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Binuclear furanyl-azine metal complexes encapsulated in NaY zeolite as efficiently heterogeneous catalysts for phenol hydroxylation



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ABSTRACT

Two different methods A and B were used for preparing binuclear furanyl-azine metal complexes encapsulated in NaY zeolite. These new heterogeneous catalysts based on Fe(II) or Cu(II) complexes with a metal/ligand molar ratio of 2:1, were characterized by different spectroscopic techniques and chemical analysis which confirm the presence of the metal complexes inside the supercages of the zeolite. Mössbauer spectroscopy technique analysis confirms the presence of the Fe³⁺- complexes in octahedral coordination. The new heterogeneous catalysts were catalytic evaluated by phenol hydroxylation and compared with the encapsulated metal furanyl-azine complexes in NaY zeolite. The zeolite themselves do not present any activity and the presence of the metal complexes improve their activity. All heterogeneous catalysts enhance higher conversion of phenol to catechol.

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1. Introduction

Hydroquinone and catechol are among the most important intermediates of organic synthesis. They are intermediates for preparing perfumes, dyes, medicines, pesticides, rubbers and other chemicals [1–3]. There are some traditional industrial processes for the synthesis of the dihydroxybenzenes, such as aniline oxidation or diisopropyl benzene oxidation [3,4]. Both processes are losing their market, aniline hydroxylation, due to its low yield and damage to the environment, and diisopropyl benzene oxidation due to the long synthetic route and the numerous by-products which are difficult to separate [4].

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Due to that, more environment friendly route, direct phenol hydroxylation, for synthesis of both dihydroxybenzenes has become a research hot spot. Nowadays, the production of dihydroxybenzenes is mainly *via* the homogeneous catalytic hydroxylation of phenol, in liquid phase, with mineral acids, simple metal ions, and complexes as catalysts. Under these conditions an excess of phenol is necessary to achieve high selectivity while phenol conversion is relatively low (4–10%) in some cases high temperature has to be applied [5]. Some investigations on this field were focused on the development of a gas-phase process for phenol oxidation. In this case, the dihydroxybenzenes are obtained in the presence of nitrous oxide (oxidant), as it was used as effective oxygen donor in direct oxidation of benzene to phenol. However, it still demands a high temperature and beside dihydroxybenzenes the production of CO_x and coke was observed [6].

Recently, with the concept of green chemistry, heterogeneous catalysts, such as, transition metals incorporated into aluminophosphate [7], titanium silicalite zeolite series [8], core shape type catalysts based on Pd nanoparticles [2], and composites of

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metal oxide nanoparticles with reduced graphene oxide [4] have been used. The heterogeneous catalysts have played a very important role in the liquid phase phenol hydroxylation due to their easy separation and reusability, which makes the entire process more environmental friendly. Among the heterogeneous catalysts, various solid catalysts containing iron and/or copper take a special position. From this group of materials for example: copper modified titanium silicate [1], ferrocene particles incorporated into Zr based MOFs [3], magnetically separable CuFe₂O₄ reduced graphene oxide composites [4], metal containing mesoporous MCM-41 [9,10], copper containing SBA-15 [11] and many others were applied as catalysts for phenol hydroxylation. However, the drawbacks of low catalytic activity and easy deactivation of the catalyst have limited its wide application.

Bearing it, we have prepared metal complexes encapsulated in NaY zeolite using heterocyclic azine derivatives which have a widespread range of applications in diverse areas such as optics, electronics and catalysis [12,13]. Heterocyclic Schiff-base and azine ligands bearing N, O and S heteroatoms in their structure should exhibit improved coordination ability as well as different catalytic activity. Therefore, several azine ligands bearing thiophene, pyrrole and furan heterocycles have been used as versatile building blocks for supramolecular chemistry [14–16], due to their capacity to form dinuclear dimers or mononuclear monomers [14,16]. The presence of two metal centers in complexes might lead to better catalytic activities. On the other hand, less attention has been paid to their study as ligands for metal complexes synthesis having in mind their further application in catalysis. Tetradentate Schiff base, Salen type transition metal complexes encapsulated in zeolite were widely studied in hydroxylation of phenol [17]. However, there are no reports for phenol hydroxylation using furanyl-azine Schiff base complexes encapsulated in Y zeolite catalysts. On the other hand, our previous studies showed that when binuclear iron pyrrolylazine complex was entrapped into NaY zeolite, highly selective catalysts were obtained [16]. Consequently, we decided to synthesize a furanyl-azine derivative to be used as ligand on the preparation of new heterogeneous catalysts based on the transition metal complexes in zeolites.

In the present study, Cu and Fe complexes with furanyl-azine derivative encapsulated in NaY zeolite were prepared as heterogeneous catalysts and used for phenol hydroxylation. All the heterogeneous catalysts were characterized *via* FTIR, XRD, elemental analysis, HR-CS AAS, SEM and N₂ adsorption to investigate the correlation between the catalyst and its activity. In the case of iron complexes, Mössbauer spectroscopy technique was additionally applied. In addition, the effects of reaction time, different catalysts, catalyst amount, metal content, solvent, reaction temperature and catalyst reusability on phenol hydroxylation were studied.

The main disadvantage of the homogeneous catalysts is their problematic separation after the catalytic cycle and possibility reuse. On the other hand, the heterogeneous catalysts (encapsulated complexes) should join both advantages: (i) high catalytic activity, due to the presence of active sites from the complexes; (ii) easy separation/simple filtration, due to the encapsulation of the complexes on the insoluble material (zeolite) and (iii) reusability, in order to make the entire process more environmental friendly [16,17].

