

MONO- AND BIMETALLIC COMPLEXES OF Mn(II), Co(II), Cu(II), AND Zn(II) WITH SCHIFF BASES IMMOBILIZED ON NANOSILICA AS CATALYSTS IN OZONE DECOMPOSITION REACTION

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Abstract. The results of the study of catalytic activity of nanocomposites containing mono- and bimetallic manganese(II), cobalt(II), copper(II), and zinc(II) complexes with Schiff bases [(salicyl-aldiminopropyl (L1) and 2-hydroxy-4-methoxybenzophenoniminopropyl (L2)] immobilized on silica in the reaction of ozone decomposition are presented. The catalytic activity dependence on a nature of complexing metal ions and ligands has been determined.

Keywords: nanosilica, Schiff bases, mono- and bimetallic complexes, ozone decomposition.

1. Introduction

Previously, it has been shown that the catalytic activity of 3d metal complexes ML_2/Si (or ML_2/SiO_2) immobilized on silicas [aerosil A-300 (Si), silica KSMG (SiO_2)] strongly depends not only on the nature of the metal M = manganese(II), cobalt(II), copper(II), zinc(II), the ligand (L = Schiff bases, NO_3^- , Cl^-), the geometry of coordination polyhedron, but also on the nature of the matrix [1]. As a result, the specific antiozonant activity of monometallic compositions immobilized on nanosilica exceeds by two orders the activity of complexes on porous matrix ML_2/SiO_2 ($L = NO_3^-$, Cl^-). In the presence of mentioned complexes, similarly to the reaction in solutions [2-4], the ozone decomposition proceeds by the radical chain mechanism, the kinetic proof of which can be the difference between the values of first-order reaction rate constant at the beginning of the reaction and at the ozone half-conversion time. Consequently, metal complex

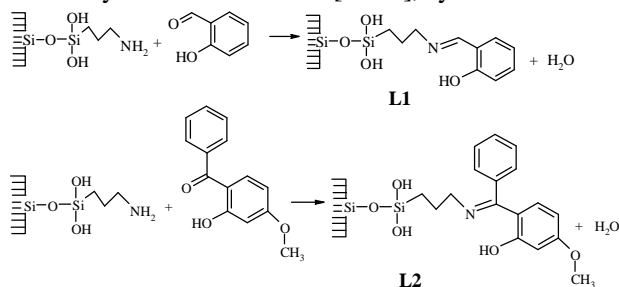
catalytic effect for these reactions is determined not only by the nature of complexing ion and ligand, but by the existence of even insignificant impurities of another metal ion. The most detailed cooperative action of two metal cations was investigated in the reactions of sulfur dioxide oxidation in conditions simulating processes in the atmosphere [5-9].

Concerning ozone, many examples of catalysts, which consist of two or more metals in different forms are mostly shown in patents [10]. Among the bimetallic complex catalysts only the catalysts with composition $PdCl_2-CuCl_2$ (or $NiCl_2$)/ Al_2O_3 are known [11]. Usually in such publications kinetic and stoichiometric parameters in ozone decomposition reaction are not presented, therefore the cross-effect of two metals remains uncertain. In bimetallic redox system the manifestation of synergetic or additive, or inhibiting effect is expected if it is based on the idea of radical chain reaction course.

Our objective is the study of catalytic activity of nanocomposites containing monometallic complexes $[ML_2]$ (M = manganese(II), cobalt(II), copper(II), and zinc(II)) and bimetallic complexes $[Mn-M_2-L]$, where M_2 = cobalt(II), copper(II), zinc(II); ($L = L1$ and $L2$).

