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«SOFT» Chemistry Methods Appear as an Effective Way for Production of Superdispersive (Nano-Sized) Materials Based on Re and d-Elements of V-VIII Groups

Dmitry V. Drobot

1

Chemical design of precursor

1. Choice of metals
Re, Mo, W, Nb, Ta, Ni

2. Choice of ligands
MeOH, EtOH, i-PrOH, BuOH

3. Creation of methods of synthesis
Electrochemical Synthesis

→

Investigation of structure in solid phase and in solution, stages of thermal decomposition, P-T diagrams of Metal-Oxygen, etc.

↑

Precursors

$M^1_x M^2_y M^3_z L^1_m L^2_n$

→ Thermal Decomposition
T, τ, atmosphere - var →

1. Preparation of metals, alloys and ligatures (Re-Mo, Re-W) at record-breaking low temperatures.
2. Regulation of grain size, preparation of **nano-sized materials** (20-50 nm).
3. Preparation of new phases in Nb(Ta)-O systems and complex oxide phases with **high** phase and chemical **purity**.
4. Usage in **catalysis** with obtaining of expressed synergetic effect.

M – metal, **L** – ligand

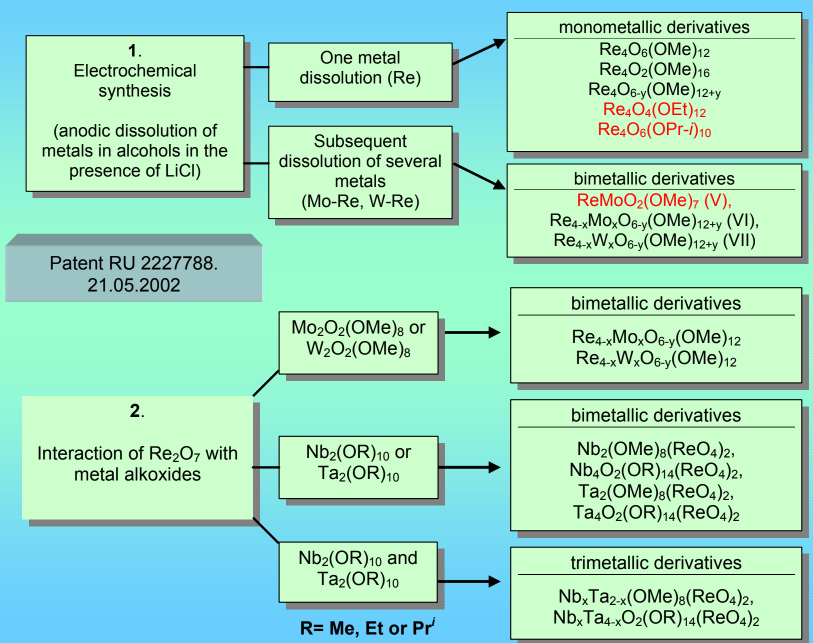
2

The main problems:

- Search for and development of methods of synthesis of rhenium alkoxides and oxoalkoxide derivatives, including cluster and heterometallic ones;
- Study of their physicochemical properties including the structure in the solid state and the thermal decomposition processes;
- Determination of the chemical and phase compositions of the products of the thermal decomposition of rhenium alkoxides and oxoalkoxide derivatives under various conditions and the search for rational applications of the materials produced in this way

3

Synthetic approaches to rhenium-containing alkoxide derivatives



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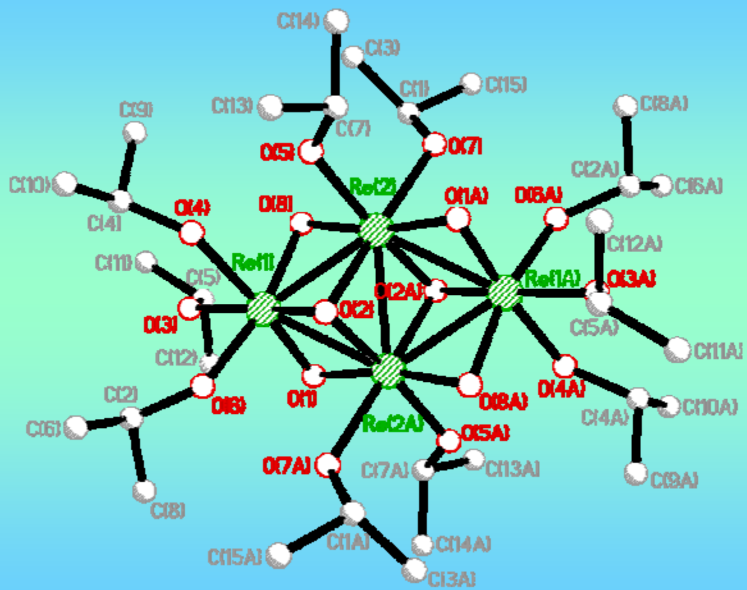
Electrochemical synthesis – a convenient approach to rhenium alkoxides