2. 2- Experimental

2.1. 1- materials

Furan-2-carbaldehyde was from Acros Organics. Hydrazine hydrate, cuprizone, KBr (FTIR grade), phenol (PhOH), chlorobenzene (PhCl), *tert*-butyl hydroperoxide solution - 5.0-6.0 M in decane (TBHP), acetonitrile (HPLC grade), dichloromethane and methanol (UV–Vis spectroscopy grade) were from Aldrich. NaY zeolite (CBV100, Si/Al = 2.83) in the powder form was obtained from Zeolyst International.

2.2. 2- Preparation of the samples

Synthesis of ligand: 1,2-bis((furan-2-yl)methylene)hydrazine (denoted as **L**). To a solution of furan-2-carbaldehyde (2.0 mmol) in 10 mL of ethanol, hydrazine hydrate (1.0 mmol) was added and the reaction mixture was heated under reflux for 5 h. The mixture was concentrated at reduced pressure, which induced precipitation of a solid. The solid product formed was separated by filtration, purified by crystallization from ethanol and then dried under vacuum.

1,2-bis(Furan-2-ylmethylene)hydrazine (L) was obtained as a brown solid (0.350 g, 93%). Mp: 121.0–123.0 °C (134–136 °C [15]). ¹H NMR (400 MHz, CDCl₃) δ = 6.54–6.55 (m, 2H, 2 × H-4), 6.90 (dd, 2H, *J* = 3.2 and 0.4 Hz, 2 × H-3), 7.60 (d, *J* = 1.6 Hz, 2H, 2 × H-5), 8.53 (s, 2H, 2 × N=CH) ppm. ¹³C NMR (100.6 MHz, CDCl₃) δ = 112.26 (2 × C4), 116.76 (2 × C3), 145.79 (2 × C5), 149.42 (2 × C2), 150.94 (2 × N=CH) ppm.

Synthesis of Cu(II) and Fe(II) complexes. To a solution of the L ligand (0.54 mmol, 0.10 g) dissolved in 15 mL of methanol was added of Cu(II) or Fe(II) chloride with 2:1 metal:ligand molar ratio, then 5 mL of methanol was added. The resulted solution was stirred and refluxed for 5 h. Complexes were formed as dark-brown solid. After cooling, the solid products were separated by filtration and left for 24 h at room temperature. The complexes obtained are denoted as [M₂LCl₄], where M = Fe or Cu.

Analytical data for the neat copper complex is as follows: [Cu₂LCl₄]; Brown solid (yield 0.2 g, 81%). Anal. Calc. For $C_{10}H_8Cl_4Cu_2N_2O_2$: C, 26.28; H, 1.76; N, 6.13, Cu, 27.80. Found: C, 26.04; H, 1.50; N, 6.00; Cu, 28.16.

Analytical data for the neat iron complex is as follows: $[Fe_2LCl_4(H_2O)_4]$; Brown solid (yield 0.2 g, 72%). Anal. Calc. For $C_{10}H_{16}Cl_4Fe_2N_2O_2$: C, 23.38; H, 3.14; N, 5.45; Fe, 21.70 Found: C, 22.38; H, 2.95; N, 5.52; Fe, 21.35.

Preparation of the heterogeneous catalysts. Two methods of encapsulation were used to prepare the heterogeneous catalysts based on NaY zeolite and reported by us elsewhere [18–20].

Method A. A solution of L ligand (22.3 mg, 0.12 mmol) and Cu(II) or Fe(II) chloride (0.24 mmol) in 50 mL ethanol was added to NaY zeolite (previously dehydrated at 120 °C overnight) suspension (1.5 g in 50 mL methanol). The mixture was further stirred for 24 h at 80 °C. The solid fraction was filtered and washed with deionized water, followed by Soxhlet extraction with ethanol. The new heterogeneous catalysts (M_2 L-Y_A, where M = Fe or Cu) were dried in the oven at 120 °C overnight under reduced pressure.

Method B. NaY zeolite was first ion-exchanged with an aqueous solution of Cu(II) nitrate or Fe(II) chloride (0.8 mM, liquid/ solid = 20 mL g⁻¹) at room temperature for 24 h, and dried at 120 °C overnight under reduced pressure. M – Y solid (1.2 g) was suspended in the solution of 40 mg (0.21 mmol) ligand **L** in 50 mL methanol and the mixture was stirred for 24 h at 80 °C. After filtration and washing, the solids were Soxhlet extracted with ethanol and dichloromethane to remove the unreacted ligand. The new catalysts (M₂L-Y_B, where M = Fe or Cu) were dried in the oven at 120 °C overnight under reduced pressure and characterized.

2.3. 3- Physical measurements

Room temperature Fourier Transform Infrared (FTIR) spectra of ligand, free complexes and solid samples of diluted 4% in KBr pellets

