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email: maksimizumsky@gmail.com**RADICAL MECHANISM OF FORMATION OF Cu-Re AND Pb-Re COMPOSITES IN GASEOUS PHASE BY THERMAL DECOMPOSITION OF *TRANS*-TETRACHLORODI- $\mu$ -PROPIONATO DIRHENIUM(III)**

Reactions of individual *trans*-tetrachloro-di- $\mu$ -propionato dirhenium(III) thermal decomposition in dynamic inert atmosphere were investigated. Using a radical reaction of *transportation* in gaseous phase, Cu-Re and Pb-Re composites were obtained on a ceramic surface. Free radicals  $C_2H_5\cdot$  were detected by reaction with metal Cu and Pb mirrors. Cu-Re and Pb-Re composites were studied by XRD, micro-X-ray spectral and SEM analysis. Cu-Re composites contain nano- dendrites of Cu which «grow» from a Re base and most likely have a nanotube structure. Dimensions of the nanotubes can vary from 100 nm to 1  $\mu$ m.

**Keywords:** rhenium, free radical, carboxylate, composite, mechanism, decomposition.

Binuclear cluster carboxylates of rhenium(III), obtained for the first time by A.S. Kotelnikova (USSR) and Cotton (USA), are the classical complexes in chemistry of clusters [1-4]. Currently information related to the radical mechanism of thermal destruction of dirhenium(III) complexes and forming Cu-Re and Pb-Re composites is not available.

The current understanding of the chemistry of rhenium carboxylates is reviewed in the book «Multiple bonds between metal atoms» [3].

Investigation of thermal decomposition is very important for the determination of a detailed radical mechanism of reactions and detecting free  $C_2H_5\cdot$  radical by interaction with metals like Cu and Pb. It provides an opportunity to obtain very pure Rhenium metal for a specialist industry, Re coatings and new composite materials using a chemical vapor deposition [5, 6].

In this article we obtained Cu-Re and Pb-Re composites by reaction of free  $C_2H_5\cdot$  radical with a Pb mirror and compact Copper. Free  $C_2H_5\cdot$  radicals were formed as a result of thermal decomposition of *trans*-tetrachloro-di- $\mu$ -propionato dirhenium(III).

**RESULTS AND DISCUSSION**

Ceramic-based Copper-Rhenium and Lead-Rhenium composites were obtained using thermal decomposition of *trans*-tetrachloro-di- $\mu$ -propionato dirhenium(III) in a quartz tube (Fig. 1).

During the procedure *trans*-tetrachloro-di- $\mu$ -propionato dirhenium(III) evaporates in a stream of inert gas at 300°C [7] on heater 1 followed by thermal decomposition on Cu or Pb surface at 800°C on heater 2. We carried out three experiments using different process conditions. Thermal decomposition of *trans*-tetrachloro-di- $\mu$ -propionato dirhenium(III) in air was studied in our previous work [6].

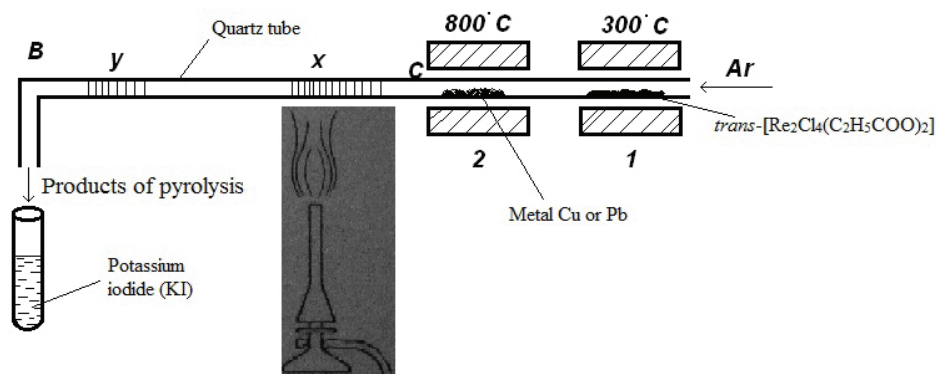


Fig. 1. Experimental set-up used for conformation of free-radical thermal decomposition of *trans*-tetrachloro-di- $\mu$ -propionato dirhenium(III) and formation of metal composites.

