Polyhedral silsesquioxanes as precursors of tailor-made heterogeneous catalyst centres

I. Water oxidation

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Abstract

Fe-, Ni-, Cu- and Mn-polyhedral oligometallasilsesquioxanes containing $(PhSiO_{1.5})_{12}(MO)_n$L-fragments (where L = ROH, H_2O; $n = 6$ for Fe, Ni, Mn and $n = 4$ for Cu; Ni_4Fe_2- and Ni_4Cu_2-complexes were also used) have been used for the preparation of heterogeneous catalysts to investigate the influence of structural factors on the catalytic properties of the hydroxides of these metals. SAXS have been used for the characterization of the distribution of complexes associated in the solution and on the supports surface. It was found that the complex distribution on the carbon support (soot) is close to monomolecular. The highest O_2 yields have been obtained when Fe_6/C were used as catalysts. It has been found that supports have a strong influence on the catalytic properties of supported complexes. The catalysts prepared based on the Fe_6 complexes were more active than those prepared from Ni_4Fe_2 complexes, in which active Fe atoms are separated by inactive Ni atoms. This observation is very important for the mechanism developed by the authors. According to this mechanism it is necessary for the formation of O_2 to have at least two metal ions associated with each other in active centre.

Key words: Silicon; Alkoxide; Iron; Nickel; Copper; Manganese; Supported catalyst

1. Introduction

Water oxidation to dioxygen is a four electrons process, requiring the strong oxidants with $E = 1.23$ V (*vs.* NHE) [1]. Furthermore, for elimination of one electron from H_2O molecule a more strong oxidant with $E = 2.8$ V is needed. However, photosystem II of green plants evolves O_2 from H_2O with a high efficiency. This system does not include strong oxidants. Moreover, its oxidant is the one-electron [2]. Oxygen evolving centre (OEC) of such system contains four Mn ions [2]. Apparently the reason of high efficiency of photosystem II is a high level of structural organization

of various groups of enzyme molecule, taking part in the process. OEC is under intensive investigation for many years. However, the mechanism of its action is still unclear. So, many Mn-complexes, which were synthesized as a structural models of OEC, are inactive in water oxidation [3]. Earlier, we investigated H_2O oxidation by one-electron oxidant $Ru(bpy)_3^{3+}$ (reaction (1)).

$$4Ru^{III} + 2H_2O \longrightarrow 4Ru^{II} + O_2 + 4H^+ \qquad (1)$$
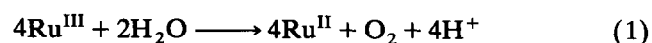
Hydroxides of Fe^{III} and Cu^{II} [4], Mn^{III}, Co^{III} and Ru^{IV} [5] were found to be efficient catalysts for this reaction.

The universal mechanism of four-electron catalytic oxidation of water, depicted in Scheme 1, was proposed on the base of quantum-chemical study [6,7].
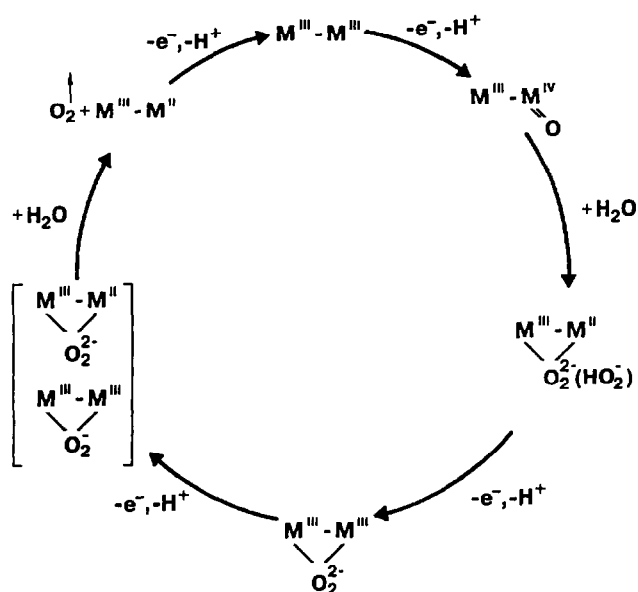
Scheme 1. Mechanism of water to dioxygen oxidation.

The main features of this mechanism are:
(i) An active site of water-oxidation catalysts should contain at least two metal atoms. One atom takes part in the redox transformation, the second atom is to stabilize the intermediates such as O_2^{2-} or HO_2^- (without changing their oxidation state). H_2O oxidation to H_2O_2 (uncoordinated molecule) requires 1.78 V (vs. NHE). This makes the process energetically unfavourable.
(ii) The metal atoms should be fixed at the optimal distance, to enable electron transfer and coordination of the intermediate products.
(iii) The activity of the catalysts depends on the properties of OH groups of the first coordination sphere of a metal atom. The OH group should be terminal and acidic, thus providing the wide pH range of operation.

