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Immobilization of chromium complexes in zeolite Y obtained from biosorbents: Synthesis, characterization and catalytic behaviour

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ABSTRACT

The goal of this study is the preparation of new heterogeneous catalytic materials to be used in oxidation reactions under mild conditions through the valuation of heavy metals in wastewater. The samples used in the immobilization of chromium complexes were prepared from a dichromate solution of 100 $mg_{Cr}\,L^{-1}$. The zeolite CrNaY was prepared from a robust biosorption system consisting of a bacterial biofilm, *Arthrobacter viscosus*, supported on zeolite NaY. The biofilm performs the reduction of Cr(VI) to Cr(III) and this cation is retained in the zeolite by ion exchange. The immobilization of chromium complexes with heterocyclic ligands in the supercages of Y zeolite was performed by the *in situ* synthesis with three different ligands, 3-methoxy-6-chloropyridazine (A), 3-piperidino-6-chloropyridazine (B) and 1-(2-pyridylazo)-2-naphthol (C). A sample loaded with Cr from a liquid solution with the same initial concentration was prepared as a reference through the traditional direct ion-exchange method and coordinated with ligand (A). The resulting catalysts were fully characterized by different techniques (FTIR, XRD, TGA, SEM, Raman, cyclic voltammetric studies and chemical analysis) and the results confirmed that the Cr complexes were immobilized in supercages of NaY. Catalytic studies were performed in liquid phase for the cyclohexene oxidation, at 40 °C, using *tert*-butyl hydroperoxide (TBHP) as the oxidizing agent. All the prepared catalysts exhibited catalytic activity for the oxidation reaction.

1. Introduction

Sustainable development concern is responsible for the concentration of research efforts on the effects of toxic metals on the environment, since they ultimately reach and accumulate in animal and human tissues. According to water standards used in many countries, heavy metal ions in wastewater must be controlled and reduced to set values. Various treatment processes are available for heavy metals removal, among which ion exchange is considered to be quite attractive if low-cost ion exchangers such as zeolites are used [1–7]. The peculiar adsorptive properties of zeolites result from the positively charged exchangeable ions, which are located inside the three-dimensional pore structure of the solid to balance the negative charge, introduced by the framework Al atoms and those can be replaced by heavy metals [8].

In recent years, the biosorption process has been studied extensively using microbial biomass as biosorbent for heavy metal removal. *Arthrobacter viscosus* is a good exopolysaccharide producer, which, by itself, would allow foreseeing good qualities for support adhesion and for metal ions entrapment. As reported in previous works [9–11], a low-cost system combining the biosorption properties of a microorganism with the ion-exchange properties of a zeolite, was able to remove hexavalent chromium from contaminated water. What is usually considered a xenobiotic pollutant, chromium(VI) in wastewater can, therefore, be transformed in a catalyst to be applied in the oxidation of persistent organic compounds [10].

After the biosorption process, the chromium retained in the zeolite was tested as a catalyst in the oxidation of volatile organic compounds. The results from the gas-phase oxidation of 1,2-dichlorobenzene showed that the presence of Cr in the zeolite improved the overall 1,2-dichlorobenzene conversion and selectivity towards CO_2 when compared to the parent zeolite NaY or NaX [10]. For liquid phase, it is know that Cr acting as catalyst in molecular sieves presents stability problems for the oxidation reactions due to the possible leaching of the small quantities of chromium into solution. Nevertheless, these chromium ions in

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solution may be responsible for the catalytic reaction [12–14]. One of the strategies to prevent the leaching of the active metal into the liquid phase under operating conditions is to immobilize the metal by coordination with organic ligands in a solid support [15,16]. The use of metal complexes immobilized into solid supports as heterogeneous catalysts has become very important for eco-friendly industrial processes [17–22].

The present work associates biosorption studies to the immobilization of transition metal complexes in zeolites for applications in heterogeneous catalysis in mild conditions. The preparation of host–guest Cr complexes entrapped in zeolite NaY was performed by a robust biosorption mediator consisting of a bacterial biofilm supported on the zeolite [3], followed by *in situ* immobilization in the liquid phase [11] and the overall process can be summarized as follows:

I Reduction of Cr(VI) to Cr(III) by *Arthrobacter viscosus* supported on NaY.

II Ion exchange of Cr(III) ions in zeolite obtained by biosorption process.

$$Na_{53}Y + xCr^{3+} \leftrightarrow Cr_xNa_{53-3x}Y + 3xNa^+ \quad (1)$$

III *In situ* immobilization of the Cr complex.

$$Cr_xNa_{53-3x}Y + \text{excess L} \leftrightarrow [Cr(L_n)]_xNa_{53-3x}Y \quad (2)$$

where *x* represents the atom fraction of Cr^{3+} ions migrating into the zeolite and L represents the heterocyclic ligand coordinated to the chromium center.