were measured using a Bomem MB104 spectrometer in the range 4000-500 cm⁻¹ by averaging 32 scans at a maximum resolution of 4 cm⁻¹. ¹H NMR spectra were obtained on a Varian Unity Plus Spectrometer at an operating frequency of 300 MHz using the solvent peak as an internal reference at 25 °C. Chemical analysis of C. H. and N was carried out on a Leco CHNS-932 analyzer. Cu(II) in a neat complex was determined by the spectrophotometric method using cuprizone as a complexing agent. The content of Cu and Fe in the heterogeneous catalysts was determined by the High-Resolution Continuum Source Atomic Absorption Spectrometry (HR-CS AAS) using a ContraAA® 300 atomic absorption spectrometer (Analytik Jena, Jena, Germany) operating in the flame (airacetylene) mode. The carefully weighted zeolite samples (0.1 g) were digested using the Anton Paar Multiwave 3000 closed system instrument. The standard two step procedure developed for silica rich matrices was applied. The initial digestion with the mixture of concentrated acids HCl, HF and HNO₃ (2:1:3, v/v) was followed by the complexation of the free HF with cold saturated H₃BO₃ solution. Scanning electron micrographs (SEM) were collected on the LEICA Cambridge S360 Scanning Microscope equipped with EDS system. To avoid the surface charging, prior to the analysis the samples were coated with gold in vacuum, by using a Fisons Instruments SC502 sputter coater. The textural characterization of the samples was based on the N₂ adsorption isotherms, determined at $-196 \degree C$ with a Quantachrome NOVA 4200e apparatus. The samples were previously outgassed at 150 °C under vacuum. Powder X-ray diffraction patterns (XRD) were recorded using a Philips Analytical X-ray model PW1710 BASED diffractometer system. The solids samples were exposed to the Cu Ka radiation at room temperature in a 2θ range between 5 and 65° . The relative crystallinity of the heterogeneous catalyst was estimated by comparing the intensities of the peaks with NaY used as a standard sample (100% crystalline) according to ASTM D-3906-80 method.

2.4. 4- Catalytic studies

The phenol hydroxylation reaction was carried out in 6.0 mL of acetonitrile at 70 °C (±5 °C) under constant stirring, and the composition of the reaction medium was; phenol (0.09 g, 1.0 mmol, substrate), chlorobenzene (0.11 g, 1.0 mmol, GC internal standard) and 0.10 g of heterogeneous catalyst. The oxygen source, TBHP (0.54 mL of 5.5 M in decane solution), was progressively added to the reaction medium at a rate of 0.02 mL·min⁻¹. The reaction was conducted under inert atmosphere (argon). Periodically, samples were taken from the solution with a hypodermic syringe, filtered through 0.2 µm syringe filters, and directly analysed by GC-FID. At the end of each run, the catalysts were sequentially extracted/ centrifuged three times with 15 mL of ethanol and once with 15 mL of dichloromethane to remove occluded reactants and products. and then dried in an oven at 120 °C before the new catalytic cycle or the FTIR characterization. A leaching test was performed to ensure that the hydroxylation was only catalysed heterogeneously.

To assess the possible catalytic activity of the support itself in the hydroxylation of phenol, the reactions using the same experimental conditions (*vide supra*) were also carried out in the presence of the support (0.1 g of the parent NaY zeolite).

The oxidation products were analysed in a SRI 8610C Gas Chromatograph equipped with a CP-Sil 8CB capillary column, using nitrogen as the carrier gas. The identification of the reaction products was additionally performed by GC-MS (Varian 4000 Performance) using helium as the carrier gas. Compound identification was based on the GC/MS spectra libraries, co-injection with authentic standards and analysis of fragmentation patterns. The products were quantitatively determined by the internal standard method. The reusability of the catalysts was studied under the same experimental conditions.

3. 3- Results and discussion

3.1. 1- Characterization of complexes

The coordination with metals by ligands containing furan through oxygen donor atom can be classified into three broad categories: free, pendant, or as a part of fused ring. There are few examples in which free furan coordinates to a metal and when it acts as an O, C - bridge [21]. Coordination by pendant furan or fused furan rings makes several examples (Scheme 1).

Most of the examples of coordination by pendant furan have been observed for furan - 2 aldehyde thiosemicarbazone $[R_1 = R_2 = H (Scheme 1)]$ complexes with Cu(II), Zn(II), Ni(II) and Co(III) [22]. In all cases, the coordination of the ligand to the metal through azomethine nitrogen and thiolate sulphur atoms was confirmed, whereas the furan oxygen appears not to be coordinated in any complexes. These complexes have different stoichiometry and molecular structure. For Cu(II) a dimeric structure with chloride bridges was confirmed, for Ni(II) and Zn(II) metal to ligand ratio was 1:2 and for Co(III) 1:3 stoichiometry was found [22]. For the same ligand family, it was found that for Ni(II) complexes the furan coordination mode strongly depends on substituents R1 and R_2 (Scheme 1). Also, when $R_1 = R_2 = H$ furan ring remained pendant, the complex stoichiometry is NiL₂. Whereas for $R_1 = -CH_3$ and $R_2 = H$ coordination through furan oxygen, azomethine nitrogen and thiolate sulphur atoms was found for series of nickel(II) complexes with different substituents in -NHR linkage from thiosemicarbazone ligand [21].

For Schiff base ligand derived from 2-furan carbaldehyde and propanediamine ($R_1 = R_2 = H$, Scheme 1) complexes with Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Fe(III) the participation of furan oxygen donor in metal coordination was confirmed by spectroscopic and analytical methods [23]. Similarly, when the amine part of Schiff base derives from 8-aminoquinoline, six- or four-coordinated complexes with Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) were synthesised and the bonding between ligand and metal by N_{C} —N and O_{furan} donor atoms was confirmed by different physico-chemical and spectroscopic methods [24].

In the present work, the metal complexes were obtained through the reaction between the metal ions and the ligand at 2:1 (M:L) ratio. The synthesised ligand and its complexes are stable at room temperature. The ligand and its metal complexes are soluble in DMF and DMSO but insoluble in water and in most of the organic solvents. The molar conductance for both complexes confirms their non-electrolytic properties, suggesting that the chloride ions are bonded to metal in the complex structure.