Besides the previously mentioned metal hydroxides, the complexes of the same metals with ligands, containing the donor N- or O-groups, were studied [8]. However, if such complexes are used as the catalyst precursors, an induction period of activation is observed owing to the oxidation of the ligand by $Ru(bpy)_3^{3+}$ and further hydrolysis of complexes yielding metal hydroxides. Virtually any other ligand, containing the donor N or O group, can be oxidized more readily than H_2O or its fragments, including hydroxyls.

The development of silsesquioxane chemistry presented new types of metal complexes, in which the transition metal can be coordinated with oxygen atoms of macrocyclic organosiloxanolate ligands (or the silsesquioxanes framework) [9]. These complexes should

be more stable under oxidation conditions and could be considered as a model of active centres of heterogeneous-metal silica-supported catalysts on the base. The synthesis of polyatomic and heterometal complexes allows us to investigate the catalytic properties of different ion clusters, which can be considered as models of catalytic centres. The catalytic properties of heteronuclear complexes, prepared on the base of cubic silsesquioxanes, were investigated previously by Feher and co-workers [10–14]. Primarily polymerization reaction were studied [13,14], which required reductive treatment of complexes with a metalloorganic compound in order to obtain the active centres. Catalytic properties of polynuclear silsesquioxanes in oxidation reactions were then not yet considered.

We have now investigated the influence of structural factors on the catalytic properties of the catalysts prepared with the use of Fe, Ni, Cu and Mn polyhedral oligometallasilscsquioxanes, and present the results of our investigations below.

2. Results and discussion

2.1. Synthesis of polyhedral silsesquioxanes

Polyhedral silsesquioxanes $\{RSiO_{1.5}\}_n(MO_x)_m$ are synthesized via interaction of sodium polyphenylsilsesquioxanes with metal chlorides. The synthesis of the complexes with organosiloxanolate have been described elsewhere [9]. This preparation includes three stages:
(i) hydrolysis of corresponded trichlorosilane to polysilsesquioxane (polysilaxonolate);
(ii) basic cleavage of polysilaxonolates to sodiumpolyphenylsilsesquioxanes;
(iii) exchange reaction of sodiumphenylsilsesquioxanes with metal chloride.

The compounds used in this work are presented in Table 1.

TABLE 1. The compounds used for catalyst preparation

| N	Composition	Structure type	Ref
1	$[PhSiO_{1.5}]_{12}(NiO)_4(NaO_{0.5})_6(BuOH)_5(OH)_{10}$	B	17
2	$[PhSiO_{1.5}]_{12}(NiO)_4(FeO1,5)_2(NaCl)(EtOH)_8(OH)_2$	A	–
3	$[PhSiO_{1.5}]_{12}(NiO)_4(CuO)_2(NaCl)(BuOH)_{3,4}(OH)_{12}$	A	–
4	$[PhSiO_{1.5}]_{12}(NiO)_6(NaCl)(BuOH)_{12}$	A	15
5	$[PhSiO_{1.5}]_{12}(FeO)_6(BuOH)_6(H2O)_{2,4}$	A	19
6	$[PhSiO1,5]_{12}(FeO_{1.5})_4$-polymer M.W.1000–2000	–	19
7	$[ViSiO_{1.5}]_{12}(CuO)_4(KO_{0.5})_4(BuOH)_{2,5}(H_2O)_3$	C	20
8	$[PhSiO_{1.5}]_{12}(CuO)_4(KO_{0.5})_4(BuOH)_{3,5}$	C	20
9	$[PhSiO_{1.5}]_{12}(MnO)_6(NaCl)(EtOH)_8$	A	16
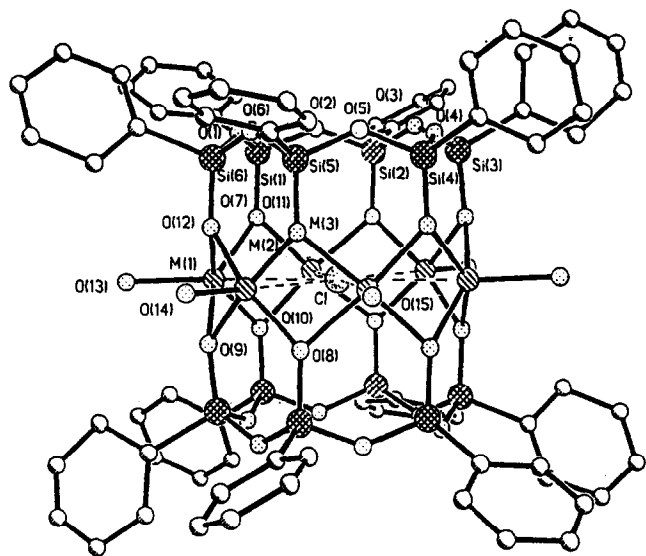
Fig. 1. The molecular structure of Na$^+$[(PhSiO$_2$)$_6$Ni$_6$(O$_2$SiPh)$_6$Cl$^-$]- (^{n}BuOH)$_{16}$ [15] and Na$^+$[[PhSiO$_2$]$_6$Mn$_6$[O$_2$SiPh]$_6$Cl$^-$](EtOH)$_8$ [16]. Hydrogen atoms and hydrocarbon parts of alcohols have been omitted for clarity (M = Mn, Ni)..