The objective of the present work is the evaluation of the catalytic behaviour of the chromium complexes immobilized in the zeolite Y obtained from biosorption. Catalytic studies were performed in liquid phase for the oxidation of cyclohexene, using *tert*-butyl hydroperoxide (TBHP) as oxygen source.

2. Experimental

2.1. Materials and reagents

A. viscosus was obtained from the Spanish Type Culture Collection of University of Valência. Chromium trichloride and potassium dichromate aqueous solutions were prepared by diluting $CrCl_3{\cdot}6H_2O$ (Merck) and $K_2Cr_2O_7$ (Panreac) in distilled water, in concentrations up to 100.0 $mg_{Cr}\,L^{-1}$. The zeolite NaY (Si/Al = 2.83) with specific surface area of 900 $m^2\,g^{-1}$, was obtained from Zeolyst. It was calcined at 500 °C during 8 h under a dry air stream prior to use. All glassware used for experimental purposes was washed in 10% nitric acid to remove any possible interference by other metals. Atomic absorption spectrometric standards were prepared from 1000 mg L^{-1} solution. The 3-methoxy-6-chloropyridazine (A) and 3-piperidino-6-chloropyridazine (B) ligands were prepared using previously described procedures in the literature [9,11]. 1-(2-pyridylazo)-2-naphthol ligand was purchased from Aldrich. All other chemicals and solvents used were reagent grade and purchased from Aldrich.

2.2. Preparation of the CrNaY host

The preparation of the CrNaY host recovered after biosorption treatment of aqueous dichromate solutions was previously reported [3,10,11]. Two sets of samples were prepared in the same conditions. The whole experimental work was conducted in triplicate. 1.0 g of the NaY was placed in a 250 mL Erlenmeyer flask to which 15 mL of *Arthrobacter viscosus* culture media and 150 mL of the dichromate solution up to 100 $mg_{Cr}\,L^{-1}$ were added and kept at 28 °C, with moderate stirring for 10 days. The CrNaY host sample, obtained from dichromate solution in biosorption assays, was calcined at 500 °C during 8 h under a dry air stream before immobilization in order to remove the organic matter of the *A. viscosus* bacterium. This heat treatment is essential to assure that the organic matter is completely burnt off and will not participate in the immobilization procedure and to allow the ion exchange between the zeolite and the residual metal ions [3,11]. As a reference, a sample with trivalent chromium, Cr(III)NaY, was prepared by direct ion-exchange method from a solution of Cr(III) with the same initial concentration as the ones used in the biosorption assays.

2.3. Immobilization of the Cr complexes with heterocyclic ligands in NaY zeolite

2.3.1. General procedure

Cr complexes immobilized with heterocyclic ligands and derived from biosorbents supported in NaY zeolite were prepared according the following experimental procedure [11,23]. Catalysts were prepared by adsorption of heterocyclic ligands (A, B and C) in CrNaY host. After drying the host, this was mixed with ligand solution and heated to stimulate diffusion of the ligand into the micropores. The heating duration and temperature depend on the thermal stability of the ligand. The resulting materials were purified by Soxhlet extraction with appropriate organic solvent to remove unreacted ligand and residual Cr complexes adsorbed onto the external surface of the zeolite crystallites. The uncomplexed metal ions present in zeolite were removed by exchanging with aqueous 0.01 M NaCl solution. Finally, the samples were dried in an oven at 90 °C, under vacuum, for 12 h. The solid samples obtained from biosorption method were denoted as $[CrL_A]_1$–NaY, $[CrL_B]_2$–NaY and $[CrL_C]_3$–NaY where L_A represents the ligand 3-methoxy-6-chloropyridazine, L_B the ligand 3-piperidino-6-chloropyridazine and L_C the ligand 1-(2-pyridylazo)-2-naphthol. The reference sample, $[Cr(III)L_A]_4$–NaY, was prepared in the same conditions with ligand A.

2.3.1.1. Synthesis of $[CrL_A]_1$–NaY and $[Cr(III)L_A]_4$–NaY. The procedure is analogous to that reported for Fe(III) complexes of pyridazine derivatives in NaY [11]. Following the retention of the metal ion in the NaY zeolite by biosorption or by ion-exchange methods, 0.5 g of the host was stirred with a solution of the ligand A, 3-methoxy-6-chloropyridazine (0.69 mmol) in 100 mL of diethyl ether. This mixture was kept in reflux for 24 h and Soxhlet-extracted for 6 h with ethanol to remove unreacted ligand. Finally, the samples $[CrL_A]_1$–NaY and $[Cr(III)L_A]_4$–NaY were dried in an oven at 90 °C, under vacuum, for 12 h. The final colour of both samples is green.

