



Oxidation of cyclohexanol and cyclohexene with triazenido complexes of chromium immobilized in biosorption FAU supports



H. Figueiredo^a, B. Silva^a, I. Kuźniarska-Biernacka^b, A.M. Fonseca^b, R. Medina^c, S. Rasmussen^c, M.A. Bañares^c, I.C. Neves^{b,*}, T. Tavares^{a,*}

^aCentro de Engenharia Biológica, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal

^bDepartamento de Química, Centro de Química, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal

^cInstituto de Catálisis y Petroleoquímica, CSIC, E-28049 Madrid, Spain

HIGHLIGHTS

- Fau supported Cr catalysts were prepared by biosorption of waste metal.
- Diphenyltriazene derivatives proved to be suitable coordination agents for CrFAU.
- CrFAU catalysts were successfully used in mild condition oxidation reactions.
- Cr leaching was effectively reduced by the immobilization procedure.

ARTICLE INFO

Article history:

Received 4 December 2013

Received in revised form 25 January 2014

Accepted 25 February 2014

Available online 10 March 2014

Keywords:

FAU zeolite

Chromium

1,3-Diphenyltriazenido ligands

Heterogeneous catalyst

Oxidation reactions

ABSTRACT

This work presents the recovery of biosorption supports as an alternative source of benign production of heterogeneous catalysts for oxidation reactions in mild conditions. Cr-containing FAU zeolite, in sodium form (NaY) and in proton form (HY), was recovered from biosorption studies and reused as support for the preparation of heterogeneous catalysts by the flexible ligand method, using 1,3-diphenyltriazene derivatives. Results showed that the ligand play an important role in the coordination of Cr inside the zeolite. The catalysts showed good activity for the oxidation of cyclohexanol, reaching a maximum of 63.5% conversion. Cr leaching was evaluated and it was found that the Cr-FAU supports lost some of the Cr into the reaction medium, whereas immobilization of Cr-complexes reduced the referred leaching. For the cyclohexene oxidation, a maximum 72.9% conversion was achieved with a HY zeolite-based catalyst.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Research on environmental protection receives considerable attention from public, academia and industry. Several technologies for pollution abatement and/or remediation have been proposed and successfully implemented. One particular critical aspect of industrial contamination of the environment is heavy metal pollution. Metals tend to accumulate in organisms, therefore posing a health risk through persistence in food chains [1]. Various technologies for the treatment/prevention of heavy metal contamination in liquid systems have been developed such as ion exchange, adsorption, precipitation, filtration and dialysis/osmosis processes [2]. More recently, environmental awareness has resulted in efforts

for developing “green processes”, whereas the current economic constraints increase the demand for recovery–reuse technologies [3,4].

In order to address these two trends, a technology for the removal and recovery of hexavalent chromium has been proposed, combining the biosorption properties of the *Arthrobacter viscosus* bacterium with a supporting zeolite [5–10]. The bacterium performs the reduction of Cr(VI) to Cr(III), while the latter is ion-exchanged by the supporting zeolite, which is intrinsically unable to perform direct ion-exchange of chromate and dichromate anions, the most common aqueous Cr(VI) species. After the biosorption process, the resulting biosorbent-zeolite system was calcined and the resulting Cr-zeolite is suitable for application in catalysis.

The use of Cr–NaY zeolite recovered from biosorption studies in gas-phase catalysis has been conducted, namely, for the oxidation of 1,2-dichlorobenzene and ethyl acetate [5,11]. However, the

* Corresponding authors. Tel.: +351 253604400 (T. Tavares).

E-mail addresses: ineves@quimica.uminho.pt (I.C. Neves), ttavares@deb.uminho.pt (T. Tavares).

utilization of Cr–NaY matrices in liquid-phase oxidation reactions requires previous immobilization of the Cr species in the support, in order to overcome the possible Cr leaching [12–14]. Since leaching of active metal centres into the solution is undesirable, various strategies for immobilization of catalytically active metal centres in inorganic matrices have been proposed. Some of the methods to obtain the heterogeneous catalysts include coordination of the metal with ligands by anchoring it to the support or by *in situ* synthesis of the complex inside the host, the so called *ship in bottle* synthesis [15–18].

Encapsulation of metal species in zeolites is a method that has been studied for a quite long time [19] and is known to be efficient for the immobilization of transition metal complexes. Faujasite (FAU) zeolites possess well-defined supercages interlinked with three-dimensional channels with wide pore openings (12 oxygen atoms), which makes these supports ideal hosts for the encapsulation of metal complexes *via* the flexible ligand method. This heterogeneous class of catalysts has found application on several fields in catalysis such as preparation of fine chemicals [15], photocatalysis and electrocatalysis [17].

Oxidation of alcohols to the corresponding ketones and aldehydes is a key reaction in organic synthesis [20–22], since the selective formation of carbonyl functional groups in hydrocarbons makes them useful intermediaries for pharmaceuticals and cosmetic products [23]. Cr-containing catalysts have found application on the oxidation of several organic substrates, including cyclohexene and cyclohexanol [24–26]. The latest is of particular interest, as the liquid-phase oxidation of secondary alcohols often employs homogeneous Cr(VI) catalysts, which requires previous preparation of catalyst and demands for an efficient disposal of the metal after reaction, given its toxicity [22].

This work reports the preparation of heterogeneous chromium catalysts from Cr-biosorption FAU supports and the application of these catalysts to liquid-phase oxidation reactions in mild conditions. For the effect, 1,3-diphenyltriazene derivatives were used as ligands for the immobilization of the Cr species inside the framework of FAU zeolite. The oxidation of cyclohexanol and cyclohexene were chosen as model reactions for the validation of the catalytic activity.

2. Experimental section

2.1. Materials and procedures

A. viscosus was obtained from the Spanish Type Culture Collection of University of Valência. Potassium dichromate aqueous solutions were prepared by diluting $K_2Cr_2O_7$ (Panreac) in distilled water, in concentrations up to 100.0 mg_{Cr}/L. The FAU supports, NaY and HY zeolites, were supplied by Zeolyst International (commercial names CBV100 and CBV400, respectively) in powder form. Bulk Si/Al ratios are 2.83 and 2.80 for NaY and HY, respectively. Both zeolites were 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. 1,3-diphenyltriazene derivatives (1a, 1b and 1c) were prepared using a previously described procedure in literature [27,28]. All the other chemicals and solvents used for the catalysts preparation and for the catalytic reactions were reagent grade and purchased from Aldrich.