Fig. 2. The molecular structure of Na$_2$[(PhSiO$_2$)$_6$Na$_4$Ni$_4$(OH)$_2$(O$_2$Si-Ph)$_6$](^{n}BuOH)$_{16}$ [17]. Hydrogen atoms and hydrocarbon parts of alcohols have been omitted for clarity.

Complexes of type A (Fig. 1) have a sandwich structure: two "outward" 12-membered cyclohexasilanolate ligands coordinate six metal ions (Ni [15], Mn [16] and presumably Fe) situated between them along the hexagon with each silanolate O atom bonded to two metal ions and each metal coordinated by four silanolate O atoms (two of each cyclic ligand). The metal–Si–O–framework has a non-crystallographic 6/mmm symmetry and cylinder form, where the Cl$^-$ anion is encapsulated in the centre of the cavity and coordinated by six metal ions along the hexagon. The Na$^+$ counterion is located outside the silaxonolate molecule and coordinated by the O atoms of the siloxane cycles and the solvent molecules. The metal atoms have a distorted tetragonal–bipyramidal coordination: four silanolate O atoms are in equatorial position and the Cl$^-$ ion is in the distant apical one; each Ni (or Mn) atom coordinates one molecule of alcohol or water and Fe ions presumably coordinate hydroxyls.

The complex of type B (Fig. 2) is Na$_2$[(PhSiO$_2$)$_6$Na$_4$-Ni$_4$(OH)$_2$(OSiPh)$_6$](^{n}BuOH)$_{16}$. The complex anion is built up out of two antiparallel cis-hexaphenylcyclohexanolate ligands with silanolate O atoms, which coordinate via a sandwich grouping ("cationic layer") of metal atoms (4Ni^{2+} and 4Na$^+$) stabilized by two bridging ligands μ-OH$^-$. The external cations of the layer (4Na$^+$ and 2Ni^{2+}) are also coordinated by O atoms of the 10 solvated n-butanol molecules. Two Na cations are situated in the external sphere of the complex, and each of them is coordinated by three O atoms of silanolate macrocycles and three n-butanol molecules.
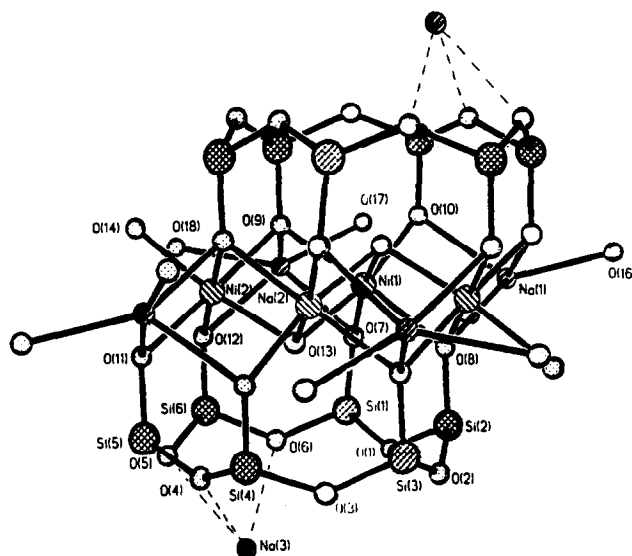
The complexes of type C (Fig. 3) are presented here by Cu complexes K$_4$[(RSiO$_2$)$_{12}$Cu$_4$](^{n}BuOH)$_8$ (R = Ph, Vi). The main structural units of these complexes are cyclododecasiloxanolate ligands (-RSiO-)$_{12}$ with a tris(cis)-trans-tris(cis) coordination and "horse saddle"
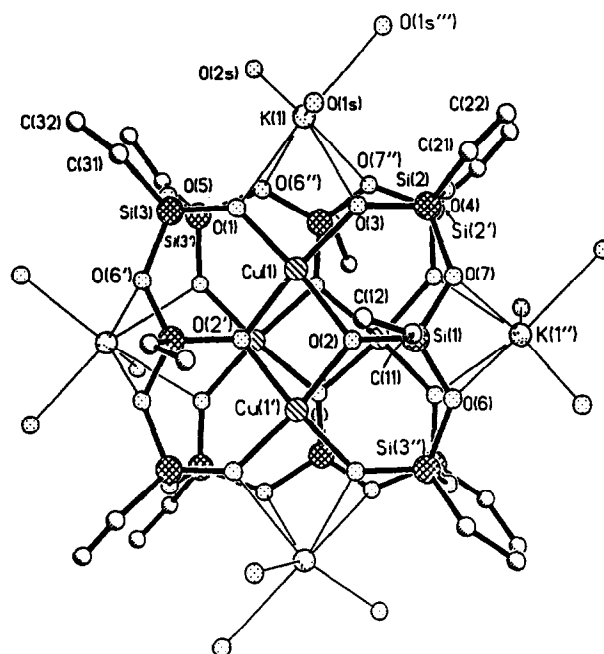