*Experiment 1.* 1 g pure *trans*-tetrachloro-di- $\mu$ -propionato dirhenium(III) was placed in zone 1 of a quartz tube (Fig. 1). Zone 2 was free. Re-mirror appeared after 5 hrs heating in zone 2 (Fig. 2). Metal rhenium was detected by XRD analysis.

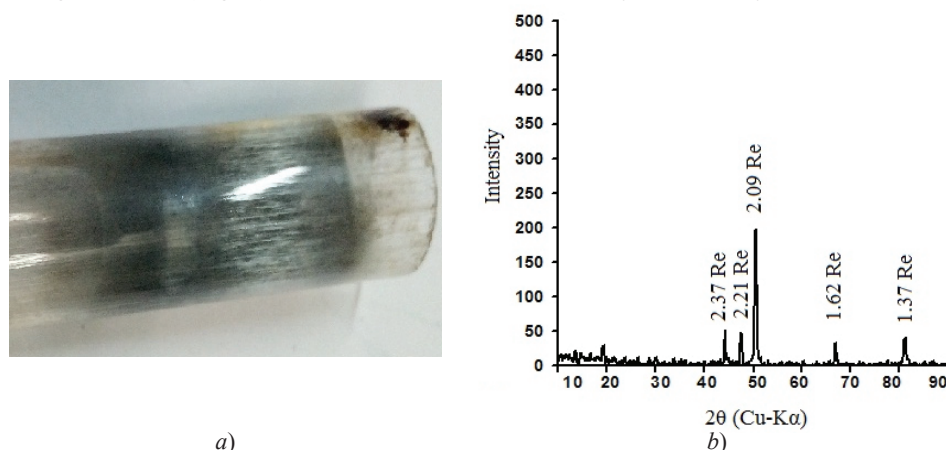
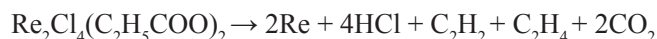


Fig. 2. Rhenium mirror (a) and X-ray diffraction (b) of a deposit formed in a quartz tube. DRON-3, Cu-K $\alpha$ -radiation.

Quantity of produced Re was detected by gravimetric method from a mass increase of the quartz tube. On the next stage, Re was dissolved in H<sub>2</sub>O<sub>2</sub>. Perrhenic acid (HReO<sub>4</sub>) was detected (tan coloured substance) by mixing with potassium thiocyanate (KSCN) and tin(II) chloride (SnCl<sub>2</sub>) [8]. HReO<sub>4</sub> was titrated using sodium hydroxide (NaOH) and a phenolphthalein indicator [8]. Quantity of the obtained rhenium was 99% by mass of the original *trans*-complex. Carbon (IV) dioxide (CO<sub>2</sub>) was detected by reaction with calcium hydroxide (Ca(OH)<sub>2</sub>). Hypothetical halogenalkyls (C<sub>2</sub>H<sub>5</sub>Cl and C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>) were dissolved in two different solvents: (tetrachloromethane (*solution 1*) and dimethyl ketone (*solution 2*)). 1-2 ml of *solution 1* was added to a tube followed by addition of 10-20 mg of sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>). The tube was placed in a glycerine bath and kept

at 180°C. the tube top was paper-covered with an infused reagent (congo indicator with hydrogen peroxide). The colour of the paper has changed to blue [9]. 1-2 ml of *solution 2* was added to a microtube followed by addition of 2 ml pyridine and 5N sodium hydroxide. The colour of pyridine has changed to light pink.

