



*Dedicated to Professor Victor-Emanuel Sahini
on the occasion of his 85th anniversary*

SUPPORTED Fe, Ni – ACETATE CLUSTER USED IN OXIDIZING PROCESSES OF ORGANIC COLORANTS

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The cluster $\text{Fe}_2\text{NiO}(\text{CH}_3\text{COO})_6(\text{Py})_3$ was prepared by classical synthesis route. The heterobimetallic compound was obtained through the reaction between the metal nitrates and the sodium acetate at room temperature, under vigorous stirring. To obtain suitable heterogeneous catalysts an immobilization reaction was carried out with a silanolic derivative. The inorganic support was functionalized with (3-Mercaptopropyl)-trimetoxysilane, and the immobilization was carried out in methanol at reflux for two hours. The final product was tested in the decomposition of hydrogen peroxide and fading of the indigo carmine organic colorant. Fading process reveals a first order kinetics towards the colorant.

INTRODUCTION

Trinuclear oxo-centrated acetate complexes have been investigated as models for electronic and magnetic extended interactions, as homogeneous catalysts and as important building blocks for supramolecular chemistry.¹⁻³

The iron acetate cluster was first isolated in 1909 by Weinland and Gussman, but at that time they weren't able to propose the correct formula. Later, Blake and the co-workers were those who showed through X-ray studies the fact that in the reality was a trinuclear structure. The first structures determined by X-ray studies were $\text{Fe}^{\text{III}}\text{M}^{\text{II}}\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3$ where M= Co or Ni.⁴

The classical way to obtain this type of compounds is by reacting a mixture composed by iron (III) salt and divalent metal salt with sodium acetate in aqueous or alcoholic solution. This method gives yields around 30% and the products are not always pure, mostly contaminated with sodium salts. To obtain pure acetate clusters the final product was

filtered washed with ethanol, water and acetone and the dissolved in pyridine. This process helps increasing the solubility of the compound.

The utilization of them in different homogeneous catalytic processes is justified by several advantages like their capability to form σ and π chemical bonds, the influence of the ligands over the electronic density of the complex generator, the modification possibility of the oxidation state of it and the coordination number.⁵⁻⁷

Intense studies were carried out, in the last period, to immobilize this type of coordinative compounds on organic/inorganic supports in order to obtain heterogeneous catalysts for oxidation reactions. The oxidation reactions was carried out using hydrogen peroxide, one of the most used oxidizing agent in the conversion process of some organic classes of compounds to obtain aliphatic acids, alcohols, phenols, ketones, epoxydes, etc.⁸

The iron-nickel polynuclear acetate cluster is used in several process as catalyst. For this reason the purpose of this study is to investigate the catalytic activity of $\text{Fe}_2\text{NiO}(\text{CH}_3\text{COO})_6(\text{py})_3$

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immobilized on a functionalized silica matrix in the fading process of the indigo carmine organic colorant.

EXPERIMENTAL PART

All reagents were purchased from Fulka Analytical and used without further purification. The solvents were distilled before they were used. The FT IR spectra were carried out using a BRUKER TENSOR 27 (ATR) apparatus, the UV-Vis were recorded with a UV-VIS VARIAN CARRY BIO100, the thermogravimetric analysis were made with a Paulik Erdey type derivatograph (MOM-BUDAPEST) with a heating rate of 10°C/min between 25-750°C. The specific surface of the silica matrix and the porosity of it were determined by liquid nitrogen adsorption at 77K using a QUANTACHROME AUTOSORB NOVA 2200e apparatus, and the surface area was calculated by Brunauer-Emmett-Teller method. The pore size distribution was calculated with Barrett-Joyner-Halenda model. The obtained catalyst was tested in the fading process of indigo-carmine using hydrogen peroxide solution 4% at room temperature.

Synthesis

The experimental procedure was carried out like is given in the literature.¹⁵ Over an ethanol solution of 4.04 g (10mmoles) of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 1.45g (5mmoles) $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added an aqueous suspension of 8.20 g (100mmoles) of CH_3COONa under vigorous stirring. The stirring was continued for 2 hours at room temperature. The formed precipitate was filtered, washed with water, ethanol and acetone and dried at room temperature over P_2O_5 . For increasing the solubility of the compound, the precipitate was dissolved at reflux in pyridine. The resulting precipitate was recrystallized from methanol. The product was obtained as a

microcrystalline form with good solubility in water, alcohol and other organic solvents.

The inorganic support was functionalized using (3-Mercaptopropyl)-trimetoxysilane. The mixture was refluxed in anhydrous toluene for 3 hours. The resulting product was washed with methanol and stored over CaCl_2 .