Fig. 3. The molecular structure of K$_4$[[ViSiO$_2$]$_{12}$Cu$_4$](^{n}BuOH)$_6$. Hydrogen atoms and hydrocarbon parts of alcohols have been omitted for clarity. Na$_4$[(PhSiO$_2$)$_{12}$Cu$_4$](^{n}BuOH)$_8$ [20] has the similar structure.
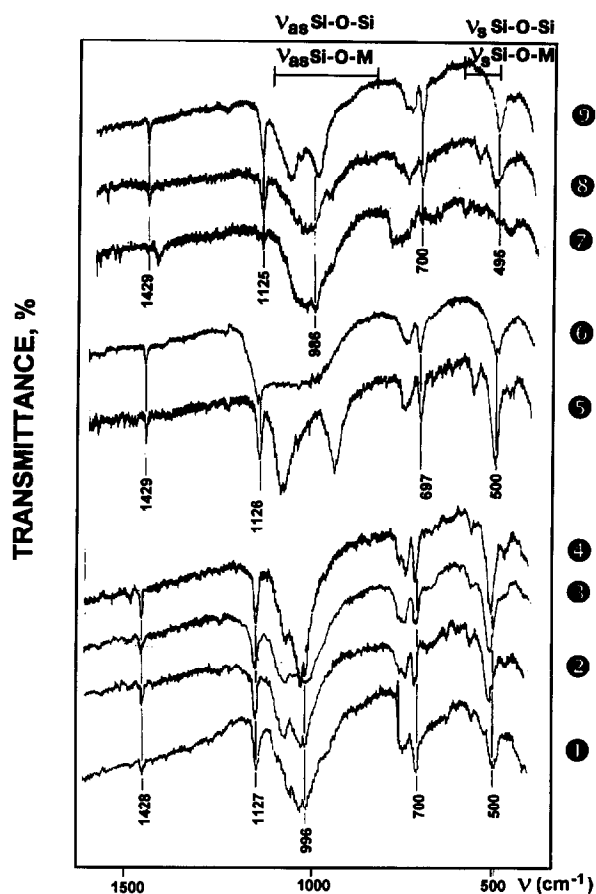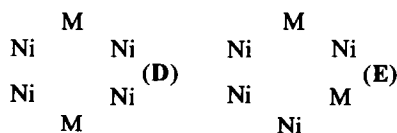
Fig. 4. IR spectra of the silsesquioxane complexes. The numbers in circles correspond to complex numbers in Table 1.

plexes of Cu allows us to attribute the bands that correspond to the organic part of the complexes. Thus, the IR bands at 1429, 1127, 700 and 500 cm^{-1} were assigned to the vibrations of Si–Ph fragments (ν_{C-C}, ν_{Si-C}, δ_{C-H} and δ_{Si-C}, respectively). The intensive bands in the 1100–950 and 570–520 cm^{-1} regions we attributed to the antisymmetrical and symmetrical vibrations of Si–O–Si and Si–O–M fragments [18]. The weak bands in these regions are assigned to the combination of ν_{as} and ν_s vibrations together with deformation and torsion ones. Note, that the crystals of the complexes are characterized by well-resolved IR bands in the vibration regions of Si–O–Si and Si–O–M fragments, even though polymer iron silsesquioxane (with mol. weight = 1000–2000) has wide bands in these regions. Thus, IR spectra of the complexes can be used to grade their quality.

The distance between the two metal atoms (Ni–Ni, Cu–Cu, Mn–Mn, Fe–Fe, Fe–Ni, Cu–Ni) in the resulting complexes do not exceed 2.9–3.0 Å, according to the X-ray data. This distance allows for the formation of bridged O_2^{2-} or HO_2^- intermediates, as assumed in the mechanism (see above) [7]. Thus, the resulting complexes could be considered as perspective models of the active centres of water-oxidation catalysts.

2.2. Catalyst preparation

The complexes that have been prepared are all insoluble in water. In order to make the complexes available for the reagent molecules we have tried to separate them on the surface of supports (silica, alumina and soot). SAXS was used to characterize this procedure.

Figure 5 presents the particle size distributions for the complexes in solutions. Along with the main peak near 30 Å small peaks corresponding to bigger particles were registered. Note that the size of the main peak at 30 Å is greater than that of complexes (20–22 Å, obtained from X-ray studies [15–17,19]), because of solvating shells. The scattering electron density of solvating complexes should be different from the electron density of a solvent. Peaks corresponding to the bigger particles (> 50 Å) can be attributed to the associates of complex molecules. Actually, the dilution of the complex solutions led to the disappearance of the high position peaks (see Fig. 5(b)).

