

The aim of this work is to investigate the structure and the potential catalytic activity of two groups of polinuclear coordinative compounds of the first row transition metals. The novelty of this research consists in the synthesis and characterization of three coordinative compounds with structures not reported in the literature. These compounds are part of the homodinuclear compounds with molecular formula $[M_2(TF)(o\text{-phen})_n](TF)$ where $M = Mn(II), Co(II), Cu(II)$, $TF = C_8H_4O_4^{2-}$ and $n=2$ for the compound that contains in molecule cooper and 4 for the other two. The crystalline structure of these compounds facilitates the eterogenization process by chemical immobilization onto functionalized silica support do to the presence of two coordinative available positions occupied by two water molecules. The loss of these two solvent molecules at moderate heating suggests the coordination of these molecules is established through weak coordination bonds. This fact suggest that the coordination compounds synthesized are able to implicate into ligand exchange reactions at low temperatures. Their immobilization was successfully realized onto inorganic supports type *Si-propyl-SH* and *Si-hexyl-NH₂*.

Another class of coordination compounds that was synthesized and successfully used in the immobilization process was the class of trinuclear oxo-centred compounds. Aldo these compounds were studied and their crystalline structure is well known, these compounds kept, during time, the attentions do to their versatility, there multiple utilizations and their ability to mime the activity of the active centers of the natural enzymes. Studies regarding their utilization into catalytic system immobilized were not found by me. The study began with the synthesis of 4 heteronuclear compounds type $[Fe_2MO(OOC-CH_3)_6(H_2O)_2(C_5H_5N)]^n$ where $M = Cr(III), Mn(II), Co(II), Ni(II)$ and $n = +1$ or 0 .

The eterogenization was made by replacing one coordination water molecule with one functional group from attached on the surface of the silica matrix. The implication of these hybrid materials in the fading process of aqueous solutions of indigo carmine and methylene blue was materialized by two articles published in one ISI indexed magazine.

The stage made into prof. Fabio Marchetti's laboratory helped me to use with success all the catalysts in the catalytic oxidation of the double bond near the aromatic nucleus. In this reaction we obtained conversions rate of styrene equal to 60% for obtaining benzaldehyde for 24h reactions time. The selectivity of the reactions was maintained 10 hours. The oxidation reactions were followed by GC-MS technique. These results were materialized by one short communication send to publish to one international ISI magazine.

The experimental part, where the original results are presented, begins in the chapter VIII with the synthesis and characterization of the trinuclear oxo-centred coordinative compounds and homodinuclear coordinative compounds. The obtaining of the two functionalized silica matrix type Si-propyl-SH and Si-hexyl-NH₂ along with their IR, thermal and textural characterization are presented into chapter IX. The immobilization and the characterization of the hybrid materials obtained are presented into chapter X and XI.

The final aim of this study was to evaluate the catalytic activity of the coordinative compounds synthesized and chemically immobilized onto the functionalized matrix. The evaluation was made in the fading reaction of aqueous solution of methylene blue and indigo-carmin using as oxidizing agent aqueous solutions of hydrogen peroxide. Was proved that the obtained materials are capable to generate *in situ* hydroxyl radicals and to facilitate the attack of these active species over the organic molecules by physical adsorption on surface.

VIII. Synthesis and characterization of di/trinuclear coordinative compounds

VIII.1. Trinuclear oxo-centred compounds

Stoichiometric ratios of iron nitrate and transition metals nitrates [Cr(III), Mn(II), Ni(II), Co(II)] were dissolved in the minimum quantity of distilled water. Under vigorous stirring, over the mixture of metallic salts was added, in excess, an alcoholic solution of sodium acetate. The reaction mixture was left under stirring, at room temperature, to react for 4 hours. The brown-red precipitate obtained was filtered, washed with distilled water and methylic alcohol and left to dry at room temperature in exicator. The dry precipitate was suspended in 100mL of anhydrous pyridine and heated to reflux temperature for 4 hours according to the protocol described in figure 21. The pyridine excess from the system was removed by distillation and the reaction product was taken with ethylic alcohol and recrystallized.