2.2. Immobilization of Cr complexes in FAU supports

Immobilization of Cr(III) complexes in the Cr–FAU supports was based in a previously established procedure [29]. Cr–FAU supports

were prepared by different biosorption treatments: the sample CrNaY was recovered from a single-batch process, whereas CrNaY_{SBR} and CrHY_{SBR} were obtained from processes involving sequential batch reactors (hence the suffix SBR) and in all cases an initial 100 mg_{Cr}/L dichromate solution was used [6]. All recovered samples were previously calcined at 500 °C under dry air flow for 8 h. For the immobilization of 1,3-diphenyltriazene chromium complex in the Cr–FAU supports the coordination was obtained with ligand 1,3-diphenyltriazene (1a). Two more ligands, 1,3-bis(*p*-methylphenyl)triazene (1b) and 1,3-bis(*p*-nitrophenyl)triazene (1c) were used for coordination with Cr in CrNaY support in order to compare the efficiency of Cr immobilization.

The catalysts were prepared *via* a flexible ligand method consisting of three steps: *in situ* complex synthesis, liquid–solid extraction and stabilization. For the first step, 0.28 mmol of the selected ligand in 100 mL of ethanol solution and 1.0 g of Cr–FAU host (previously dried at 150 °C under vacuum) were refluxed for 24 h with moderate stirring. The solid is recovered by filtration and dried overnight at 60 °C. Liquid–solid Soxhlet extraction was conducted with 50 mL of dichloromethane for 5 h. Finally, the stabilization of the catalyst was performed under moderated stirring at room temperature for 24 h with 50 mL of 0.01 M NaNO₃ solution. The solid is recovered from this solution by filtration, followed by overnight drying at 60 °C.

2.3. Catalytic oxidation of cyclohexene and cyclohexanol

The oxidation reaction of cyclohexene is conducted in a 50 mL three-way flask equipped with a condenser and thermometer. The reaction mixture is as follows: 5.8 mL decane (solvent), 0.2 mL cyclohexene (substrate), 0.4 mL toluene (internal standard for GC analysis) and 2.0 mL of *tert*-butyl hydroperoxide (TBHP) 5.5–6.0 M in decane (oxygen source). For the catalyzed reactions, an amount of 50.0 mg of previously dried catalyst is transferred into the reaction mixture before the addition of TBHP. The reactor is placed in an oil bath at the desired reaction temperature (controlled by a thermostat at 50 °C) and the mixture is moderately stirred for 23 h. The evolution of cyclohexene and oxidation products is followed by GC analysis.

The oxidation reaction of cyclohexanol is conducted in similar conditions as for the oxidation of cyclohexene, with the exception of the composition of the reaction mixture which is as follows: 5.0 mL diethylketone (solvent), 0.3 mL cyclohexanol (2.9 mmol of substrate), 0.4 mL chlorobenzene (standard for GC analysis) and 2.0 mL of 5.5–6.0 M TBHP in decane. The reaction temperature is set to 60 °C and the mixture is moderately stirred for 23 h. All blank experiments, without catalyst and using NaY and HY zeolites as catalyst, were performed under the same conditions.

2.4. Characterization procedures

Scanning electron microscopy (SEM) surface analysis was performed on a Nova NanoSEM 200 microscope under high vacuum, coupled to EDAX – Pegasus X4M energy-dispersive spectrometer (EDS), with beam energy of 15.00 kV. X-ray photoelectronic spectra (XPS) of the supports/catalysts were obtained with a VG Escalab 200 R XPS spectrometer fitted with an Mg K α X-ray source at 120 W. Carbon was used as internal standard for all samples, with correction of the corresponding binding energy of C to 284.6 eV. Fourier-Transform Infrared spectra (FTIR) of solid samples were recorded within the 4000–500 cm⁻¹ range with a Bomem MB104 spectrometer, using KBr pellets (sample/KBr mass ratio was 1:100). Raman spectra of solid samples were recorded on a Perkin–Elmer Raman Station 400F fitted with a 785 nm wavelength laser with a maximum power at sample of 100 mW. Accumulations, total accumulation time and power at sample

parameters were adjusted in order to minimize the effect of background fluorescence on each sample. EPR spectra were collected with a Bruker EMX EPR spectrometer at 77 K using a finger dewar inserted into a Bruker standard ER4102ST cavity. The microwave frequency was around 9.42 GHz. Before acquisition of EPR spectra, the samples were dried overnight at 120 °C. Chemical analysis of C, N and H was conducted on a Leco CHNS-932 analyzer. The determination of Cr content of each solid support was carried out by inductively coupled plasma atomic emission spectrometry (ICP-AES) using a Philips ICP PU 7000 Spectrometer. Thermogravimetric analysis (TGA) was conducted on a Shimadzu TGA-50 instrument. Samples were placed in aluminium crucibles and were characterized between 25 and 580 °C under a constant heating rate of 6 °C/min and 50 mL/min of N₂ flow. BET areas of the supports/catalysts were determined from N₂ adsorption isotherms performed on an automatic Micromeritics ASAP-2000 apparatus. Samples were previously outgassed at 140 °C for 2 h. Acid digestion of liquid samples from catalytic reactions were performed in a microwave (0.5 mL of sample for 10.0 mL of HNO₃) and analysed for Cr in a Varian SpectraAA-250 atomic absorbance spectrometer. Liquid samples from catalytic reactions were analysed by gas chromatography on a SRI Instruments 8610C gas chromatograph, fitted with a CP-Sil 8CB capillary column and FID detector.