Complexes were supported by conventional techniques, such as impregnation from solutions accompanied by the solvent evacuation at 20°C. Weak adsorption of complexes was observed on carbon support (soot) and γ-Al_2O_3 (solutions of complexes became less coloured). The particle size distributions of complexes supported on soot, γ-Al_2O_3 and SiO_2 are presented in Fig. 6.

conformation. Cu atoms have a square-planar coordination by the silanolate O atoms. Electroneutrality of the complexes is arranged by four K cations, which are coordinated by two olate O_m, two siloxane O_c atoms of the ligand and three O_s atoms of the solvated ^nBuOH molecules.

The possible mutual transformation of the Ni complexes of type A and B via anionic exchange has been proposed [17]. We have successfully exchanged four external Na ions by two Fe or Cu atoms (see Table 1, complexes 2 and 3). It is likely that complexes Ni_4M_2 can co-exist as a mixture of two isomers (types D and E) with the different mutual position of introduced metal atoms.

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        M                    M
Ni      Ni        Ni        Ni
           (D)                   (E)
Ni      Ni        Ni        M
        M                    Ni
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Further investigation of these complexes by EXAFS can provide additional information on their structure.

IR spectra of the complexes are presented in Fig. 4. The comparison of spectra of phenyl- and vinyl-com-

particle size distributions contain a peak near 10 Å and large wide peaks corresponding to the particles bigger than 50 Å. Peaks near 10 Å can be attributed to the molecular form of complex adsorption, or to the Si–O–metal core of the products of complex decomposition (which can be proposed for the interaction of complexes with acidic alumina surface).

2.3. Catalytic properties

Dioxygen yields in water oxidation by $Ru(bpy)_3^{3+}$ (reaction (1)) are presented in Table 2. Note that the oxidant $(Ru(bpy)_3^{3+})$ takes part not only in reaction (1) but also in the oxidation of bpy ligands. Furthermore, the reaction study is complicated by the adsorption of the reaction product, $Ru(bpy)_3^{2+}$, on the active sites of the catalysts, thus poisoning the latter. Hence, the efficiency of the catalysts under consideration could be characterized by its selectivity, *e.g.* by yield of O_2 at the complete oxidant conversion. The higher the yield,
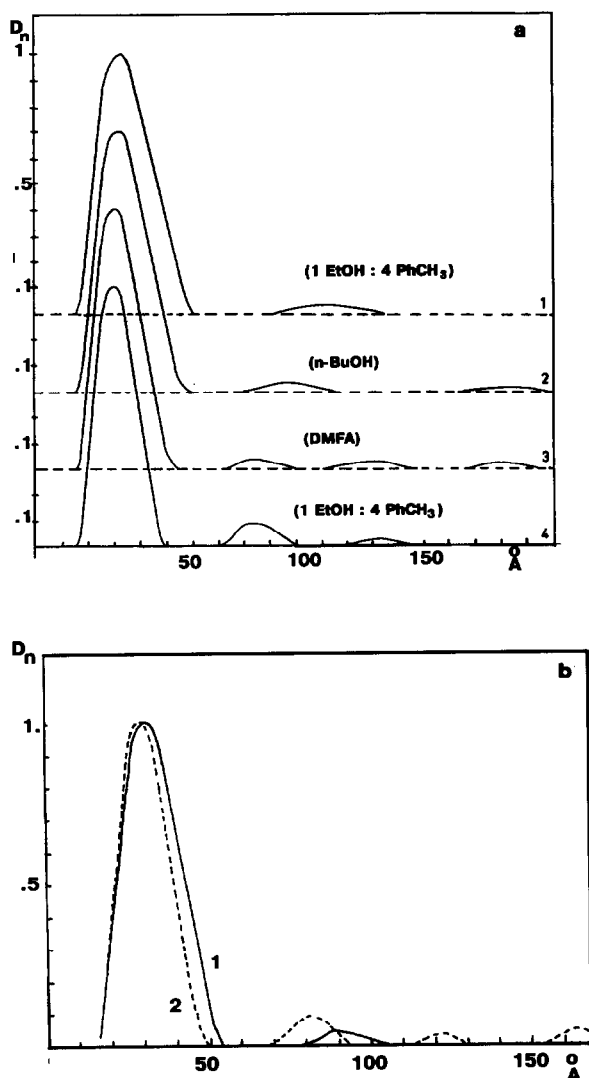
Fig. 5. (a) The particle size distributions of complex solutions: 1-Fe₆ (1EtOH:4toluene); 2-Ni₄Fe₂ (ⁿBuOH); 3-Fe₆ (DMFA); 4-Mn₆ (1EtOH:4toluene). (b) Effect of dilution of the Ni₆ complex solution in ⁿBuOH: 1-2 mg ml⁻¹; 2-20 mg ml⁻¹.