2.3.1.2. Synthesis of $[CrL_B]_2$–NaY. An analogous procedure is followed using the ligand 3-piperidino-6-chloropyridazine (ligand B). A solution of the ligand B (0.51 mmol) in 100 mL of diethyl ether was added to 0.5 g of dry CrNaY host obtained from biosorption method. After 24 h in reflux and Soxhlet extraction with ethanol, a green sample is obtained.

2.3.1.3. Synthesis of $[CrL_C]_3$–NaY. The procedure is analogous to that reported for (1-(2-pyridylazo)-2-naphthol)copper(II) encapsulated in zeolite Y [24]. A solution of ligand C, 1-(2-pyridylazo)-2-naphthol, (0.76 mmol) in 50 mL THF was added to 0.5 g of CrNaY obtained by biosorption method. The suspension was stirred for 12 h at room temperature. After Soxhlet extraction for 12 h with ethanol, violet solid sample was obtained.

2.4. Characterization procedures

The quantitative analysis (Si, Al, Na and Cr) has been carried out by inductively coupled plasma atomic emission spectrometry (ICP-AES) using a Philips ICP PU 7000 Spectrometer. Chemical analyses of C, H and N were carried out on a Leco CHNS-932 analyzer. A Varian SpectrAA 400 GTA 96 Plus (AAS) was used for the determination of total Cr in aqueous solutions. Phase analysis was performed by XRD using a Philips PW1710 diffractometer. Scans were taken at room temperature in a 2θ range between 5 and 60°, using Cu Kα radiation. Scanning electron micrographs (SEM) were collected on a LEICA Cambridge S360 Scanning Microscope equipped with an EDX system. In order to avoid the surface charging, samples were coated with gold in vacuum prior to analysis, by using a Fisons Instruments SC502 sputter coater. Room temperature Fourier transform infrared (FTIR) spectra of the ligands and of the catalysts samples in KBr pellets were measured using a Bomem MB104 spectrometer in the range 4000–500 cm^{-1} by averaging 20 scans at a maximum resolution of 4 cm^{-1}. Raman spectra were run with a single monochromator Renishaw System-1000 microscope Raman equipped with a cooled CCD detector (−50 °C) and holographic super-Notch filter. The holographic Notch filter removes the elastic scattering while the Raman signal remains high. The powder samples were excited with the 514 nm Ar^+ line; spectral resolution was ca. 3 cm^{-1} and spectrum acquisition consisted of 40 accumulations of 10 s. The power applied to the sample was 0.9 mW. The spectra were obtained under hydrated and dehydrated conditions in a hot stage (Linkam TS-1500). The catalysts were dehydrated in synthetic airflow at 500 °C at a rate of 10 °C min^{-1}. Raman spectrum of dehydrated sample was run at 500 °C and after cooling in synthetic air at room temperature. Thermogravimetric analyses (TGA) of samples were carried out using a TGA 50 Shimadzu instrument under high purity helium supplied at a constant 50 mL min^{-1} flow rate. All samples were subjected to a 6 °C min^{-1} heating rate and were characterized between 25 and 600 °C. The voltammetric study was performed in a thermostated three-electrode glass cell. A saturated calomel electrode and a platinum foil (99.95%) were used as reference and counter electrode, respectively. Before each experiment, the solutions were deaerated with ultra pure nitrogen (U Quality from Air Liquide) and a nitrogen stream was maintained over the solution during the measurements. The electrochemical instrumentation consists on a potentiostat/galvanostat from Amel Instruments coupled to a microcomputer (Pentium II/500 MHz) through an AD/DA converter. The Labview software (National Instruments) and a PCI-MIO-16E-4 I/O module were used for generating and applying the potential program as well as acquiring data such as current intensities. The zeolite-modified electrodes were prepared according the following experimental procedure [24,25]: 20 mg of samples were dissolved in a Nafion/water solution (120 μL Nafion/120 μL ultra pure water). The resulting solutions were homogenized using an ultrasound bath and totality deposited on a carbon Toray paper with an area of 2 cm × 2 cm. Finally the carbon Toray paper was glued to the platinum electrode using conductive carbon cement (Quintech) and was dried at room temperature during 24 h.