The immobilization process was made in methanol at reflux for two hours. The obtained catalyst was filtered, washed with methanol and acetone and dried at room temperature. After the immobilization process the concentration of the metal complex over the silica support is about $2.056 \cdot 10^{-4}$ mol/g silica support.

RESULTS AND DISCUSSION

FT-IR spectroscopy

In the FT-IR spectra of the studied compound appear the specific vibrations bands for this type of structure (Fig. 1). At 1538.31 cm^{-1} can be found the asymmetric vibration of the COO^- group. The principal vibrations band found in the spectra of the polynuclear compound are: 1538.31 cm^{-1} ($\nu_{\text{asym}} \text{COO}^-$), 1411.38 cm^{-1} ($\nu_{\text{sim}} \text{COO}^-$), 1340.14 cm^{-1} ($\nu_{\text{sym}}^{\text{bent}} \text{CH}_3$), 1039.35 cm^{-1} (rock CH_3), 655.00 and 618.75 cm^{-1} (in plane bent and out of plane of COO^-) 564.15 cm^{-1} ($\nu_{\text{Fe}_2\text{NiO}}$). At 3400 cm^{-1} can be observed a large band due to the water presented in the system. The frequency difference between the antisymmetric and symmetric stretching mode of carboxylate group is typically for acetate ligand bridging between two metal ions.

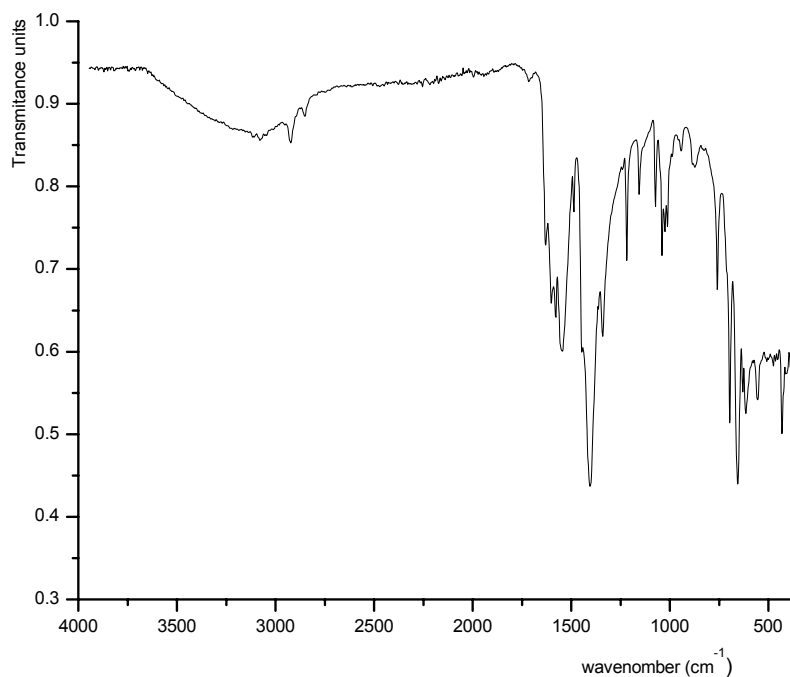


Fig. 1 – FT-IR spectra of the polynuclear compound.

UV-Vis spectroscopy

In the visible spectra of the coordinative compound the three transitions specific for the Ni^{2+} cation are very weak and partially masked by the specific absorption band of the Fe^{3+} in the polynuclear compounds. This large band that can be attributed to the transition ${}^4\text{T}_1 \rightarrow {}^4\text{T}_2$ due to the partial coupling of the electrons from the Fe^{3+} . The other band specific to Fe^{3+} due to the ${}^4\text{T}_1 \rightarrow {}^4\text{A}_1$ transition is situated at 506.7 nm and is present as a shoulder for the other transition. A weak signal appears at 749.0 nm and can be attributed to one of the Ni^{2+} transitions (${}^3\text{T}_{2g} \rightarrow {}^3\text{A}_{1g}$). In the UV region appear the specific transitions bands for the solvent at 203.6 nm, another one at 256 nm due to the $\pi \rightarrow \pi^*$ transition of the aromatic system of the pyridine and another one at 307 nm that can be attributed to a $n \rightarrow \pi^*$ specific to the pyridine molecule.

Thermogravimetric analysis

Specific to this type of compounds is their low thermal stability. The decomposition of the metal complex starts at 80°C with the elimination of the solvent molecules from the system and the break of

the H₂O/Py bond from the cluster. The basic decomposition process finishes at 240°C with the total destruction of the metal cluster and the formation of a mixed oxide NiFe_2O_4 with some organic impurities. After this temperature the mass of the investigated system remains stable due to the relative stability of the formed metallic oxide.