Alcohol	LiCl, M	U, V	I, A	j_a, A/cm^2	Duration, h	Products	Re-Re distance, Å (X-ray single crystal study)
MeOH	0,025	25 - 110	0,055 - 1	0,01- 0,56	8 - 38	$Re_4O_{6-y}(OMe)_{12+y}$	3,45; 3,65
EtOH	0,025	170	0,08- 0,01	0,04- 0,05	24	$Re_4O_4(OEt)_{12}$ [*]	2,54(2); 2,648(19); 2,65(2)
i-PrOH	0,2	250	0,025	0,025	20,5	$Re_4O_6(OPr\text{-}i)_{10}$ [*]	2,5204(7) - 2,5501(5)

[*] Cluster compounds

5

Structure of $Re_4O_6(OC_3H_7\text{-}i)_{10}$ (Re-Re 2.52-2.55 Å)



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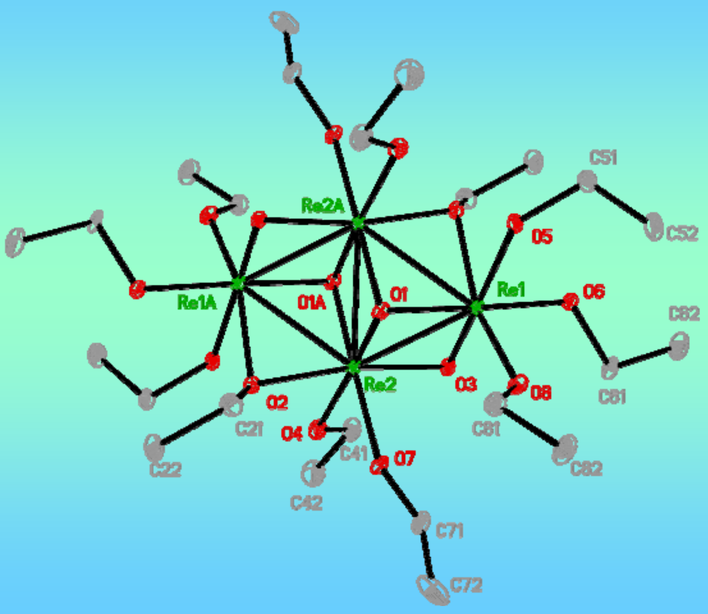
Structure of **$Re_4O_4(OC_2H_5)_{12}$** (Re-Re 2.54-2.65 Å)



7

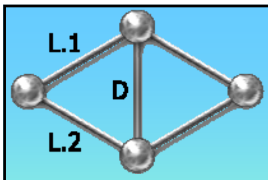
Characteristics of metal-metal bonds in alkoxide compounds

Compound	r(M–M), Å	M–M bond order	Refs.
$Re_4O_{6-y}(OMe)_{12+y}$	3,45; 3,65	no bond	*
$Re_4O_4(OEt)_{12}$	2,54(2); 2,648(19); 2,65(2)	>1, ~1	*
$Re_4O_6(OPr^i)_{10}$	2,5204(7) - 2,5501(5)	>1	*
$ReMoO_2(OMe)_7$	2,658(2)	1	*
$Re_2O_3(OMe)_6$	2,559(1)	1	1
$Re_2(OMe)_{10}$	2,5319(7)	2	2
$Re_3(OPr^i)_9$	2,36	2	3
$Re_3(OCH_2Bu^t)_9$	2,365(1) - 2,372(1)	2	4

* Own data

1. P. G. Edwards, G. Wilkinson, M. B. Hursthouse, K. M. Abdul Malik, *J. Chem. Soc. Dalton Trans.*, 1980, 2467.
2. J. C. Bryan, D. R. Wheeler, D. L. Clark, J. C. Huffman, A. P. Sattelberger, *J. Am. Chem. Soc.*, 1991, 113, 3184.
3. D. M. Hoffman, D. Lappas, D. A. Wierda, *J. Am. Chem. Soc.*, 1993, 115, 10538.
4. W.-W. Zhuang, B. E. Truitt, D. M. Hoffman, *Inorg. Chem.*, 1997, 36, 3330.

8



Metal–Metal Bonds in clusters based on $Ti_4(OMe)_{16}$ core structure

Compound	L.1, Å	L.2, Å	D, Å	Number of core cluster electrons	Ref.
$Ba_{1,14}Mo_8O_{16}$	2,616(1)	2,578(1)	2,578(1)	10	[1]
$Ba_{1,14}Mo_8O_{16}$	2,847(1)	2,546(1)	2,560(1)	8,28 (average)	[1]
$W_4(OEt)_{16}$	2,936(2)	2,646(2)	2,763(1)	8	[2]
$Re_4O_4(OEt)_{12}$	2,54(2)	2,648(19)	2,65(2)	8	[*]
$Re_4O_6(OPr\text{-}i)_{10}$	2,5501(5)	2,5399(5)	2,5204(7)	6	[*]
$Mo_4O_8(OPr\text{-}i)_4(Py)_4$	3,472(1)	2,600(1)	3,218(1)	4	[2]

[*] Own data

[1] *Torardi C.C., McCarley R.E.* J. of Solid State Chem. 1981. 37, 3. 393
[2] *Chisholm M.H., Huffman J.C., et al.* J. Amer. Chem. Soc. 1981. 103, 20. 6093

9

Computer Aided Composition of Atomic Orbitals (C.A.C.A.O.)