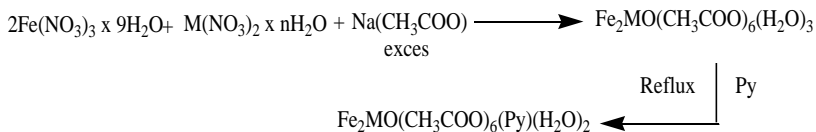


Figure 21 Synthesis protocol used to obtain oxo-trinuclear compound through classical method

One original improvement to the synthesis method presented in the literature was utilization of pyridine as solvent and ligand, with the obtaining of 80% reaction yields.

VIII.1.2.2 Characterization by IR absorption spectroscopy

The characteristic maxims of the symmetric and asymmetric vibration of the (COO) group appear in the IR spectra of this class of compounds, at wavenumbers close to 1590cm^{-1} value and 1450cm^{-1} . The difference between these two wavenumbers of the absorption maxima that correspond to (COO) groups is smaller (140cm^{-1}) than the difference corresponding to the sodium acetate (200cm^{-1}). This fact suggests a greater possibility that the acetate anion to coordinate to the metallic cations than to be found as sodium acetate uncoordinated. The presence of the nitrate anion in the structure of the coordinative compound is associate to the presence in the IR spectra of one strong, sharp absorption band at 1375cm^{-1} . The vibration frequency associated to the structural unit M3O from the center of the coordinative compound can be found in the IR spectra in the interval $560\text{-}430\text{cm}^{-1}$.

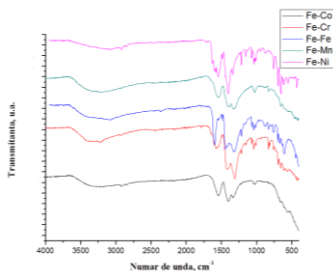


Figure 24 The IR spectra of the oxo-trinuclear compounds synthesized

VIII.1.2.3. Characterization by UV-Vis absorption spectroscopy

In the interval 200-400 nm (Figure 25) can be found the specific absorption bands of the used solvent along with the characteristic absorption bands of the coordinated pyridine. In the case of trinuclear oxo-centred coordinative compounds, the visible spectra include large absorption bands with relatively low intensity. The UV-Vis spectra of Fe-Fe specie is composed from a wide charge transfer band from metal to ligand. The appearance of this band in the Vis spectra make difficult to identify the d-d forbidden transitions characteristic to $3d^5$ configuration of trivalent iron. Magnetic moment determinations ($\mu = 3.11\text{MBP}$ - specific to 3 uncoupled electrons in the valence shell) led to the possible existence of a temporary electronic

coupling into the valence shell of trivalent iron, making possible the appearance of transitions specific to the splitting of type 4I fundamental spectral term.

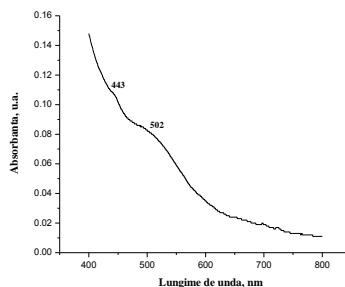
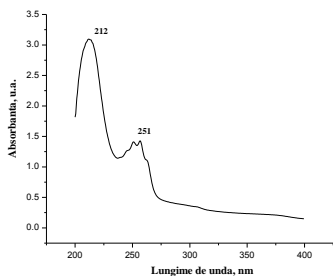


Figure 25 UV spectra of **Figure 26** Vis spectra of $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_2(\text{Py})]\text{NO}_3$

VIII.1.2.4. Thermal analysis

The thermogravimetric studies made for the oxo-trinuclear coordinative compounds displayed that this class of compounds is made from low thermal stability members. They decompose before passing into liquid faze. The decompose process is explained by breaking the hydrogen bond network.

By analyzing the thermogram obtained for the compound with molecular formula $[\text{Fe}_2\text{MnO}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_2(\text{C}_5\text{H}_5\text{N})]$ can be observed different mass loss that can be attributed to different molecular fragments that are present in the compound molecular structure. The temperature interval in which the mass loss occurs along with the molecular fragment that is lost are presented in table 4.

