



*Dedicated to Professor Ionel Haiduc  
on the occasion of his 75<sup>th</sup> anniversary*

## SUPPORTED OXO-TRINUCLEAR Fe-ACETATE CLUSTER WITH CATALYTIC ACTIVITY

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In this paper are presented the physico-chemical characterization of the trinuclear  $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6(\text{Py})_3]\text{NO}_3$  acetate cluster and the catalytic fading of methylene blue organic colorant in the presence of diluted solutions of hydrogen peroxide using the metal complex immobilized on functionalized with (3-Mercaptopropyl)-trimetoxysilane silica matrix through chemical bond. The catalytic fading suggests a first order kinetics towards the hydrogen peroxide. Further test using p-nitrosodimethylaniline reveals a radical mechanism.

### INTRODUCTION

The oxidation of hydrocarbons and derivatives is used in many purposes with the scope to prepare other functionalized classes of compounds such as aliphatic acids alcohols, phenols, ketones, epoxides etc.<sup>1-3</sup>

As a general rule the oxidation process takes place more selectively using a proper catalyst. The observed selectivity in this case is explained through much soft reaction conditions due to the formation of a complex between the catalyst and the oxidizing agent, after which the formed metal complex is decomposed with formation of free radicals, or the emergence of a non-radical phase in the reaction between the oxidizing agent and the catalyst.

Hydrogen peroxide is one of the most used oxidizing agents that is capable to react with different organic compounds. It can be considered an ecological redox agent due to the fact that the residual product obtained are water and dioxigen.<sup>4-7</sup>

One of the most important classes of industrial and/or laboratory catalysts is constituted by the polynuclear transitional metals complexes.

The utilization of them in different homogeneous catalytic processes is justified by several advantages, like their capability to form  $\sigma$  and  $\pi$  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.<sup>11-13</sup>

In the last period, intense research was made for the immobilization of this coordinative compound on organic/inorganic supports in order to obtain so-called heterogenized homogeneous catalysts.

This new catalysts class combines the advantages of both classes and eliminates the disadvantages.<sup>7-10</sup> Silica based hybrid materials can be used as suitable catalysts for liquid phase reaction due to its possibility to offer a good diffusion coefficient of the liquid reactants to the catalytic active sites. Their silanol groups can be easily tuned using different organic functions to improve its ability to attach different coordinative species with catalytic active role. The iron polynuclear coordinative compounds are used in several processes as catalysts.<sup>21</sup> For this reason we intended to study the catalytic activity of polynuclear

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$[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6(\text{Py})_{3-n}(\text{H}_2\text{O})_n]\text{NO}_3$  immobilized on functionalized silica matrix.

## EXPERIMENTAL

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 recorded with a BRUKER TENSOR 27 (ATR) apparatus, the UV-Vis were recorded with a UV-VIS VARIAN CARRY BIO100, the thermogravimetric analysis were carried out using a Paulik Erdey type derivatograph (MOM-BUDAPEST) with a heating rate of  $10^\circ\text{C}/\text{min}$  between  $25\text{--}750^\circ\text{C}$ . The surface area of the silica matrix and its porosity were determined from the adsorption isotherms of the material at the temperature of liquid nitrogen ( $-196^\circ\text{C}$ ) using a QUANTACHROME AUTOSORB NOVA 2200e apparatus. The surface area was calculated using the Brunauer-Emmett-Teller method while pore size distribution using the Barrett-Joyner-Halenda model.

### Synthesis

Over an ethanol solution of 6.06 g (15 mmol) of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , it was added an aqueous suspension of 8.20 g (100 mmol) of  $\text{CH}_3\text{COONa}$  under vigorous stirring.<sup>19</sup> The formed precipitate was filtered, washed with water, ethanol and acetone and dried at room temperature over  $\text{P}_2\text{O}_5$ . For better solubility the compound was solubilized in pyridine at reflux and left to crystallize at room temperature. The resulting precipitate was recrystallized from methanol. The inorganic support was functionalized using (3-Mercaptopropyl)-trimethoxysilane. The mixture was refluxed in anhydrous

toluene for 3 hours. The resulting product was washed with methanol and stored at room temperature over  $\text{CaCl}_2$ .