FTIR spectrum of ligand (Fig. 1) shows the presence of medium intensity bands at 1216, 1598 and 3090 cm^{-1} which could be



Scheme 1. Possible coordination to metals by ligands containing furan: pendant mode (left) and fusel mode (right).



Fig. 1. FTIR spectra of 1) $[Fe_2LCl_4(H_2O)_4]$ complex and 2) free ligand in whole measured region.

assigned to $\nu(C-O-C)$ stretching vibration of furan, $\nu(C=N)$ vibrations of azomethine groups and $\nu(C-H)$ aromatic stretching vibrations, respectively [25–28]. Moreover, bands appearing in the regions 1440-1480 cm⁻¹, 1060-1100 cm⁻¹ and 720-775 cm⁻¹ were usual modes of aromatic ring vibrations [29]. A comparison of FTIR spectra of metal complexes with the ligand, as representative example of Fe(II) complex, is shown in Fig. 1. The FTIR spectra of both Cu(II) and Fe(II) complexes showed band due to azomethine group $\nu(CH=N)$ at 1617 and 1629 cm⁻¹ for Cu(II) and Fe(II) complexes, respectively. This band is shifted of 11 and 23 cm^{-1} to lower energy regions in comparison to free ligand. This confirms the coordination by $N_{C==N}$ donor [30]. The furan oxygen stretching band is shifted to higher wavenumbers in the complexes spectra and appears at 1230 and 1224 cm⁻¹ for Cu(II) and Fe(II) complexes. This positive shift in the $\nu(C-O-C)_{\text{furan}}$ stretching mode suggesting the coordination of ligand through O_{furan} donor [31]. The combined results from the elemental analysis and FTIR data confirmed that the coordination of Schiff base ligand to the metal is through $N_{C=N}$ and O_{furan} [23–25,31]. Moreover, it was found that the copper complex is four-coordinated with two Cl ligands and in the case of iron, the six-coordinated complex is formed (coordination of two additional H₂O molecules).

Elemental analysis confirmed the purity of the free complexes and the maximum difference between calculated and found values was of 0.5% for Fe complex [Fe₂LCl₄(H₂O)₄], where each Fe forms six-coordinated complex (N,O- from organic ligand, two chloride ions and two water molecules). For Cu complex [Cu₂LCl₄] where each Cu forms four-coordinated complex (N,O- from organic ligand and two chloride ions) and the maximum difference between calculated and found values was 0.2%. For free ligand, as well as for free complexes the C/N ratio is 4.3 (Scheme 2).

3.2. Characterization of the heterogeneous catalysts

Based on our previous studies [16], we can state that furanylazine ligand can easily diffuse into the zeolite and form the ML complex (M = Cu or Fe) by both A and B methods. The metal complexes were *in situ* synthetized into supercages of zeolite NaY and are too large to effectively pass through the free aperture of the zeolite pores (*ca.* 7.4 Å), but they are small enough to be confined within the supercages (internal diameter ca. 13.0 Å) (Scheme 3).

The metal contents in Cu₂L-Y_A, Cu₂L-Y_B, Fe₂L-Y_A and Fe₂L-Y_B samples were determined by the HR-CS AAS. The loading of copper immobilized was found 0.48 and 0.89% (wt%) of Cu on the zeolite for Cu₂L-Y_A and Cu₂L-Y_B. The elemental analysis of the organic matter in the hybrid catalysts Cu₂L-Y_{A/B} gives C/N ratio similar to that for the neat complex (Table 1). The results suggest that both methods (A and B) lead to the complete Cu(II) complexation inside the zeolite matrix and that the metal complex structure is maintained. Thus Cu(II) complex loading is of 38 and 70 µmol per gram for Cu₂L-Y_A and Cu₂L-Y_B, respectively.

A significantly higher iron content was found 2.61 and 2.99% (wt %) for Fe₂L-Y_A and Fe₂L-Y_B samples, respectively. Whereas for both Fe(II) containing catalysts the loading of C and N is lower than it was found for respective Cu(II) containing catalysts. The C/N ratio suggests ligand incorporation into the zeolite matrix. For all encapsulated complexes the C/N is 4.2–4.5 which is the same as was found for free complexes and confirmed the presence of organic ligand on zeolite. Additionally, Cu/N ratio for copper encapsulated complexes is 4.4 (Cu₂L-Y_A) and 4.7 (Cu₂L-Y_B) which is nearly the same ratio as it was found for free complex is maintained in the zeolite structure. The higher content of Fe suggests some interaction of the metal with the zeolite framework. This will be discussed in more detail later.

FTIR spectra of parent zeolite and the heterogeneous catalysts are shown in Fig. 2A. All samples displayed bands at 3150 and 3720 cm⁻¹. In general, the bands at 3500–3680 cm⁻¹ correspond to the bridging OH groups in \equiv Al–OH–Si \equiv linkage and are attributed to the location of hydrogen atoms on different oxygen atoms in the zeolite framework and adsorbed water molecules. Upon the incorporation of the complexes the bands become sharper and some shoulders are more visible. This effect suggests that water content is decreasing during complex encapsulation or/and some specific O–H bonds are replaced with metal species. The latter effect was observed for iron complex containing catalysts, where the \equiv Al–OH–Si \equiv surface groups together with \equiv Al–OH and \equiv Si–OH groups can lose their hydrogen ions via \equiv Si–OH–Al⁺ \equiv + OH⁻ \leftrightarrows



Scheme 2. Schematic representation of the coordination complexes of [Cu₂LCl₄] and [Fe₂LCl₄(H₂O)₄].