Table 4 The calculated mass loss and those found experimental at thermal decomposition of $[\text{Fe}_2\text{MnO}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_2(\text{C}_5\text{H}_5\text{N})]$

Fragment	Temperature interval °C	Mass loss %	Calculated mass %
solvent	50-90	1,998	-
2 x H_2O coordination 1x H_2O crystallization	100 - 230	7,508	7,03
Coordinated pyridine	275-340	9,509	10,29
2 (CH ₃ COO) x	450 - 640	17,841	17,84

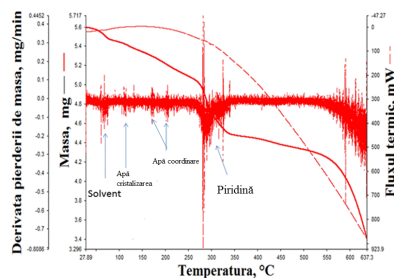
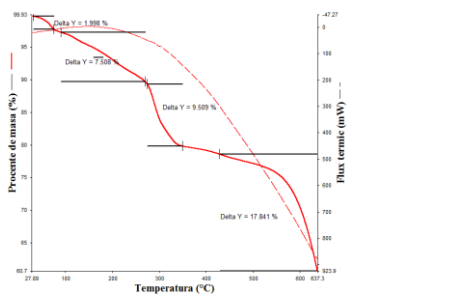


Figure 27 Obtained thermogram for **Figure 28** DTA curve for Fe-Mn specie $[\text{Fe}_2\text{MnO}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_2(\text{PY})]$

VIII.1.3. Structural model description

The oxo-trinuclear compounds contain in molecule a structural arrangement made from 3 metallic cations connected into triangle fashion by 5 acetate groups and one μ_3 -oxo bridge. This structural arrangement induces a C3 symmetry. The coordination environment is completed with 3 neutral molecules (water, pyridine) coordinated into apical positions. The three metallic centers are crystallographic equivalent due to the presence of μ_3 oxygen atom, that is placed into a special position. The coordination environment of every metallic cation is made from 4 oxygen atoms

came from carboxyl groups, the μ_3 oxygen atom and the donor atom from the neutral molecule. The four carboxylate groups form an equatorial plane in a *sin-sin* fashion, while the central oxygen atom and the donor atom from the neutral molecule are placed into axial positions.

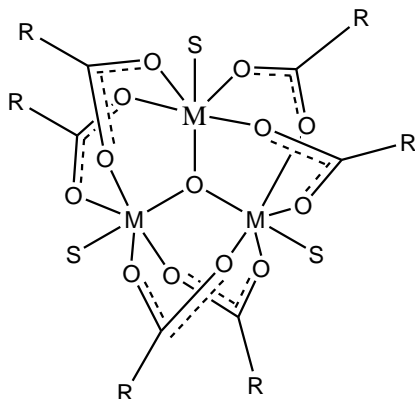


Figure 32 The structure of the unit $[M_3O(OOCR)_6S_3]$, where S = solvent molecule

VIII.2. Homodinuclear compounds with terephthalate bridge ligand

The synthesis protocol of this type of compounds was realized in two steps. In the first step the precipitation of the metallic cations was made with an aqueous solution of sodium terephthalate in a molar ratio of 2:1. In the second step the obtained precipitate, washed and dried, was suspended in distilled water under continuous magnetic stirring. Over this suspension was added, in excess, an alcoholic solution containing 1,10-phenanthroline until complete dissolution of the precipitate. The solution was left to evaporate slowly at room temperature until crystals of coordinative compound appeared. The recrystallization was carried out from ethyl alcohol at low temperature giving crystalline products.

Using this synthesis protocol we successfully obtained 3 homodinuclear coordinative compounds with coordinative compound generators the ions Mn(II), Co(II) and Cu(II). The compounds $[Mn_2(TF)(o\text{-phen})_4](TF)$ and $[Co_2(TF)(o\text{-phen})_4](TF)$ were obtained as single crystals and $[Cu_2(TF)(o\text{-phen})_2](TF)$ as microcrystalline powder.