Thermal decomposition of *trans*-tetrachloro-di- $\mu$ -propionato dirhenium(III) in a stream of inert gas runs according to Schematic 1.



Scheme 1. Thermal decomposition at 800°C of *trans*-tetrachloro-di- $\mu$ -propionato dirhenium(III) in a stream of inert gas.

*Experiment 2.* 1 g pure *trans*-tetrachloro-di- $\mu$ -propionato dirhenium(III) was placed in zone 1 of the quartz tube (Fig. 1). At the same time, 0.1 g metal Cu, ceramic ( $\text{Mg}_2\text{Al}_4\text{Si}_6\text{O}_{18}$ ) and a quartz plate were placed in zone 2 of the quartz tube. A Copper-Rhenium composite was obtained after 5h heating in the end of zone 2 (Fig. 3) and detected by XRD analysis.

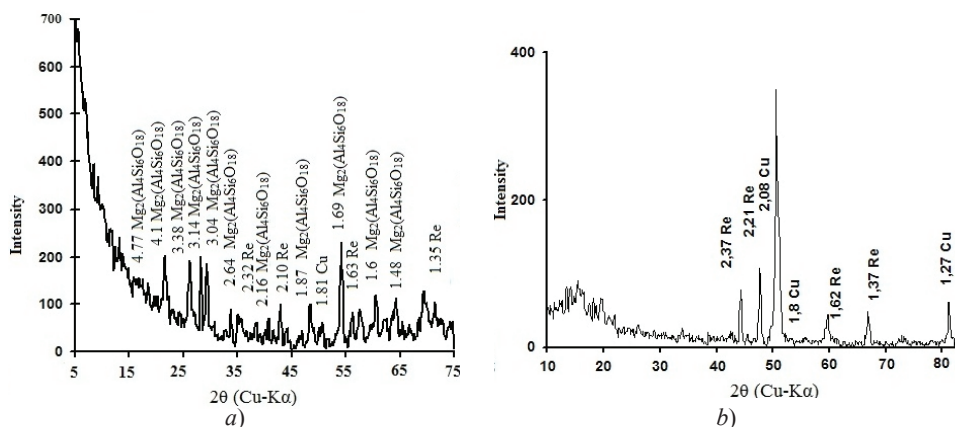
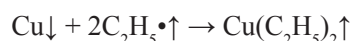
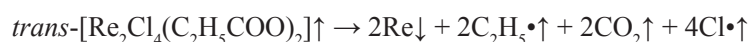
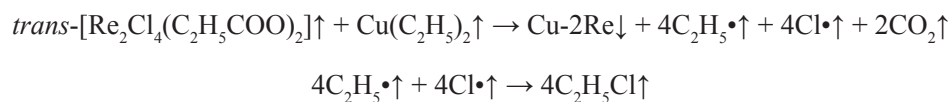


Fig. 3. X-ray diffraction of Copper-rhenium composite formed on cordierite ( $\text{Mg}_2\text{Al}_4\text{Si}_6\text{O}_{18}$ ) (a) and quartz tube (b). DRON-3, Cu-K $\alpha$ -radiation.