2.5. Catalytic experiments

Cyclohexene oxidations were carried out in a 50 mL round-bottom flask equipped with a condenser and a magnetic stirrer. In a typical batch, the reactor was charged with: (i) 5.8 mL of decane (solvent); (ii) 0.2 mL of cyclohexene (0.20 mmol of substrate); (iii) 0.4 mL of toluene (GC internal standard). 50 mg of the catalysts, previously activated in an oven at 150 °C under vacuum for 12 h, were transferred into the reactor and then agitated for 30 min at 40 °C. Finally, 2 mL of TBHP (12 mmol of solution 6 M of *tert*-butyl hydroperoxide in decane) acting as an oxygen source were added to the reactor under stirring. Samples of the reaction mixtures were withdrawn at fixed time intervals and analyzed by gas chromatography (GC, SRI 8610C, equipped with a CP-Sil 8CB capillary column and a FID detector) and allowed to qualitatively and quantitatively determine (by the internal standard method) the cyclohexene substrate and the following reactions products: 2-cyclohexene-1-one, 2-cyclohexene-1-ol and 1-*tert*-butylperoxy-2-cyclohexene. The identities of these reaction products were confirmed by GC–MS (Varian 4000 Performance). Turnover number (TON) was defined by the ratio between the converted cyclohexene (mol) and the amount of metal ions in the catalyst (mol).

3. Results and discussion

3.1. Characterization of the heterogeneous catalysts

The CrNaY zeolite host was recovered from an initial 100 mg_{Cr} L^{-1} dichromate solution, with 20% of maximum removal of the initial amount of dichromate [3,10]. *Arthrobacter viscosus* bacterium supported on the zeolite performs the reduction of Cr(VI) to Cr(III), and then the Cr(III) is retained in the zeolite by ion exchange. The low removal ratio of Cr(VI) seem to be connected to the limited bioreduction capacity of the bacterium and the charge repulsions with the zeolite [3].

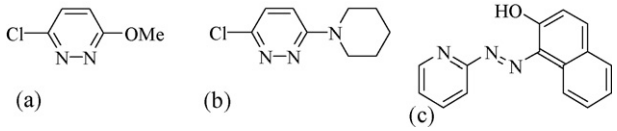
In order to test the CrNaY zeolites as catalysts in liquid phase and to prevent the leaching of the metal, Cr complexes were immobilized within the host zeolites by the flexible ligand method using an excess of the heterocyclic ligands to assure a complete coordination of the chromium inside the zeolite [9,11]. Three heterocyclic ligands were used: 3-methoxy-6-chloropyridazine (L_A), 3-piperidino-6-chloropyridazine (L_B) and 1-(2-pyridylazo)-2-naphthol (L_C) (Scheme 1).

The molecular diameters of these heterocyclic ligands are smaller than the limiting pore diameter of the zeolite. All ligands present nitrogen atoms available for coordination. Moreover, the ligand L_C offers also the oxygen atom for coordination [9,11,24].

The results from different techniques of characterization reveal the unequivocal evidence for the immobilization of Cr complexes in the supercages of the host zeolite. The powder XRD diffraction patterns of the NaY and of the immobilized Cr complexes in NaY were recorded at 2θ values between 5 and 60° and some representative patterns are presented in Fig. 1.

All samples exhibited the typical and similar pattern of highly crystalline zeolite Y, with no obvious change in the position or in the relative intensity of the diffraction lines for zeolite Y after immobilization of the complexes. The similarity between the diffractograms of the zeolite after chromium biosorption and after the immobilization of the complex, and the diffractograms of the original one reveal that those processes do not promote any structural modification in the zeolite NaY.

Fig. 2 presents the field emission scanning electron micrographs of the starting NaY and the samples before and after calcination of CrNaY obtained from biosorption process.



Scheme 1. Structures of the ligands: (a) 3-methoxy-6-chloropyridazine, (b) 3-piperidino-6-chloropyridazine and (c) 1-(2-pyridylazo)-2-naphthol.

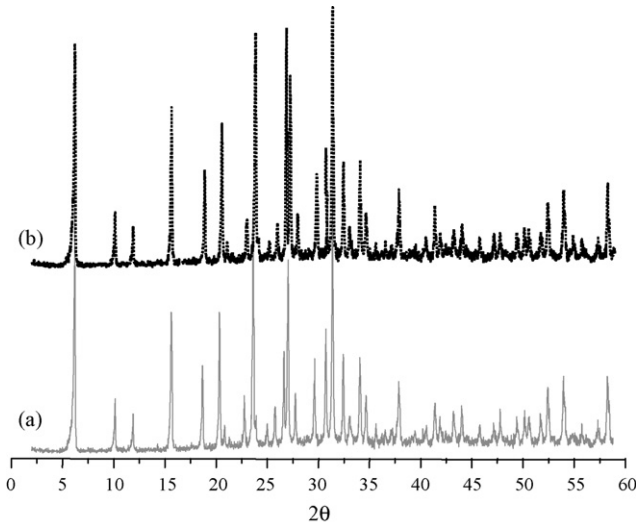


Fig. 1. XRD patterns of NaY (a) and of $[CrL_A]_1$–NaY(b).

