Heteronuclear Fe-Mn Cyclopentadienyl Complexes Supported on Boehmite. Thermochemistry and Thermodynamics of their Decomposition

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Article info	Abstract
Received: 5 June 2024	Boehmite samples with compounds of the composition $(C_5H_5)_2FeMnX_2(\mu-CO)_n$, where X=Cl, Br and n=1.2, precipitated at room temperature from tetrahydrofuran solutions and then heated in an air flow up to 873 K were obtained and characterized using X-ray diffractometry, infrared Fourier spectroscopy, electron magnetic resonance and temperature-programmed desorption methods. It was shown that
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Accepted: 10 September 2024	in the range from room temperature to 873 K occurs stepwise and consists of at least two stages. The first stage of thermal decomposition occurs in the range of 453–753 K, and the second – in the range of 813–843 K. The XRD data show that when
Keywords: Supported Fe-Ni cyclopentadienyl complexes, Boehmite, Thermal decomposition	calcining at 873 K the boehmite samples with the applied compounds of the above composition and containing these compounds less than 10 wt.%, the diffraction patterns show only reflections characteristic of poorly crystallized aluminum oxide. However, the electron paramagnetic resonance (EPR) spectra of these samples clearly show intense signals characteristic of superpara/ferromagnetic particles of iron and manganese oxides, as well as EPR signals from isolated Fe ³⁺ substituting Al ³⁺ ions in the aluminum oxide structure. EPR spectra most of the iron and manganese is stabilized on the surface of poorly crystallized aluminum oxide in the form of nanostructured iron and manganese oxides.

1. Introduction

Over the past few decades, a new field of heterogeneous catalysis has emerged- organometallic chemistry on the surface of solids, which gradually opened the way to organometallic catalysis by organometallic compounds deposited on the surface of solids [1,2]. The chemistry of organometallic compounds supported on solid supports is one of the most important and rapidly developing areas of modern catalysis. Being at the intersection of various fields of chemistry, it is closely related to inorganic chemistry, in particular with the chemistry of coordination and element-organic compounds. Recently, new catalytic systems have been actively developed, in which organometallic compounds play a key role, acting as catalysts for many practically important chemical processes [3,4]. The application of organometallic compounds to solid supports makes it possible to obtain catalysts with active centers with controlled composition and structure. In this case, preparation technologies play an important role in controlling the type of catalysts obtained and using the capabilities of organometallic chemistry for the targeted production of catalytically active centers with desired properties. New catalytic reactions were discovered, and the catalytic characteristics - activity, selectivity, and service life - were significantly improved [5-8]. Note that methods

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based on the attachment of organometallic compounds of transition metals to strongly dehydroxylated metal oxide supports in a strictly controlled atmosphere make it possible to generate catalytic centers with controlled composition and structure. This strategy provides significant advantages over traditional methods for preparing heterogeneous catalysts, such as impregnation, which lead to the formation of an ensemble of active sites with different compositions and structures. The coordination sphere of anchored complexes can be designed with a high degree of confidence into a specific catalytic site because all preparatory steps can be carefully controlled using organometallic and/or coordination chemistry concepts and tools. Another advantage of this chemistry is that the surface is treated as a rigid ligand, preventing in most cases unwanted interactions between catalytic sites. Organometallic chemistry on the surface of oxides makes it possible to obtain, for example, bimetallic catalysts, the active centers of which are highly homogeneous in nature [9,10]. The vast majority of supports currently used in industry are inorganic materials (SiO₂, Al₂O₃, aluminosilicates). Energy and environmental issues have become a major focus of research efforts to develop more active and selective catalytic systems for key chemical processes. Organometallic surface chemistry with an established concept, with specific tools, allows the design and preparation of catalysts with well-defined properties of catalytically active sites. The goal of these studies is to create catalytic cycles through putative catalytic intermediates derived from organometallic or coordination compounds, designing surface organometallic moieties coordinated to a surface with a specific composition and structure. These ideas underlie the structure-activity strategy, which allows us to better understand the mechanistic aspects of the catalytic process and improve the characteristics of the catalysts being developed. Application of this strategy for the development and preparation of catalysts for industrially important processes that are critical for energy and environmental ecology, such as the oxidative conversion of methane into C_2 and C_{2+} hydrocarbons, into oxygen-containing methanol, formic aldehyde, formic acid, etc., hydrogenation CO₂ into lower alkenes, formic acid, etc. [11-20].