VIII.2.1.2. Characterization by IR absorption spectroscopy

One particularity discovered after the complete determination of crystalline structure by X ray diffraction was the presence, in the structure lattice, of an terephthalate counter ion. This thing is well correlated with the existence in the IR spectra, in the $1650 - 1350\text{cm}^{-1}$ region, of two sets of absorption maxima specific to the symmetric and asymmetric vibration of the coordinated and uncoordinated (COO) group.



Figure 36 The IR spectra of the compound $[\text{Co}_2(\text{TF})(\text{o-phen})_4](\text{TF})$

By calculating the difference between the characteristic wavenumbers of the symmetric and asymmetric vibration of the carboxyl groups information about the coordination modes of this group can be found. The peaks from 1622 and 1361cm^{-1} can be attributed to the vibration of the coordinated terephthalate group and those from 1563 and 1421cm^{-1} to that uncoordinated. The presence in the IR spectra of one wide band at 3244cm^{-1} suggests the existence in the molecular structure of a network made from hydrogen bonds.

VIII.2.1.3. Characterization by IR absorption spectroscopy

The UV part of the UV-Viz spectrum is composed from the specific absorption bands of the aromatic fragments from the molecule. By comparison with the aqueous solutions spectra of the sodium terephthalate and 1,10-phenanthroline can be observed the shift of the absorption maxima from 352nm from the free 1,10-phenanthroline to 344nm , fact that suggests the coordination of it to the metallic cations.

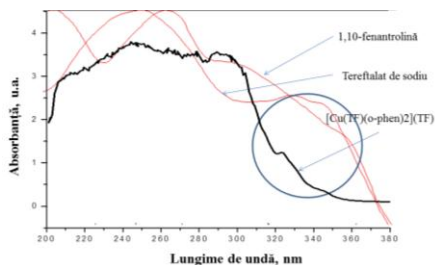


Figure 38 The UV spectra of the aqueous solution of coordinative compound $[\text{Cu}_2(\text{TF})(\text{o-phen})_2](\text{TF})$

The visible region of the spectra is made from the absorption bands characteristic to d-d transitions, specific to metallic cations.

VIII.2.1.4. Thermal analysis

Thermal decomposition of $[\text{Co}_2(\text{TF})(\text{o-phen})_4](\text{TF})$ starts at low temperatures. In the 72-132°C interval can be observed a mass loss attributed to the loss from the molecular structure of the coordination water molecules and crystallization water. After 132°C the coordinative compound is thermal stable until 241°C, after this point in the compound thermogramme can be seen two mass loss attributed to the elimination of terephthalate fragments coordinated and uncoordinated. After 414°C, the rest of the compound becomes stable until 700°C. The residual mass percent is in a good accordance with the cobalt mass cation and the mass of 4 molecules of 1,10-phenanthroline.

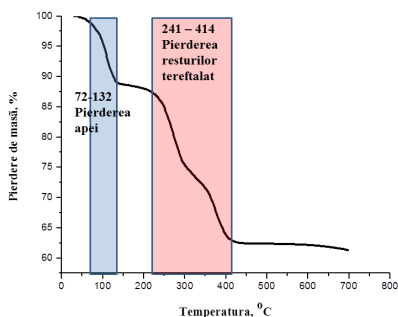


Figure 40 Thermogramme of $[\text{Co}_2(\text{TF})(\text{o-phen})_4](\text{TF})$

VIII.2.1.6. Determination of molecular structure by X ray diffraction

The two compounds present ionic type structure in which the cation is represented by $[M(o\text{-phen})n(\text{TF})m]^{2+}$ and TF^{2-} represents the counterion. The crystalline structure of bought chemical species la initial moment were similar, in alcoholic solutions the structures are dimer type $[\text{M}_2(\text{TF})(o\text{-phen})](\text{TF})$. The recording of the diffraction spectra after a while indicated a structural reorganization at molecular scale for the manganese containing coordinative compound. This transformed into a simple compound type $[\text{Mn}(o\text{-phen})_3](\text{TF})$.