Table 1
IR spectroscopic data of ligands and catalysts samples.

Samples	IR (cm^{-1})		
	ν(OH)[c]	ν(OH)[d]	ν(N=N)
NaY	ca. 3450	1640	–
CrNaY[a]	ca. 3450	1640	–
	ca. 3450	1640	–
Cr(III)NaY[b]	ca. 3400	1638	–
L_A	–	–	1580
L_B	–	–	1583
L_C	3362	1605	1504
$[CrL_A]_1$–NaY	ca. 3450	1642	1410
$[CrL_B]_2$–NaY	ca. 3450	1640	1405
$[CrL_C]_3$–NaY	ca. 3450	1639	1406
$[Cr(III)L_A]_4$–NaY	ca. 3450	1640	1410

[a] Host obtained by biosorption method.
[b] Host obtained by ion-exchange method.
[c] ν(O–H) stretching vibration bond.
[d] ν(O–H) deformation bond.

SEM confirmed that the calcination step after biosorption process is important to assure that the bacterium is not present on the zeolite (Fig. 2c). Energy-dispersive X-ray analysis plots support this conclusion as no organic matter was detected on the spotted surface in the CrNaY sample after calcination. From SEM observations, the heterogeneous catalysts have well defined crystals and there is no indication of the presence of the complexes on the surface. In addition, no morphological changes on the surface upon immobilization of the complexes are seen due to their low loading.

A partial list of IR spectroscopic data is presented in Table 1.

The FTIR patterns of the heterogeneous catalysts are very similar and are dominated by the strong bands assigned to the vibration of zeolite structure [9–11,23,24]. The intensity of the peaks in immobilized complexes is, however, weak because their low concentrations in the zeolite host [11,24]. The spectra of the ligands A and B exhibit a band around 1580 cm^{-1} attributed to the ν(N=N) of the pyridazine group. However, in the spectrum of the ligand C a band at 1504 cm^{-1} is attributed to the azo group [24]. Comparison of the spectra of these ligands with the spectra of the respective immobilized complexes provides evidence for the coordinating mode of ligands in complexes. The shifts of the ν(N=N) to lower wavenumbers in complexes suggest the coordination of the ligands nitrogen atoms.

Immobilization of Cr complexes in zeolite was further supported by thermogravimetric analyses (TGA) and chemical analysis. Table 2 presents the analytical data from TGA and chemical analysis.

The TGA curves of the NaY and of the host supports show a weight loss at 110 °C attributed to the removal of intra-zeolite water. After immobilization of Cr complexes, two major stages of weight loss can be evidenced in a broad temperature range (i.e. 80–580 °C). The first stage occurs at 120 °C and is due to the contributions from the physisorbed water within the zeolite structure. For temperature near 540 °C, the weight loss is associated with progressive decomposition of the immobilized complexes.

As expected, the bulk Si/Al ratio (Table 2) for all heterogeneous catalysts did not change substantially after the biosorption and the immobilization processes which indicate that no dealumination occurred during these steps [3,10,11]. The successful synthesis of the immobilized Cr complexes in zeolite was confirmed by the analytical data of carbon and metal. For immobilized complexes in host obtained from biosorption, a stoichiometry of metal/ligand for L_A and L_B is 1:2 and for L_C is 1:1. In these syntheses the totality of each ligand is coordinated with the metal in agreement with our previous works [9,11,24]. However, the higher Cr/C ratio observed for the sample obtained from ion-exchange method, $[Cr(III)L_A]_4$–NaY, suggests the presence of a fraction of chromium not coordinated with the ligand. Probably, the higher Cr loading in NaY is also placed in framework sites that are inaccessible for the ligand [11,26].