3. Results and discussion

3.1. Preparation and characterization of the heterogeneous Cr–FAU catalysts

In the present study, Cr–FAU structures are used as hosts for the preparation of catalysts and their application in liquid-phase oxidation reactions is reported. The Cr–FAU zeolites were recovered from different batch assays supporting Cr(VI) biosorption studies. In short, the *A. viscosus* bacteria, supported on FAU zeolites, bioreduces Cr(VI) species to Cr(III) ions and these cations in aqueous medium are then easily ion-exchanged by the zeolitic support. All Cr–FAU zeolites were recovered from an initial 100 mg_{Cr}/L dichromate solution, with uptake values of 11.7, 8.3 and 6.7 mg_{Cr}/g_{zeolite} for CrNaY, CrHY_{SBR} and CrNaY_{SBR}, respectively. This difference in uptake performance results in different Cr loadings of the supports. Full details on the biosorption-recovered supports were described elsewhere [6].

The recovered structures were calcined in order to remove the supported biomass and other organic matter, resulting in Cr–FAU materials. These starting materials for preparation of the different catalysts were named CrHY_{SBR} and CrNaY_{SBR}, for those recovered from the sequential batch process (SBR), whereas CrNaY was recovered from a single-batch process [6].

The *in situ* synthesis of Cr(III) complexes in FAU zeolite supercages was performed by the flexible ligand method in the liquid phase using an excess of the 1,3-diphenyltriazene derivatives, named **1a**, **1b** and **1c** (Fig. 1). Three triazenido derivatives ligands with different donor and acceptor substituents in *para*-phenyl group were used: 1,3-diphenyltriazene (**1a**), 1,3-bis(*p*-methylphenyl)triazene (**1b**) and 1,3-bis(*p*-nitrophenyl)triazene (**1c**). All ligands could be chelated by the 1,3-nitrogen atoms [30].

The coordination of chromium by these ligands is strongly affected by the substituents in *para*-aryl position. The nitro group in *para* position of the aromatic ring decreases the coordination of triazenido as a result of its electrowithdrawing ability. However, methyl groups in *para* position increase the electronic density in the triazenido group, resulting in enhanced coordination. The environment medium for the coordination has also an important influence on the final complexes because it is necessary to ensure that

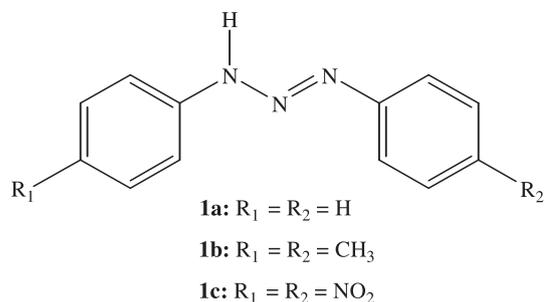


Fig. 1. Structure of 1,3-diphenyltriazene derivatives.

the deprotonation of the acidic hydrogen in triazene group occurs [31].

Several different techniques were used to evaluate the immobilization of 1,3-diphenyltriazenido chromium complexes in the supercages of the host zeolites obtained by different processes in the Cr catalysts.

SEM analysis is important to confirm that the calcination step after the biosorption process removes the biofilm from the zeolite [29,32]. Fig. 2 presents the field emission scanning electron micrograph (Fig. 2a) and the surface EDS spectrum (Fig. 2b) of CrHY_{SBR} as a representative example.

The typical faujasite zeolite morphology was preserved and has well defined particles with average sizes between 0.2 and 0.5 μm (Fig. 2a). No changes in the zeolite morphology or structure upon complex encapsulation were observed. Energy-dispersive X-ray analysis shows the presence of Cr in the matrix by the respective Kα line at 5.40 keV [33] and a residual amount of phosphorus was detected at 2.03 keV [34], which is most likely a scattered biomass residue from calcination (Fig. 2b).

The XPS analysis provided valuable information about the presence of chromium on the surface layer of supports, as well as about the oxidation state of the metal. All catalysts revealed the presence of oxygen, sodium, silicon, nitrogen and aluminium in their XPS resolution spectra. The presence of chromium was detected in region of Cr 2p. The spectrum showed two bands at binding energies of 577.4 eV and 586.6 eV. The first corresponds to a Cr 2p_{3/2} and the second to a Cr 2p_{1/2}. Fig. 3 presents the peak fitting of the signal on the Cr 2p XPS spectrum of CrNaY, as an example.

After deconvolution in the Cr 2p_{3/2} region, the peak at 577.4 eV is attributed to Cr(III), while signals at 581.3 and 579.5 eV may be due to the presence of Cr(VI) [26,35]. The presence of Cr(III) is due to the reduction of Cr(VI) to Cr(III) during the biotreatment process. The biomass is responsible for this reduction, while the zeolite performed the entrapment of Cr(III) by ion-exchange [6,9]. Similar results were observed by Park et al. [36], who concluded that the biomass by itself would only retain Cr(III) ions. The presence of Cr(VI) in CrNaY could be due to the calcination treatment re-oxidating a fraction of the exchanged Cr(III) species to Cr(VI). This fact was reported by Weckhuysen et al., who stated that Cr(III) ion-exchanged Y zeolites would form chromate species upon calcination in an oxygen-rich atmosphere [37]. Since the recovered biosorption supports were calcined under dry air flow, it is likely that a partial oxidation occurred and the supports contained both Cr(VI) and Cr(III) species.

Additional structural information was obtained by Raman spectroscopy that can identify chromium species present in these catalysts. Fig. 4 presents the Raman spectra of CrNaY support and the homologous catalysts prepared with the three different ligands. Although the spectra are dominated by the intrinsic background fluorescence of calcined zeolitic samples [38], it is possible to identify peaks at 1360 and 942 cm⁻¹ in [CrL_{1a}]NaY and [CrL_{1b}]NaY. The spectrum of [CrL_{1c}]NaY is similar to the one

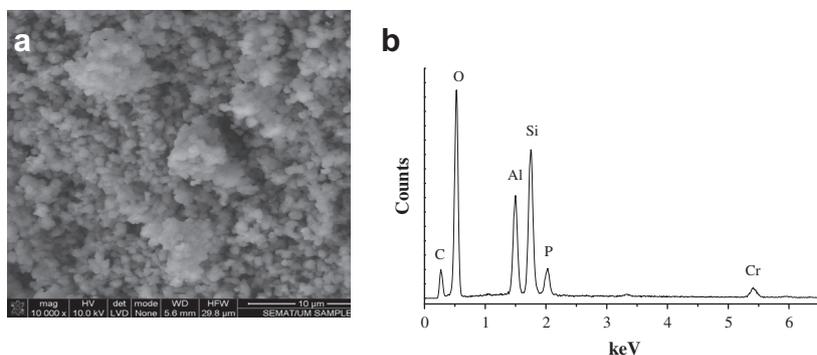


Fig. 2. (a) Scanning electron microscopy (10,000 \times) and (b) energy dispersive spectrum of CrHY_{SBR}.