2. Experimental

Nanosilica (aerosil) A-300 brand ($S_{sp} = 280 m^2/g$) was used for synthesis of γ -aminopropylsilica, from which immobilized Schiff bases ($L1$ – salicylaldiminopropyl, $L2$ – 2-hydroxy-4-methoxybenzophenoniminopropyl) were obtained by the known methods [12-14], by the schemes:



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Table 1

The chemical composition of mono- and bimetallic complexes of 3d metals with Schiff bases

Sample	$C_L \cdot 10^4$, mol/g	$C_M \cdot 10^4$, mol/g			
		Mn ²⁺	Co ²⁺	Cu ²⁺	Zn ²⁺
L1	9.0	—	—	—	—
[Mn(L1) ₂]	9.0	3.0	0	0	0
[Co(L1) ₂]	9.0	0	3.0	0	0
[Cu(L1) ₂]	9.0	0	0	3.0	0
[Zn(L1) ₂]	9.0	0	0	0	3.0
[Mn-Co-L1]	9.0	2.4	2.4	0	0
[Mn-Cu-L1]	9.0	2.4	0	2.4	0
[Mn-Zn-L1]	9.0	2.4	0	0	2.4
L2	5.3	—	—	—	—
[Mn(L2) ₂]	5.3	2.5	0	0	0
[Co(L2) ₂]	5.3	0	2.5	0	0
[Cu(L2) ₂]	5.3	0	0	2.5	0
[Zn(L2) ₂]	5.3	0	0	0	2.5
[Mn-Co-L2]	6.0	2.5	2.5	0	0
[Mn-Cu-L2]	6.0	2.5	0	2.5	0
[Mn-Zn-L2]	6.0	2.5	0	0	2.5

Monometallic complexes [M(L)₂] with deprotonated ligands (see Subsection 3.1) were obtained by the adsorption of metal ions from ethanol (manganese(II) chloride) or acetone (chlorides of cobalt(II), copper(II), zinc(II)) solutions. Bimetallic complexes [Mn-M2-L] were obtained by the compatible sorption of manganese(II) from alcohol solution of MnCl₂ and M2(II) from the corresponding (CoCl₂, CuCl₂, ZnCl₂) acetone solution and so from mixture of ethanol-acetone solutions (sorption was not full and only 80% of cations from the solutions were adsorbed). Concentration of immobilized ligands L1, L2, metal ions and chemical composition of synthesized mono- and bimetallic complexes are shown in Table 1.

IR spectra were recorded by a Fourier transform Perkin Elmer Spectrum BX FT-IR instrument (400–4000 cm⁻¹) from transparent tablets obtained by pressing of bare samples and with adding of KBr as well.

Diffuse reflectance spectra were recorded at room temperature in the wave number range of 30000–11000 cm⁻¹ by a Specord M-40 in stainless steel cells where samples were pressed.

ESR-spectra were obtained on PX-100 Adani Instruments at 293 K.

The catalyst samples ($m = 0.2$ g) were tested using a gas flow setup with a fixed bed reactor at 293 K, relative humidity of 65 %, and the ozone-air mixture linear velocity of 6.2 cm/s. Ozone decomposition was monitored by measuring the final ozone concentration ($C_{O_3}^f$). The initial ozone concentrations ($C_{O_3}^{in}$) and $C_{O_3}^f$ were measured by a Tsycon-Revers optical gas analyzer (detection limit of 1 mg/m³).

The first order rate constant ($k_{1/2}$, s⁻¹) at the ozone half-conversion time ($t_{1/2}$) was calculated by the formula:

$$k_{1/2} = \frac{0.69}{\tau_{1/2}} \quad (1)$$

The amount of ozone (Q_{exp} , moles of O₃) entering into the reaction over the whole period of its proceeding (t_{exp} , min.) was measured as a square of the corresponding ozonogram plotted as a ΔC_{O_3} vs. t function. The stoichiometric parameter of the reaction n was calculated by formula (2) for monometallic complexes

$$n = \frac{Q_{exp}}{Q_{M1}} \quad (2)$$

and by formula (3) for bimetallic complexes

$$n = \frac{Q_{exp}}{Q_{Mn} + Q_{M2}} \quad (3)$$

where Q_{M1} , Q_{M2} , Q_{Mn} – are the amounts of metal ions in the nanocomposite.