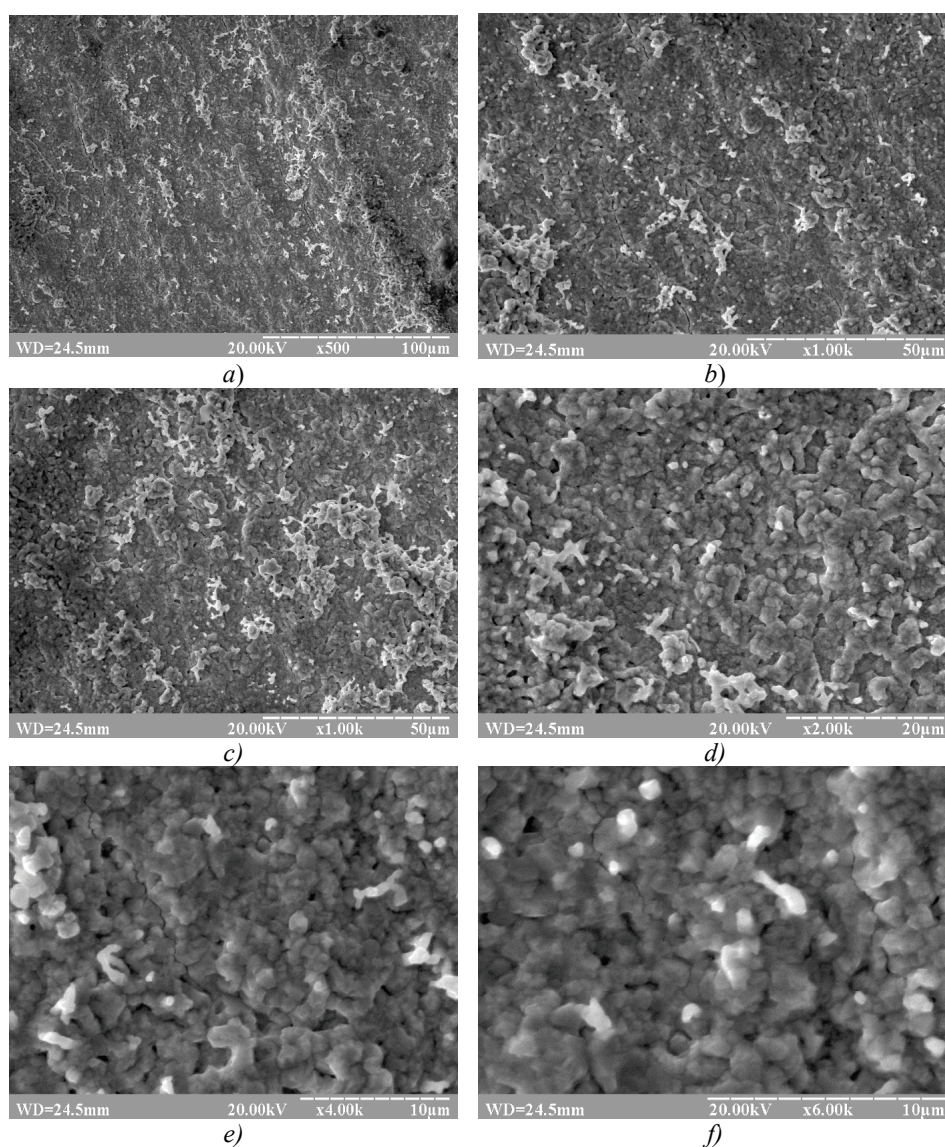
The halogenalkyls were analyzed in the same way as described in *Experiment 1*. Because of instability of  $\text{Cu}(\text{C}_2\text{H}_5)_2\uparrow$  or  $\text{Cu}(\text{C}_2\text{H}_5)_n\uparrow$ , their presence is theoretically based on the publications data [10-19]. As a matter of fact,  $\text{Cu}(\text{C}_2\text{H}_5)_n\uparrow$  cannot be obtained in a solid state. The reaction of thermal decomposition of *trans*-tetrachloro-di- $\mu$ -propionato dirhenium(III) with metal Cu in a stream of inert gas runs according to Schematic 2.





Scheme 2. Thermal decomposition of *trans*-tetrachloro-di- $\mu$ -propionato dirhenium(III) with metal Cu in a stream of inert gas.