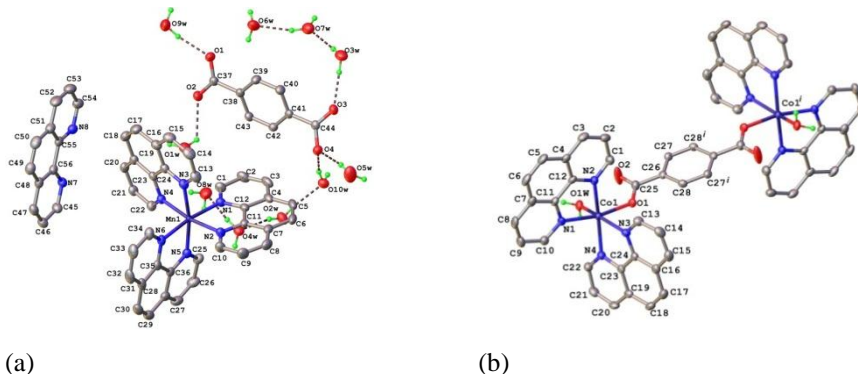


Figure 45 Crystalline structure for the compounds (Mn(TF)-(a) and Co(TF)-(b)

IX. Functionalization of the silica base support

The functionalization process of the support material was achieved in two ways:

- By using a silica based chemical agent chemically attached on the silica base matrix
- By generating functional groups using specific reaction sequence.

IX.1. Obtaining and characterization of support material type Si-propyl-SH

IX.1.1 Functionalization

The functionalization of the silica based matrix was realized according to the methods presented in the literature. In one tree neck reactor equipped with vertical condenser and magnetic stirrer was suspended 20 g chromatographic silica in anhydrous toluene. The resulting mixture was magnetically stirred under nitrogen atmosphere for 20 minutes in order to assure the diffusion of the reactants into porous system of the material. Over the mixture was added 45 mL (3-mercaptopropyl)-trimetoxysilane under vigorous stirring. The stirring was continued for another half an hour. The reaction mixture was then heated to reflux temperature and left to react for 24hours. The resulted material was filtered, washed abundantly with toluene and dichloromethane and the Soxhlet extracted in dichloromethane for 24h in order to deactivate the acid centers remained unreacted on the silica surface and to eliminate the excess of silanization agent unreacted. The obtained material was dried under vacuum for 48 h at 80°C.

IX.1.2. Characterization by FT-IR spectroscopy

In the IR spectra of the functionalized matrix appear the characteristic bands of the $[\text{SiO}_4]^{4-}$ characterized by an increased intensity by compare with the characteristic vibrations of the silanization agent from the system. By plotting the IR spectra of the Si-propyl-SH specie only in $4000\text{-}1500\text{cm}^{-1}$ interval can be observed the vibration maxima specific to C-H bond at 2936cm^{-1} , the vibration of the Si-O-C bonds at 1609cm^{-1} and the vibration band characteristic to thiol group shifted to lower wavenumbers (theoretic 2500cm^{-1} practical 2160cm^{-1}).

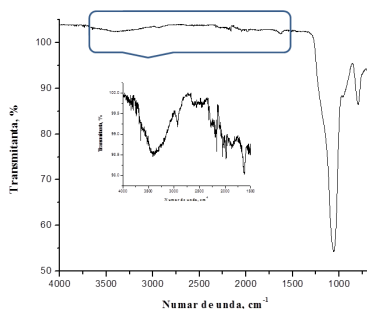


Figure 51 FT-IR spectra of Si-propyl-SH

IX.1.3. Characterization by thermal analysis

By analyzing the compound thermogramme can be observed a mass loss about 1.45% correlated with the loss of water molecules and methylic alcohol physically adsorbed in the porous system. The material relative thermal stability is present until 150°C after which temperature a constant thermal decomposition of the material occurs along with thermal decomposition of the organic faze.

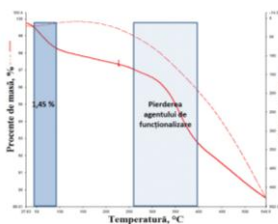


Figure 53 The thermogramme of Si-propyl-SH

IX.1.4. Surface area determination

The surface area determination at 77K by nitrogen adsorption into the material pores indicated type IV isotherms specific to micropores (Figure 54). After coupling the adsorption isotherm with the desorption one was obtained a H2 hysteresis loop specific to materials that contain in structure interconnected micropores with different dimensions.