A Package for Molecular Orbital Analysis
[PC Beta-Version 5.0 , 1998]

Carlo Mealli u Davide M. Proserpio
With major contribution of Andrea Ienko.

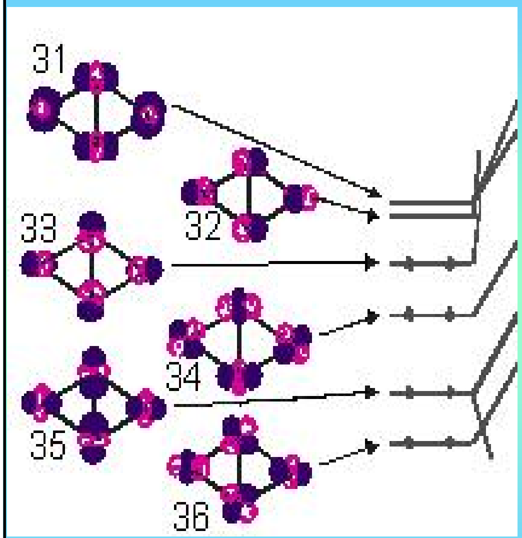
10

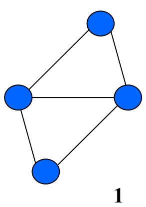
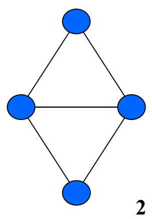
Package Technical Information

- ***Method – Extended Method of Hukkel.***
  - *Molecules geometry is approximate to the real.*
  - *The radicals $-CH_3$ and $-CF_3$ are used as $-C_2H_5$ and $-CH_2CF_3$*

11

Cluster Re_4

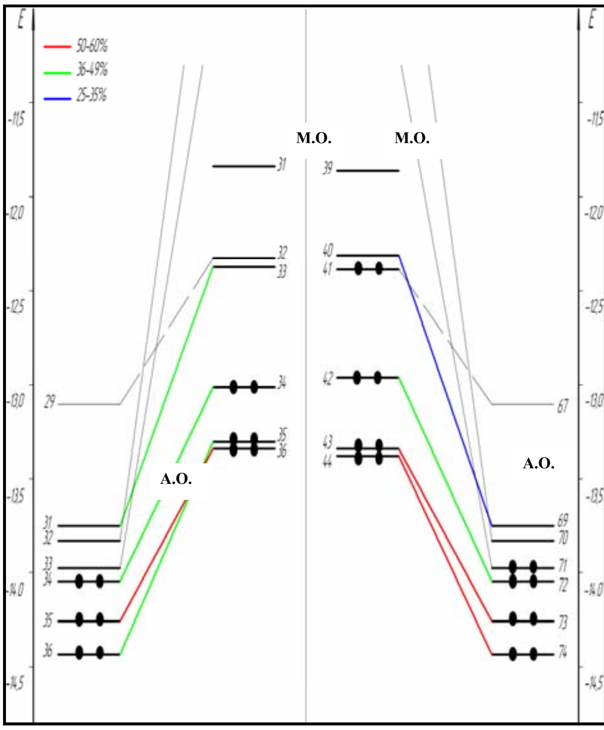


№1	№2
$Re_4O_4(OEt)_{12}$	$Re_4O_6(OPr^i)_{10}$
Re (V)	Re (V, VI)
$[Re4]^{20+}$	$[Re4]^{22+}$
e=8	e=6
C2h	D2h
 1	 2

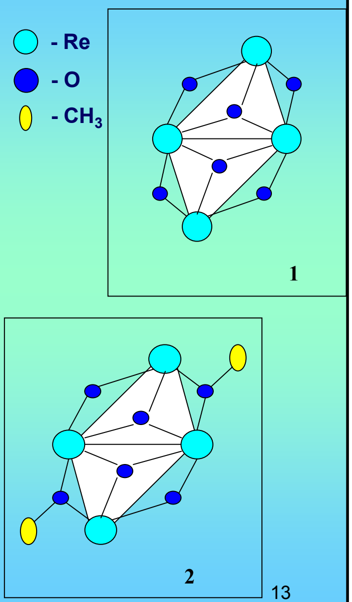
- Re

Olesya A. Nikonova, Kjell Jansson, Vadim Kessler, Margareta Sundberg, Alexei I. Baranov, Andrei V. Shevelkov, Dmitrii V. Drobot and Gulaim A. Seisenbaeva . Inorg. Chem. 2008, 47, 1295-1300.

12



Models 1, 2.