This paper presents the results of a study of the thermal stability of bimetallic heteronuclear compounds of the composition $(C_5H_5)_2FeMnX_2(\mu-CO)_n$, where X=Cl, Br and n=1.2 deposited on boehmite, and the thermodynamics of their decomposition.

2. Materials and methods

Synthesis and characterization of compounds $(C_5H_5)_2FeMnX_2(\mu-CO)_n$, where X=Cl, Br and n=1.2. These compounds were synthesized according to the procedure in [21] and characterized by physical-chemical methods of analysis.

Synthesis of oxide samples with supported FeMn cyclopentadienyl compounds. Fine boehmite powder produced by Qualikems, India was used as a solid carrier. FeMn cyclopentadienyl compounds were applied to boehmite samples from tetrahydrofuran solutions with different concentrations of these compounds at room temperature. Then each sample dried at 323 K for 6 h and then calcined at 473, 673 and 873 K for 4 h [22]. The thermal decomposition of the obtained samples was studied by TG/DTA methods on a NETZSCH STA 449 F3 Jupiter thermal analyzer in an air flow in the range of 298–1173 K at a temperature rise rate of 10 °C/min.

The phase composition of aluminum oxide samples with these deposited compounds was determined by X-ray diffractometry using a Phaser D2 diffractometer, Bruker; the infrared spectra of these samples were recorded on an FT-IR Alfa spectrometer and EPR spectra on an EMRmicro spectrometer, Bruker, Germany.

3. Results and discussion

Figure 1a,b shows thermograms, obtained in a stream of air, respectively, of compounds, applied from the tetrahydrofuran solutions to samples of boehmite dried at 323 K for 6 h in air a stream of air.

As can be seen from the thermograms presented in Fig. 1, when heating samples of boehmite with compounds $(C_5H_5)_2FeMnX_2(\mu-CO)_n$, where a) X=Cl, n=2 and b) X=Br, n=1 from room temperature to 1173 K in a flow of air, the residual masses were 90.89 wt.% and 88.15 wt.%, respectively, for the first and second samples of their initial mass. If we assume that the residue of thermal decomposition of aluminum oxide samples with deposited compounds I consists of a mixture of iron, manganese and aluminum oxides, then in accordance with Eqs. 3-6 the mass of iron and manganese oxides is in solid residues should be ~ 9.70 by weight of the mixture. This circumstance is mainly due to the desorption of a significant portion of these compounds deposited from the organic liquid phase during heating of the samples. Under experimental conditions, when heated from room temperature to 1173 K in a flow of air, the initial mass of samples with these com-



Fig. 1. (a), (b) thermograms, obtained in a stream of air, respectively, of compounds $(C_5H_5)_2FeMnX_2(\mu-CO)_n$, where (a) X=Cl, n=2 and (b) X=Br, n=1 in an amount of 2.44 wt.%, applied from the tetrahydrofuran solutions to samples of boehmite dried at 323 K for 6 h in air.

pounds decreases by ~10 and 11%, respectively. The thermal decomposition of these compounds deposited on aluminum oxide in a stream of air under the specified conditions occurs in two stages – within the range of 453–753 and 813–843 K and ends with the formation of oxides of iron, manganese (exothermic effect at 813 K).