Diffuse reflexion spectroscopy

By this technique the bond between the metal complex and the functionalized silica support was evidenced, though the red shift of the absorption bands in the spectra of the catalyst. The band that was previously attributed to ${}^4\text{T}_1 \rightarrow {}^4\text{T}_2$ transition characteristic to Fe^{3+} is shifted to 590 nm and the intensity increases. The other band that is attributed to the ${}^4\text{T}_1 \rightarrow {}^4\text{A}_1$ transition is shifted to 690 nm. The specific band attributed previously to the Ni^{2+} remained weak and is covered by the large absorption band attributed to Fe^{3+} . In the UV region we can observe the transition band of the solvent that remained in the pores of the silica support and the transition band specific to the -SH bond from the silane derivative.

Table 1

UV-Vis data for the investigated metal complex

Wavelength (nm)	Transition that occur	Chemical species
201		Ethanol
256	$\pi \rightarrow \pi^*$	Pyridine molecule
307	$n \rightarrow \pi^*$	Pyridine molecule
490	${}^4\text{T}_1 \rightarrow {}^4\text{T}_2$	Fe^{3+}
506.7	${}^4\text{T}_1 \rightarrow {}^4\text{A}_1$	Fe^{3+}
749.0	Shoulder to the other band ${}^3\text{T}_{2g} \rightarrow {}^4\text{A}_{2g}$	Ni^{2+}

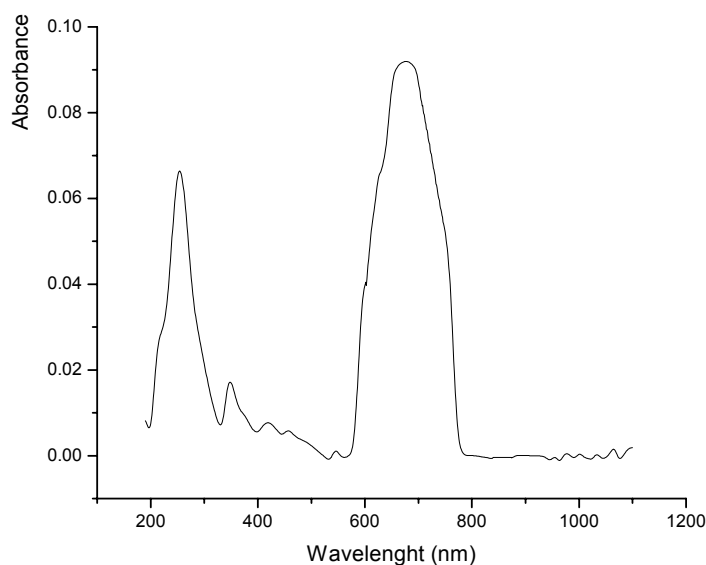


Fig. 3 – UV-Vis spectra of the solid catalyst.

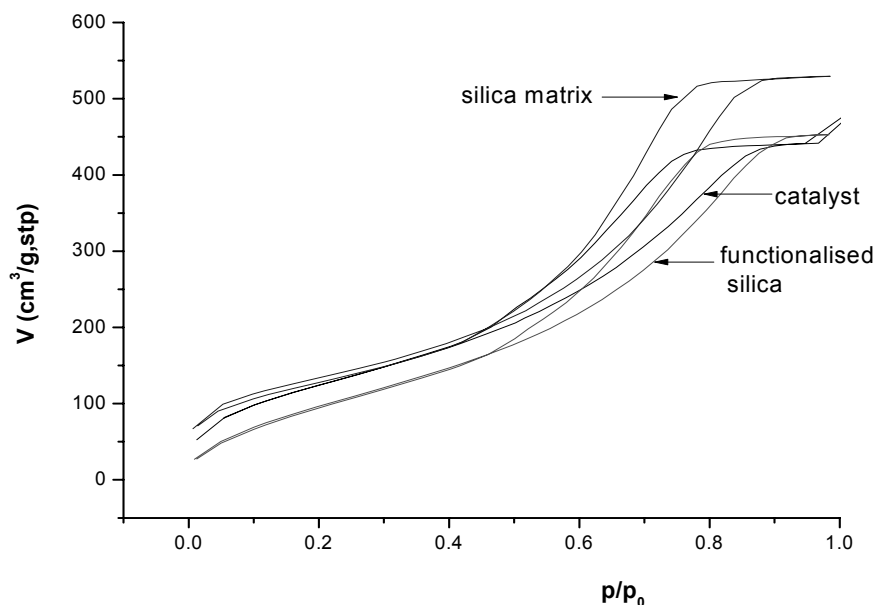


Fig. 4 – Adsorption/desorption isotherms for the catalyst, functionalised support and support.

