the ionic radii of Nb^v and Ta^v for coordination number 6 are almost the same and equal to 0.64 Å [28].

The purpose of the present work was to investigate the possibility to obtain new trimetallic oxoalkoxocomplexes on the basis of Re, Nb and Ta in a wider range of compositions and test their applicability for the synthesis of porous complex oxide materials.

2. Experimental

All the preparative procedures were carried out in dry nitrogen atmosphere using a dry box. Toluene was dehydrated by refluxing over $LiAlH_4$ with subsequent distillation. Methanol was purified by distillation over magnesium methoxide.

IR spectra of Nujol and hexachlorobutadiene (HCB) mulls were obtained with a Perkin Elmer FT-IR spectrometer Spectrum-100. Mass-spectra were recorded using a JEOL JMS-SX/SX-102A mass-spectrometer, applying electron beam ionization ($U = 70$ eV) with direct probe introduction. Microanalysis studies of all samples were carried out using a Heraeus CHN-O-RAPID instrument (standard deviations: $C \pm 0.3\%$, $H \pm 0.1\%$).

Thermal analysis (DTA–TGA) was carried out in air at a heating rate 5 °C/min, using the Q-1500 D instrument (Derivatograph-C, system developed by F. Paulik, J. Paulik, L. Erdey; MOM, Hungary) with 120–300 mg samples (weighing accuracy, ± 0.4 mg).

Thermo-gravimetric (TG) studies were carried out with a Perkin-Elmer TGA-7 device and the measurements were performed in nitrogen atmosphere, with the samples of 10–15 mg.

X-ray powder diffraction (XRD) studies were carried out on a DRON-3M powder diffractometer (CuKα radiation, scan step of 0.05–0.1°, counting time of 2–4 s per data point) and by the Guinier–Hägg method using CuKα radiation and silicon as the internal standard and with an STADI-P (STOE) diffractometer.

Table 1
Crystal data and details of diffraction experiments for compounds **I**, **II**, and **III**

Samples	$(Nb_{0.7}Ta_{0.3})_4O_2(OMe)_{14}(ReO_4)_2$	$(Nb_{0.5}Ta_{0.5})_4O_2(OMe)_{14}(ReO_4)_2$[a]	$(Nb_{0.3}Ta_{0.7})_4O_2(OMe)_{14}(ReO_4)_2$
Parameters			
Temperature of crystallization (°C)	22	22	22
Crystal system, space group	Monoclinic, $P2_1/c$		
Formula	$C_{14}H_{42}O_{24}Nb_{2.80}Ta_{1.20}Re_2$	$C_{14}H_{42}O_{24}Nb_2Ta_2Re_2$[a]	$C_{14}H_{42}O_{24}Nb_{1.20}Ta_{2.80}Re_2$
M (g/mol)	1444.16	1514.60	1585.03
Parameters of unit cell			
a (Å)	9.845(6)	9.745(9)	10.002(2)
b (Å)	16.001(1)	15.882(1)	13.451(4)
c (Å)	12.331(8)	12.204(1)	14.233(3)
β (deg)	100.860(1)	100.98(2)	109.763(6)
Volume of unit cell V (Å³)	1908(2)	1854(3)	1802.1(8)
Independent reflection (R_{int})	2179 (0.0706)	5594 (0.0977)	5374 (0.0540)
Observed reflection $I > 2\sigma[I]$	1321	2402	1640
Refined parameters	739	208	200
R_1	0.0868	0.0591	0.0493
wR_2	0.1197	0.1134	0.1001
Goodness of fit	0.974	0.864	0.925

[a] Literature data [26].