Different phases of Cu and Re can be clearly seen from Fig. 3. SEM images of Cu-Re composite are shown in Fig. 4. Images *g* and *h* in Fig. 4 show dendrites of Cu that «grow» from a Re base and most likely have a nanotube structure. Dimensions of the nanotubes can vary from 100 nm to 1  $\mu\text{m}$ . Micrographs in Fig. 4 demonstrate a complex





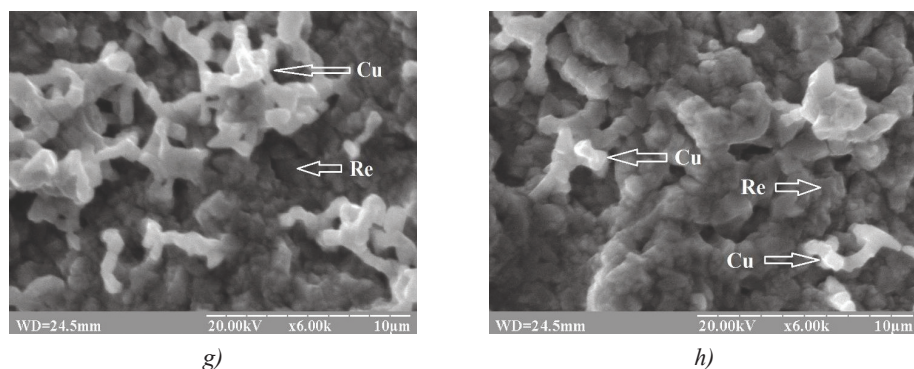


Fig. 4. SEM images of Cu-Re deposits formed on cordierite ( $Mg_2Al_4Si_6O_{18}$ ). Re and Cu were detected by micro-X-ray spectral analysis.

structure of crystals with dimensions from 0.5  $\mu m$  to 20  $\mu m$ . Their composition was confirmed by micro-X-ray spectral analysis. Co-deposition of Re and Cu was carried out using a non-metallic substrate in order to eliminate red-ox reactions with Fe or other active metals.

*Experiment 3.* 1 g pure *trans*-tetrachloro-di- $\mu$ -propionato dirhenium(III) was placed in zone 1 of the quartz tube (Fig. 1). At the same time, 0.1 g metal Pb, was placed in zone 2 of the quartz tube. Lead-Rhenium composite was obtained after 5hrs heating in the end of zone 2 (Fig. 1 and Fig. 5). Lead-rhenium composite was detected by XRD analysis.

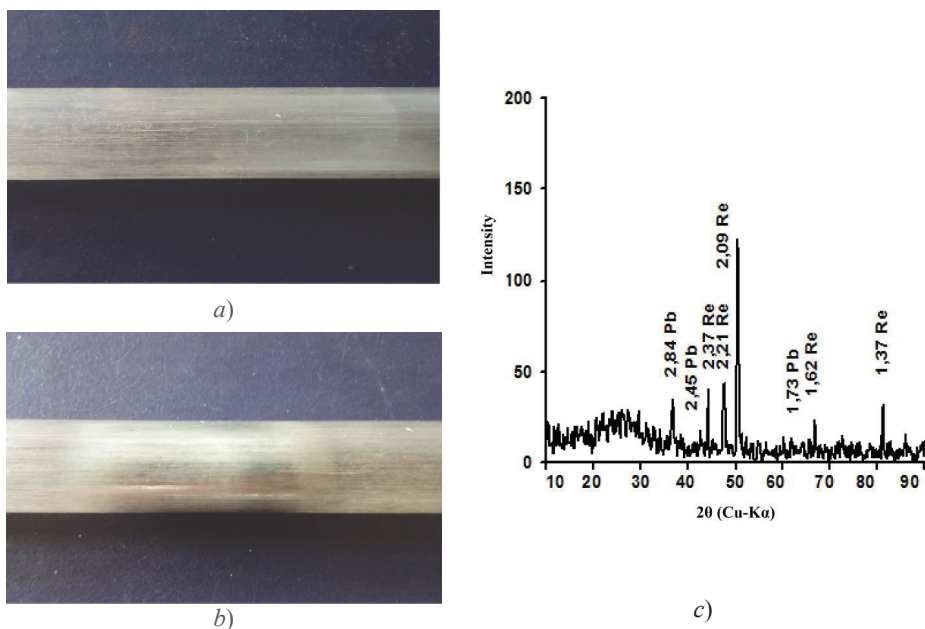


Fig. 5. Lead-rhenium composite and its XRD analysis. a) Photo of a quartz tube before deposition.; b) Photo of a quartz tube after deposition.