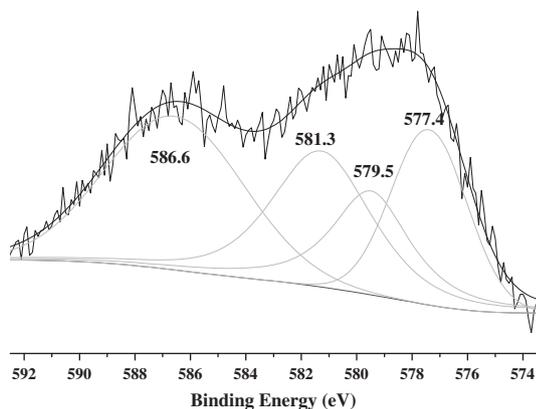


Fig. 3. Peak fitting of the Cr 2p region on the XPS spectrum of CrNaY.

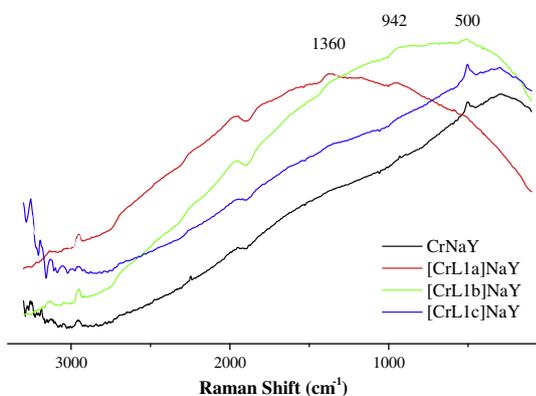


Fig. 4. Raman spectra of CrNaY and of the respective catalysts.

of CrNaY. The first signal corresponds to the D-band of carbon compounds [39], while the second peak resembles the most intense Raman band of alkali chromates species [26]. The presence of these species could be related to the calcination conditions that favour the oxidation of Cr(III) to Cr(VI). Cr(III)-related Raman bands are expected at 550 cm^{-1} but are not visible in the spectra, mainly due overlapping with the intense 500 cm^{-1} Raman band that is typical for FAU zeolites [40].

The immobilization of chromium complexes in the biosorption FAU supports was demonstrated by FTIR and EPR analysis. All FTIR spectra of biosorption FAU supports and of the catalysts are dominated by the strong bands attributed to the zeolite structure. No shift or broadening of the zeolite vibration bands is observed upon incorporation of the chromium complex. The FTIR spectra of NaY

and HY are characterized by a very intense broad band at ca. 3460 cm^{-1} , with a poor resolved shoulder at ca. 3600 cm^{-1} attributed to the hydroxyl groups in the supercages and in the sodalite cages, respectively [41,42]. In the low energy region, the spectrum showed a band at 1640 cm^{-1} characteristic of the $\delta(\text{H}_2\text{O})$ mode of absorbed water [43]. The band at ca. 1020 cm^{-1} is usually attributed to the asymmetric stretching of Al–O–Si chain of zeolite. The symmetric stretching and bending frequency bands of Al–O–Si framework of zeolite appear at ca. 727 and 513 cm^{-1} , respectively [44]. As an example, the spectra for CrNaY and [CrL_{1a}]NaY provide evidence that the zeolite framework is preserved throughout calcination and immobilization of the 1,3-diphenyltriazenido chromium complex (Fig. 5). The spectrum of [CrL_{1a}]NaY shows the bands at 1492 and 1593 cm^{-1} , attributed to the $\nu(\text{N}=\text{N}=\text{N})$ of the triazene group, which proves that this ligand was successfully coordinated into the framework zeolite.

The EPR spectra of the triazenido chromium complexes on NaY and CrNaY are shown in Fig. 6, while Table 1 presents characteristic EPR data. The principal *g*-value of the samples was calculated from their EPR spectra by using the standard procedure [26,45].

CrNaY exhibit a fairly sharp, slightly anisotropic signal at a g_{\perp} value around 1.97 (denoted g_1 in Table 1), which probably represents Cr species in square pyramidal conformation, since the g_{\parallel} line appears to be around 1.957 [26]. The immobilized samples contain similar bands and in addition to that a signal at $g = 2.0$ (denoted g_2 in Table 1). However, it should be noted that the spectral features of the [CrL_{1c}]NaY sample are quite similar to those of the parent CrNaY. The EPR lines for FAU supports and for CrL_{1a} and CrL_{1b} in FAU supports appear as a combination of the mentioned signals at $g = 1.97$ and 2.0. Especially in the case of the [CrL_{1a}]HY_{SBR} sample an anisotropic broadening of the $g = 1.97$ signal is observed, which could suggest some change in the coordination environment of Cr

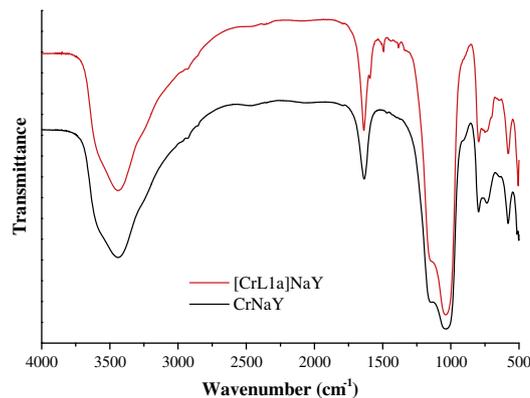


Fig. 5. Infrared spectra of CrNaY and [CrL_{1a}]NaY.