The immobilization process was made in methanol at reflux for two hours with the liberation of a pyridine molecule from the metal complex. The presence in the liquid of a free pyridine molecule was put in evidence by UV spectroscopy. In the spectra of the solution appeared the specific absorption bands of free pyridine at 250, 256 and  $262\text{nm}$ .<sup>20</sup> The obtained catalyst was filtered, washed with methanol and acetone and dried at room temperature. The catalytic activity was tested toward fading process of methylene blue colorant.

## RESULTS AND DISCUSSION

### FT-IR spectroscopy

The FT-IR spectra for the synthesized compound with formula  $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6(\text{C}_5\text{H}_5\text{N})_3](\text{NO}_3)$  is presented in Fig. 1. In the spectra are present the typical bands at  $1592.26\text{ cm}^{-1}$  ( $\nu_{\text{asym}} \text{COO}^-$ ),  $1427.5\text{ cm}^{-1}$  ( $\nu_{\text{NO}_3^- \text{ s}}$ ),  $1324.5\text{ cm}^{-1}$  ( $\nu_{\text{sym bent}} \text{CH}_3$ ),  $1042.0\text{ cm}^{-1}$  (rock  $\text{CH}_3$ ),  $822.67$  ( $\delta \text{NO}_3^-$ , w),  $666.00$  and  $618.75\text{ cm}^{-1}$  (in plane bent and out of plane of  $\text{COO}^-$ )  $560.00\text{ cm}^{-1}$  ( $\nu_{\text{Fe}_3\text{O}}$ ). The frequency difference between the antisymmetric and symmetric stretching mode of carboxylate group is typical for acetate ligand bridging between two metal ions.

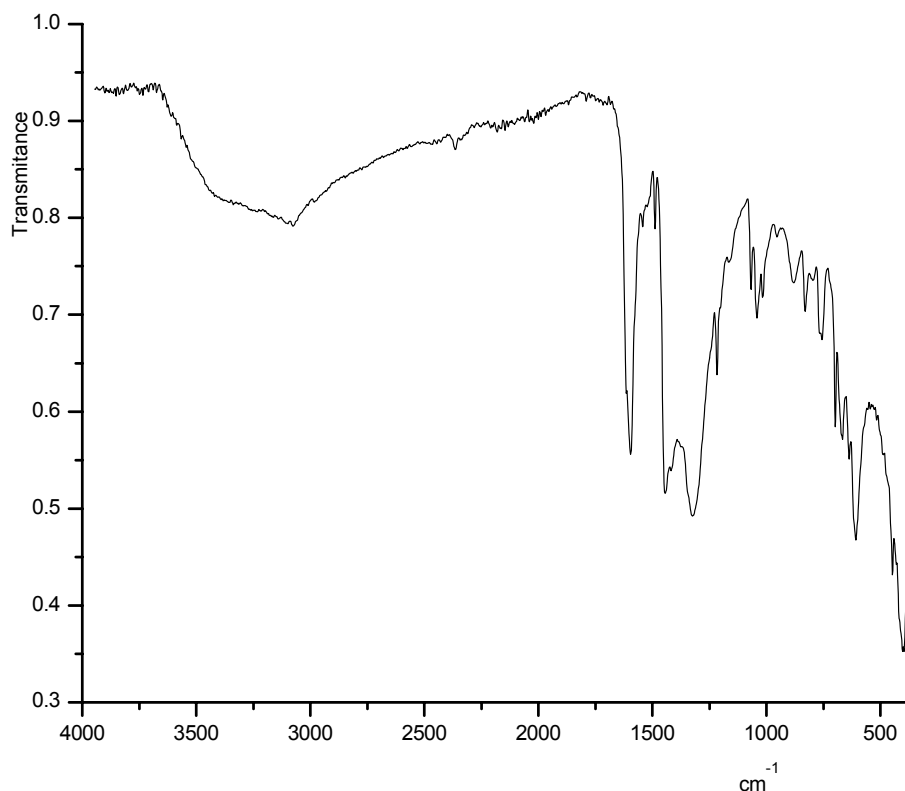


Fig. 1 – FT IR spectra of  $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6(\text{C}_5\text{H}_5\text{N})_3](\text{NO}_3)$ .