Additionally structural information of samples was obtained by Raman spectroscopy. This technique together with cyclic voltammetry studies provided the identification of chromium species present in these heterogeneous catalysts. For the samples prepared from ion-exchange method, only the chromium trivalent is identified. The micro-Raman spectra of CrNaY host obtained from biosorption method underline a non-homogeneous distribution of chromium species. The Raman bands observed between 200 and 600 cm^{-1} are assigned to the motion of the oxygen atom in a plane perpendicular to the T–O–T bonds in the zeolite structure. The presence of hexavalent chromium was observed at bands 1001 and 882 cm^{-1} and are related to surface Cr(VI) species. The presence of

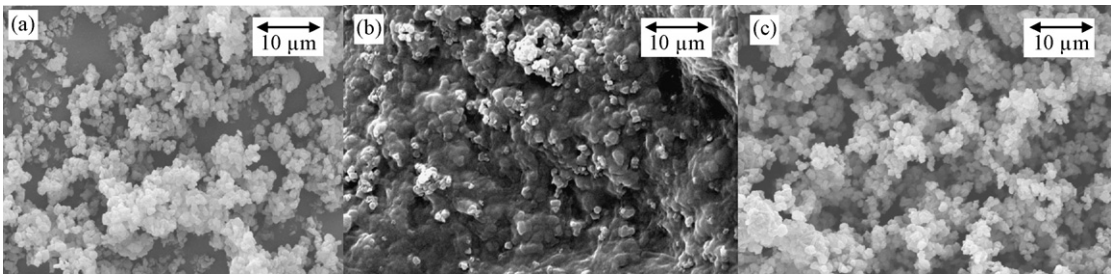


Fig. 2. Scanning electron micrographs (SEM) with resolution (3000×): NaY (a), CrNaY before calcination (b) and after calcination (c).

Table 2
Analytical data of the catalysts samples.

Samples	Elemental analysis (wt%)				
	TGA (°C)	Si/Al[a]	Cr[a]	C[b]	Cr/C
NaY	120	2.83	–	–	–
CrNaY[c]	110	2.97	0.14	–	–
	120	2.90	0.07	–	–
Cr(III)NaY[d]	110	2.77	0.62	–	–
$[CrL_A]_1$–NaY	120/540	2.81	0.09	0.82	0.11 (0.10)[e]
$[CrL_B]_2$–NaY	120/546	2.61	0.09	0.67	0.13 (0.06)[e]
$[CrL_C]_3$–NaY	110/470	2.78	0.07	0.75	0.09 (0.07)[f]
$[Cr(III)L_A]_4$–NaY	120/538	2.70	0.58	0.65	0.89 (0.10)[e]

[a] Bulk Si/Al ratio and Cr loading on NaY determined by ICP-AES analysis.
[b] Carbon from Cr complexes obtained by elemental analysis.
[c] Host obtained by biosorption method.
[d] Host obtained by ion-exchange method.
[e] Value in parentheses refers to the theoretical ratio Cr/C (w/w) in the chromium complex for a 1:2 stoichiometry.
[f] Value in parentheses refers to the theoretical ratio Cr/C (w/w) in the chromium complex for a 1:1 stoichiometry.

Table 3
Data from oxidation of cyclohexene with TBHP for different catalysts (reaction time = 24 h).

Catalyst	Conversion (%)	Selectivity (%)			TON[a]
		CyOL[b]	CyONE[c]	CyOX[d]	
–	16.2	–	–	100.0	–
NaY	14.2	–	–	100.0	–
CrNaY[e]	40.3	–	34.3	65.7	614
Cr(III)NaY[f]	51.2	20.1	79.9	–	160
$[CrL_A]_1$–NaY	27.6	–	17.0	83.0	647
$[CrL_B]_2$–NaY	30.3	–	18.4	81.6	717
$[CrL_C]_3$–NaY	31.8	–	21.5	78.5	851
$[Cr(III)L_A]_4$–NaY	37.9	9.5	44.5	46.0	137

[a] TON = the converted cyclohexene (mol)/the amount of metal ions in the added catalyst (mol).
[b] CyOL is 2-cyclohexene-1-ol product.
[c] CyONE is 3-cyclohexene-1-one product.
[d] CyOX is 1-*tert*-butylperoxy-2-cyclohexene product.
[e] Host obtained by biosorption method.
[f] Host obtained by ion-exchange method.

these species could be related to the calcination conditions and to the limited bioreduction of the *A. viscosus* bacterium.

The electrochemical techniques such as cyclic voltammetry can be successfully used for the characterization of electron-transfer processes involving zeolite-immobilized complexes. In order to determine the electroreactivity by cyclic voltammetry, Cr complexes immobilized in NaY were deposited on carbon Toray (CT). The cyclic voltammetry studies performed with a new method for the preparation of zeolite-modified electrodes [24,25] show evidence for electroactivity restricted to boundary associated Cr complexes. It was found that the voltammograms of immobilized complexes are very similar and the sample $[CrL_C]_3$–NaY has been selected as an example. The voltammograms of NaY/CT and $[CrL_C]_3$–NaY/CT in 0.1 M NaCl are presented in Fig. 3.