After removal of Pb from zone 2 and heating zone **x** and zone **y** in a stream of gaseous mixture of *trans*-tetrachloro-di- $\mu$ -propionato dirhenium(III) and argon pure metal Re was obtained in zone **x** (Fig. 6) and Pb-Re composite – in zone **v**.

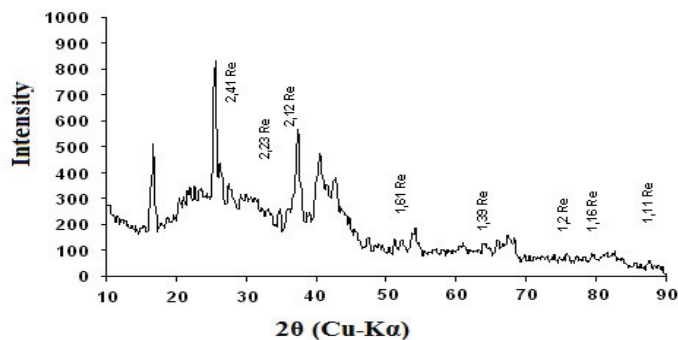


Fig. 6. X-ray diffraction of Rhenium formed in zone **x**.

Formation of yellow precipitate took place after gaseous mixture passed through a solution of potassium iodide (KI), with further addition of sodium thiosulfate. XRD analysis of yellow precipitate is shown in Fig. 7.

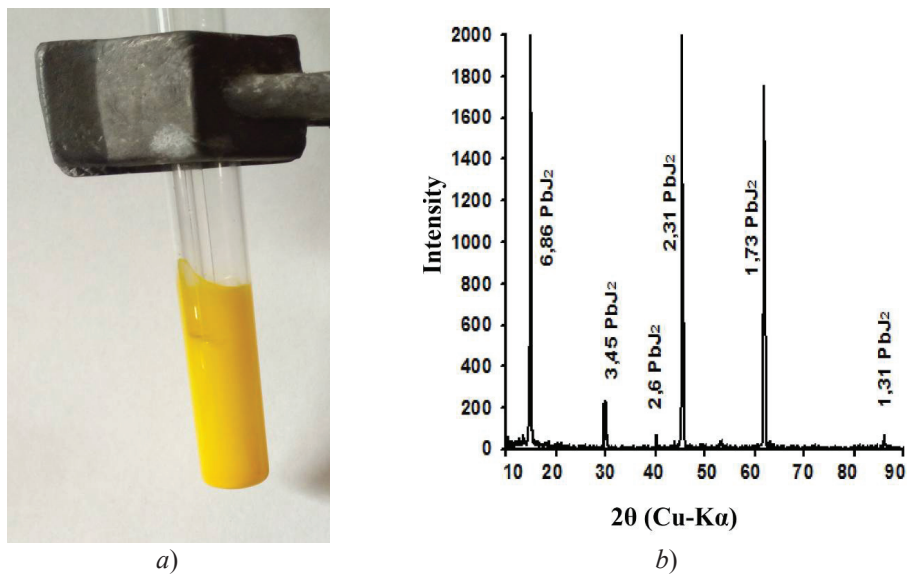
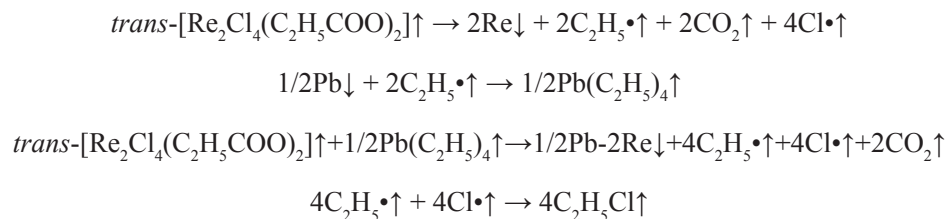


Fig. 7. X-ray diffraction of yellow precipitate.