These distributions are close to monomolecular (at least 80% of complexes should be available for interaction with reagents), and were obtained for the complexes adsorbed on the soot. Note that for those curves the main peak is situated near 10-12 Å, the value corresponding to the Si–O–metal core of adsorbed complexes (phenyl groups of siloxanes rings were not registered owing to the similarities of their electron densities and those of the carbon soot network formed by hexagon rings).

For SiO₂-adsorbed complexes the particle size distributions correspond to surface associate's formation. These associates are likely to contain more than 5-6 molecules. For the γ-Al₂O₃ supported complexes the
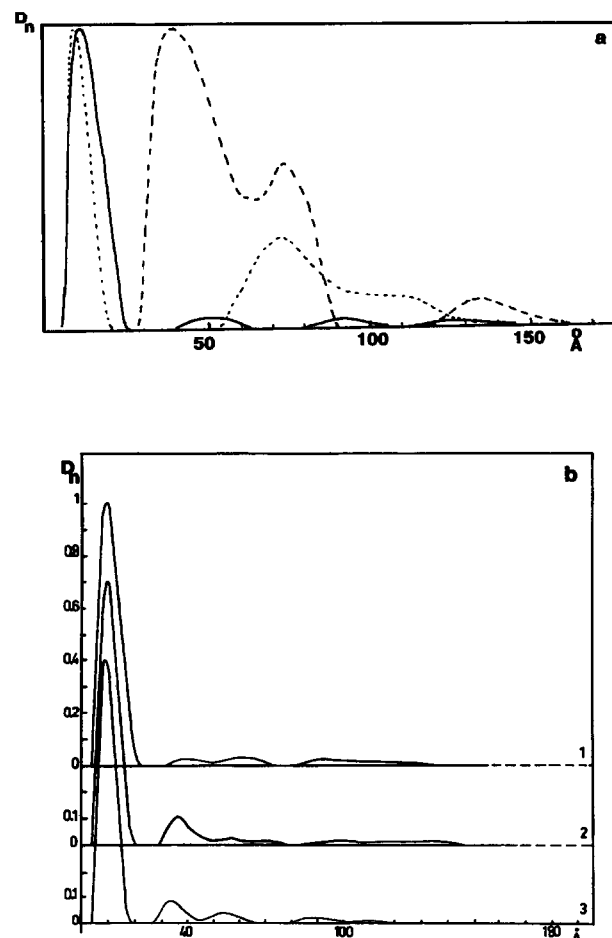
Fig. 6. The particle size distributions of the complexes supported on soot, γ-Al₂O₃, SiO₂: (a) Fe-complexes supported on soot (———), γ-Al₂O₃ (······), SiO₂ (-----); (b) complexes of type A supported on soot: 1-Ni₄Fe₂/C; 2-Fe₆/C; 3-Mn₆/C.

TABLE 2. Dioxygen yields in water oxidation by Ru(bpy)$_3^{3+}$ (20 ml of 0.05 M pyrophosphate buffer and 0.001 M Ru(bpy)$_3^{3+}$, 298 K, pH = 8–10)

Catalyst	O_2 yield (%)	R_{M-M} (Å)
Fe$_6$/C	55	2.9–3.0
Fe$_6$/SiO$_2$	29	2.9–3.0
Fe$_6$/Al$_2$O$_3$	17	2.9–3.0
Mn$_6$/C	18	2.9
Ni$_6$/C	< 5	2.89
Ni$_4$Fe$_2$/C	2	> 4 (Fe–Fe)
Ni$_4$Cu$_2$/C	traces	> 4 (Cu–Cu)
Cu$_4$K$_4$Ph$_{12}$/C	traces	2.9
Cu$_4$Na$_4$Ph$_{12}$/C	traces	2.9
Cu$_4$K$_4$Vi$_{12}$/C	traces	2.9
Fe$_4$(OH)$_{10}$SO$_4$	85	3.0
NaFe$_3$(OH)$_6$(SO$_4$)$_2$	5	3.6

the higher the rate of catalytic reaction, compared with side reactions.

Amongst the silsesquioxanes under consideration, the Fe and Mn complexes were active in the reaction (1), but the Ni and Cu complexes were not.

Note that Ni$_6$- and Cu$_4$-supported complexes are not active in reaction (1), in contrast with bulk hydroxides [4]. Ni and Cu atoms on the surface of bulk hydroxide seem to change the oxidation state more readily than in the rigid oxygen framework of the silanolate complex.

Mn$_6$ complexes were active in the reaction, but less than the Fe$_6$ one.

The highest yields of O$_2$ for the supported catalysts were obtained with the Fe/C ones. The efficiency of the catalyst decreases in the following series:

Fe/C > Fe/SiO$_2$ > Fe/Al$_2$O$_3$

This series corresponds to the decrease of the particle dispersion of the Fe complex on the different supports and/or resistance against deactivation by the reaction product. Thus, one can observe the support (SiO$_2$ and γ-Al$_2$O$_3$) colouring in the Ru(bpy)$_3^{2+}$ solution.