### UV-Vis spectroscopy

The transitions that appear in the visible spectra of the  $\text{Fe}^{3+}$  compound can be attributed to a partial coupling of the electrons from the  $d^5$  structure due to the influence of the pyridine directly bonded to the  $\text{Fe}^{3+}$  cation. The partial couplings of the electrons lead to the appearance of a  ${}^4G$  spectral term that gives multiple transitions. From those only two have acceptable energies. The first one can be attributed to a  ${}^4T_1 \rightarrow {}^4T_2$ . The intensity of this band is very intense, and is specific to polynuclear compounds that contain  $\text{Fe}^{3+}$ . The second absorption band can be attributed to a  ${}^4T_1 \rightarrow {}^4A_1$ . This band is weak and is partially masked by the other one. In the UV region there is present the absorption band of the solvent at 211 nm and the absorption band specific to the pyridine molecule at 255.9 nm.

### Thermogravimetric studies

A specific feature of the investigated complex is related to its low temperature stability. On TG and DTG curves of the investigated compound, it is visible that the basic processes of decomposition finishes in the range 300–360°C. The first decomposition endothermic stage corresponds to removal of solvent molecules (Py and  $\text{H}_2\text{O}$ ) and some quantity of intrasphere solvent molecules. It is very probable that the removal of intrasphere molecules of solvent is accompanied by reorganization of the cluster in such a way to

assure all coordination places of the  $\text{Fe}^{3+}$  ion.<sup>9</sup> The subsequent second process for all three clusters is characterized by several super positioned processes: removal of coordinated molecules of pyridine, decomposition of acetic acid anions and reorganization of the complexes with the formation of the final product,  $\text{Fe}_3\text{O}_4$ , with a small quantity of impurities.

### Surface area determination

The absorption process taken at 77K using liquid nitrogen showed a surface area about 447,926  $\text{m}^2/\text{g}$  and a pore diameter smaller than 130 nm (Fig. 2). The decrease of the external and internal surface area and pore volume value shows an immobilization of the inorganic compound on the internal surface of the pore system and on the exterior of the material.

The H2 type adsorption hysteresis is explained as a consequence of the interconnectivity of pores. In such systems, the distribution of pore sizes and the pore shape is not well-defined or irregular. A sharp step on the desorption isotherm is usually understood as a sign of interconnection of the pores. If a pore connected to the external vapor phase via a smaller pore, in many cases the smaller pore acts as a neck (often referred to as an “ink-bottle” pore). In the cases when adsorption is expected to happen homogeneously over the entire volume of a porous material, desorption may happen by different mechanisms.

Table 1

UV-Vis data for the investigated metal complex

Wavelength (nm)	Transition that occur	Chemical species
211.9		Ethanol
261	$\pi \rightarrow \pi^*$	Pyridine molecule
445.9	${}^4T_1 \rightarrow {}^4T_2$	$\text{Fe}^{3+}$
500.1	${}^4T_1 \rightarrow {}^4A_1$	$\text{Fe}^{3+}$

Table 2

Obtained data from the adsorption isotherms

Parameter	Silica	Functionalized silica	Catalyst
Surface area ( $\text{m}^2/\text{g}$ )	615.829	522.759	447.926
Total pore volume ( $\text{cc}/\text{g}$ )	0.866	0.747	0.694