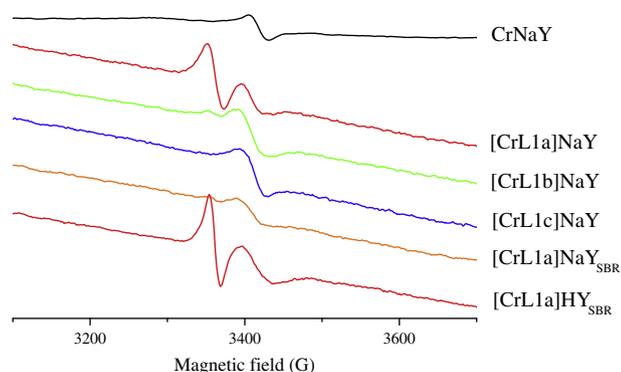


Fig. 6. EPR spectra for CrNaY and the respective catalysts. Data collected at 77 K.

Table 1
EPR data for the different samples.

Sample	EPR signals			
	g_1	Band width (pp ^a) (G)	g_2	Band width (pp) (G)
CrNaY	1.971	25		
[CrL _{1a}]NaY	1.973	28	2.002	22
[CrL _{1b}]NaY	1.978	35	2.003	20
[CrL _{1c}]NaY	1.972	32		
[CrL _{1a}]NaY _{SBR}	1.976	32	2.001	19
[CrL _{1a}]HY _{SBR}	1.975	39	2.002	15

^a pp: Peak to peak band width on derivative EPR spectra.

due to the complexation into FAU supercages [26]. Since the samples were only dried at 120 °C, it is reasonable to assume that some intra-zeolitic water might still be present, which coordinates to Cr(III) in the *in situ* synthesis of the complex.

Combined chemical, thermogravimetric and textural analyses were performed to compare the immobilization of chromium complexes within the different biosorption supports. The combined data are detailed in Table 2.

The immobilization of the Cr complexes in biosorption supports was confirmed by the analytical data of carbon, nitrogen and metal. The highest Cr/N ratio observed for CrNaY_{SBR} suggests the presence of a fraction of chromium not coordinated with the ligand. It was found that a part of this chromium could be located in framework sites that are inaccessible for the ligands [27,45]. The lower nitrogen amount in the [CrL_{1c}]NaY catalyst shows that the complex with 1,3-bis(*p*-nitrophenyl)triazene (**1c**) ligand was not achieved, in agreement with Raman, FTIR and EPR analyses. These results are due to the decrease of the donor groups strength of the triazenido ligand by the NO₂ group in *para* position in acidic medium [31].

Table 2
Characterization data of the materials.

Support	Ligand	Elemental analysis (% w/w)				Cr/N	TGA analysis Complex mass (% w/w)	BET surface area (m ² g ⁻¹)
		Cr ^a	C ^b	N ^b				
CrNaY		0.75	0	0			593	
	1a	0.71	0.75	0.19	3.74	2.5	196	
	1b	0.71	1.23	0.20	3.55	2.1	317	
	1c	0.72	0.10	0.02		0.2	563	
CrNaY _{SBR}		0.46	0	0			590	
	1a	0.47	0.32	0.05	9.40	0.8	540	
CrHY _{SBR}		0.59	0	0			496	
	1a	0.55	1.04	0.29	1.89	2.5	201	

^a Cr loading on FAU supports determined by ICP-AES analysis.

^b Carbon and nitrogen from Cr complexes obtained by elemental analysis.

It should be referred that the biosorption assays were performed at pH 4.00 in order to increase the reduction of the Cr(VI) species.

The low amount of Cr complexes is related to the presence of the different Cr species in the biosorption FAU supports. Cr(VI) species detected by XPS and Raman are not coordinated with the triazenido ligands which means that only a small fraction of chromium takes part in the synthesis of the complex and this fraction is trivalent.

Thermogravimetric analysis also confirmed that immobilization of Cr complexes was achieved. TG and DTG curves of the biosorption FAU supports and of the catalysts show a weight loss at 110 °C which is attributed to the loss of water molecules present in the framework of the zeolite. After the synthesis, the catalysts based in 1,3-diphenyltriazene (**1a**) and 1,3-bis(*p*-methylphenyl)triazene (**1b**) ligands presented a secondary weight loss, taking place at a higher temperature, around 410 °C, which is attributed to the decomposition of the organic matter from the complexes. Fig. 7 presents the TGA–DTG data for [CrL_{1a}]NaY, as an example.

The different weight losses observed for the catalysts confirm that the 1,3-bis(*p*-nitrophenyl)triazene (**1c**) ligand is not coordinated with chromium. In the case of the chromium complex formed in CrNaY_{SBR} the TGA results show that the lower amount of the complex is related to the lower amount of entrapped chromium.

The extent of the secondary weight loss varied with the different combinations of support and 1,3-diphenyltriazene (**1a**) ligand. This ligand was able to form up to 2.5% (w/w) mass of chromium complex within CrNaY and CrHY_{SBR}. Despite having different chromium loadings, the formation of complex with **1a** ligand was comparable between these two supports.

For all catalysts, the total surface areas were calculated by the BET equation (S_{BET}) and the data show a reduction in area after the complexation, when compared to the respective parent supports, which is a further indication of successful immobilization [46,47]. The decreasing of the BET area is specially significant for the catalysts obtained from CrNaY and CrHY_{SBR}.

3.2. Oxidation of cyclohexanol

The catalytic behaviour of the different chromium complexes in biosorption FAU supports was tested for the oxidation of cyclohexanol using TBHP as an oxygen source. Blank experiments without catalyst and in the presence of parent NaY or HY were performed under identical experimental conditions. Cyclohexanone was found to be the only significant product of the reaction studied [48]. Table 3 presents the results achieved by different catalysts after 23 h.

From the results presented in Table 3, it is seen that the presence of chromium ions on the support greatly increases cyclohexanol conversion, while parent NaY and HY zeolites proved to be

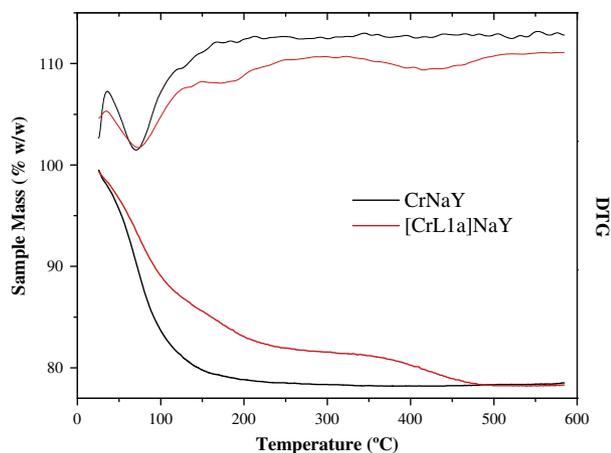


Fig. 7. TG and DTG curves of CrNaY and [CrL_{1a}]NaY.