Surface area determination

The adsorption-desorption process carried out at 77 K using nitrogen revealed for the catalyst an surface area about 444.776 m²/g, surface smaller than the original surface area of the silica matrix (491.277m²/g). The pores volume is lowered up to 0.6924cc/g. From this fact can be concluded that the immobilization of the metal compound is carried out inside the pores.

The isotherms show a H2 type hysteresis loops that can be correlated to “ink-bottle” shape pores with diameter smaller than 59.7 nm. The immobilization of the metal complex is achieved without destroying the inner architecture of the pores.

Catalytic activity

The catalytic activity was tested in the fading process of the indigo carmine organic colorant¹⁰⁻¹². The measurements were made at 610 nm, constant volume, constant temperature and ph 7.09. The absorbance were recorded with a CECIL CE 1020 single beam spectrophotometer. The initial

concentration of the colorant was 10⁻¹M. The reaction speed was calculated with the relation:

$$V = \frac{\Delta A}{\Delta t \cdot \Sigma \cdot l} \quad (1)$$

Where:

ΔA = variation of the system absorbance for the time interval considered

Σ = extinction molar coefficient

l = the thickness of the vat

1mL I_c + 39-n mL tampon solution + n mL H₂O₂ + 50mg catalyst.

The obtained curves correspond to 1mL, 2mL and 5 mL of hydrogen peroxide (4%) in the system (Fig. 5). The fading process follows a first order kinetics with rate constant about 10⁻⁷ molL⁻¹s⁻¹ calculated from the values obtained from the optical densities of the reaction system. All the determinations were made at room temperature and constant pH. After 10 hour of continuous stirring the reaction mixture became completely fade. Supplementary tests for the decomposition of hydrogen peroxide over the same catalyst using p-nitrosodimethylaniline as radical acceptor and revealed a radical mechanism, radicals that are responsible for the fading process of the organic colorant.

Table 2

Data obtained at the fading of the indigo carmine in the presence of the catalyst

Time (min)		0	5	10	15	20	V(mol/L*s)
Absorbance	n=1	0.453	0.444	0.438	0.431	0.424	2.67·10 ⁻⁷
	n=2	0.453	0.436	0.425	0.411	0.393	5.537·10 ⁻⁷
	n=5	0.453	0.415	0.385	0.350	0.324	1.19·10 ⁻⁶

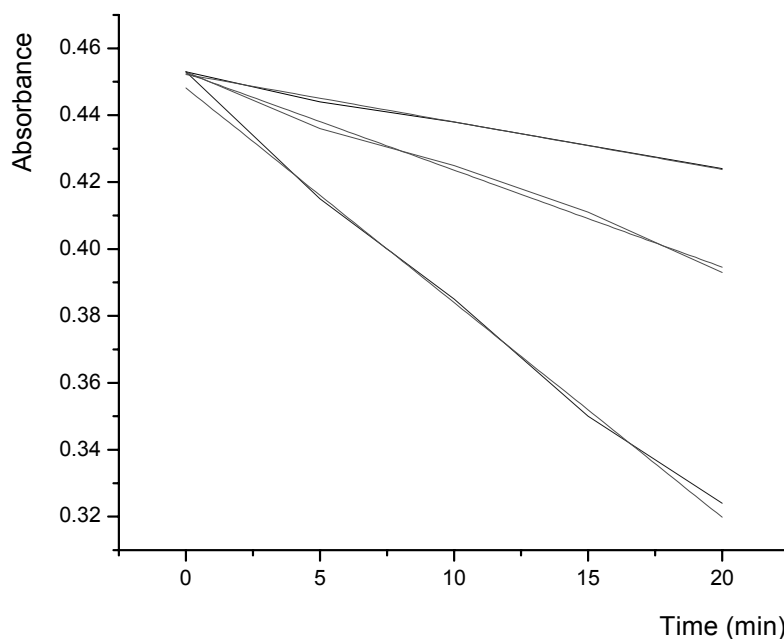


Fig. 5 – Obtained curves at the catalytic fading of indigo carmine.

CONCLUSIONS

In conclusion we successfully prepared a suitable catalyst that can be used in the oxidation process of the organic substrates. Through this catalyst we successfully combine the advantages of heterogeneous and homogeneous catalysis through the immobilization process of a soluble metal complex on an insoluble inorganic matrix, and eliminate their disadvantages directly bonded to the removal process of the catalyst from the reaction mixture.

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