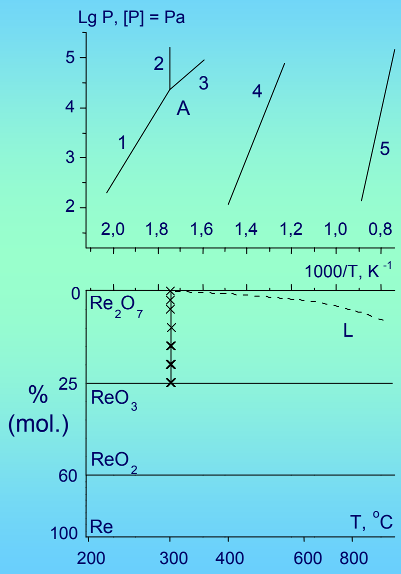
13

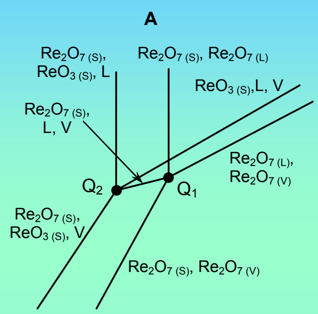
The main results of the calculations are:

- Anodic oxidation of Rhenium in EtOH-PrOH^{i} allows to obtain heteroligand derivatives with general composition $Re_4O_n(OEt)_x(OPr^i)_y$. Probability of the formation compounds containing Re4 cluster and based on the structure of $Re_4O_4(OEt)_{12}$ or $Re_4O_6(OPr^i)_{10}$ is equal.
- In the structure of the $Re_4O_4(OEt)_{12}$ part of Et-groups can be substitute by (OCH_2CF_3) groups. Replacement of hydrogen atoms by fluorine atoms at μ_2 position increases the heteroligand complex stability;
- It is possible to prepare compound containing Re4 cluster and μ_3-S ligands.

14

P–T and T–x diagrams for the rhenium–oxygen system (without the vapor line)

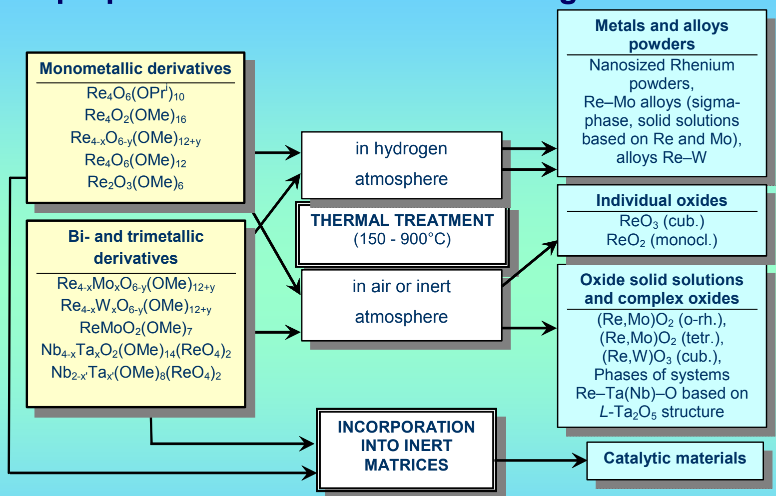




1 – Re_2O_7 (S), ReO_3 (S), V;
2 – Re_2O_7 (S), ReO_3 (S), L;
3 – ReO_3 (S), L, V;
4 – ReO_3 (S), ромб. ReO_{2+x^*} (S), V;
5 – ромб. $ReO_{2+x^{**}}$ (S), Re (S), V;
A – detailed fragment of P–T projection;
Q_1 – Re_2O_7 (S), Re_2O_7 (L), Re_2O_7 (V);
Q_2 – Re_2O_7 (S), ReO_3 (S), L, V.

15

Application of the metal alkoxide derivatives for the preparation of rhenium-containing materials

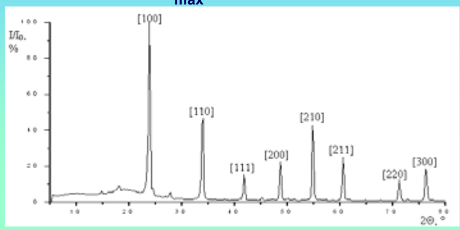


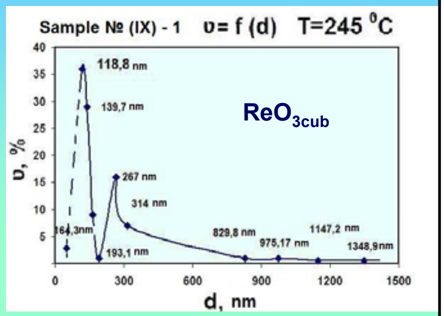
1. **Drobot D.V., Seisenbaeva G.A., Kessler V.G., Shcheglov P.A., Nikonova O.A., Mikhnevich S.N., Petrakova O.V. (2008) Journal of Cluster Science. № 10876**
2. **P. A. Shcheglov, D. V. Drobot (2005). Russian Chemical Bulletin.International Edition. 54, 2247.**