The catalysts with only Fe complexes were more active than those prepared with Ni$_4$Fe$_2$ complexes, in which the active atoms (Fe) are separated by inactive Ni-atoms. This observation is very important for the mechanism suggested in the literature [6,7]. According to this mechanism of O$_2$ formation, the active centre should possess at least two neighbouring metal ions associated to each other. Note, that the distance (R_{M-M}) between the two Fe atoms in complex Ni$_4$Fe$_2$, which can have D or E structures, is larger than 4.5 Å. These data are in a good agreement with the data obtained for the bulk hydroxo complexes. Thus, the suspension of NaFe$_3$(OH)$_6$(SO$_4$)$_2$, where the distance

between the iron atoms is 3.6 Å, was not active in reaction (1), whereas Fe$_4$(OH)$_{10}$SO$_4$, with the typical Fe–Fe distance of ~3.0 Å, exhibited a high activity.

According to the proposed mechanism (Scheme 1) one of two metal atoms in the active centre takes part in redox transformation, whilst the other assists stabilization of the reaction intermediates (O$_2^{2-}$ and/or O$_2$H$^-$). In the supported Ni$_4$Fe$_2$ complex the active Fe atoms are separated by Ni atoms. This formally meets the proposed mechanism, because the pair Ni–Fe can be considered as the active centre. However, Ni^{2+} is a weaker coordination centre for both hydroxyl groups and intermediates when compared with Fe^{3+} ions. Furthermore, the oxidation of Ni^{2+} to Ni^{3+} is not possible without coordination of OH and cleavage of Ni–O bond in the square-planar Ni–O fragment.

It should be mentioned that the activity of the catalyst depends on the properties of OH groups of the first coordination sphere of the metal atom, as the yield of O$_2$ depends on the pH of the reaction mixture.

The lower yields of O$_2$ for the supported complexes when compared with that for the suspension of Fe$_4$(OH)$_{10}$SO$_4$, and the poor activity of NaFe$_3$(OH)$_6$-(SO$_4$)$_2$ can be explained not only in terms of optimal distances between active metals in the catalytic centres but also in terms of the differences of acidic properties of the surface hydroxyl groups. Thus, Fe$_4$(OH)$_{10}$SO$_4$ is characterized by the high content of sufficiently-acidic OH groups with pK$_a$ > 7, and will be efficient at pH = 6–10 [4]. It is likely that the supported catalysts that are under consideration have pK > 9. Hence, the yields of O$_2$ are limited for them by pH = 8–10. Furthermore, NaFe$_3$(OH)$_6$(SO$_4$)$_2$ has no acidic hydroxyl groups at all [4], and is characterized by poor activity in reaction (1).

3. Experimental details

All manipulations and reactions were carried out using either standard Schlenk vessel or vacuum-line techniques under dry, oxygen-free dinitrogen. Chemical grade solvents were purified by standard procedures. IR spectra were obtained with a Specord 75 IR (KBr-mixture of complexes) apparatus.

The particles size distributions were obtained with KRM-1 instrument (Cu$_{K\alpha}$-radiation, Russian Federation). The scattering of the corresponding solvent (or support) were subtracted from $I(s)$-scattering intensities of the complex solution (or supported sample). The size distribution function of the particles $j_n(R)$ was calculated from the integral equation

$$I(h) \sim \int f_n(R) R^6 i_0(hR) \, dR$$

where $I(h)$ is the experimental scattering-intensity curve and $i_0(hR)$ is the scattering form factor. For spherical particles we have

$$i_0(hR) = \frac{3(\sin hR - hR \cos hR)}{h^3 R^3}$$

where $h = 2\pi(\sin \theta)/\lambda$ and θ is the scattering angle.

3.1. Complex preparation

The synthesis of polyphenylsilsesquioxane was described previously [9]. It was used for the preparation of all the silsequioxanes.

3.1.1. Synthesis of $Na_2[(PhSiO_2)_6Na_4Ni_4(OH)_2(O_2\text{-}SiPh_6)]("BuOH)_{16}$

This complex was prepared according to ref. 17. Yield: 4.64 g (67.84%). Found: C 43.48; H 4.89; Na 6.08; Ni 9.19; Si 14.36%. $C_{136}H_{222}Na_6Ni_4O_{42}Si_{12}$. Calcd.: C 50.43; H 6.91; Na 4.26; Ni 7.25; O 20.75; Si 10.41%.