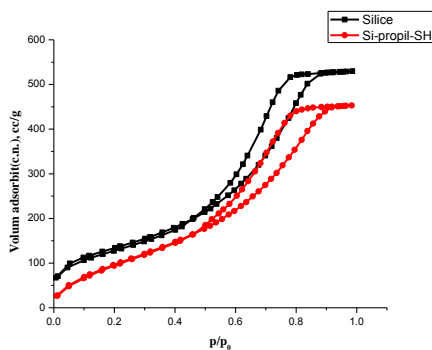


Figure 54 The representation of the adsorption/desorption isotherms for silica material and functionalized silica material

X. Immobilization of coordinative compounds

The immobilization process has as immediate effect the heterogenization of the coordinative compounds and considerable increase of the specific surface area and accessibility of the catalytically active centers. The immobilization of studied coordinative compounds was realized by coordination process of functional groups from the surface of the support in the place of one weak coordinated water molecule. Over an alcoholic solution that contains the coordinative compounds was added one amount of functionalized silica. The reaction mixture was heated at reflux under magnetic stirring for 4 hours.

0.5g of coordinative compound dissolved in 100mL methylic alcohol was added over 2g of functionalized support into a three neck flask. The obtained suspension was magnetically stirred and heated to reflux temperature with obtaining of hybrid materials with possible catalytic activity. The active component is distributed on the internal and external surface.

The presence in the molecular structure of weak coordinated molecules to metallic cations is viewed as an advantage. These materials are susceptible to heterogenization processes. On this thing is based the heterogenization process of the homodinuclear compounds with terephthalate bridge onto functionalized silica. At a close look on the molecular structure of this class of compounds can be seen the two sterically available positions.

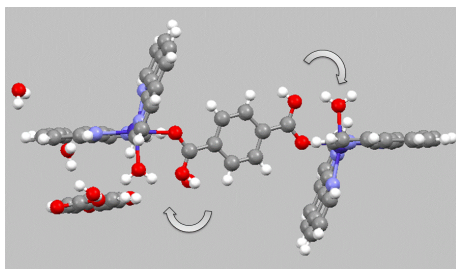


Figure 60 structural unit of $[\text{Co}_2(\text{TF})(\text{o-phen})_4](\text{TF})$ suggesting the two coordinative available positions

XII. The catalytic activity evaluation of polinuclear immobilized compounds

XII.1. Preliminary tests – hydrogen peroxide decomposition

The preliminary catalytic activity of the immobilized coordinative compounds onto silica based matrix was carried out in the hydrogen peroxide decomposition reaction at constant temperature and constant pH. The interaction hydrogen peroxide-surface active center takes place by generating HO· radicals that combines after that in order to form oxygen and water.

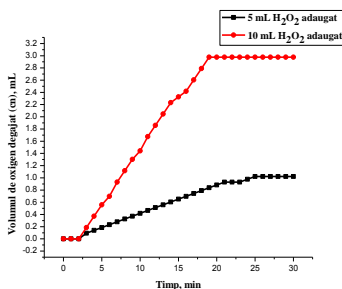


Figure 67 Hydrogen peroxide decomposition curves catalyzed by Si-propyl-Fe-Co using different volumes of hydrogen peroxide solutions (4%)

XII.2.1. Indigo carmine fading

The speed determining step for these chemical reactions is given by the diffusion process of the reactants into the porous system of the support material.

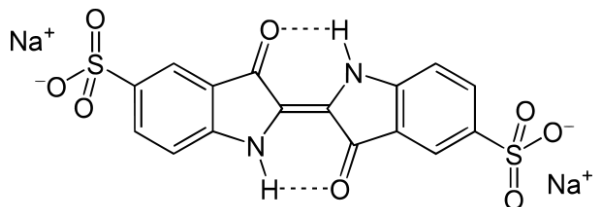


Figure 70 Chemical structure of the sodium salt of indigo carmine

The fading reaction takes place after the physical sorption of colorant molecule onto the surface of the material, the attack of the hydroxyl radicals occurs when the dye molecule is adsorbed onto the surface.