The halogenalkyls were analyzed in the same way as described in *Experiment 1*. The reaction of thermal decomposition of *trans*-tetrachloro-di- $\mu$ -propionato dirhenium(III) with metal Pb in a stream of inert gas runs according to Schematic 3.

Knowledge about formation of  $\text{Pb}(\text{C}_2\text{H}_5)_4 \uparrow$  or  $\text{Pb}(\text{C}_2\text{H}_5)_n \uparrow$  is based on previous publications [10-19] and reactions with KI and metal mirrors.



Scheme 3. Thermal decomposition of *trans*-tetrachloro-di- $\mu$ -propionato dirhenium(III) with metal Pb in a stream of inert gas.

### EXPERIMENTAL SECTION

In this research initial  $[\text{N}(n\text{-C}_4\text{H}_9)_4]_2[\text{Re}_2\text{Cl}_8]$  and *trans*-carboxylates were synthesized without using an autoclave. The complexes obtained in the present study have been evaluated by electron absorption and elemental analysis [20-23]. All reagents and solvents are commercially available.

Preparation of compounds.  $[\text{N}(n\text{-C}_4\text{H}_9)_4]_2[\text{Re}_2\text{Cl}_8]$ . 2.0 g of  $[\text{N}(n\text{-C}_4\text{H}_9)_4\text{ReO}_4]$  was added to 20 ml of benzoylchloride ( $\text{C}_6\text{H}_5\text{COCl}$ ). The solution was heated under reflux in a Nitrogen atmosphere at 210°C for 5 hours. Consequently, 3.33 g of  $[\text{N}(n\text{-C}_4\text{H}_9)_4\text{Br}]$  was dissolved in 30 ml of saturated with a hydrogen chloride ethanol and added to the solution. This mixture remained under reflux at 210°C for 1.5 hrs in a Nitrogen atmosphere. Using filtration, a blue crystalline substance was obtained. It was washed using three 10 ml portions of isopropyl alcohol then ethanol and dried under vacuum. The substance yield is 2.2462 g or 97%.

*Analysis.* Calculations for  $\text{C}_{32}\text{H}_{72}\text{N}_2\text{Cl}_8\text{Re}_2$ : C, 33.69; H, 6.36; N, 2.45; Cl, 24.9; Re, 32.65. Found: C, 33.0; H, 6.15; N, 2.5; Cl, 24.8; Re, 32.6. UV-vis (acetonitrile),  $\lambda_{\text{max}}$ ,  $\text{cm}^{-1}$ : 14700, 20940, 23645, 27000, 28100, 32600, 39215. [24-26]

The synthesis of *trans*-tetrachloro-di- $\mu$ -propionato dirhenium(III) is reviewed in [6]

Diffractometer DRON-3 with Cu-K $\alpha$  radiation was used for X-ray diffraction analysis. Scanning Electron Microscope with Micro-Analyzer SEMMA-102-02 was used to obtain SEM images.

### CONCLUSIONS

Radical mechanism of thermal decomposition of *trans*-tetrachloro-di- $\mu$ -propionato dirhenium(III) was confirmed. Mechanism of free-radical reactions was established by reaction of  $\text{C}_2\text{H}_5 \cdot$  with Cu and Pb metal mirrors. Microstructure of Cu-Re composite was revealed. This research may be used for explanation of the CVD processes while obtaining coatings, composites and new precision materials.