Below are the results of a thermodynamic analysis of the thermal decomposition reactions of compound $(C_5H_5)_2FeMnX_2(\mu-CO)_n$ deposited on boehmite samples AlO(OH), calcined at 873 K in a stream of air for 4 h (3–6). The temperature dependences of the Gibbs free energy of these reactions (Eqs. 3a–6a) were determined based on the Uhlich equation using the method described in [18,23,24]:

$$\Delta G_T^0 = \Delta H_T^0 - T \Delta S_{298}^0 - \Delta C_{P,298}^0 T \left[\ln \left(\frac{T}{298} \right) + \frac{298}{T} - 1 \right]$$
(1)

In the computer version, Eq. (1) has the form (T denoted by x):

$$\Delta G_{x} = \Delta H_{x}^{0} - x \cdot \Delta S_{298}^{0} - \Delta C_{P,298}^{0} \cdot x \left[\ln \left(\frac{x}{298} \right) + \frac{298}{x} - 1 \right]$$
(2)

In Eqs. (1) and (2): ΔG_T^0 is the standard Gibbs free energy change at temperature T, ΔH_T^0 – is the standard enthalpy change at temperature T, ΔS_{298}^0 – is the standard entropy change at 298 K, T – is the temperature in Kelvin; which are determined on the basis of the thermodynamic functions of the substances involved in the reactions. $\Delta C_{p,298}^0$ is the difference in the molar isobaric heat capacities of the products and starting materials of the reactions. The values of the thermodynamic parameters of inorganic substances in reactions (3–6) are taken from [25]. The values of the thermodynamic parameters of bimetallic heteronuclear compounds of the composition $(C_5H_5)_2FeMnX_2(\mu-CO)_n$, where X=Cl, Br and n=1.2 are not available in the literature. They were determined (Table) by calculation based on the values of the thermodynamic parameters of ferrocene [26–29], the corresponding manganese chlorides (bromides), and the binding energy between the iron atom and CO. The last value was determined based on the values of the thermodynamic parameters of iron pentacarbonyl Fe(CO)₅ [25].

Table. Thermodynamic parameters of compounds $(C_5H_5)_2FeMnX_2(\mu-CO)_n$

Compounds	$-\Delta H^0_{p,298},$	$S_{298}^{0},$	$C_{p,298}^{0},$
	kJ/mol	J/(K mol)	J/(K mol)
$(C_5H_5)_2FeMnCl_2(\mu-CO)$	396	575	350
$(C_5H_5)_2FeMnCl_2(\mu-CO)_2$	541	664	372
$(C_5H_5)_2FeMnBr_2(\mu-CO)$	301	599	348
$C_{5}H_{5})_{2}FeMnBr_{2}(\mu-CO)_{2}$	446	688	370

Below (Fig. 2) are the temperature dependences of the Gibbs free energy for the thermal decomposition reactions of bimetallic heteronuclear compounds supported on boehmite $(C_5H_5)_2FeMnX_2(\mu-CO)_n$.

 $2(C_5H_5)_2FeMnCl_2(\mu-CO) + 2AIO(OH) + 27.5O_2 \rightarrow Fe_2O_3 + 2MnO + 2Cl_2 + 11H_2O + 2CO + 20CO_2 + Al_2O_3$ (3)

 $\Delta G_T^0(kJ) = -11270 + 0.7625 * x + 0.486 * x^* (\ln(x/298) + 298/x-1)$ (3a)

$$\begin{split} & 2(C_5H_5)_2 FeMnCl_2(\mu\text{-CO})_2 + 2AlO(OH) + 27.5O_2 \rightarrow Fe_2O_3 + \\ & 2MnO + 2Cl_2 + 11H_2O + 4CO + 20CO_2 + Al_2O_3 \end{split}$$

 $\Delta G_T^0(kJ) = -11202 + 0.545 * x + 0.472 * x^* (\ln(x/298) + 298/x-1)$ (4a)

 $2(C_{5}H_{5})2FeMnBr_{2}(\mu-CO) + 2AIO(OH) + 27.5O_{2} \rightarrow Fe_{2}O_{3} + 2MnO + 2Br_{2} + 11H_{2}O + 2CO + 20CO_{2} + AI_{2}O_{3}$ (5)