3. Results and Discussion

3.1. Composition and Structure of Complexes

The formation, the way of coordination and the structure of coordination sphere of manganese(II), cobalt(II), copper(II), and zinc(II) complexes with Schiff bases immobilized on nanosilica were established by the following results (Table 2).

Table 2

**Spectral data for Schiff bases immobilized on nanosilica and their complexes
with manganese(II), cobalt(II), copper(II), and zinc(II)**

Ligand Complex	IR	Electronic reflectance spectra	
	$n_{C=N}, \text{cm}^{-1}$	$n_{p-p^*}, \text{cm}^{-1}$	n_{d-d}, cm^{-1}
L1	1635	24600	—
[Mn(L1) ₂]	1630	26900; 25200; 24600sh	—
[Co(L1) ₂]	1622	26900; 25200; 24600sh	17400; 15800sh
[Cu(L1) ₂]	1620	26700; 25200; 24600sh	13500
[Zn(L1) ₂]	1620	26900; 25100; 24600sh	—
[Mn-Co-L1]	1625	26900; 25200	17300; 16200, 15800sh
[Mn-Cu-L1]	1625	26900; 25200	13500
[Mn-Zn-L1]	1625	26900; 25200	—
L2	1595	26400	—
[Mn(L2) ₂]	1590	26470	—
[Co(L2) ₂]	1590	26470	16900; 15300
[Cu(L2) ₂]	1592	26500	14100
[Zn(L2) ₂]	1592	26450	—
[Mn-Co-L2]	1590	26500	16700; 15200
[Mn-Cu-L2]	1591	26500	14100
[Mn-Zn-L2]	1591	26500	—

Table 3

**Kinetic and stoichiometric factors of ozone decomposition reaction over immobilised Schiff bases,
mono- and bimetallic complexes ($C_{O_3}^{\text{in}} = 4.2 \cdot 10^{-6} \text{ mol/l}$)**

Sample	$t_{\text{exp}}, \text{min}$	$t_{1/2}, \text{s}$	$k_{1/2} \cdot 10^4, \text{s}^{-1}$	$Q_{\text{exp}} \cdot 10^4, \text{mol O}_3$	n
L1	140	420	16.0	1.1	—
[Mn(L1) ₂]	360	9600	0.7	6.6	11.0
[Co(L1) ₂]	180	5880	1.2	3.3	5.5
[Cu(L1) ₂]	80	2220	3.1	1.2	2.0
[Zn(L1) ₂]	80	1920	3.6	1.0	2.0
[Mn-Co-L1]	260	6000	1.2	5.1	5.0
[Mn-Cu-L1]	360	5100	1.4	4.5	5.0
[Mn-Zn-L1]	260	4500	1.5	3.7	4.0
L2	120	2340	2.9	1.5	—
[Mn(L2) ₂]	360	8100	0.9	6.0	12.0
[Co(L2) ₂]	180	3300	2.1	1.9	4.0
[Cu(L2) ₂]	120	1500	4.6	1.1	2.0
[Zn(L2) ₂]	120	1680	4.1	1.1	2.0
[Mn-Cu-L2]	360	12000	0.6	7.7	8.0
[Mn-Co-L2]	340	10860	0.64	6.9	7.0
[Mn-Zn-L2]	320	10260	0.55	6.7	7.0

The main feature of coordination of immobilized ligands to metal ion is the low-frequency shift of azometine (C=N) group peak in IR spectra. In UV-VIS spectra after complexation, the high-frequency shift occurs for the peaks characterizing the electron density transfer in ligand n_{p-p^*} , compared with free immobilized Schiff base. Furthermore, in some cases, additional bands appear in the range of 26000–27000 cm^{-1} . The appearance