Scheme 3. Schematic representation of the synthesis of M_2L - $Y_{A/B}$ catalysts, where M = Cu or Fe. To simplify the coordinating water molecules, for iron complex, are not presented in the scheme.

Elemental analysis [%] and C/N and Si/Al ratios of heterogeneous catalysts.	

Sample	С	Ν	М	C/N	IR/cm ⁻¹		Si/Al ^b	
					$w_{\rm DR}^{\rm a}$	w _{TOT} ^a	$w_{\rm DR}^{\rm a}$	w _{TOT} ^a
NaY	_		_	_	578.6		2.63	
Cu ₂ L-Y _A	0.473	0.108	0.475	4.3	578.6	1021	2.63	0.28
Cu ₂ L-Y _B	0.800	0.190	0.885	4.2	578.6	1027	2.63	0.26
Fe ₂ L-Y _A	0.346	0.076	2.610	4.5	563.1	1010	3.60	0.33
Fe_2L-Y_B	0.427	0.103	2.990	4.2	578.6	1022	2.63	0.28

^a w_{DR} and w_{TOT} are respectively the double ring and asymmetrical valence.

^b S/Al ratio obtained from FTIR spectra.

negatively charged sites through \equiv Si(or Al)–OH + OH⁻ $\Leftrightarrow \equiv$ Si(or Al)–O⁻ + H₂O Fe³⁺ [32]. Intermolecular hydrogen bonding causes the appearance of the band at 3550–3200 cm⁻¹. The band at ~3450 cm⁻¹ is due to monomeric structures whereas the shoulder near 3200 cm⁻¹ arises from "polymeric" structures [33].

A strong T-O stretching vibration for the clinoptilolite and mordenite phases in zeolites is expected in the range of 1000–1100 cm⁻¹. The broad band in the range of 1240–1020 cm⁻¹ in parent zeolite becomes sharper following the introduction of iron resulting in a band at 1133 cm⁻¹. This indicates the interaction of iron species with Al³⁺. The peak at ~792 cm⁻¹ occurs in all the



Fig. 2. A) FTIR spectra and B) XRD patterns of the samples: 1 - NaY, 2 - Cu₂L-Y_B, 3 - Cu₂L-Y_A, 4 - Fe₂L-Y_B and 5 - Fe₂L-Y_A; SEM images of Cu₂L-Y_B C) and Fe₂L-Y_B D).

spectra and can be assigned to quartz or amorphous SiO_2 which is consistent with the XRD patterns of the natural zeolites.

The band at ~500 cm⁻¹ can also be attributed to the Si–O–Si bending mode. The intensity of this band is increased with the concentration of iron introduced [34]. The bands in the range of 600–800 cm⁻¹ are due to the presence of exchangeable cations in zeolites. The bands in the range between 800 and 550 cm⁻¹ in all FTIR patterns are typically assigned to the lattice vibrations of *faujasite* zeolites.

Besides providing the information on the structure or/and functional groups of even very poorly crystalline products, FTIR can be used to determine quantitatively the Si/Al ratios of amorphous or semicrystalline aluminosilicates (Table 1). Based on the observation of aluminosilicates with different Si/Al ratios that the Si-O bands (980-1030 cm⁻¹) are observed to shift to higher frequencies, and the Si–O–Al (~700 cm^{-1}) bands to decrease continuously in intensity, with increasing Si/Al ratios of the sample, suggesting a continuous replacement of Al^{3+} for Si^{4+} in the framework. In the literature data two different frequency shifts are used to determine Si/Al ratios, namely the band at ~1000 cm^{-1} or at ~600 cm⁻¹ assigned to asymmetrical TOT vibration (w_{TOT}) and the zeolite specific double ring mode (w_{DR}) . It is known that the asymmetrical TOT vibration w_{TOT} sensitively depends on the Si/Al ratio of zeolites and therefore has often been used for their determination [35], Eq. (1).

$$\begin{split} X &= 3.857 - \ 0.00621 \text{wDR cm} - 1 \text{ for } 0.1 < x < 0.3, \\ \text{where } X &= (1 + (\text{Si}/\text{Al}))^{-1} \end{split} \tag{1}$$

However, using a linear relation (2) may leads to an overestimation of the framework Si/Al ratio as it was observed for steamed Y zeolites [36].

$$X = 4.766 - 0.00439 \text{wTOT cm}^{-1}$$
 (2)

In the presented study both DR and TOT frequencies were used to calculate the Si/Al ratio and the values obtained (Table 1) suggests that no dealumination process took place during encapsulation of the complexes.

The X-ray structure of the *in situ* metal complexes (Cu₂L-Y and Fe₂L-YB) was not performed because the low amount of the synthetized complexes is stabilized within the zeolite structure and cannot be extracted from it. However, the structure obtained by powder XRD method could be possible but this method is much less accurate than single-crystal XRD especially for low symmetry compounds. In powder XRD, the reflections from differently oriented crystallites are measured simultaneously, so reflections with similar d-values are overlapped in the powder X-ray diffraction pattern, which hinders structure solution by powder XRD methods [37]. Thus the metal coordination in the *in situ* complexes was assumed based on FTIR and elemental analyses (see discussion above).