16

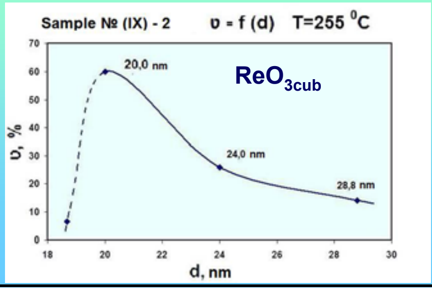
Particle-size distribution of the products of thermal decomposing of $Re_4O_n(OEt)_x(OPr^i)_y$, T_i=const

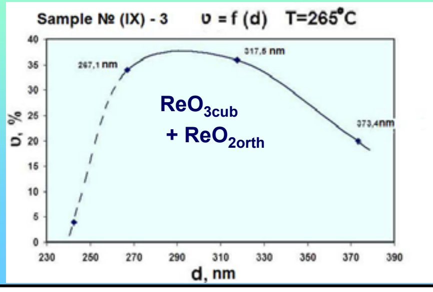
XRDA data of ReO_{3cub} obtained at thermal decomposition of $Re_4O_n(OEt)_x(OPr^i)_y$, T_{max} = 470 °C





ReO_{3cub} a=3,745 Å (a = 3,748A, ICDD–JCPDS, No.33-1096)

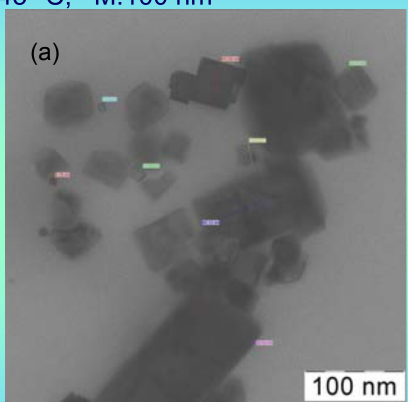


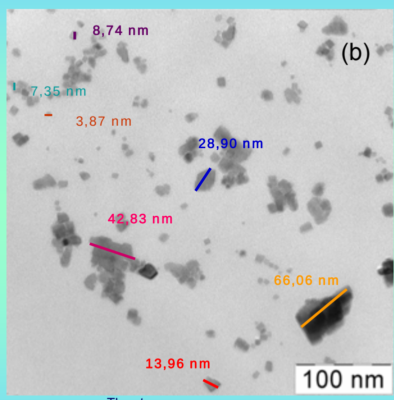


Photography of nano-sized particles

(a) $ReO_{3\ cub}$, obtained at polythermal decomposing of $Re_4O_n(OEt)_x(OPr^i)_y$, Tmax = 470 °C,

(b) ReO_{3cub}, obtained at iso-thermal annealing of $Re_4O_n(OEt)_x(OPr^i)_y$, T=245 °C; M:100 nm

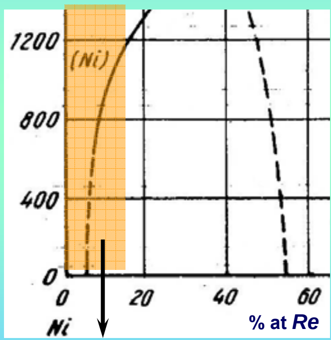




Re+EtOH+ i-PrOH n(i-PrOH) : n(EtOH) = 1:1 mole/mole, membrane → electrolysis (U=200-240 V, I, 10-50 mA, τ =112,0 h, LiCl=0,1 mole/l) → $(Re_4O_n(OEt)_x(OPr^i)_y)$ → The step thermal decomposition in air medium (T=245 °C τ=8,2 h; T=255 °C τ=34,0 h) → $ReO_{3(cub)}$ d=24 ± 5 nm (υ ~100%)

The aim

Our aim is to obtain fine (nanosized) powders of alloys Re-Ni, Re-Co, Re-Ni-Co; simple and complex oxides.



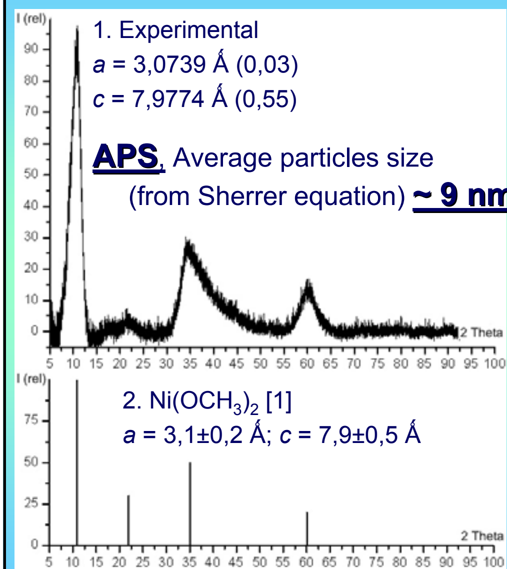
Alloys for aerospace application

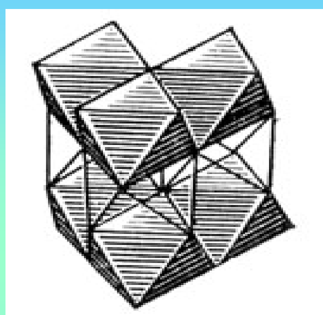
		27 **Co** T_m=1495 C	28 **Ni** T_m=1455 C
75 **Re** T_m=3168 C			

Main questions:

1. Whether Re-Ni alloys can be obtained at low (< 500 °C) temperatures?
2. What particles size thus obtained powders have?