Table 3
Results for the catalytic oxidation of cyclohexanol.

Catalyst	Cyclohexanol conversion (%)	Analytical error (%)	TON ^a	Cr Leaching (μg)
(blank reaction)	18.6	±3.5		
NaY zeolite	15.8	±5.3		
HY zeolite	14.2	±1.4		
CrNaY	61.2	±1.2	246	47.8
[CrL _{1a}]NaY	57.3	±3.0	243	28.5
[CrL _{1b}]NaY	54.1	±1.7	201	17.5
[CrL _{1c}]NaY	63.5	±2.8	266	40.9
CrNaY _{SBR}	56.8	±4.5	373	29.6
[CrL _{1a}]NaY _{SBR}	49.1	±4.6	315	18.3
CrHY _{SBR}	48.0	±1.1	245	20.1
[CrL _{1a}]HY _{SBR}	42.9	±2.9	235	4.4

^a Turnover number (TON) was determined from the converted cyclohexanol moles over the initial molarity of Cr in the respective catalyst.

inefficient for this reaction, as the substrate conversion is very close to blank. TON values are higher for the catalysts based on NaY prepared by SBR method. This might be due to the presence of chromium species in zeolite sites that are accessible to the reactants [49].

The samples with immobilised chromium complex present a slight decrease in cyclohexanol conversion when compared to biosorption FAU supports except [CrL_{1c}]NaY. The CrNaY and [CrL_{1c}]NaY catalysts led to very close cyclohexanol conversion values. This result supports the characterization data that indicated

almost no complexation took place in the latter material. Since chromium leaching from Cr-containing catalysts is acknowledged, even when TBHP oxidant is used [13], liquid samples of each reaction were digested and analysed for total chromium content. The result of this determination is presented in Table 3. It may be seen that chromium was detected on the reaction medium of all modified materials, proving that there is a contribution from homogeneous catalysis to the overall conversion. However, the immobilized catalysts prepared from biosorption FAU supports presented a smaller amount of leached chromium when compared to the correspondent untreated biosorption supports. CrHY_{SBR} is the least leaching-prone material, while leaching from its complex immobilized counterpart, [CrL_{1a}]HY_{SBR} is negligible. Catalysts based on NaY show higher leaching of active species.

3.3. Oxidation of cyclohexene

The catalysts were also tested for the oxidation of cyclohexene. The reaction mechanism in the presence of Cr-containing catalysts has already been proposed [29] and the main products obtained from this reaction are 2-cyclohexene-1-ol (CyOL), 2-cyclohexene-1-one (CyONE), and 1-*tert*-butylperoxy-2-cyclohexene (CyOX), proving that only allylic oxidation takes place. The latter was found to behave as an intermediary towards the formation of CyONE and CyOL, which has been reported by other authors [46].

The overall conversion of cyclohexene, product selectivity and TON are presented in Table 4.

It was found that the presence of chromium in the biosorption FAU supports greatly increases the conversion of cyclohexene. The products distribution depends on catalyst used. The NaY and HY zeolites were just able to originate the intermediary CyOX. CyONE was the main product when chromium modified catalysts were used and for these catalysts a small decrease in cyclohexene conversion was observed, when compared to the parent biosorption supports.

The highest cyclohexene conversion was achieved for the CrHY_{SBR} catalyst. The comparison of substrate conversion reached in blank reaction and in the presence of NaY and HY, shows that HY zeolite is slightly active in this reaction, whereas NaY is inactive. The substrate conversion values with allowance for the background reaction (HY) are 61.1% and 59.8% for CrHY_{SBR} and for [CrL_{1a}]HY_{SBR}, respectively, and they are of the same order of magnitude as for CrNaY_{SBR} based counterparts. This fact explains the higher conversion of CrHY based catalysts and they can be considered as bifunctional catalysts for this particular reaction.

[CrL_{1c}]NaY catalyst leads to lower substrate conversion than CrNaY. This might be due to the retardation effect on TBHP decomposition (free radical formation) by the presence of small amounts of free **1c** ligand in [CrL_{1c}]NaY [50].

Table 4
Conversion, product selectivity and turn-over numbers for the oxidation of cyclohexene.

Catalyst	Cyclohexene conversion (%)	Analytical error (%)	Product selectivity (%)			TON
			CyOL	CyONE	CyOX	
(blank reaction)	16.9	±5.9			100.0	
NaY	11.1	±2.2			100.0	
HY	28.7	±4.8			100.0	
CrNaY	69.0	±1.8	21.6	67.8	10.7	190
[CrL _{1a}]NaY	56.0	±1.5	12.2	69.4	18.5	164
[CrL _{1b}]NaY	55.1	±2.5	15.1	74.0	10.8	140
[CrL _{1c}]NaY	60.4	±3.1	15.4	71.6	13.0	173
CrNaY _{SBR}	61.2	±1.0	16.7	68.9	14.3	278
[CrL _{1a}]NaY _{SBR}	60.8	±1.1	14.4	63.0	22.7	267
CrHY _{SBR}	72.9	±1.4	25.0	65.0	10.0	255
[CrL _{1a}]HY _{SBR}	71.6	±1.3	22.8	66.8	10.3	269

The lower substrate conversion for chromium complex modified catalysts is observed as it was for cyclohexanol oxidation. As it was mentioned above, the chromium entrapped in the zeolite by the biosorption process is in the trivalent form before calcination. The experimental evidences clearly demonstrated that part of the trivalent chromium impregnated onto zeolite surface is oxidised to hexavalent chromium during the calcination process, as it was seen for chromium(III) acetate impregnated onto silica gel [51]. During the calcination process, the bulky CrO_3 can be gradually grafted onto zeolite surface through esterification reaction with surface hydroxyl groups [51,52]. It is still very difficult to distinguish between anchored Cr(VI) species from bulky CrO_3 by XPS. Nevertheless, according to the results from Raman, TGA and XPS the existence of mixed oxidation states of chromium species, namely Cr(III) and Cr(VI) in the studied catalysts may be postulated. It is known from literature that Cr(III) complexes are active in oxidation of cyclohexene [53], as well as free CrO_3 and anchored Cr(VI) species [54]. Thus, the triazenido complexes formed in zeolite matrix are also catalytically active but probably restrain the access of the substrate and oxidant to other catalytic active sites. The lowering of substrate conversion (cyclohexanol and cyclohexene) can be explained by the blocking effect of the complex formed.