It can be seen that the cyclic voltammogram of NaY/CT did not exhibit any redox process in the scan potential of −1.5 to 1.5 V vs. SCE. The cyclic voltammogram of the modified electrode of $[CrL_C]_3$–NaY displays one reversible wave observed at −0.20 and 0.25 vs. SCE, which is assigned to the redox couple of Cr(III)/Cr(II) from the complex immobilized in zeolite NaY. The shapes and the positions of these waves are not affected by variable scan rates indicating reproducibility of the electrode reaction. Similar electrochemical behaviour was observed by other authors [27] for the chromium(III) complexes with Schiff base ligands.

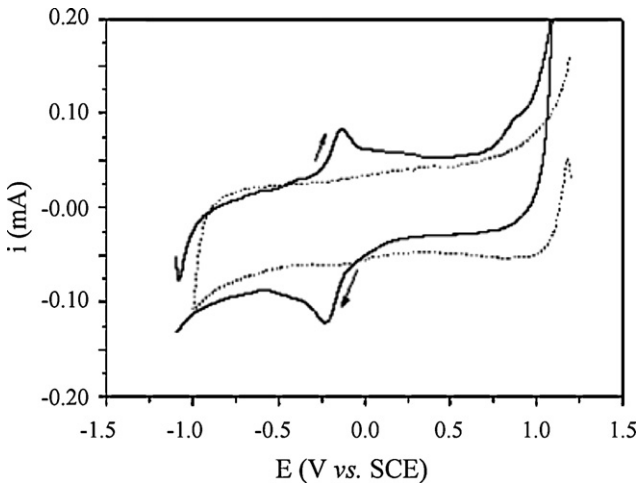


Fig. 3. Cyclic voltammograms of NaY/CT (...) and of $[CrL_C]_3$–NaY/CT (—) in 0.1 M NaCl at room temperature (scan rate: 50 mV s^{-1}).

3.2. Catalytic behaviour of the heterogeneous catalysts

The catalytic behaviour of the different heterogeneous catalysts was tested for the oxidation of cyclohexene. TBHP was employed as oxidizing agent, always in excess with respect to the substrate and the reaction was carried out at 40 °C. Blank experiments without catalyst and with parent NaY were performed under identical test conditions. The outcome of the reaction was followed by GC and the catalytic results are summarized in Table 3 and Fig. 4.

The observed reaction products were identified as 2-cyclohexene-1-ol (CyOL), 2-cyclohexene-1-one (CyONE), and 1-*tert*-butylperoxy-2-cyclohexene (CyOX), which are the typical expected products for this reaction [28–32].

Blank runs were performed to check the contribution of the radical mechanism. It was found that it accounted for about 16% of cyclohexene conversion and only allylic oxidation product has occurred with the formation of 1-*tert*-butylperoxy-2-cyclohexene [12,23,28]. NaY showed a similar behaviour. The formation of 2-cyclohexene-1-ol (CyOL) and 2-cyclohexene-1-one (CyONE) occurs by the preferential attack of the activated C–H bond over the C=C bond and 1-*tert*-butylperoxy-2-cyclohexene (CyOX) is an intermediary product [23,28–31,33]. The existence of this product in all catalysts indicates the occurrence of the radical reactions [32–34].

As expected the presence of Cr in the host NaY prepared from two different methods resulted in improvement of conversion and selectivity. However, a high conversion of cyclohexene (>50%) was obtained when sodium is ion-exchanged with Cr(III) in NaY.

From the indicated results in Table 3 and Fig. 4a it is evident that 2-cyclohexene-1-one is selectively formed in the presence of the Cr(III)NaY. The evolution of the allylic oxidation products for this host shows that chromium improves the CyONE production, reducing the selectivity towards CyOL and CyOX is an intermediary product of the reaction. However, all heterogeneous catalysts show the same selectivity towards the formation of CyONE and CyOX (Fig. 4a). The selectivity analysis shows that the 1-*tert*-butylperoxy-2-cyclohexene (CyOX) is an unstable product, while the 2-cyclohexene-1-one (CyONE) appears as a secondary and stable product.

The reaction mechanism proposed for the formation of the allylic oxidation products 2-cyclohexene-1-ol and 2-cyclohexene-1-one is more related to the cage controlled metal–OH chemistry rather than to free radical mechanism. The formation of 1-*tert*-butylperoxy-2-cyclohexene proceeds through a radical mechanism (Scheme 2) [23,28–34].