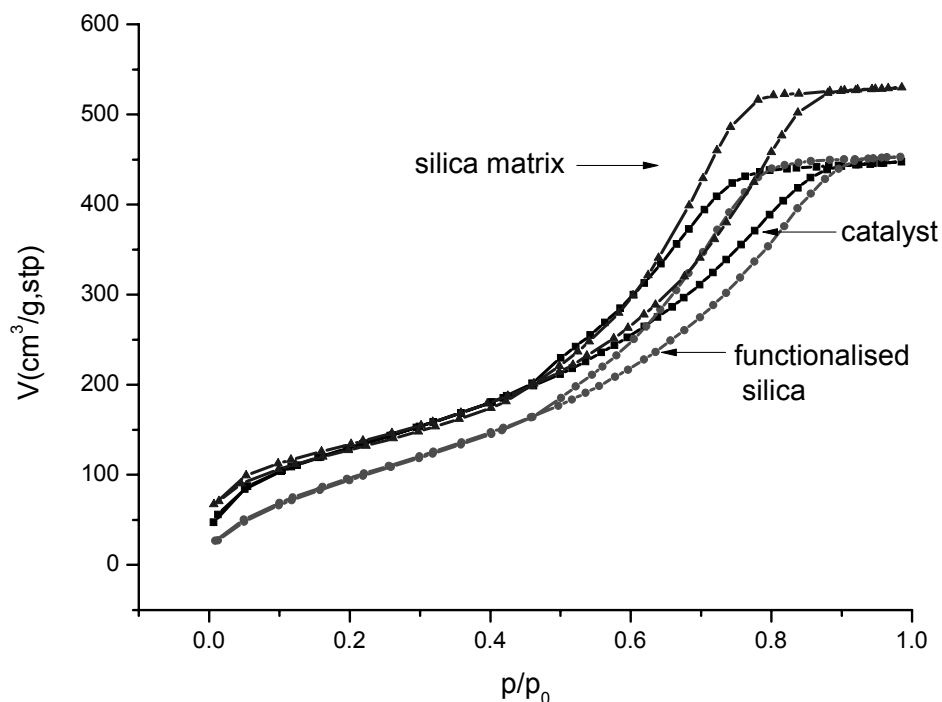


Fig. 2 – Adsorption isotherm of the functionalized silica.

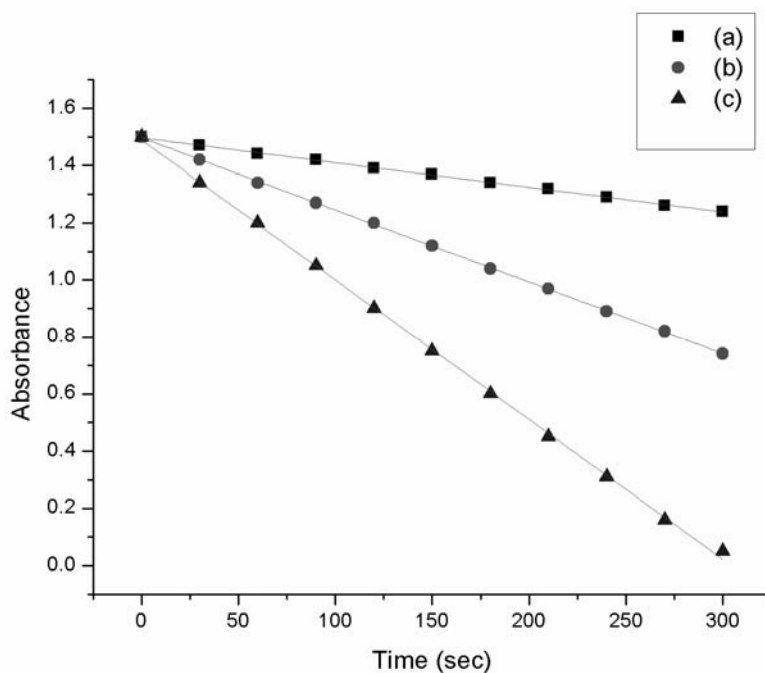


Fig. 3 – The optical density variation of (a) methylene blue with 5mL of hydrogen peroxide, (b) methylene blue with 10mg catalyst and 5mL hydrogen peroxide and (c) methylene blue with 10mg catalyst and 10mL hydrogen peroxide.

### Catalytic activity

#### *Catalytic fading of methylene blue solution*

The fading process of the methylene blue was carried out in aqueous solution. The optical densities of the reaction mixture were recorded at 666.00 nm using a single beam spectrophotometer

CECIL CE 1020 with glass vats. The fading experiments were realized using hydrogen peroxide as oxidizing agent. The measurements were made at room temperature under vigorous steering at a constant volume. First curve represents the fading process of the organic compound in absence of the catalyst. The other

two curves correspond to a volume of 5mL respectively 10 mL of hydrogen peroxide 3% added in the system. The fading process started immediately after the addition process of the oxidizing agent. The difference between the absorbance values corresponding to the last two curves suggests a first order kinetics for the fading process. After two hours from the starting of the catalytic reaction the optical density of the reaction mixture decrease linear below 0.05 absorbance units.

## CONCLUSIONS

We successfully prepared a suitable catalyst that can be used in further oxidation processes for organic substrates. Through this catalyst we successfully combine the advantages of heterogeneous and homogeneous catalysis, and eliminate their disadvantages. The use of this catalyst improves the velocity of the oxidation reaction of methylene blue solution.

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