4. Conclusions

Chromium complexes have been successfully prepared within biosorption FAU supports, using 1,3-diphenyltriazene derivatives. The electrowithdrawing properties of substituents of these ligands play an essential role in the coordination process. The supports, based in a low-cost system combining the biosorption properties of a microorganism with the ion exchange properties of a zeolite, were able to remove hexavalent chromium from contaminated water and were used for this immobilization. After the biosorption processes, FAU zeolites loaded with chromium were used as competitive catalysts in the oxidation of cyclohexanol and cyclohexene. CrNaY -derived catalysts promoted higher cyclohexanol conversion, whereas CrHY -derived catalysts presented bifunctionality for the oxidation of cyclohexene, ultimately yielding a higher conversion. The immobilization of chromium complexes proved to be efficient on limiting the metal leaching proneness observed on the untreated biosorption supports.

Acknowledgments

H. Figueiredo and B. Silva are thankful to the “FCT – Fundação para a Ciência e Tecnologia” for their respective research grants. IKB thanks FCT for the contract under the program Ciência 2007. This work was partially funded by the Centre of Biological Engineering and the Centre of Chemistry (University of Minho, Portugal) through FCT strategic projects PEst-OE/EQB/LA0023/2013 and PEst-C/QUI/UI0686/2011 (nF-COMP-01-0124-FEDER-022716), the Project “BioEnv – Biotechnology and Bioengineering for a sustainable world”, REF. NORTE-07-0124-FEDER-000048, co-funded by the Programa Operacional Regional do Norte (ON.2 – O Novo Norte), QREN and FEDER, and by the Spanish Ministry of Science and Innovation (CTQ2008-04261/PPQ).