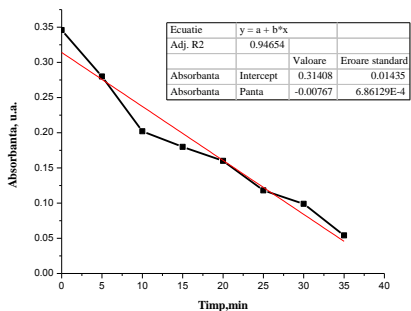


Figure 72 Optical density variation in function of time obtained for the fading process of indigo carmine using as catalyst Si-propyl-Fe-Co

The rapid decrease of the optical density for the first part of the curve can be explained by possible adsorption into surface of the dye molecule. This adsorption is made through one big hydrogen bonds network established between the heteroatoms from the dye structure and the acid groups Si-O-H from the surface of the matrix.

XII.2.2. Methylene blue fading

Methylene blue is a tyazine class compound and was firstly synthesized in 1876. The fading reaction was carried out in presence of 5mL of aqueous solution of hydrogen peroxide (4%), 10 mL of oxidizing agent, in presence of catalyst and in absence of it.

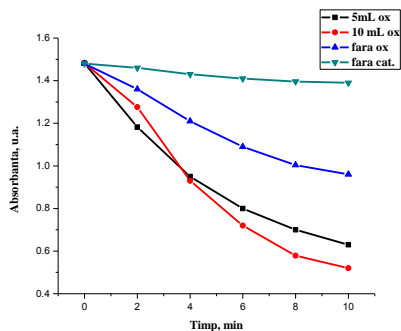


Figure 78 Comparative results obtained into fading reaction of aqueous solutions of methylene blue using as catalyst Si-propyl-Fe-Fe

Firs part of the reaction takes place at high speed thanks to no problem diffusion of the methylene blue molecules into the porous system of the material. In the same time the fading process occurs. Once the reaction takes place can be seen a diminishing of the reaction speed due to the possible crowding of the internal cavities of the support material with organic type molecules.

XII.3. Partial styrene oxidation

The catalytic activity of the supported synthetized compounds into silica based matrix was evaluated in the oxidation process of the double bond near the aromatic nucleus from styrene molecule. In function of the reaction products identified at this type of oxidation process, the chemical reaction can be symbolized in this way:

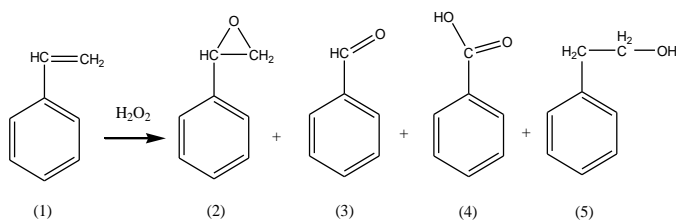


Figure 82 general reaction scheme for partial oxidation of styrene molecule

Table 22 Selectivity and the calculated number of reaction cycles on each active center for the oxo-trinuclear species immobilized onto functionalized silica matrix.

Chemical specie	Conversion %	TON , min ⁻¹	Selectivity, %			
			Styrene oxide	benzaldehyde	Benzoic acid	2-phenylethan-1-ol
Si-propyl-Fe-Fe	27	9.03	0	100	0	0
Si-propyl-Fe-Cr	22	4.74	0	100	0	0
Si-propyl-Fe-Ni	24	2.76	0	84.16	15.84	0
Si-propyl-Fe-Mn	13	2.97	0	100	0	0
Si-propyl-Fe-Co	11	2,64	0	100	0	0

In order to check the ability of the synthesized compounds to maintain the reaction selectivity for a longer period of time the most active sample was put to react using the same conditions for 24h. The results from table 23 were obtained.

Table 23 Data obtained in the partial oxidation of styrene into 24h time interval using as catalyst Si-propyl-Fe-Fe.

Time, h	Sample content, %				
	Unreacted styrene	Styryl oxide	Benzaldehyde	Benzoic acid	2-phenil- etan-1-ol
2	93.094	0	6.906	0	0
4	87.465	0	12.535	0	0
6	84.108	0	15.892	0	0
8	81.678	0	18.322	0	0
10	81.709	0	18.291	0	0
24	55.396	0	38.197	6.407	0

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