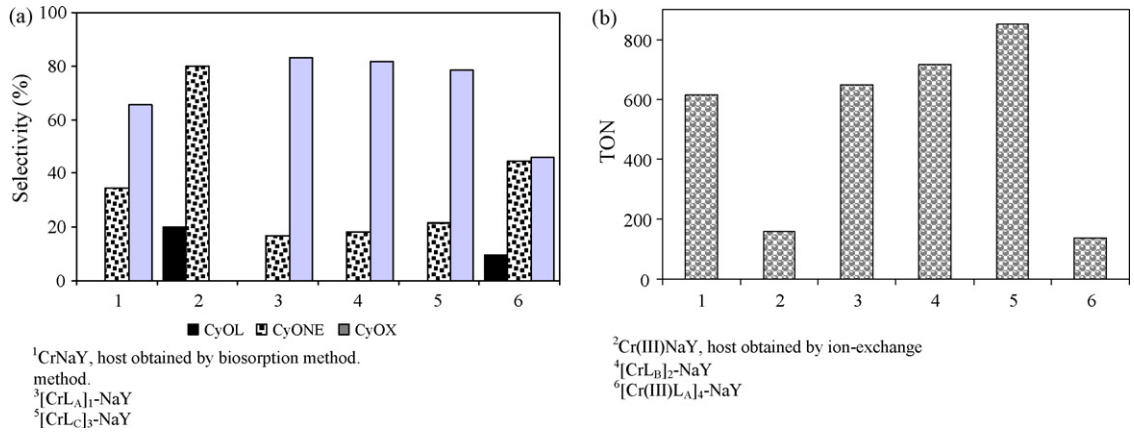
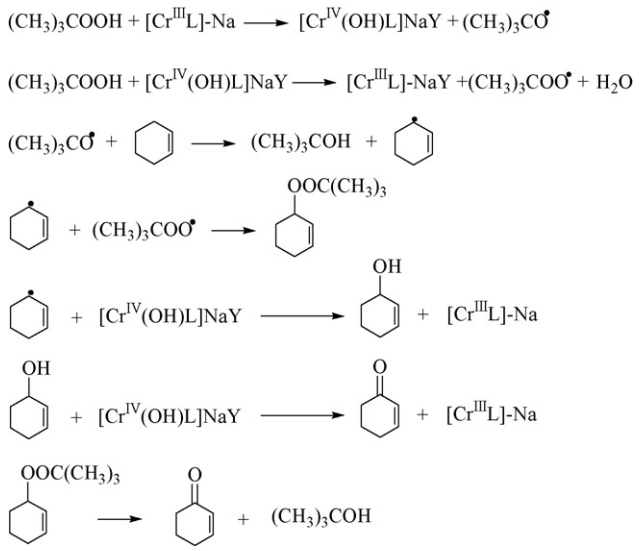


Fig. 4. Data of the catalytic oxidation of cyclohexene: oxidation products distribution (a) and TON (b).



Scheme 2. Reaction mechanism for the oxidation of cyclohexene.

The turnover number (TON) determined for all catalyst is given in Table 3 and presented in Fig. 4b. CrNaY host obtained by biosorption process exhibited a TON of 614 and it was 3.8 times higher than the one for Cr(III)NaY. This suggests that chromium obtained by biosorption is accessible and active for the oxidation reaction. It is clear that the heterogeneous catalyst presents a much higher TON than its parent hosts.

After chromium immobilization by different heterocyclic ligands in both hosts, the conversion of cyclohexene decreased and remained similar for all heterogeneous catalysts after 24 h of reaction. However, TON for [CrL$_C$]$_3$–NaY is higher than for the other immobilized catalysts. The decrease observed in TON is more pronounced in the ion-exchanged sample, [Cr(III)L$_A$]$_4$–NaY. The highest TON of 640–850 was achieved by the heterogeneous catalysts prepared from biosorption method. The lower TON for [Cr(III)L$_A$]$_4$–NaY confirms the presence of chromium coordinated with the ligand, where only a fraction of the metal is active or accessible to substract.

4. Conclusions

Chromium complexes immobilized with heterocyclic ligands in zeolite Y have been prepared by means of combined biosorption processes with heterogenization of transition metal complexes in zeolites. The catalytic results prove that the catalysts prepared from the biotreatment of Cr(VI) solutions have activity for the oxidation of cyclohexene using *tert*-butyl hydroperoxide as an oxidant. The higher turnover numbers of heterogeneous catalysts make the immobilized Cr complexes in NaY prepared from biosorption method interesting catalysts for oxidation reactions in mild conditions. The results open the way to prepare active catalysts to be applied in the oxidation of persistent organic compounds by using xenobiotic pollutants from wastewater recovered by a robust biosorption system consisting of a bacterial biofilm, *Arthrobacter viscosus*, supported on zeolite NaY.

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