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## РАДИКАЛЬНЫЙ МЕХАНИЗМ ОБРАЗОВАНИЯ Cu-Re И Pb-Re КОМПОЗИТОВ ИЗ ГАЗОВОЙ ФАЗЫ ПУТЕМ ТЕРМОРАСПАДА ТРАНС-ТЕТРАХЛОРО-ДИ- $\mu$ -ПРОПИОНАТА ДИРЕНИЯ(III)

### Резюме

Исследованы реакции термической деструкции в динамической инертной атмосфере индивидуального транс-тетрахлоро-ди- $\mu$ -пропионата дирения(III). Композиты Cu-Re и Pb-Re на керамике получены газофазной радикальной транспортной реакцией. Сво-



бодные радикалы  $C_2H_5\cdot$  обнаружены по реакции с металлическими зеркалами Cu и Pb. Композиты Cu-Re и Pb-Re изучены методами РФА, микрорентгеноспектральным анализом и растровой электронной микроскопией. Cu-Re композит состоит из нано дендритов меди, которые «ростут» из рениевой основы, и имеют размеры от 100 нм до 1 мкм, также возможно что они имеют структуру нанотрубок.

**Ключевые слова:** рений, свободный радикал, карбоксилат, композит, механизм, разложение.

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### **РАДИКАЛЬНИЙ МЕХАНІЗМ УТВОРЕННЯ Cu-Re ТА Pb-Re КОМПОЗИТІВ З ГАЗОВОЇ ФАЗИ ШЛЯХОМ ТЕРМОРОЗКЛАДУ ТРАНС-ТЕТРАХЛОРО-ДИ- $\mu$ -ПРОПІОНАТУ ДИРЕНІЮ(III)**

#### **Резюме**

Досліджено реакції термічної деструкції в динамічній інертній атмосфері індивідуального транс-тетрахлоро-ди- $\mu$ -пропіонату диренію(III) та встановлено якісним хімічним аналізом утворення металічного ренію, хлороводню, карбон(IV) оксиду, первинних та вторинних галогеноалкілів. Первинні галогеноалкіли визначено нагріванням з натрій тіосульфатом за зміною кольору на синій паперу змоченого сумішшю індикатору конго з гідроген пероксидом. Вторинні галогеноалкіли визначалися взаємодією з 5 N натрій гідроксидом та зміною кольору шару піридином на світло-рожевий. Кількість утвореного металічного ренію складає 99,1% від вмісту у вихідному транс-тетрахлоро-ди- $\mu$ -пропіонаті диренію(III), що визначено кількісним аналізом, шляхом розчинення металічного ренію у концентрованому гідроген пероксиді та подальшому титруванні утвореної перренатної кислоти розчином 0,1 N натрій гідроксиду з індикатором фенолфталеїном. Композити Cu-Re та Pb-Re на кераміці одержано у вигляді дзеркал газофазною радикальною транспортною реакцією, через взаємодію транс-тетрахлоро-ди- $\mu$ -пропіонату диренію(III) з компактними міддю та свинцем. Вільні радикали  $C_2H_5\cdot$  виявлено за реакцією з металічними дзеркалами чистих Cu та Pb. Утворення легкої сполуки  $Pb(C_2H_5)_4$  або  $Pb(C_2H_5)_n$  доведено здатністю реакційного газу з установки, при пропусканні через розчин калій йодиду утворювати жовтий осад плюмбум(II) йодиду, який визначено рентгенофазовим аналізом. Взаємодія реакційного газу з калій йодидом доводить утворення легких алкільних сполук плюмбуму при взаємодії з транс-тетрахлоро-ди- $\mu$ -пропіонатом диренію(III), та показує радикальний механізм терморозкладу. Склад та морфологію поверхні композитів Cu-Re та Pb-Re охарактеризовано методами рентгенофазового та микрорентгеноспектрального аналізів і растровою електронною микроскопією. Cu-Re композит складається з нанодендритів міді, які «ростуть» з рениевой основы, та мають розміри від 100 нм до 1 мкм, також можливо що вони мають структуру нанотрубок.

**Ключові слова:** рений, вільний радикал, карбоксилат, композит, механізм, розклад.

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