of characteristic $d-d$ transfer peaks for Co^{2+} complexes in the range of 17500–15000 cm^{-1} shows that metal ion has pseudotetrahedral surrounding. Pseudotetrahedral surrounding can also be proposed for Cu^{2+} bischelates depending on their electronic (Table 2) and ESR ($g_{\parallel} = 2.248$; $g_{\perp} = 2.04$; $A_{\parallel} = 173 \cdot 10^{-4} \text{ cm}^{-1}$) spectra [14]. The free ligand peaks of low intensity as shoulders to main peaks are also present in spectra for monometallic L1

complexes. In the case of L2 ligand the same spectral features (except free ligand peaks) are observed. Such spectra alterations argue in favour of the biligand monometallic complexes formation with deprotonated ligands [17]. The same complexes are formed with both metals in case of L1 for bimetallic systems but for L2 preferably monoligand complexes take place due to low specific concentration of L2.

3.2. Testing Nanocompositions in the Reaction of Ozone Decomposition

The catalytic activity of monometallic $[ML_2]$ and bimetallic $[Mn-M2-L]$ complexes was determined by the study of ozone decomposition kinetics. In each case the ozone concentration ($C_{O_3}^f$) increases with time and attains the initial concentration ($C_{O_3}^{in}$), but after the different periods of time. The highest duration of the experiment (360 min) (Table 3) was observed for the most catalytically active nanocomposites. Since the most substantial kinetic differences were observed during the period of 50% ozone decomposition at its initial concentration, $C_{O_3}^{in}$, of $4.2 \cdot 10^{-6}$ mol/l, the graphical changes in $C_{O_3}^f$ with time are presented for the half-conversion time ($t_{1/2}$).

Kinetic curves demonstrated a change in the final ozone concentration with the time of its decomposition by immobilized ligand L1 and monometallic complex $[M(L1)_2]$ (Fig. 1a) show that the free ligand (curve 1) also decomposes ozone, but coordination compounds (curves 2-5) are much more effective in the reaction. This affects a view of initial portions of kinetic curves, a period of time required for reaching 50 % of the initial ozone concentration and the whole period of reaction proceeding. It should be noted that, in case of the complexes, the portions of kinetic curves where the final ozone concentration is

constant appear. Fig. 1b shows the kinetics of ozone decomposition by bimetallic complexes $[Mn-M2-L1]$, where M2 = cobalt(II), copper(II), zinc(II) (curves 1-3) as compared with the most active complex $[Mn(L1)_2]$ (curve 4). As can be seen, only in the case of bimetallic complex $[Mn-Cu-L1]$ the starting portion of the kinetic curve differs significantly from others: just in 1 min $C_{O_3}^f = 15$ mg/m³, but the time of ozone half-conversion is almost the same as for $[Mn-Zn-L1]$ complex.

The ozone decomposition kinetics and the half-conversion time for ligand L2 and $[M(L2)_2]$ complexes are shown in Fig. 2a. As well as in the case of ligand L1, $[Mn(L2)_2]$ complex is characterized by higher activity in ozone decomposition. $[Cu(L2)_2]$ complexes demonstrate the lowest activity even in comparison with L2 ligand. As can be seen from Fig. 2b (curves 2-4), both the durability of the portion where the final concentration is constant and $t_{1/2}$ parameter increase for bimetallic complexes $[Mn-M2-L2]$ denoting a positive effect of the second metal ion on ozone decomposition by nanocomposites.

As shown in the previous papers [1, 14-17], the first-order reaction rate constants can be calculated in many cases from the initial portions of kinetic curves of ozone decomposition. Their values are invariable at the beginning of the reaction but change at the half-conversion time confirming the radical chain mechanism of the reaction. Analyzing the results obtained (Figs. 1, 2), one can deduce that in all cases except for L1, $[Zn(L1)_2]$, $[Mn-Cu-L1]$ and $[Cu(L2)_2]$, the final concentration does not change at the beginning of the reaction. This fact allows to use such parameters as the ozone half-conversion time, $t_{1/2}$, and the first-order reaction rate constant, $k_{1/2}$, calculated by Eq. (1) for determination of the influence of ligands and complexing metal ions on kinetic parameters. The results of analyzing kinetic ($t_{1/2}$, $k_{1/2}$) and stoichiometric (Q_{exp} , n) parameters for all nanocomposites under study are summarized in Table 3.