XRD and structure of $Ni(OCH_3)_2$

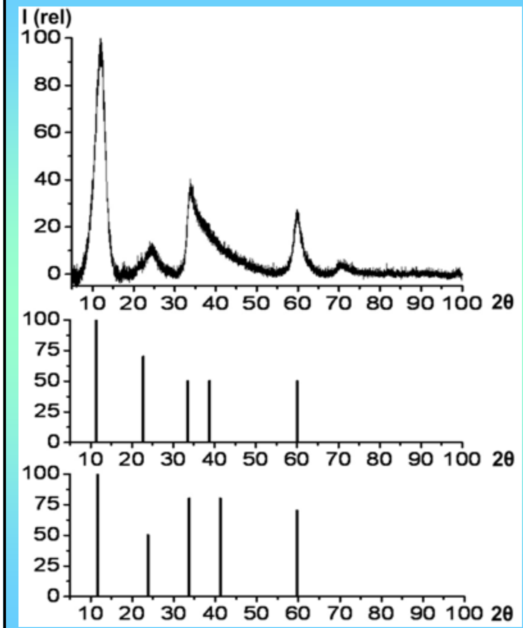




$Mg(OH)_2$ – type hexagonal structure.

[1] – Rogova T.V., Turova N.Ya., Zhadanov B. V. About nickel alkoxides // Coordination chemistry, 1985, vol. 11, № 6, pg. 784-788.

XRD of $Ni(OCH_3)_2$ hydrolysis product



1. **Experimental**
   a = 3,0811 Å (0,000)
   c = 23,4128 Å (0,035)

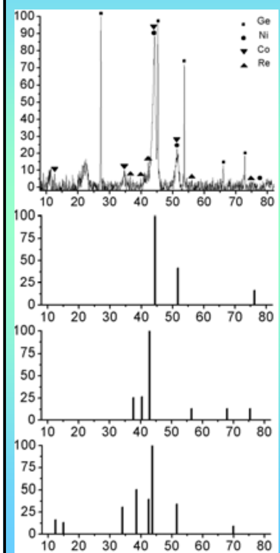
APS, Average particles size (from Sherrer equation) **~14 nm**

2. **Ni(OH)2·0.75H2O**
   ICDD 38-715
   a = 3,080 Å
   c = 23,410 Å

3. **Ni(OH)2·0.67H2O**
   ICDD 22-444
   a = 5,340 Å
   c = 7,500 Å

21

XRD of $Ni_xRe_yCo_z(OCH_3)_n$ thermal decomposition (in hydrogen medium) product

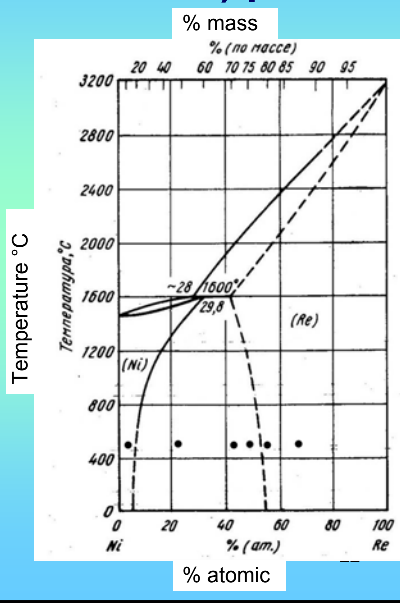


1. **Experimental**
   (Tdecomp = 400°C)

2. **Ni (cub.)**
   ICDD 65-0380

3. **Re (hex.)**
   ICDD 88-1735

4. **Co**
   ICDD 70-2633

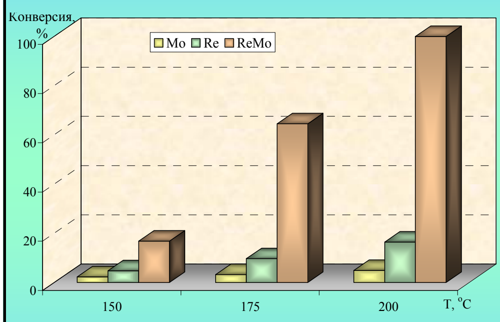


Re, Ni, Co methoxocomplexes decomposition products

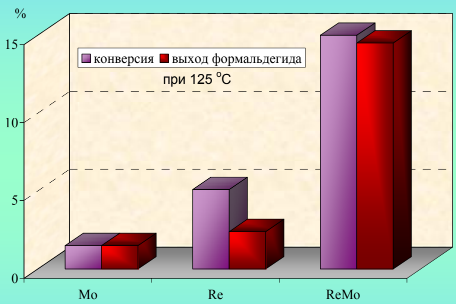
Compound	Hydrolysis product	Thermal decomposition products		
		In air medium	In argon medium	In hydrogen medium
$Re_xNi_y(OCH_3)_z$	**-**	**$NiReO_4$**	**-**	**Re – Ni alloy**
$Ni_xCo_y(OCH_3)_4$	**$Ni(OH)_2$ $Co(OH)_2$**	**$NiCo_2O_4$ NiO**	**NiO•CoO**	**Ni – Co alloy**
$Ni(OCH_3)_2$	**$Ni(OH)_2$**	**NiO**	**NiO**	**Ni**
$Co(OCH_3)_2$	**$Co(OH)_2$**	**Co_3O_4**	**CoO**	**Co**
$Re_4O_6(OCH_3)_{12}$	**-**	**ReO_3**	**-**	**Re**
$Ni_8Re_1Co_1(OCH_3)_{14}$	**-**	**$NiReO_4$ NiO**	**-**	**Ni-Re-Co alloy**

Catalyst production by incorporation of alkoxides into zeolites matrix allows to max out synergetic effect

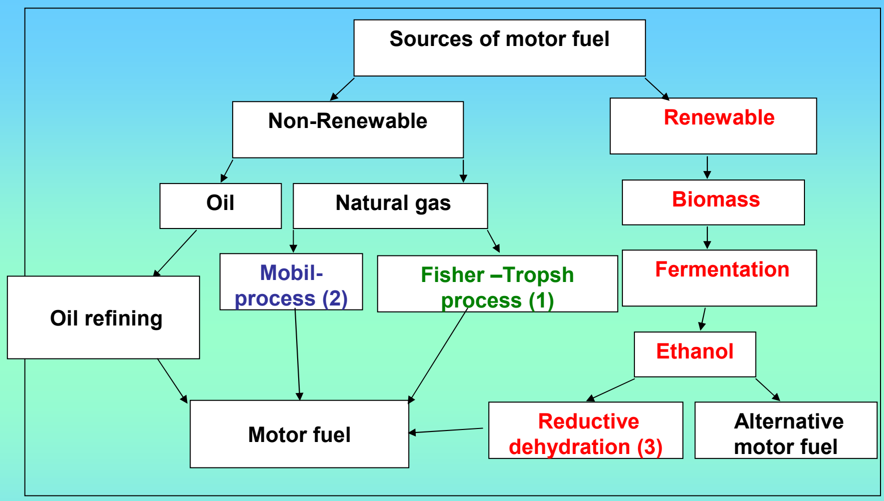
a



b



Methanol oxidation using catalysts produced by incorporation methoxo-derivativs into zeolites NaY:
Mo – $[MoO(OMe)_4]_2$; Re – $Re_2O_3(OMe)_6$; ReMo – $ReMoO_2(OMe)_7$;
A – conversion temperature dependence;
b – conversion and formaldehyde yield of 125°C.



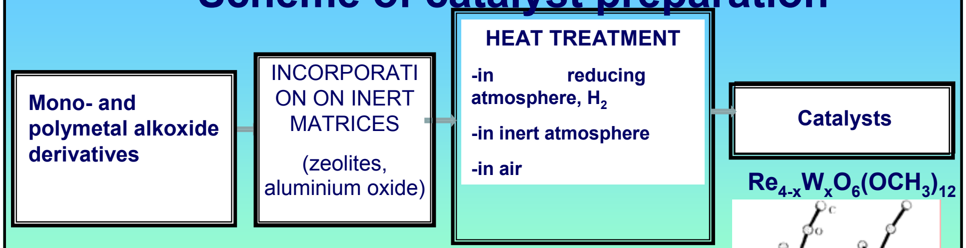
$\nu XO+(2\nu+1)H_2 \square X_\nu H_{2\nu+2}+\nu H_2O$ (1)

$XH_3OH \xrightarrow{H^+} [H_2O + (XH_3)_2O] \xrightarrow[400\text{–}420°X,\ 2\text{–}15\ \Diamond\int\lceil]{Z\Sigma M\text{–}5} X_\nu H_{2\nu+2} + A\rho H + X_\nu H_{2\nu} + H_2O$ (2)

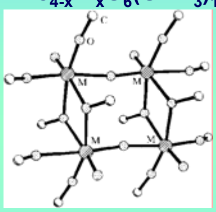
$\nu/2X_2H_5OH + H_2 = X_\nu H_{2\nu+2}+\nu/2H_2O$ (3)