The powder X-ray diffraction patterns of the parent NaY zeolite and the heterogeneous catalysts were recorded in order to see their crystalline nature and to ensure encapsulation of complexes inside the zeolite supercages (Fig. 2B). No appreciable loss in crystallinity was observed as a consequence of *in situ* metal complex encapsulation. It has been reported that an empirically derived relationship exists between the (331), (311) and (220) XRD peak intensities and the non-coordinated free cation location in the faujasite type zeolites [39]. In NaY, the relative intensities of the peaks varied in the order (331) > (220) > (311), indicating a random distribution of the exchangeable cations within the zeolite lattice. However, after the complex encapsulation the peak intensities slightly varied in the order (331) > (311) ~ (220), suggesting some displacement of cations in the supercages by the complexes. This effect is especially visible for Cu_2L-Y_B sample and it is commonly observed for encapsulated transition metal complexes in zeolites [38–41]. The change in the relative peak intensity between (220) and (311) suggests that copper complex is formed (located) in the supercages of Y-zeolite [39]. These observations indicate that the framework of the zeolite has not undergone any significant structural change during incorporation of the complexes. No new crystalline phases could be detected in complex encapsulated zeolite samples probably due to the low loading of them in the zeolite framework [42].

The scanning electron micrographs (SEM) of the zeolite encapsulated complexes (Cu_2L-Y_B and Fe_2L-Y_B) are presented in Fig. 2C. The micrographs indicate the presence of well-defined zeolite particles with a morphology and analogous to the parent zeolite, free from any shadow of the complexes/ligands present on their external surface. The typical octahedral shape of parent zeolite (NaY) with the same particle size was preserved in all complex encapsulated catalysts.

 N_2 adsorption measurements show a decrease of the S_{BET} and the total volume of the parent zeolite in comparison with the complex encapsulated catalysts (Table 2).

All heterogeneous catalysts show the same Type-I isotherm as NaY, typical of solid with a microporous structure, according to the IUPAC classification. The BET surface areas (S_{BET}) were calculated by the BET equation and all heterogeneous catalysts present a smaller surface area than NaY, due to the encapsulation of the metal complexes. In addition, the heterogeneous catalysts exhibit a decrease in the micropore volume being mainly important for the catalysts with iron.

Since the FTIR spectra and XRD patterns confirmed that the crystallinity of the zeolite was retained after the encapsulation, these changes are consistent with the presence of the complexes in the zeolite supercages rather than the external surface. Interestingly, regardless of the method used for the preparation of the heterogeneous catalysts almost the textural parameters decrease when compared with the parent zeolite. This finding is due to the presence of the complexes encapsulated inside the zeolite.

To deepen further our study at the atomic level, ⁵⁷Fe Mössbauer spectroscopy measurements were performed at room temperature for the samples with iron complexes. The Mössbauer spectroscopy was applied to show the existence of both Fe²⁺ complexed (with furanyl-azine ligand) and not complexed Fe³⁺ species inside the zeolite matrix. As the latter (not coordinated iron) are located in zeolite framework sites that are inaccessible for the organic ligand and these can oxidize during exposed to air and form Fe³⁺ species. The experimental spectra (Fig. 3A) show a strong central quadrupole doublet without any additional weaker magnetic features in the wings. The hyperfine interactions parameters of iron complexes encapsulated into zeolite are outlined in Table 3. All the samples show quite well resolved doublet with isomer shift δ in the range of (0.21–0.32 mm/s) and quadrupole splitting Δ (0.64–0.72 mm/s).

Textural properties of the parent zeolite and the heterogeneous catalysts.								
Sample	$\frac{S_{BET}^{a}}{(m^{2}/g)}$	V _{total} ^b (cm ³ /g)	S _{ext} ^c (m ² /g)	V _{micro} ^c (cm ³ /g)	V _{meso} ^d (cm ³ /g)			
NaY [7]	792	0.378	19	0.340	0.038			
Cu ₂ L-Y _A	730	0.346	14	0.325	0.021			
Cu ₂ L-Y _B	769	0.350	16	0.323	0.027			
Fe ₂ L-Y _A	763	0.350	17	0.307	0.043			
Fe ₂ L-Y _B	740	0.330	17	0.308	0.022			

^a Surface area calculated from the BET equation.

Table 2

^b Total pores volume determined from the amount adsorbed at $P/P_o = 0.95$.

^c External surface area and micropores volume calculated by the *t*-method.

^d Mesopores volume calculated by the difference V_{total}-V_{micro}.



Fig. 3. A) Room-temperature ⁵⁷Fe Mössbauer spectra of Fe–Y zeolite (for comparison) and samples Fe_2L1-Y_B , Fe_2L1-Y_B , Fe_2L-Y_B , and Fe_2L-Y_A ; B) enlarged spectrum of the sample Fe_2L-Y_B with two components – main doublet coming from Fe^{3+} and small doublet from Fe^{2+} . The dots represent the experimental data and the solid lines the fitted spectra.

 Table 3

 Hyperfine interactions parameters of the samples derived from Mössbauer spectra^a.

Sample	⊿ [mm/s]	⊿ [mm/s]	Г [mm/s]	χ^2
Fe-Y	0.23 (2)	0.65(1)	0.25(2)	1.05
$Fe_2L1-Y_B^{D}$	0.21(2)	0.70(2)	0.26(2)	1.11
Fe ₂ L1–Y _A ^b	0.32(1)	0.72(1)	0.33(1)	0.85
Fe ₂ L-Y _B	0.27(1)	0.69(1)	0.30(2)	1.13
Fe_2L-Y_A	0.25(2)	0.64(2)	0.36(2)	2.40

^a δ – isomer shift relative to α -iron, Δ – quadrupole splitting, Γ – half width at half maximum of spectral lines (uncertainty of all values is given in parentheses for the last significant number); χ^2 – goodness of fit parameter.

^b binuclear pyrrole-azine metal complexes encapsulated in NaY zeolite (comparison reason).