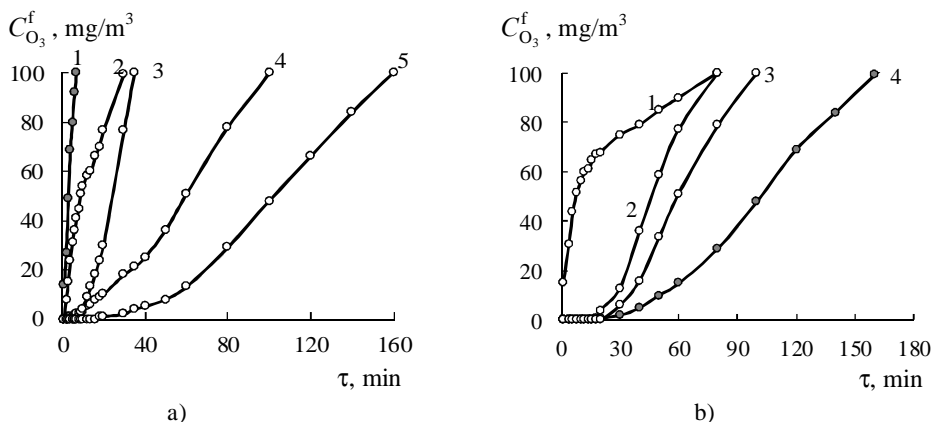


Fig. 1. Time dependences of the final ozone concentration up to the moment of 50 % ozone decomposition over immobilized L1 ligand (a, 1) and its complexes. $[M(L1)_2]$: 2 – $[Zn(L1)_2]$, 3 – $[Cu(L1)_2]$, 4 – $[Co(L1)_2]$, 5 – $[Mn(L1)_2]$ (a); $[Mn-M2-L1]$: 1 – $[Mn-Cu-L1]$, 2 – $[Mn-Zn-L1]$, 3 – $[Mn-Co-L1]$, 4 – $[Mn(L1)_2]$ (b)

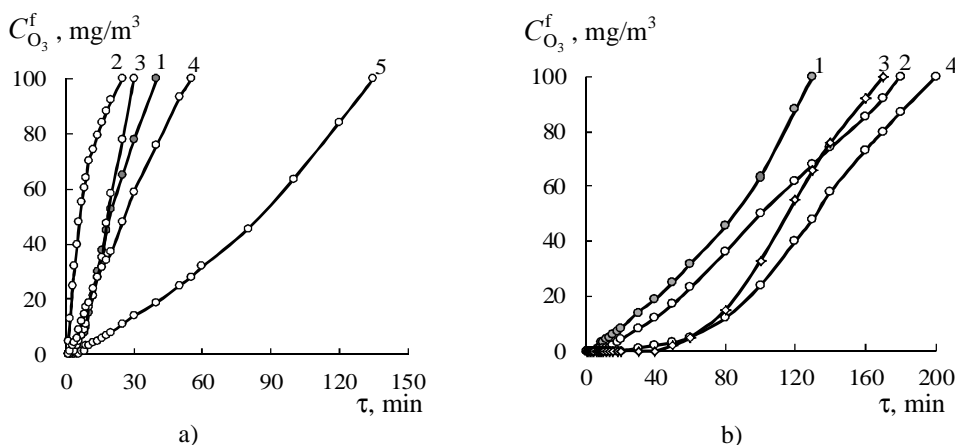


Fig. 2. Time dependences of the final ozone concentration up to the moment of 50 % ozone decomposition over immobilized L2 ligand (a, 1) and its complexes. [M(L2)₂]: 2 – [Cu(L2)₂]; 3 – [Zn(L2)₂]; 4 – [Co(L2)₂]; 5 – [Mn(L2)₂] (a); [Mn-M2-L2]: 1 – [Mn(L2)₂]; 2 – [Mn-Co-L2]; 3 – [Mn-Zn-L2]; 4 – [Mn-Cu-L2] (b)