3.1.2. Synthesis of $(PhSiO_{1.5})_{12}(NiO)_4(FeOHO)_2(Na\text{-}Cl)("BuOH)_5(H_2O)_2$

Phenylsilsesquioxane (10 g, 0.076 mol), NaOH (1.77 g, 0.44 mol) and Na (1.02 g, 0.44 mol) were boiled in 200 ml of n-butanol for 20 min. Hexaamminenickel chloride (5.87 g, 0.025 mol) was then added, and the mixture was boiled for a further 30 min, after which a solution of anhydrous iron chloride (2.05 g, 0.013 mol) in n-butanol (40 ml) was added dropwise to the boiling mixture. Continued boiled for 1 h, filtering of NaCl, and cooling gave yellow-brown crystals, which were filtered off, washed by pure n-butanol and dried in vacuum (1 Torr) at 80°C. Yield: 4.76 g (36%). Found: C 44.83; H 4.79; Si 13.64; Ni 9.35; Fe 3.94; Na 0.91; Cl 1.46%. $C_{72}H_{62}Si_{12}O_{26}Ni_4Fe_2NaCl$. Calcd: C 44.34; H 4.69; Si 13.63; Ni 9.42; Fe 4.48; Na 0.92; Cl 1.42%.

3.1.3. Synthesis of $(PhSiO_{1.5})_{12}(NiO)_3(CuO)_3(NaCl)("BuOH)_3(OH)_4(H_2O)_4$

This compound was obtained as above, but with phenylsilsesquioxane (7.86 g, 0.06 mol), NaOH (1.4 g, 0.035 mol), Na (0.81 g, 0.035 mol), n-butanol (120 ml), $(Ni(NH_3)_6)Cl_2$ (4.632 g, 0.02 mol) and a solution of anhydrous $CuCl_2$ (2.02 g, 0.015 mol) in n-butanol (30 ml). Yield: 4.94 g (48%). Found: C 42.98; H 4.03; Si 14.38; Ni 7.57; Cu 6.69; Na 0.98; Cl 1.61%. $C_{72}H_{60}Si_{12}Ni_4Cu_2O_{24}NaCl$. Calcd: C 42.64; H 4.18; Si 14.25; Ni 7.44; Cu 8.06; Na 0.97; Cl 1.50%.

3.1.4. Synthesis of $Na^+[(PhSiO_2)_6Ni_6(O_2SiPh)_6\text{-}Cl^-]("BuOH)_{14}$

This complex was prepared according to ref. 15, with a yield of 1.9 g (16%). Found: C 45.15; H 4.99; Si 13.27; Ni 11.12; Cl 1.28; Na 0.74%. $C_{120}H_{180}ClNaNi_6O_{36}Si_{12}$. Calcd.: C 48.91; H 6.17; Si 11.44; Ni 11.95; Na 0.78; O 19.55; Cl 1.20%.

3.1.5. Synthesis of $K_4[(ViSiO_2)_{12}Cu_4]("BuOH)_6$

This complex was prepared according to ref. 20, with a yield of 9.02 g (47.42%). Found: C 24.48; H 4.04; Si 19.87; Cu 13.46; K 10.42; O 27. 73%. $C_{34}H_{34}Cu_4K_4O_{29.5}Si_{12}$ Calcd.: C 24.08; H 3.98; Si 19.88; Cu 14.99; K 9.23; O 27.84%.

3.1.6. Synthesis of $Na_4[(PhSiO_2)_{12}Cu_4]("BuOH)_8$

This compound was obtained as above, but with phenylsilsesquioxane, according to ref. 20. Yield: 12.71 g (63.8%). Found: C 43.00; H 4.02; Cu 11.24; Na 4.72; Si 14.84%. $C_{104}H_{140}Cu_4Na_4O_{32}Si_{12}$. Calcd.: C 48.31; H 5.45; Cu 9.83; Na 3.56; O 19.80; Si 13.04%.

3.1.7. Synthesis of $Na^+[(PhSiO_2)_6Mn_6(O_2SiPh)_6\text{-}Cl^-](EtOH)_8$

This complex was prepared according to ref. 16.

The results of the elemental analyses do not agree too well with those calculated on the basis of the X-ray crystallography. This can be explained by partial loss of the solvent during crystallisation, when the sample was dried prior to analysis.

3.2. Catalyst preparation

Soot KGO-300 (surface area, $S = 400$ m² g⁻¹), SiO_2 ($S = 250$ m² g⁻¹) and $\gamma\text{-}Al_2O_3$ ($S = 200$ m² g⁻¹) were used as the catalyst supports. Catalysts were prepared by impregnation of supports with complex solution in ethanol-toluene and further drying of supports under vacuum. The metal content in the catalysts was measured with atom absorption spectroscopy.

3.3. Catalyst testing

The kinetics of the formation of O_2 was monitored by use of the Clark electrode and Bekman monitor. All experiments were carried out at 298 K and at the initial oxidant concentration of $Ru(bpy)_3^{3+} = 1 \times 10^{-3}$ M. The yields of O_2 after termination of the reaction were measured with reference to the stoichiometry of reaction (1). All experiments were carried out with pyrophosphate as buffer.

Acknowledgements

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