 $\Delta G_T^0(kJ) = -11460 + 0.953 * x + 0.412 * x^* (\ln(x/298) + 298/x-1)$ (5a)

 $2(C_5H_5)_2FeMnBr_2(\mu-CO)_2 + 2AIO(OH) + 27.5O_2 \rightarrow Fe_2O_3 + 2MnO + 2Br_2 + 11H_2O + 4CO + 20CO_2 + AI_2O_3$ (6)

 $\Delta G_T^0(kJ) = -11392 + 0.734 * x + 0.398 * x^* (\ln(x/298) + 298/x-1)$ (6a)

From Fig. 2 it follows that over the entire temperature range of 600–1200 K, the Gibbs free energies of reactions (3–6) are negative, which indicates complete oxidative pyrolysis of bimetallic heteronuclear compounds $(C_5H_5)_2FeMnX_2(\mu-CO)_n$ deposited on boehmite to form oxides of iron and manganese.



Fig. 2. Dependence of the Gibbs free energy of reactions (3–6) on temperature by Eqs. 3a–6a, accordingly.

Figure 3 shows X-ray diffraction patterns recorded at room temperature of boehmite samples coated with $(C_5H_5)_2FeMnX_2(\mu-CO)_n$, where X=Br, n=1 in an amount of 2.44 wt.%, applied from the tetrahydrofuran solutions to samples of boehmite dried at 323 K for 6 h in air and calcined at: a) 383, b) 473, c) 673 and d) 873 K for 2 h.



Fig. 3. X-ray diffraction patterns recorded at room temperature of boehmite samples coated with $(C_5H_5)_2FeMnX_2(\mu-CO)_n$, where X=Br, n=1 in an amount of 2.44 wt.%, applied from the tetrahydrofuran solutions to samples of boehmite dried at 323 K for 6 h in air and calcined at: (a) 383; (b) 473; (c) 673; (d) 873 K for 2 h.

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Fig. 4. EPR spectra recorded at room temperature of boehmite samples recorded at room coated with $(C_5H_5)_2FeMnX_2(\mu-CO)_n$, where X=Br, n=1 in an amount of 0.5 (a,a') and 2.44 (b) wt.%, respectively, applied from the tetrahydrofuran solutions to samples of boehmite dried at 323 K for 6 h in air and calcined at 873 K for 2 h.

X-ray diffraction patterns of catalyst samples prepared based on boehmite with compounds $(C_5H_5)_2FeMnX_2(\mu-CO)_n$, where ΔX =Cl, Br and n=1,2 deposited on them from the liquid organic phase (tetrahydrofuran) with a content of less than 10 wt.% and calcined at a temperature of 383–673 K, show only peaks belonging to boehmite [30]. X-ray diffraction patterns of these samples calcined at 873 K are characteristic of aluminum oxides (Fig. 3d). The formation of boehmite samples upon calcination at 873 K is due to dehydration of boehmite (2AIO(OH) = Al₂O₃ + H₂O). The absence of peaks from the oxide structures of iron, and manganese indicates their presence in these samples in a highly dispersed amorphous state [31–33].

Figure 4 shows EPR spectra recorded at room temperature of boehmite samples recorded at room coated with $(C_{s}H_{s})_{2}FeMnX_{2}(\mu$ -CO)_n, where X=Br, n=1 in an amount of 0.5 (a,a') and 2.44 (b) wt.%, respectively, applied from the tetrahydrofuran solutions to

samples of boehmite dried at 323 K for 6 h in air and calcined at 873 K for 2 h.