This is in agreement with the spectra of Fe^{3+} species at room temperature and indicates that high-spin Fe^{3+} ions occur in approximately octahedral coordination. This suggests that some post preparation oxidation process occurs and supports our hypothesis of oxidation of not coordinated Fe^{2+} species to species containing high-spin Fe^{3+} ions.

In Fig. 3A a small asymmetry in the Mössbauer spectra may be seen on the right side of the doublets. Fitting the second doublet with $\delta = 1.05$ mm/s and $\Delta = 1.60$ mm/s does not worsen the match quality (spectrum with two doublets for Fe₂L–Y_B sample is shown in Fig. 3B, as an example). The values of δ in the range of 1.0–1.3 mm/s and $\Delta > 1.5$ mm/s are characteristic of ferrous lowspin Fe²⁺ species in octahedral coordination [42]. However, the contribution of the second doublet is very small, of the order of 3–5% for all the spectra. This means that concentration of Fe²⁺ in complexes forming rigid crystalline structure is very low.

3.3. Catalytic studies

The catalytic activities of the heterogeneous catalysts prepared were evaluated by phenol hydroxylation. Before that, a blank reaction was realized in which there was phenol and TBHP as an oxygen source, but no catalyst. The reaction using NaY as a catalyst was also evaluated under the same experimental conditions. In both cases, the phenol concentration was remained, even when the reaction time was prolonged for 72 h. It indicated that NaY had no significant adsorption for phenol and no catalytic activity for phenol hydroxylation. It is known that the use of peroxides in the presence of heterogeneous catalysts as oxygen source in hydroxylation of phenol [43,44] generally leads to the formation of phenolate anion, which facilitates resonant stabilisation to hydroxylate phenol at *para* and *ortho* positions. So, the presence of the metal complexes encapsulated in zeolite enhance the catalytic properties of the heterogeneous catalysts. When the reaction was performed under homogeneous conditions high phenol conversion was observed for both complexes, namely (91%) for Cu₂L and (88%) for Fe₂L. These results were similar for heterogeneous catalysts obtained by the method B.

3.3.1. Influence of reaction time

The effect of reaction time on phenol hydroxylation on heterogeneous zeolite catalysts was studied in the range of 0-48 h. It was found that the conversion of phenol increases with an increase in the reaction time and becomes constant after 24 h except when Cu₂L-Y_B (6 h) was used (first run).

Moreover, selectivity of catechol (CAT) is almost constant in addition, neither hydroquinone (HQ) nor benzoquinone (BQ) were detected during the catalytic run. These results are in agreement with our previously obtained results for the pyrrolyl-azine complexes encapsulated in NaY zeolite [16]. The catalytic results after the time when phenol conversion becomes constant are summarised in Table 4.

Table 4

The catalytic hydroxylation of phenol in the presence of NaY and heterogeneous catalysts.

Entry	Run	Catalyst	t ^b (h)	%C ^{c,d}	CAT ^a		Others	
					%S ^{c,e}	%Y ^{c,f}	%S ^{c,e}	%Y ^{c,f}
1	1	NaY	72	4	_	_	_	_
2	1	Cu ₂ L-Y _B	6	92	63	58	37	34
3	2		24	79	100	79	0	0
4	1	Cu ₂ L-Y _A	24	64	30	19	70	45
5	2		24	52	100	52	0	0
6	1	Fe ₂ L-Y _B	24	87	56	49	44	38
7	2		24	44	73	32	27	12
8	1	Fe ₂ L-Y _A	<24	82	31	25	69	57
9	2		24	42	76	32	24	10
10	1 ^g	Cu ₂ L	24	91	63	57	38	34
11	1 ^g	Fe ₂ L	24	88	58	50	42	38

^a CAT – catechol.

^b Reaction time at which the substrate conversion starts to become constant.

^c Determined by GC against internal standard.

^d Phenol conversion.

^e Product selectivity.

^f Product yield.

^g Reaction performed under homogeneous conditions where the free complexes were used as the catalysts.



Fig. 4. The effect of the heteroatom in the heterocyclic ring moiety on phenol hydroxylation, for Fe₂L1-Y_A (1), Fe₂L-Y_A (2), Fe₂L1-Y_B (3), Fe₂L1-Y_A (4), Cu₂L1-Y_A (6), Cu₂L1-Y_A (6), Cu₂L1-Y_A (6), Cu₂L1-Y_A (7) and Cu₂L-Y_B (8), where L1 and L – ligand containing pyrrole [16] or furan ring, respectively, and phenol conversion (blue column) and CAT selectivity (red column).

3.3.2. Influence of the different catalysts

Comparison of catalytic properties of the heterogeneous Cu and Fe complexes with azine derivatives is given in Fig. 4. The study concerns on the zeolite encapsulated complexes with N or O heteroatom in the five-member heterocyclic ring. The ligand contains the pyrrole ring is denoted as **L1** [16], the preparation methodology was the same as in the present work.

A high phenol conversion (>60%) is observed for all samples except Cu₂L1-Y_A, whereas CAT selectivity is lower for complexes with furan ring than for these with pyrrole heterocycle. In both cases no HQ was detected. Furthermore, it is clearly observed that the highest phenol conversion ($C_{phenol} = 100\%$) is obtained on phenol hydroxylation over the Fe₂L1-Y_A. For zeolites with Cu(II) complexes encapsulated, higher phenol conversion was observed on Cu₂L containing heterogeneous catalysts compared to their Cu₂L1 counterparts. The Cu(II) heterogeneous catalysts obtained by method A lead to lower phenol conversion than their counterparts obtained by method B. This result from lower Cu(II) loading in both methods copper samples preparation. It should be mentioned that for the Fe(II) complex containing heterogeneous catalysts almost the same iron loading was obtained regardless the method and the donor atoms were applied. This effect is in agreement with that observed for Cu-SBA-15 heterogeneous catalyst used for phenol hydroxylation in water in the presence of H_2O_2 [11], where the %C of phenol strongly depends on Cu loading and was found that the % C value increases from 28.6 to 49.7 with an increase in the copper content. The CAT selectivity and yield depend on the preparation methodology, being close to 60% for method B and lower for Cu catalysts prepared by method A.