References

- [1] M. Gavrilescu, Removal of Heavy Metals from the Environment by Biosorption, *Eng. Life Sci.* 4 (2004) 219–232.
- [2] E. Erdem, N. Karapinar, R. Donat, The removal of heavy metal cations by natural zeolites, *J. Colloid Interface Sci.* 280 (2004) 309–314.
- [3] H. Eccles, Treatment of metal-contaminated wastes: why select a biological process?, *Trends Biotechnol.* 17 (1999) 462–465.
- [4] A. Agrawal, V. Kumar, B.D. Pandey, Remediation options for the treatment of electroplating and leather tanning effluent containing chromium – a review, *Miner. Process. Extr. Metall. Rev.* 27 (2006) 99–130.
- [5] H. Figueiredo, I.C. Neves, C. Quintelas, T. Tavares, M. Taralunga, J. Mijoin, P. Magnoux, Oxidation catalysts prepared from biosorbents supported on zeolites, *Appl. Catal. B Environ.* 66 (2006) 274–280.
- [6] H. Figueiredo, B. Silva, C. Quintelas, I.C. Neves, T. Tavares, Effect of the supporting zeolite structure on Cr biosorption: performance of a single step reactor and of a sequential batch reactor – a comparison study, *Chem. Eng. J.* 163 (2010) 22–27.
- [7] H. Figueiredo, B. Silva, C. Quintelas, M.F.R. Pereira, I.C. Neves, T. Tavares, Biosorption of hexavalent chromium based on modified Y zeolites obtained by alkaline treatment, *Environ. Eng. Manage. J.* 9 (2010) 305–311.
- [8] B. Silva, H. Figueiredo, I.C. Neves, T. Tavares, The role of pH on Cr(VI) reduction and removal by *Arthrobacter Viscosus*, *Int. J. Chem. Biomol. Eng.* 43 (2009) 59–62.
- [9] B. Silva, H. Figueiredo, C. Quintelas, I. Neves, T. Tavares, Zeolites as supports for the biorecovery of hexavalent and trivalent chromium, *Microporous Mesoporous Mater.* 116 (2008) 555–560.
- [10] M.T. Tavares, C. Quintelas, H. Figueiredo, I. Neves, Comparative study between natural and artificial zeolites as supports for biosorption systems Maria Teresa Tavares, *Mater. Sci. Forum.* 516 (2006) 1294–1298.
- [11] B. Silva, H. Figueiredo, O.S.G.P. Soares, M.F.R. Pereira, J.L. Figueiredo, A.E. Lewandowska, M.A. Bñares, I.C. Neves, T. Tavares, Evaluation of ion exchange-modified Y and ZSM5 zeolites in Cr(VI) biosorption and catalytic oxidation of ethyl acetate, *Appl. Catal. B Environ.* 117–118 (2012) 406–413.
- [12] I.W.C.E. Arends, R.A. Sheldon, Activities and stabilities of heterogeneous catalysts in selective liquid phase oxidations: recent developments, *Appl. Catal. A Gen.* 212 (2001) 175–187.
- [13] Z. Lounis, A. Riahi, F. Djafri, J. Muzart, Chromium-exchanged zeolite (CrE-ZSM-5) as catalyst for alcohol oxidation and benzylic oxidation with t-BuOOH, *Appl. Catal. A Gen.* 309 (2006) 270–272.
- [14] R.A. Sheldon, M. Wallau, I.W.C.E. Arends, U. Schuchardt, Heterogeneous catalysts for liquid-phase oxidations: philosophers' stones or Trojan Horses?, *Acc Chem. Res.* 31 (1998) 485–493.
- [15] D.E. De Vos, M. Dams, B.F. Sels, P.A. Jacobs, Ordered mesoporous and microporous molecular sieves functionalized with transition metal complexes as catalysts for selective organic transformations, *Chem. Rev.* 102 (2002) 3615–3640.
- [16] D.E. Vos, P.P. Knops-Gerrits, R.F. Parton, B.M. Weckhuysen, P.A. Jacobs, R.A. Schoonheydt, Coordination chemistry in zeolites, *J. Incl. Phenom. Macrocycl. Chem.* 21 (1995) 185–213.
- [17] A. Corma, H. Garcia, Supramolecular host–guest systems in zeolites prepared by ship-in-a-bottle synthesis, *Eur. J. Inorg. Chem.* 2004 (2004) 1143–1164.
- [18] P. McMorn, G.J. Hutchings, Heterogeneous enantioselective catalysts: strategies for the immobilisation of homogeneous catalysts, *Chem. Soc. Rev.* 33 (2004) 108–122.
- [19] C.R. Jacob, S.P. Varkey, P. Ratnasamy, Selective oxidation over copper and manganese salens encapsulated in zeolites, *Microporous Mesoporous Mater.* 22 (1998) 465–474.
- [20] M. Salavati-Niasari, E. Zamani, M.R. Ganjali, P. Norouzi, Synthesis, characterization and liquid phase oxidation of cyclohexanol using tert-butylhydroperoxide over host (zeolite-Y)/guest (copper(II) complexes of 12- and 13-membered diaza dioxo Schiff-base macrocyclic ligand) nanocomposite materials (HGNM), *J. Mol. Catal. A Chem.* 261 (2007) 196–201.
- [21] M. Jhansi, L. Kishore, K. Anand, A. Kumar, Kinetic study of oxidation of cyclohexanol using bimetallic iron–copper macrocyclic complex catalyst, *Catal. Commun.* 10 (2008) 285–290.
- [22] J.-D. Lou, L.-H. Zhu, L.-L. Pan, L. Li, F. Li, C.-L. Gao, Solvent-Free Oxidation of Secondary Alcohols with Chromium Trioxide, *Synth. React. Inorg. Met. Nano-Metal Chem.* 36 (2006) 585–587.
- [23] C. Jin, W. Fan, Y. Jia, B. Fan, J. Ma, R. Li, Encapsulation of transition metal tetrahydro-Schiff base complexes in zeolite Y and their catalytic properties for the oxidation of cycloalkanes, *J. Mol. Catal. A Chem.* 249 (2006) 23–30.
- [24] J. Muzart, Homogeneous Cr(VI)-catalyzed benzylic, allylic and propargylic oxidations by tert-butyl hydroperoxide, *Mini. Rev. Org. Chem.* 6 (2009) 9–20.
- [25] J. Muzart, Chromium-catalyzed oxidations in organic synthesis, *Chem. Rev.* 92 (1992) 113–140.
- [26] B.M. Weckhuysen, I.E. Wachs, R.A. Schoonheydt, Surface chemistry and spectroscopy of chromium in inorganic oxides, *Chem. Rev.* 96 (1996) 3327–3350.
- [27] M. Menon, A. Pramanik, S. Chattopadhyay, N. Bag, A. Chakravorty, Chemistry of $[\text{Ru}(1,3\text{-diaryltriazene})_2(\text{PPh}_3)_2]_z$ ($z = 0, +$), a hindered Ru(II), IIIN_2P_2 family with valence-independent geometry, *Inorg. Chem.* 34 (1995) 1361–1367.
- [28] A.F.M.J. Van der Ploeg, G. Van Koten, K. Vrieze, Synthesis of novel dinuclear formamidino and triazenido compounds $[\text{2,6-(Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3](\text{p-tolN}_2\text{N})\text{PtAgBr}$ ($Y = \text{CH, N}$) containing a platinum–silver bond, *Inorg. Chem.* 21 (1982) 2026–2031.
- [29] H. Figueiredo, B. Silva, C. Quintelas, M.M.M. Raposo, P. Parpot, A.M. Fonseca, A.E. Lewandowska, M.A. Bñares, I.C. Neves, T. Tavares, Immobilization of chromium complexes in zeolite Y obtained from biosorbents: Synthesis, characterization and catalytic behaviour, *Appl. Catal. B Environ.* 94 (2010) 1–7.
- [30] D. Pfeiffer, I.A. Guzei, L.M. Liable-Sands, M.J. Heeg, A.L. Rheingold, C.H. Winter, Synthesis, structure, and characterization of lanthanide complexes bearing 1,3-diphenyltriazene ligands, *J. Organomet. Chem.* 588 (1999) 167–175.
- [31] J.J. Nuricumbo-Escobar, C. Campos-Alvarado, G. Ríos-Moreno, D. Morales-Morales, P.J. Walsh, M. Parra-Hake, Binuclear palladium(I) and palladium(II) complexes of ortho-functionalized 1,3-bis(aryl)triazene ligands, *Inorg. Chem.* 46 (2007) 6182–6189.

- [32] H. Figueiredo, B. Silva, M.M.M. Raposo, A.M. Fonseca, I.C. Neves, C. Quintelas, T. Tavares, Immobilization of Fe(III) complexes of pyridazine derivatives prepared from biosorbents supported on zeolites, *Microporous Mesoporous Mater.* 109 (2008) 163–171.
- [33] P. Echlin, Low-voltage energy-dispersive X-ray microanalysis of bulk biological materials, *Microsc. Microanal.* 4 (1999) 577–584.
- [34] S.-Y. Li, J. Millstone, C. Mirkkin, V. Dravid, Detection of phosphorus in biological samples with analytical electron microscopy, *Microsc. Microanal.* 13 (2007) 456–457.
- [35] L. Dambies, C. Guimon, S. Yiacoumi, E. Guibal, Characterization of metal ion interactions with chitosan by X-ray photoelectron spectroscopy, *Colloids Surfaces A Physicochem. Eng. Asp.* 177 (2000) 203–214.
- [36] D. Park, Y.-S. Yun, J.M. Park, XAS and XPS studies on chromium-binding groups of biomaterial during Cr(VI) biosorption, *J. Colloid Interface Sci.* 317 (2008) 54–61.
- [37] B.M. Weckhuysen, H.J. