

Review

Rhenium Nanochemistry for Catalyst Preparation

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Abstract: The review presents synthetic approaches to modern rhenium-based catalysts. Creation of an active center is considered as a process of obtaining a nanoparticle or a molecule, immobilized within a matrix of the substrate. Selective chemical routes to preparation of particles of rhenium alloys, rhenium oxides and the molecules of alkyltrioxorhenium, and their insertion into porous structure of zeolites, ordered mesoporous MCM matrices, anodic mesoporous alumina, and porous transition metal oxides are considered. Structure-property relationships are traced for these catalysts in relation to such processes as alkylation and isomerization, olefin metathesis, selective oxidation of olefins, methanol to formaldehyde conversion, *etc.*

Keywords: heterogeneous catalysis; rhenium oxides; porous matrices; active centers; oxidation catalysis; olefin metathesis; methanol-to-formaldehyde conversion

1. Introduction

Rhenium and its compounds such as sulfides, oxides, alloys and complexes have found application as catalysts in petroleum production, different organic syntheses and radiotherapy.

Rhenium metal is broadly used as a component of catalysts for alkylation in organic synthesis and for industrial processes such as reforming of petroleum feedstock and metathesis of alkenes [1–3]. These catalysts have shown good activity in the hydrocarbon cracking and selective hydrogenation, hydrodesulfurization of heavy crude oil and also selective dehydroaromatization of methane and ethane to benzene [4–12]. Applying a nanocomposite of Pt-Re alloy nanoparticles deposited onto TiO₂

matrix it has been proven possible to transform tertiary amides into their corresponding amines using high pressure hydrogen atmosphere [13]. Rhenium-nickel oxide has been reported as an efficient catalyst for the water gas shift reaction [14]. Re-containing catalysts showed high performance for selective oxidation of methanol and ethanol [15–17]. Recently, it was discovered that Rhenium/zeolite catalyst is very active in the selective oxidation of benzene to phenol [18].

Rhenium heptoxide has shown high catalytic activity in olefin metathesis and is the only catalyst, which can work efficiently at room temperature [19]. Moreover, this heterogeneous catalyst can also be used to convert oleate esters when activated by organo-tin, which use, however, is detrimental to the regeneration process [20]. Re_2O_7 dispersed on mesoporous alumina (abbreviated as meso- Al_2O_3) with a narrow pore-size distribution centered at 3 nm in the metathesis of internal as well as terminal olefins without functional groups has shown higher catalytic activity than Re_2O_7 on common $\gamma\text{-Al}_2\text{O}_3$ in liquid phase [21,22]. Rhenium oxide supported on ordered mesoporous alumina has even been claimed as a more active and selective catalyst than $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3$ for alkenes metathesis [23].

The most efficient catalyst based on Rhenium is the well-known methyltrioxorhenium (CH_3ReO_3 , MTO). This catalyst is particularly useful in oxidation chemistry and shows high activity for epoxidations, C-H and Si-H oxidations but it can also be applied in other types of catalytic reactions such as olefin metathesis and aldehyde olefinations [24–28].

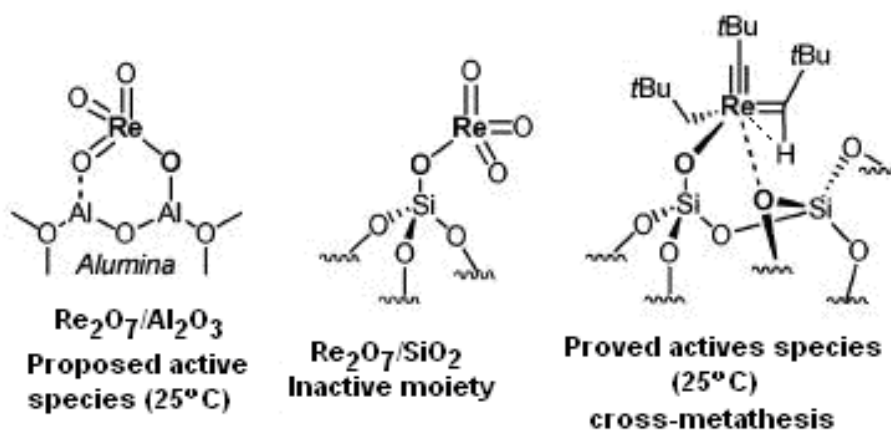
Rhenium complexes, in particular, of the type *fac*- $[\text{Re}(\text{L})(\text{CO})_3\text{Cl}]$ (where L is a bidentate ligand such as 2,2'-bipyridyl or two monodentate ligands such as 4,4'-bipyridyl), was used as heterogeneous catalyst in the reduction of CO_2 [29–31].

Molecular design principles for the creation of efficient heterogeneous catalysts for olefin metathesis with a specific focus on rhenium compounds have been reviewed by C. Coperet [32].

2. Rhenium (VII) Oxide Based Nanostructures

The activity of rhenium (VII) oxide catalyst on the surface of an oxide substrate in their most attractive application, olefin metathesis, is, according to Coperet, due to formation of either multiply bridged oxo-centers or alkyldene-substituted moieties on the surface. Single oxygen bridge connected $-\text{O}-\text{ReO}_3$ unit does not in fact display any appreciable activity [32] (see Scheme 1).

Scheme 1. Molecular fragments (potential active centers) derived from the rhenium oxide attached to oxide matrices.

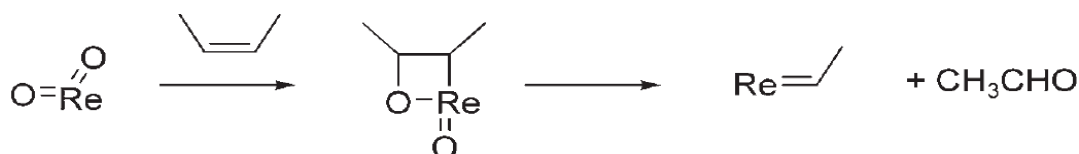


It is commonly agreed that the attachment of rhenium (VII) oxide in the not alkyldene-substituted form occurs in an advantageous way to the surface of alumina (and not silica) in the view of higher negative charge and better bridging capacity of the oxygen atoms on its surface. The catalysts can be prepared by thermal diffusion of the oxide via heating of a close mixture of ammonium perrhenate, NH_4ReO_4 , and alumina powder [33]. An alternative approach exploits wetting of the alumina with a water solution of ammonium perrhenate or perrhenic acid, HReO_4 [22]. Activation of the nanocomposite is always achieved by short term heat-treatment in oxygen atmosphere [34]. The subsequent application has always been tested in argon atmosphere to avoid the loss of rhenium in the form of volatile Re_2O_7 .

The activity of the rhenium oxide-on-alumina catalysts is a function, in the first hand, of the porosity of applied matrix. According to [33], the most efficient catalysts are characterized by more-or-less uniform mesoporosity. The commercial γ -alumina gives much less efficient catalysts in the view of micro porosity domination in relation to the total pore volume. Formation of the support with reproducible wormhole type mesoporosity is possible to achieve through application of block-copolymer surfactants in the synthesis starting either from aluminium alkoxides as precursors or using an aqueous sol-gel approach based on application of aluminium chloride or nitrate [33,35]. Triblock-copolymers of the Pluronic series such as, for example, $(\text{EO})_{19}(\text{PO})_{70}(\text{EO})_{19}$ (Pluronic P84) are efficiently applied for this purpose [35].

The activity of rhenium oxide catalysts is revealed in the starting (activation) step for the internal olefins, implying the formation of cyclic intermediates as a compulsory moment in realization of the reaction mechanism [34] (see Scheme 2).

Scheme 2. Oxometalla-cyclobutane (pseudo-Wittig) mechanism in activation of grafted rhenium oxide (alkyldene formation).



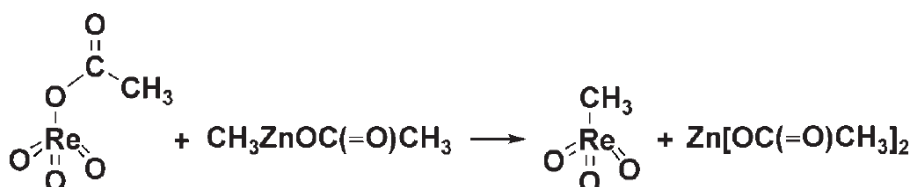
A lot of attention has been put on investigation of the effects connected with the porosity and the chemical composition of the substrate. In fact, the synthesis of highly ordered mesoporous silica is already a straightforward procedure, while the same approach to metal oxide matrices results commonly only in limited order of pores with wormhole porosity dominating the structure. It has been demonstrated, however, that pure silicas are not able to produce catalytically active nanocomposite. In the silica-alumina systems the activity increases with the aluminium content, while the ordering in porosity is a matter of simultaneous decay [22].

3. Methyltrioxorhenium Based Nanocomposites and Nanostructures

In spite of the known efficiency of methyltrioxorhenium (MTO) as a catalyst in numerous organic reactions, even the synthesis of this compound itself has until recently been extremely expensive and inefficient. It involved either direct alkylation of dirhenium heptoxide (Re_2O_7) with the non-reducing alkyl-transfer reagent tetramethyltin, wasting half of the expensive metal in the form of inactive

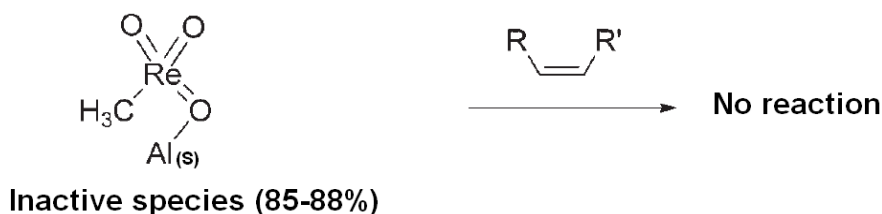
$(\text{CH}_3)_3\text{SnOReO}_3$ species, or alkylation of Re_2O_7 by the same reagent in the presence of trifluoroacetic anhydride (“anhydride route”) with formation of extremely poisonous methyltin trifluoroacetates. An unexpectedly clean and efficient synthesis of MTO has recently been reported by Herrmann *et al.*, exploiting interaction of trioxorhenium acetate, derived from rhenium oxide and acetic anhydride, with methyl zinc acetate (see Scheme 3) [36,37].

Scheme 3. Alkylation of trioxorhenium acetate by alkyl zinc acetate.



Mechanistic studies revealed very interesting intrinsic features in the activity of MTO on the oxide supports: it turned out that the influence of the support on the olefin metathesis is almost the opposite of the one observed for the rhenium (VII) oxide. In fact, the oxo-bridges species formed predominantly with a support displaying pronounced Lewis basicity are not active at all (Scheme 4) [25].

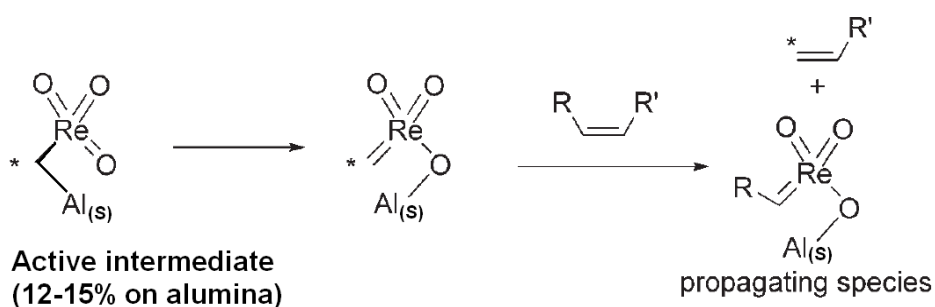
Scheme 4. O-bridged grafting dominating on a Lewis basic support.



In contrast, the supports with well expressed Lewis acidity and, especially, doped with metal atoms able to form stable metal-carbon bonds such as, for example, zinc display pronounced activity in metathesis reaction [38]. The proposed explanation lies in the need in intermediate formation of a methylene bridging unit between the oxide support and the rhenium center. This bridge is converted then into an alkyldene unit and a new oxo-bridge is formed instead (see Scheme 5) [25].

The molecular models of this surfaced intermediate complex have shown activity in the ring-opening polymerization [39].

Scheme 5. CH_2 -bridging is enhanced on a Lewis acid support and especially on a Zn-doped support.



Methyltrioxorhenium as oxidation catalyst is most efficient when a zeolite matrix is applied. For example, ZSM-5 zeolite-supported rhenium catalysts, prepared by chemical vapor deposition (CVD) of methyl trioxorhenium, are active for selective oxidation of benzene to phenol with molecular oxygen, where coexisting ammonia is prerequisite to the direct phenol synthesis. The direct synthesis of phenol from benzene with molecular oxygen proceeds with selectivity of 88% in the steady state and 94% for the pulse experiment. The phenol selectivity highly depends on the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the HZSM-5 and also on the Re loading [40–42].

4. Metal Alkoxide Derived Nanocomposites

Application of metal alkoxides—salts of alcohols, which are extremely weak, volatile and even thermally poorly stable acids—is a broadly recognized approach to the synthesis of nanocomposite materials [43]. In the catalytic applications the solutions of metals alkoxides in organic solvents are used to wet the porous matrices, which are then most often treated thermally to convert the alkoxides into oxide molecules/clusters.

The alkoxide chemistry of rhenium has been pioneered by the works of Edwards and Wilkinson in the 1980s [44]. It turned out, however, that the traditional synthetic approaches to metal alkoxides of early transition metals based on metathesis reactions of metal halides with alkali alkoxides were not efficient in this case. They were complicated by numerous side reactions and even by redox and polymerization processes. A principal breakthrough in the synthesis of homometallic rhenium alkoxides has been achieved with application of the electrochemical synthesis. The anodic oxidation of rhenium metal in alcohols turned out to be a facile and practically quantitative pathway to the corresponding oxo alkoxides. The reaction in methanol provided a derivative of rhenium (VI) $\text{Re}_2\text{O}_3(\text{OMe})_6$ as a primary product [45]. This compound, obtained earlier by halide metathesis reaction in [41], turned to be unstable in solution and prone to dimerization into $\text{Re}_4\text{O}_6(\text{OMe})_{12}$. This process was additionally enhanced by the partial reduction in the course of electrochemical synthesis of rhenium (VI) into rhenium (V). The latter led to formation of much less soluble complex of variable composition, $\text{Re}_4\text{O}_{6-x}(\text{OMe})_{12+2x}$ [46]. Formation of a principally much more soluble and solution stable alkoxide complex was achieved through interaction of the in situ produced rhenium (V) methoxide with molybdenum (VI) methoxide, $\text{MoO}(\text{OMe})_4$ [47].

Rhenium and Molybdenum oxo methoxide complexes $\text{Re}_2\text{O}_3(\text{OMe})_6$, $\text{ReMoO}_2(\text{OMe})_7$ and $\text{MoO}_2(\text{OMe})_8$ were used as precursors to prepare highly dispersed mono- and bimetallic oxide species, which were supported on the microporous NaY zeolite and mesoporous SiO_2 and Al_2O_3 . It should be mentioned, that oxomethocomplexes of Re and Mo lose their ligands when loaded into the microporous NaY zeolite, so that just metal suboxide cores, ReO_3 and MoO_3 , remain in the intracrystalline voids and reside there as nanosized particles (see Scheme 6). The obtained clusters reveal both acidic and redox properties [48], acting as efficient catalyst for methanol-to-formaldehyde conversion (Figure 1).

It is worth noting that the encapsulated rhenium oxide molecules did not show any sign of complete reduction up to the temperatures over 800 °C in pure hydrogen atmosphere in the temperature programmed reduction experiments, demonstrating high stability of this type of nanocomposite catalyst.

Scheme 6. Transformations of an alkoxide molecule on adsorption inside a pore of NaY-zeolite.

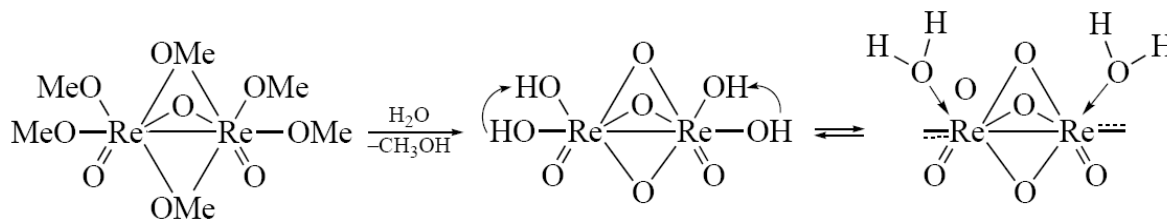
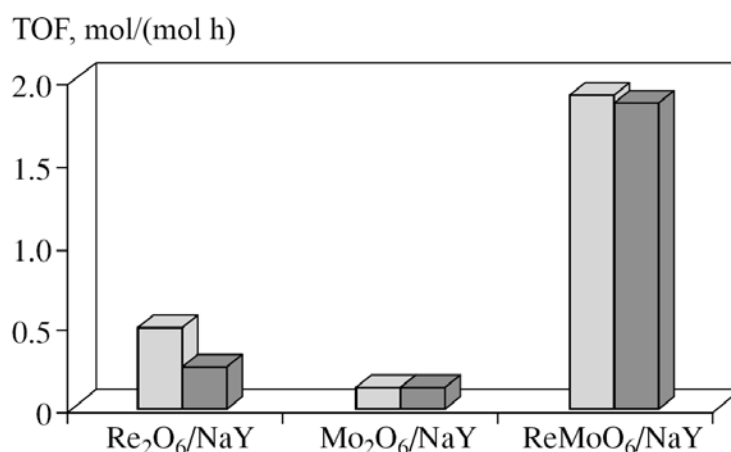
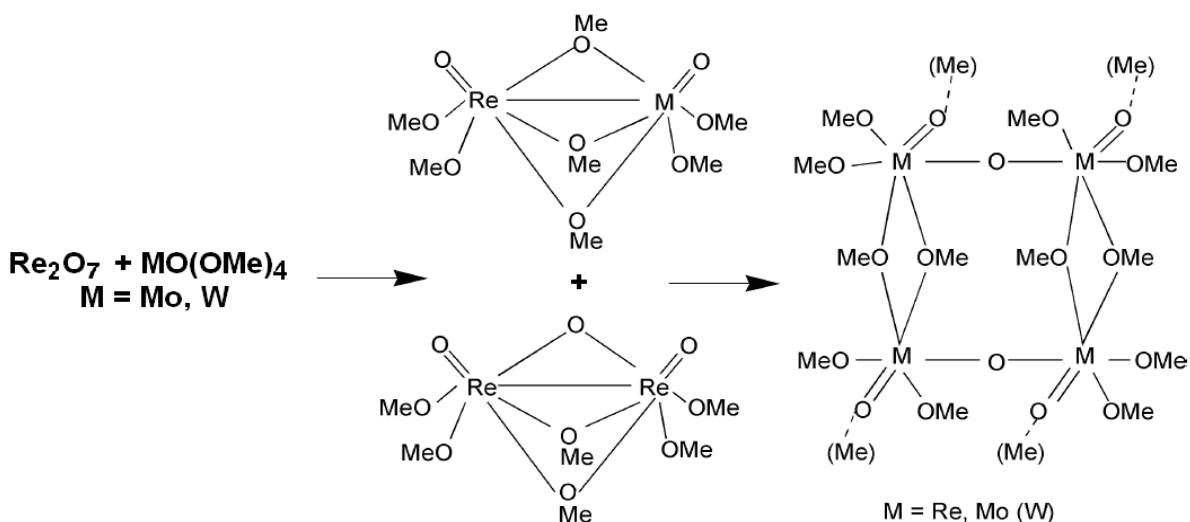


Figure 1. Catalytic activity of rhenium oxide nanocomposites in methanol-formaldehyde conversion.



The bimetallic methoxides of rhenium-molybdenum and even tungsten-molybdenum could even be prepared via thermal co-condensation of rhenium (VII) oxide with molybdenum (VI) or tungsten (VI) methoxides in toluene [45]. The higher temperature of the reaction turned out, however, to promote dimerization with formation of insoluble compounds (see Scheme 7).

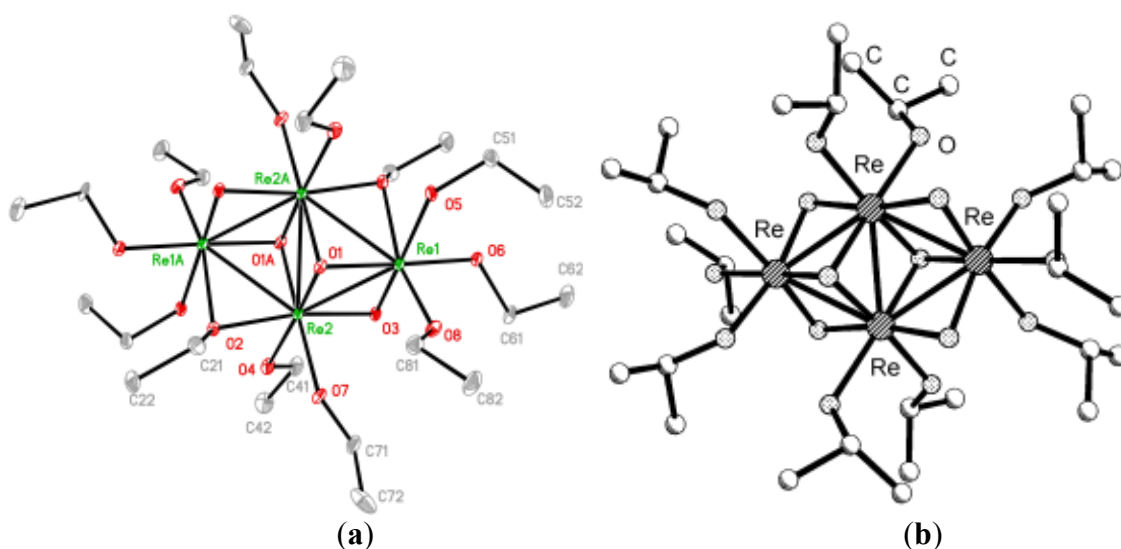
Scheme 7. Generation and dimerization of bimetallic rhenium methoxide complexes.



The lack of solution stability for the methoxide derivatives urged the search for other homologues in hope for better solubility and solution stability for them.

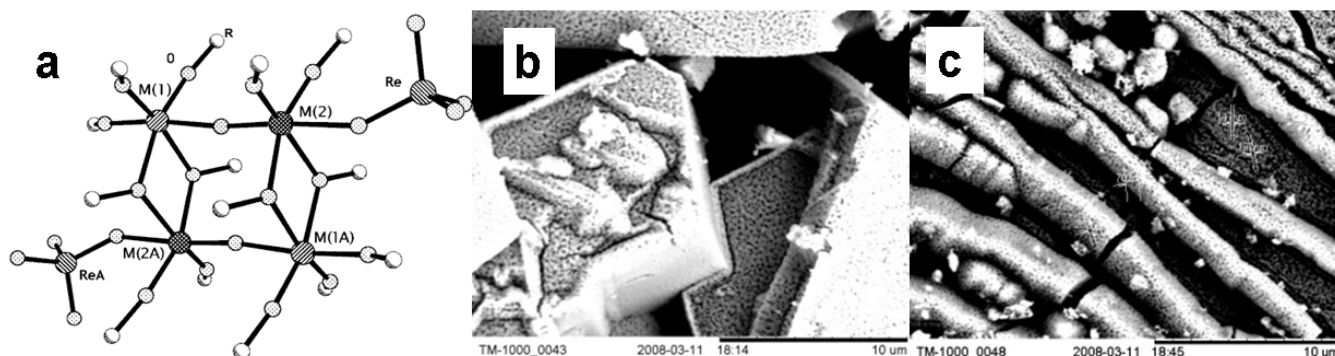
Unfortunately, the produced tetranuclear clusters (see Figure 2) turned to be completely insoluble in organic solvents. An advantage, however, compared to other known alkoxide derivatives lay for all the described tetranuclear complexes (including Re-Mo and Re-W) in their stability in ambient atmosphere. The metal alkoxides are otherwise known to be rapidly deteriorating in ambient atmosphere, which often makes the work with them rather difficult. The tetranuclear rhenium complexes, however, can be handled in open air. Their thermal treatment under extremely mild conditions provides facile access to nanopowders of rhenium metal and of corresponding alloys [49,50].

Figure 2. Molecular structures of rhenium (a) oxo-ethoxide and (b) oxo-isopropoxide.



The search for stability and possibility of applications in solution synthesis of nanocomposites led then logically to the broadening of the spectrum of available bimetallic and even trimetallic complexes obtained through co-condensation of rhenium (VII) oxide with niobium or/and tantalum alkoxides. The produced species turned out to be heterometallic alkoxide perrhenates with alkoxide cores and perrhenate groups attached via an oxygen bridge (see Figure 3).

Figure 3. Molecular structures of niobium and tantalum methoxoperrhenates including mixed-metal species, $(\text{Nb}_x\text{Ta}_{x-1})_4\text{O}_2(\text{OMe})_{14}(\text{ReO}_4)_2$ (a) and the SEM views of the complex oxide monoliths produced by their thermal decomposition, 70% Nb (b) and 50% Nb (c).

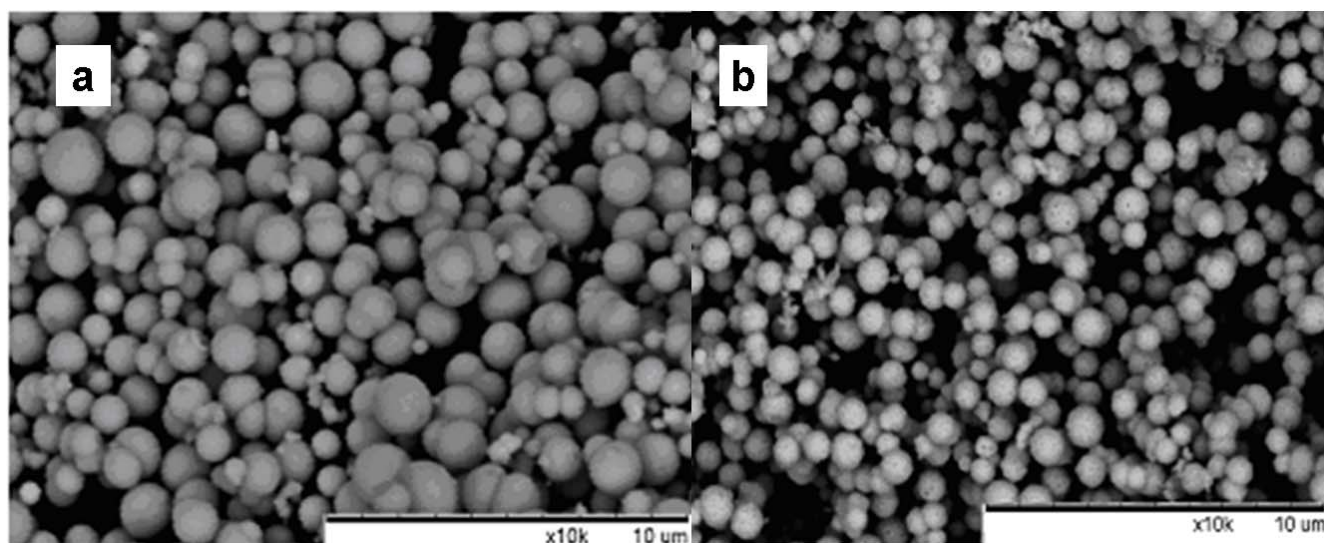


The methoxide derivatives of this family are poorly soluble but their thermal decomposition under thoroughly controlled conditions offered an attractive approach to organized porous solids with the prospect of incorporating rhenium oxide into a simultaneously formed hierarchical matrix [51]. Unfortunately, a major part of the rhenium content in the thermal decomposition processes is reduced into an inactive form and then re-oxidized and removed in volatiles at higher temperatures (over 500 °C).

Further steps in the synthesis of rhenium oxides nanocomposites derived from metal alkoxides have successfully exploited high solubility and solution stability of bimetallic ethoxide complexes of rhenium with niobium or tantalum. These complexes are prepared with quantitative yields via interaction of rhenium (VII) oxide with the ethoxides of those metals. Their structure follows the same principal construction as that of their methoxide analogs [52]. Even n-propoxide derivatives following the same motive in the molecular structure could successfully be produced [53].

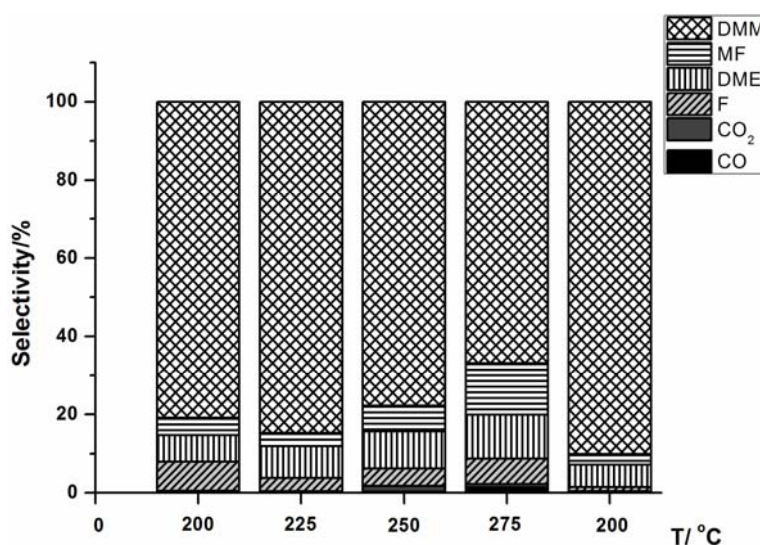
The use of an inorganic perrhenate ligand in the structure of early transition metal alkoxide precursors permits to achieve uniform self-assembly of the primary nanoparticles produced by their hydrolysis. The latter has been carried out in hydrocarbon reaction medium by addition of water on vigorous stirring, either in the pure form or in solutions in parent alcohols. The self-assembly is guided in this case by the surface charge enhanced by the presence of strongly coordinated anions as determined by zeta-potential measurements. The reaction products turned to be spherical aggregates with the size that could efficiently be controlled through polarity of the reaction medium (see Figure 4). Their inner porosity is, unfortunately, closed with residual surface area of about 25 m²/g. The coordination of metal centers has been investigated using EXAFS-spectroscopy revealing preservation of perrhenate ligands through the whole sol-gel procedure. The coordination of the tantalum atoms remained also the same. The aggregates remained amorphous on thermal treatment up to 700 °C (24 h treatment), but crystallized, when treated at 1000 °C. This latter process was, unfortunately, associated with the total loss of rhenium content and offered early transition metal oxides as products.

Figure 4. Typical appearance of nanobeads produced by controlled hydrolytic sol-gel process in mixed (hydrocarbon-alcohol) solvent media using ethoxide Ta (a) and Nb (b) perrhenates. .



The most attractive application of soluble and solution stable alkoxide perrhenate precursors for preparation of heterogeneous catalysts was exploiting deposition of *in situ* produced oxide perrhenates nanoparticles onto mesoporous titanium dioxide matrix. The Ta₂O₅-based particles with the size of about 5 nm as shown by TEM were distributed in the pores of meso-TiO₂ practically conserving its surface area thus creating an advantageous microstructure for the catalytic application. This permitted to maintain high surface area and expose both oxidative ReO₄- sites and acidic tantalum oxide sites to the methanol substrate. This resulted in efficient and highly selective conversion of methanol into dimethoxy-methane (DMM) in one step [54]. It is also important to note that the prepared catalysts were displaying high activity at relatively low temperatures and was not losing it and even improving the selectivity through the temperature cycling. It can be explained through efficient conservation of the perrhenate sites along with formation of Ta-OH functions on interaction with released water molecules in the course of the process (see Figure 5).

Figure 5. Temperature dependence of the selectivity as a function of temperature for methanol-to-formaldehyde conversion using alkoxide-derived rhenium-tantalum oxide catalyst on mesoporous titania support [54]. Abbreviations: DMM—dimethoxymethane, MF—methyl formiate, DME—dimethyl ether, F—formaldehyde.



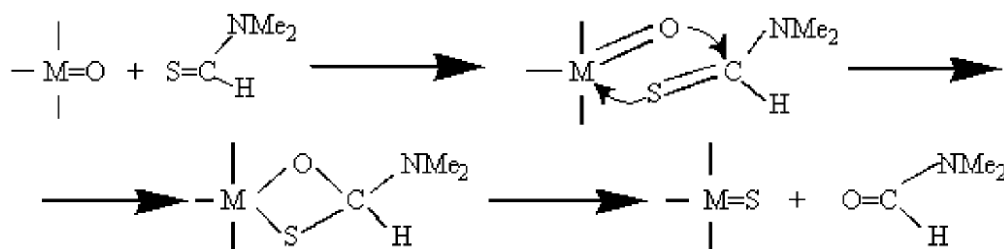
An alternative approach to creation of active centers of rhenium oxide within titanium dioxide matrix has been developed through oxidative dispersion of rhenium metal [55]. The thus prepared catalyst demonstrated predominantly oxidative activity, producing formaldehyde as major product in the methanol conversion.

5. Rhenium Sulfide Based Nanocomposites

Preparation of nanocomposite materials based on metal sulfides has until relatively recently been a considerable challenge. The traditional approach involved first preparation of corresponding metal oxide nanocomposites and then their sulfidation by hydrogen sulfide gas. Another approach involved impregnation of matrices with in advance obtained thioperrhenate salts with their subsequent thermal decomposition within the matrix [56].

A principally new approach has been reported recently based on solution sulfidation of rhenium complexes with O-donor ligands using thiocarbonyl compounds. This reaction permits to avoid application of poisonous gases and occurs at ambient conditions. Its mechanism exploits the strong affinity of rhenium to S-donor ligands (see Scheme 8).

Scheme 8. Proposed mechanism of solution sulfidation by thiocarbonyl compounds [57].



This new sulfidation method permitted to obtain highly active catalysts for hydrodesulfurization (HDS) and especially for the hydrodenitrogenation process, especially important for the purification of lower quality crude oils. Mesoporous alumina was used as support. It was impregnated by freshly prepared solutions of rhenium (VII) oxide in toluene/dimethylthioformamide mixture.

The thus prepared nanocomposites revealed considerably higher activity and selectivity than the commercial catalysts prepared by standard perrhenate impregnation and hydrogen sulfide treatment sequence [57]. Under the reaction conditions employed the catalysts in question gives rise to the following reactions. Dibenzothiophene (DBT) is desulfurized by two parallel routes, yielding either biphenyl (BP) or cyclohexylbenzene (CHB) as products. Indole is denitrogenated to yield ethyl benzene and ethyl cyclohexane as products. Naphthalene is hydrogenated to tetralene. The conversions determined were expressed as pseudo-first-order rate constants for hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and hydrogenation (HYD), respectively (Table 1).

Table 1. Catalytic activities of hydrodesulfurization catalysts prepared by a traditional method and by the new solution sulfidation method (rate constants in h^{-1}).

Preparation technique and catalyst load	$k(\text{HDS})$	$k(\text{BP})$	$k(\text{CHB})$	$k(\text{HDN})$	$k(\text{HYD})$
New method, 9 wt % Mo/ Al_2O_3	2.4	1.9	0.5	9.2	5.1
Traditional method, 8 wt % Mo/ Al_2O_3	2.7	2.4	0.3	4.6	3.3
New method, 6 wt % Re/ Al_2O_3	2.0	2.0	0.0	6.4	0.5
Traditional method, 6 wt % Re/ Al_2O_3	3.7	3.7	0.0	2.0	0.4

6. Conclusions

Nanochemistry approaches apparently render a possibility of strong improvement in the activity of rhenium based catalysts in combination with principal decrease in the content of this expensive constituent. These two features in combination open for broad and successful future use of rhenium catalysts.

Acknowledgments

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References

1. Mol, J.C. Industrial applications of olefin metathesis. *J. Mol. Catal. A Chem.* **2004**, *213*, 39–45.
2. Xiao, J.; Puddephatt, R.J. Pt–Re clusters and bimetallic catalysts. *Coord. Chem. Rev.* **1995**, *143*, 457–500.
3. Guryev, Y.V.; Ivanova, I.I.; Lunin, V.V.; Grünert, W.; van den Berg, M.V.E. Characterization of metal segregation in Pt–Re/Al₂O₃ reforming catalysts. *Appl. Catal. A* **2007**, *329*, 16–21.
4. Laurenti, D.; Ninh Thi, K.T.; Escalona, N.; Massin, L.; Vrinat, M.; Llambias, F.J.G. Support effect with rhenium sulfide catalysts. *Catal. Today* **2008**, *130*, 50–55.
5. Okal, J.; Kubicka, H. Influence of oxidation-reduction treatment on activity and selectivity of Re supported on gamma-alumina. *Appl. Catal. A* **1998**, *171*, 351–359.
6. Escalona, N.; Vrinat, M.; Laureni, D.; Llambias, F.J.G. Rhenium sulfide in hydrotreating. *Appl. Catal. A* **2007**, *322*, 113–120.
7. Rätty, J.; Pakkanen, T.A. Controlled gas-phase preparation and HDS activity of Re-2(CO)(10)/alumina catalysts. *Catal. Lett.* **2000**, *65*, 175–180.
8. Escalona, N.; Llambias, F.J.G.; Vrinat, M.; Nguyen, T.S.; Laurenti, D.; Agudo, A.L. Highly active ReS₂/gamma-Al₂O₃ catalysts: Effect of calcination and activation over thiophene hydrodesulfurization. *Catal. Comm.* **2007**, *8*, 285–288.
9. Escalona, N.; Ojeda, J.; Cid, R.; Alves, G.; Agudo, A.L.; Fierro, J.L.; Llambias, F.J.G. Characterization and reactivity of Re(x)/gamma-Al₂O₃ catalysts in hydrodesulfurization and hydrodenitrogenation of gas oil: Effect of Re loading. *Appl. Catal. A* **2002**, *234*, 45–54.
10. Wang, L.; Ohnishi, R.; Ichikawa, M. Selective dehydroaromatization of methane toward benzene on Re/HZSM-5 catalysts and effects of CO/CO₂ addition. *J. Catal.* **2000**, *190*, 276–283.
11. Shu, Y.; Ohnishi, R.; Ichikawa, M. Improved methane dehydrocondensation reaction on HMCM-22 and HZSM-5 supported rhenium and molybdenum catalysts. *Appl. Catal. A* **2003**, *252*, 315–329.
12. Wang, L.S.; Murata, K.; Inaba, M. Production of pure hydrogen and more valuable hydrocarbons from ethane on a novel highly active catalyst system with a Pd-based membrane reactor. *Catal. Today* **2003**, *82*, 99–104.
13. Burch, R.; Paun, C.; Cao, X.M.; Crawford, P.; Goodrich, P.; Hardacre, C.; Hu, P.; McLaughlin, L.; Sa, J.; Thompson, J.M. Catalytic hydrogenation of tertiary amides at low temperatures and pressures using bimetallic Pt/Re-based catalysts. *J. Catal.* **2011**, *283*, 89–97.
14. Chayakul, K.; Srithanratana, T.; Hengrasmee, S. Catalytic activities of Re–Ni/CeO(2) bimetallic catalysts for water gas shift reaction. *Catal. Today* **2011**, *175*, 420–429.
15. Chang, A.S.Y.; Chen, W.; Wang, H.; Rowe, J.E.; Madey, T.E. Methanol reactions over oxygen-modified Re surfaces: Influence of surface structure and oxidation. *J. Phys. Chem. B* **2004**, *108*, 14643–14651.

16. Yuan, Y.; Shido, T.; Iwasawa, Y. The new catalytic property of supported rhenium oxides for selective oxidation of methanol to methylal. *Chem. Comm.* **2000**, 1421–1422.
17. Tsoncheva, T.; Vankova, S.; Bozhkov, O.; Mehendjiev, D. Rhenium and manganese modified activated carbon as catalyst for methanol decomposition. *Can. J. Chem.* **2007**, *85*, 118–123.
18. Kusakari, T.; Sasaki, T.; Iwasawa, Y. Selective oxidation of benzene to phenol with molecular oxygen on rhenium/zeolite catalysts. *Chem. Comm.* **2004**, 992–993.
19. Salameh, A.; Baudoin, A.; Daravong, S.; Boehm, V.; Roeper, M.; Basset, J.M.; Coperet, C. CH₃-ReO₃ on gamma-Al₂O₃: Activity, selectivity, active site and deactivation in olefin metathesis. *J. Catal.* **2008**, *253*, 180–190.
20. Mol, J.C. Catalytic metathesis of unsaturated fatty acid esters and oils. *Topics Catal.* **2004**, *27*, 97–104.
21. Onaka, M.; Oikawa, T. Olefin metathesis over mesoporous alumina-supported rhenium oxide catalyst. *Chem. Lett.* **2002**, 850–851.
22. Bakala, P.C.; Briot, E.; Millot, Y.; Piquemal, J.Y.; Bregeault, J.M. Comparison of olefin metathesis by rhenium-containing γ -alumina or silica-aluminas and by some mesoporous analogues. *J. Catal.* **2008**, *258*, 61–70.
23. Oikawa, T.; Ookoshi, T.; Tanaka, T.; Yamamoto, T.; Onaka, M. A new heterogeneous olefin metathesis catalyst composed of rhenium oxide and mesoporous alumina. *Micropor. Mesopor. Mater.* **2004**, *74*, 93–103.
24. Jain, K.R.; Kühn, F.E. Immobilization of organorhenium (VII) oxides. *J. Organomet. Chem.* **2007**, *692*, 5532–5540.
25. Salameh, A.; Joubert, J.; Baudouin, A.; Lukens, W.; Delbecq, F.; Sautet, P.; Basset, J.M.; Coperet, C. CH₃ReO₃ on γ -Al₂O₃: Understanding its structure, initiation, and reactivity in olefin metathesis. *Angew. Chem. Int. Ed.* **2007**, *46*, 1–5.
26. Mandelli, D.; van Vliet, M.C.A.; Arnold, U.; Sheldon, R.A.; Schuchardt, U. Epoxidation of alkenes with hydrogen peroxide catalyzed by ReO₄-SiO₂ center dot Al₂O₃ and ReO₄-Al₂O₃. *J. Mol. Catal. A* **2001**, *168*, 165–171.
27. Buffon, R.; Auroux, A.; Lefebvre, F.; Leconte, M.; Choplin, A.; Basset, J.M. A surface organometallic approach to the synthesis of rhenium-based catalysts for the metathesis of olefins: CH₃ReO₃/Nb₂O₅. *J. Mol. Catal.* **1992**, *76*, 287–295.
28. Buffon, R.; Choplin, A.; Leconte, M.; Basset, J.M. Surface organometallic chemistry of rhenium: Attempts to characterize a surface carbene in metathesis of olefins with the catalyst CH₃ReO₃/Nb₂O₅. *J. Mol. Catal.* **1992**, *72*, L7–L10.
29. Scheiring, T.; Klein, A.; Kaim, W. EPR study of paramagnetic rhenium (I) complexes (bpy(center dot-))Re(CO)₃X relevant to the mechanism of electrocatalytic CO₂ reduction. *J. Chem. Soc., Perkin Trans.* **1997**, *2*, 2569–2571.
30. Cecchet, F.; Alebbi, M.; Bignozzi, C.A.; Paolucci, F. Efficiency enhancement of the electrocatalytic reduction of CO₂: fac-[Re(v-bpy)(CO)₃Cl] electropolymerized onto mesoporous TiO₂ electrodes. *Inorg. Chim. Acta* **2006**, *359*, 3871–3874.
31. Chen, Y.; Liu, W.; Jin, J.S.; Liu, B.; Zou, Z.G.; Zou, J.L.; You, X.Z. Rhenium (I) tricarbonyl complexes with bipyridine ligands attached to sulfur-rich core: Syntheses, structures and properties. *J. Organomet. Chem.* **2009**, *694*, 763–770.

32. Coperet, C. Molecular design of heterogeneous catalysts: the case of olefin metathesis. *New. J. Chem.* **2004**, *28*, 1–10.
33. Balcar, H.; Hamtil, R.; Zilkova, N.; Zhang, Z.; Pinnavaia, T.J.; Cejka, J. Re(VII) oxide on mesoporous alumina of different types—Activity in the metathesis of olefins and their oxygen-containing derivatives. *Appl. Catal. A* **2007**, *320*, 56–63.
34. Salameh, A.; Coperet, C.; Basset, J.M.; Böhm, V.P.W.; Röper, M. Rhenium (VII) oxide/ aluminum oxide: More experimental evidence for an oxametallacyclobutane intermediate and a pseudo-Wittig initiation step in olefin metathesis. *Adv. Synth. Catal.* **2007**, *349*, 238–242.
35. Marquez-Alvarez, C.; Zilkova, N.; Perez-Pariente, J.; Cejka, J. Synthesis, characterization and catalytic applications of organized mesoporous alumina. *Catal. Rev. Sci. Eng.* **2008**, *50*, 222–286.
36. Herrmann, W.A.; Rost, A.M.J.; Mitterpleininger, J.K.M.; Szesni, N.; Sturm, S.; Fischer, R.W.; Kühn, F.E. A cheap, efficient, and environmentally benign synthesis of the versatile catalyst methyltrioxorhenium (MTO). *Angew. Chem. Int. Ed.* **2007**, *46*, 7301–7303.
37. Jain, K.R.; Herrmann, W.; Kühn, F. Synthesis and catalytic applications of chiral monomeric organomolybdenum (VI) and organorhenium (VII) oxides in homogeneous and heterogeneous phase. *Coord. Chem. Rev.* **2008**, *252*, 556–568.
38. Oikawa, T.; Masui, Y.; Tanaka, T.; Chujo, Y.; Onaka, M. Lewis acid-modified mesoporous alumina: A new catalyst carrier for methyltrioxorhenium in metathesis of olefins bearing functional groups. *J. Organom. Chem.* **2007**, *692*, 554–561.
39. Frech, C.M.; Blacque, O.; Schmalle, H.W.; Berke, H.; Adlhart, C.; Chen, P. Unprecedented ROMP activity of low-valent rhenium–nitrosyl complexes: Mechanistic evaluation of an electrophilic olefin metathesis system. *Chem. Eur. J.* **2006**, *12*, 3325–3338.
40. Bal, R.; Tada, M.; Kusakari, T.; Iwasawa, Y. Direct phenol synthesis from Benzene with molecular oxygen on rhenium/zeolite catalysts. *Catal. Catal.* **2005**, *47*, 72–74.
41. Viswanadham, N.; Shido, T.; Iwasawa, Y. Performances of rhenium oxide-encapsulated ZSM-5 catalysts in propene selective oxidation/ammoxidation. *Appl. Catal. A* **2001**, *219*, 223–233.
42. Viswanadham, N.; Shido, T.; Sasaki, T.; Iwasawa, Y. Ammonia-promoted rhenium-cluster formation in CH₃ReO₃-encapsulated H-ZSM-5 relevant to the performance of the catalytically selective oxidation/ammoxidation of propene. *J. Phys. Chem. B.* **2002**, *106*, 10955–10963.
43. Seisenbaeva, G.A.; Gohil, S.; Kessler, V.G. *Sol-Gel Methods for Materials Processing*; Innocenzi, P., Zub, Y., Kessler, V.G., Ed.; Springer: Dordrecht, The Netherlands, 2008; pp. 397–403.
44. Edwards, P.G.; Wilkinson, G.; Hursthouse, M.B.; Malik, K.M.A. Improved syntheses of tetrachloro-oxorhenium (VI) and chlorotrioxo-rhenium (VII). Synthesis of alkoxo- and dialkylamido-rhenium compounds. The crystal and molecular structures of di- μ -methoxy-tetramethoxy- μ -oxo-dioxodirhenium (VI) (Re–Re), bis [lithium pentaiso-propoxo-oxorhenate (VI)–lithiumchloride–tetrahydrofuran(1/1/2)], and trans-tetraphenoxobis(trimethylphosphine)rhenium (IV). *J. Chem. Soc. Dalton Trans.* **1980**, 2467–2472.
45. Seisenbaeva, G.A.; Shevelkov, A.V.; Kloos, L.; Gohil, S.; Tegenfeldt, J.; Kessler, V.G. Homo- and heterometallic rhenium oxomethoxide complexes with a M₄(μ -O)₂(μ -OMe)₄ planar core—a new family of metal alkoxides with peculiar structural disorder. Preparation and X-ray single crystal study. *J. Chem. Soc. Dalton Trans.* **2001**, 2762–2768.

46. Kessler, V.G.; Shevelkov, A.V.; Khvorykh, G.V.; Seisenbaeva, G.A.; Turova, N.Y.; Drobot, D.V. Electrochemical synthesis and physicochemical properties of rhenium(V) oxomethoxide, $\text{Re}_4\text{O}_2(\text{OMe})_{16}$. *Russ. J. Inorg. Chem.* **1995**, *40*, 1477–1483.
47. Kessler, V.G.; Seisenbaeva, G.A.; Shevelkov, A.V.; Khvorykh, G.V. Synthesis, crystal, molecular and electronic structure of a novel heterobinuclear alkoxide cluster $(\text{MeO})_2\text{ReO}(\mu\text{-OMe})_3\text{MoO}(\text{OMe})_2$. *J. Chem. Soc. Chem. Commun.* **1995**, 1779–1780.
48. Kustov, A.L.; Kessler, V.G.; Romanovsky, B.V.; Seisenbaeva, G.A.; Drobot, D.V.; Shcheglov, P.A. Supported Re and Mo oxides prepared using binuclear precursors: Synthesis and characterization. *J. Mol. Catal.* **2004**, *216*, 101–106.
49. Seisenbaeva, G.A.; Sundberg, M.; Nygren, M.; Dubrovinsky, L.; Kessler, V.G. Thermal decomposition of the methoxide complexes $\text{MoO}(\text{OMe})_4$, $\text{Re}_4\text{O}_6(\text{OMe})_{12}$ and $(\text{Re}_{1-x}\text{Mo}_x)\text{O}_6(\text{OMe})_{12}$ ($0.24 \leq x \leq 0.55$). *Mater. Chem. Phys.* **2004**, *87*, 142–148.
50. Nikonova, O.A.; Jansson, K.; Kessler, V.G.; Sundberg, M.; Baranov, A.I.; Shevelkov, A.V.; Drobot, D.V.; Seisenbaeva, G.A. Electrochemical synthesis, structural characterization and decomposition of rhenium oxoethoxide. *Inorg. Chem.* **2008**, *44*, 1295–1300.
51. Nikonova, O.A.; Kessler, V.G.; Seisenbaeva, G.A. Substitution features in the isomorphous replacement series for metal-organic compounds $(\text{Nb}_x\text{Ta}_{1-x})_4\text{O}_2(\text{OMe})_{14}(\text{ReO}_4)_2$, $x = 1/4, 0.7, 0.5, 0.3$ —Single-source precursors of complex oxides with organized porosity. *J. Solid State Chem.* **2008**, *181*, 3294–3302.
52. Nikonova, O.A.; Kessler, V.G.; Drobot, D.V.; Shcheglov, P.A.; Seisenbaeva, G.A. Synthesis and X-ray single crystal study of niobium and tantalum Oxo-ethoxo-perrhenates, $\text{MV}_4\text{O}_2(\text{OEt})_{14}(\text{ReO}_4)_2$. *Polyhedron* **2007**, *26*, 862–866.
53. Nikonova, O.; Nedelec, J.M.; Kessler, V.G.; Seisenbaeva, G.A. Precursor-directed assembly of complex oxide nanobeads. The role of strongly coordinated inorganic anions. *Langmuir* **2011**, *27*, 11622–11628.
54. Nikonova, O.A.; Capron, M.; Fang, G.; Faye, J.; Mamede, A.S.; Jalowiecki-Duhamel, L.; Dumeignil, F.; Seisenbaeva, G.A. Novel approach to rhenium oxide catalysts for selective oxidation of methanol to DMM. *J. Catal.* **2011**, *279*, 310–318.
55. Secordel, X.; Yoboue, A.; Cristol, S.; Lancelot, C.; Capron, M.; Paul, J.F.; Berrier, E. Supported oxorhenate catalysts prepared by thermal spreading of metal $\text{Re}(0)$ for methanol conversion to methylal. *J. Solid State Chem.* **2011**, *184*, 2806–2811.
56. Davenport, W.H.; Kollonitsch, V.; Kline, C.H. Advances in rhenium catalysts. *Ind. Eng. Chem.* **1968**, *60*, 10–11.
57. Seisenbaeva, G.A.; Gohil, S.; Jansson, K.; Herbst, K.; Brorson, M.; Kessler, V.G. Solution interaction of O-donor ligand metal complexes with thiocarbonyl compounds—a new general route to metal sulfide materials. *New J. Chem.* **2003**, *27*, 1059–1064.