The EPR spectra shown are typical for samples containing isolated iron ions Fe^{3+} , manganese Mn^{2+} , nano-sized particles of iron, and manganese oxides Fe(Mn)Ox [34,35]. In the EPR spectra (Fig. 4a,b) in low magnetic fields ($\Delta H \sim 150$ mT), a narrow signal with a g-factor value of ~4.3 and a six-component signal with g-factor values of ~2.00 and hyperfine interaction constants of 9.4 mT (Fig. 4,a,a') are observed. These signals are detected against the background of broad signals, the intensity of which increases with increasing content of these compounds. These broad signals belong to nanosized Fe(Mn)Ox particles [36,37].

Figure 5a,b shows IR-Fourier spectra recorded at room temperature of compound $(C_5H_5)_2FeMnX_2(\mu-CO)_n$, where X=Br, n=1 deposited on boehmite in an amount of 2.44 wt.% after drying at 323 K (a) and calcination at 473 K (b) on air for 2 h.



Fig. 5. FT-IR spectra recorded at room temperature, IR-Fourier spectra recorded at room temperature of compound $(C_5H_5)_2$ FeMnX₂(μ -CO)_n, where X=Br, n=1 deposited on boehmite in an amount of 2.44 wt.% after drying at 323 K (a) and calcination at 473 K (b) on air for 2 h.

The Fourier transform FT-IR spectrum shown in Fig. 5a is characteristic of cyclopentadiene compounds $(C_5H_5)_2FeMnX_2(\mu-CO)_n$. As can be seen from (Fig. 5), there is a significant decrease in the intensity of the absorption bands when they are calcined in air at 473 K [38,39]. The peaks appear at 3316.79, 1601 belong to surface OH – groups of boehmite matrix.

The peaks between 1190 and 810 cm⁻¹ arising from the out of-plane vibration of cyclopentadiene and the peaks between 400–500 cm⁻¹ due to the asymmetric ring metal stretching vibration, which is characteristic of metal-cyclopentadiene complexes, are clear evidence of the presence of $(C_5H_5)_2FeX_2(\mu-CO)$ molecules in the sample. It is interesting to note that the effect of heating of the boehmite samples with adsorbed iron-manganese-cyclopentadiene complex resulted in decreasing the intensity of FTIR spectrum of iron-manganese complex and of surface OH groups of boehmite. The decrease in the intensity of absorption bands in the FT-IR spectra in this case may be due to their partial evaporation and/or decomposition of the complex $(C_5H_5)_2FeX_2(\mu-CO)$ deposited on boehmite due to the reaction with the surface OH groups of boehmite.

4. Conclusion

Thermal decomposition of organo-bimetallic $(C_5H_5)_2FeMnX_2(\mu-CO)_n$, where X=Cl, Br and n=1.2 compounds deposited on boehmite samples from tetrahydrofuran solutions at room temperature, studied in dynamic mode in the range from room

temperature up to 1173 K. It was shown that the thermal decomposition in a flow of air of these compounds proceeds according to a staged scheme with the formation at the final stage of nanostructured iron and manganese oxides with superpara/ ferromagnetic properties with a poorly crystallized aluminum oxide base. Based on the Uhlich equation, a thermodynamic analysis of the thermal decomposition of these compounds deposited on boehmite was carried out, and the values of the thermodynamic parameters were calculated. It was shown that in the X-ray diffraction patterns of these samples containing less than 10 wt.% of these compounds, calcined at temperatures \leq 673 K, only peaks due to boehmite are observed. Registration of EPR signals characteristic of iron and manganese oxides shows that the thermal decomposition of boehmite samples with deposited compounds of the specified composition in an air flow at the temperature 873 K is accompanied by the introduction of a small part of iron in the form of Fe³⁺ ions into the structure of aluminum oxide, replacing aluminum ions Al³⁺, and most of the iron and manganese is stabilized on the surface of poorly crystallized aluminum oxide in the form of nanostructured oxides of iron and manganese. XRD data also show that when the above samples with a boehmite base are calcined below 873 K, the boehmite structure is preserved, and when these samples are calcined at a temperature of 873 K, the boehmite structure is transformed into the structure of aluminum oxide $(2AIO(OH) = AI_2O_3 + H_2O).$

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