25

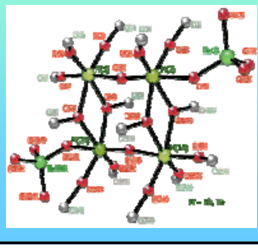
Scheme of catalyst preparation



$Re_{4-x}W_xO_6(OCH_3)_{12}$



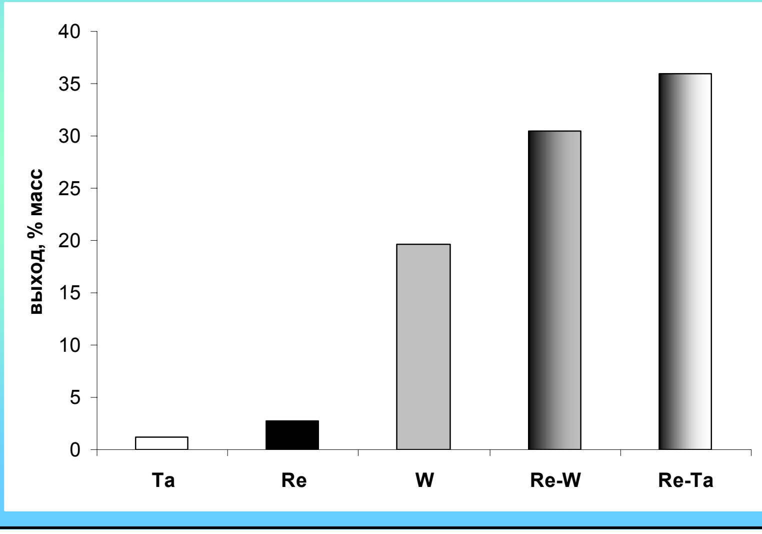
$Ta_4O_2(OCH_3)_{14}(ReO_4)_2$



Created catalysts

Catalyst	Precursor
Re/ γ-Al_2O_3	$Re_4O_2(OMe)_{12+y}$ – solution in ethanol
W/ γ-Al_2O_3	$[WO(OCH_3)_4]_2$ – solution in methanol
Ta/ γ-Al_2O_3	$Ta_2(OMe)_{10}$ – solution in methanol
Re - W/ γ-Al_2O_3	$Re_{4-x}W_xO_6(OCH_3)_{12}$ – solution in methanol
Re - Ta/ γ-Al_2O_3	$Ta_4O_2(OCH_3)_{14}(ReO_4)_2$ – solution in toluene
Re- Ta/ γ-Al_2O_3	Mixture solutions $Re_4O_2(OMe)_{12+y}$ and $Ta_2(OMe)_{10}$ in methanol

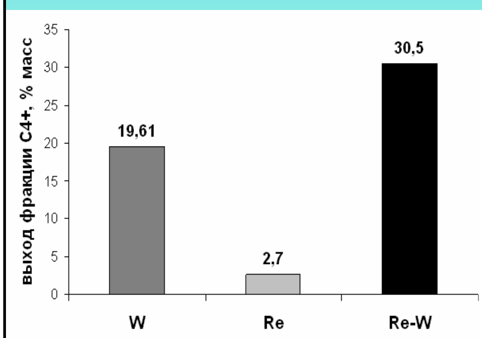
The relationship between alkane-olefins fraction C5 – C9 yield and composition of active components in cross-coupling reaction of ethanol and glycerin.

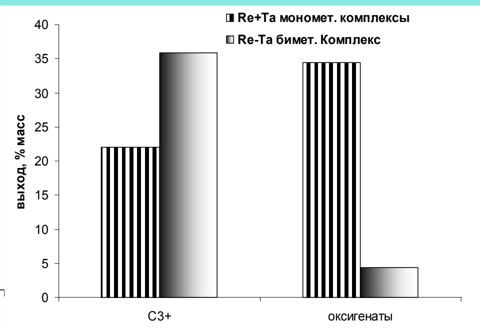


27

Socatalitic effect of rhenium and tungsten obtained by using bimetallic precursor $W_xRe_{4-x}O_6(CH_3O)_{12}$

The dependence of catalytic activity and selectivity on the precursor chemistry





1. M. V. Tsodikov, A. V. Chistyakov, F. A. Yandieva, V. Ya. Kugel, O.V. Bukhtenko, T.N. Zhdanova, A. E. Gekhman, I. I. Moiseev, D.V. Drobot, O.V. Petrakova // Patent RU № 2391133, 10.06.2010.
2. M. V. Tsodikov, A. V. Chistyakov, F. A. Yandieva, V. Ya. Kugel, O.V. Bukhtenko, T.N. Zhdanova, A. E. Gekhman, I. I. Moiseev, D.V. Drobot, O.V. Petrakova // Patent RU 2008139448. Applied 30.11.2009

28

Fabrication of fine powders of metallic and oxide materials based on rhenium using alkoxide derivatives as precursors

BASIC CONCEPT

Synthesis of alkoxide derivatives containing one or several metals → Thermal treatment provides oxide (oxides, solid solutions, complex oxides) and metallic (fine metals and alloys) materials

ADVANTAGES

1. An approach to single-phase products with required stoichiometry: the control of the composition and the degree of homogeneity that preserves through the technological process

2. The decrease of the temperature and duration of synthesis

3. The preparation is feasible of both fine (several nanometers grain size) products and coarse-crystalline products (with micrometers scale grain sizes)

29

I am sorry, that have extended my time

30

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31