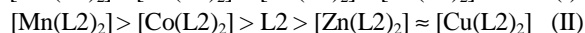
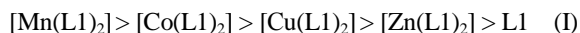
Based on the classic conceptions concerning the mechanism of ozone decomposition [2-4] and our studies of kinetics of ozone decomposition by 3d metal complexes with Schiff bases immobilized on nanosilica [1, 14-17], it can be deduced that metal ions taking part in the chain propagation reaction increase the time of ozone half-conversion attainment ($k_{1/2}$ decreases) and the amount of ozone entering the reaction over the whole period of its proceeding (Q_{exp}). In this case, the higher the $t_{1/2}$ and Q_{exp} the more actively complex decomposes ozone. For all complexes, except for [Zn(L)₂] and [Cu(L)₂], Q_{exp} is much higher than for free ligands L1 and L2 but in all cases $n \gg 1$ (n is the stoichiometric coefficient) indicating the multiple participation of metal ions in the reaction of ozone decomposition. It should be noted that the amount of ozone entering the reaction for bimetallic [Mn-M2-L2] complexes (M2 = cobalt(II), copper(II), zinc(II)) is higher than that for the monometallic [Mn(L2)₂] complex, however, parameters n for bimetallic complexes considering the total amount (moles) of two metal ions (Eq. (3)) is less than sums of n values for corresponding pairs of metal ions.

Thus, mono- and bimetallic complexes with Schiff bases immobilized on nanosilica (L1, L2) demonstrate catalytic behavior in the reaction of low-temperature ozone decomposition, however, the use of bimetallic nanocompositions produces no synergistic result when Mn : M2 ratio is equal to 1.

4. Conclusions

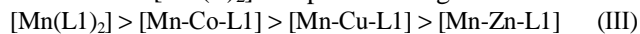
Based on the data obtained, the following conclusions can be drawn:

1. The catalytic activity of monometallic complexes has been found to depend on the nature of central atoms and ligands:



The complexes in order (I) are more active than the complexes in order (II) and positions of ligands L1 and L2 in the orders change.

2. When the Mn : M2 ratio is equal to 1, the catalytic activity of bimetallic complexes [Mn-M2-L] (M2 = cobalt(II), copper(II), zinc(II)); L = L1, L2) in the reaction of ozone decomposition as compared with monometallic [Mn(L)₂] complexes changes as follows:



Order (III) shows a decrease in the catalytic activity of bimetallic complexes and correlates with row (I) for monometallic complexes: the lower the activity of the second metal M2, the higher the inhibitory effect it induces. In the case of bimetallic complexes with ligand L2 (order (IV)), the second metal M2 = cobalt(II), copper(II), zinc(II), to the contrary, amplifies the catalytic effect of manganese(II).

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**МОНО- ТА БІМЕТАЛІЧНІ КОМПЛЕКСИ Mn(II), Co(II),
Cu(II), Zn(II) З ОСНОВАМИ ШИФФА
ІМОНІЛІЗОВАНИМИ НА НАНОСИЛІЦІЮ ЯК
КАТАЛІЗАТОРИ В РЕАКЦІЇ РОЗКЛАДАННЯ ОЗОНУ**

Анотація. В роботі представлені результати дослідження каталітичної активності наноконпозицій, що містять моно- та біметалічні комплекси 3d-металів – Mn(II), Co(II), Cu(II), Zn(II) з імонілізованими на аеросилі основами Шиффа [саліцил-альдімінпропіл (L1) і 2-гідрокси-4-метокси-бензофенонімінпропіл (L2)] в реакції розкладання озону. Визначені ряди каталітичної активності моно- та біметалічних комплексів в залежності від природи комплексоутворювача та ліганду.

Ключові слова: наносиліка, основи Шиффа, моно- та біметалічні комплекси, розкладання озону.