The reusability of the $M_2L-Y_{B/A}$ catalysts in the phenol hydroxylation reaction was examined. The Cu(II) containing heterogeneous catalysts during the second reaction run show small activity loss and its phenol conversion is about 80 and 50% for B and A methods, respectively. For the Fe(II) containing heterogeneous catalysts, a significant drop in phenol conversion was observed during the second run. These results support our hypothesis that not all Fe(II) was complexed in the zeolite cavity, and can probably leach after the first run. The increase in the CAT selectivity in the second run also supports this hypothesis as CAT is a unique product of phenol hydroxylation in the presence of free complexes [16]. Some ligand oxidation and/or complex deactivation cannot be excluded either.

The direct comparison of catalytic results presented here with the literature data is not easy. Nevertheless, some of the research published earlier focuses on the influence of the ligand structure on ortho-selectivity in hydroxylation of phenol catalysed by Cu(II) and Fe(III) complexes with selected commercially available or easy synthesised enamines (N,N and N,O ligands) under homogeneous conditions [45]. The results obtained indicated the Cu(II) complexes are able to mediate the region-specific ortho-hydroxylation of phenol in the presence of hydrogen peroxide under homogeneous conditions. The iron complexes did not catalyse selective hydroxylation to the ortho isomer. Although for the copper complexes the conversion of phenol was lower than that of the iron complexes. The yields of products based on H₂O₂ after 30 min of the reaction varied between 2 and 9% for commercially available ligands. The selectivity on dihydroxybenzene was more than 95%, and the selectivity on catechol was more than 85%. The Cu(II) complexes with enamine ligands were shown to provide good catechol selectivity 82-90%.

Cu(II) complexes with monofunctional and dendrimeric pyrrole-Schiff base ligands were evaluated as catalysts in the liquid phase hydroxylation of phenol under homogeneous conditions [46]. It was found that all the catalysts investigated were active for phenol hydroxylation. Under the conditions used, the mononuclear Cu(II) catalyst was found to be the most active with phenol conversion 82%.

In the literature data, different factors on catalytic activity of Schiff base complexes encapsulated in Y zeolite were studied. The electron-donating and electron-withdrawing effects of substituents in the ligand on phenol oxidation reaction was investigated for two copper complexes with tridentate thiophene containing ligands [47]. The heterogeneous complex with an additional electron-withdrawing group was more active probably due to enhanced Lewis acidity of the copper centre and leads to 89% phenol conversion, with high CAT selectivity 72%. Other heterogeneous Cu(II) and Fe(III) complexes with bidentate (N, O) thio-Schiff bases were tested as catalysts in hydroxhylation of phenol [48]. The phenol conversion for both catalysts enhances with the reaction time and attains a steady state after ~6 h. The copper containing catalyst shows the highest %C = 18, while the catalyst containing iron achieves ca. 12%. Both catalysts show high selectivity to CAT (>95%). Better results were found for the encapsulated Cu(II) complex with the bidentate (N, O) Schiff base derived from salicylaldehye and 2-aminoethyl-benzimidazole [42]. The heterogeneous catalyst leads to higher substrate conversion (42%) and CAT selectivity (74%) than its homogeneous counterpart (%C = 35 and % S = 69). The highest phenol conversion (79%) and CAT selectivity (84%) were obtained for the Cu(II) complex with the tetradentate Schiff base encapsulated in NaY [49].

4. Conclusion

Four novel heterogeneous catalysts based on binuclear furanylazine Fe(II) or Cu(II) metal complexes were prepared by common encapsulation methods. The Cu(II) loading depends on encapsulation methods and the higher metal content was found for the sample obtained by the method B, whereas the iron loading is much higher and almost the same for the catalysts obtained by both proposed methods. The analytical and spectroscopic methods confirmed the complex formation in zeolite cavity in the case of iron some uncomplexed ions indicating the interaction of the metal with the zeolite framework was found. All the heterogeneous catalysts are active in phenol hydroxylation and the substrate conversion under homogeneous conditions is close to that obtained under heterogeneous conditions for catalysts prepared by method B. The heterogeneous catalysts can be re-used with small activity lost. Comparison of the catalytic activity of the catalysts obtained in this work with other copper and iron encapsulated complexes in zeolite Y reported on the literature, showed that, our catalysts exhibit higher phenol conversion and similar or superior selectivity towards catechol formation.

Author contribution

I. Kuźniarska-Biernacka: Conceptualization, Investigation, Writing - original draft, Validation. M.M.M. Raposo: Conceptualization, Writing - review & editing. R.M.F. Batista: Investigation. O.S.G.P. Soares: Investigation. M.F.R. Pereira: Investigation. P. Parpot: Investigation. C. Oliveira: Investigation, Writing - original draft. E. Skiba: Investigation, Writing - review & editing. E. Jartych: Investigation, Writing - original draft. A.M. Fonseca: Conceptualization, Writing - review & editing. I.C. Neves: Conceptualization, Supervision, Writing - original draft, Validation.

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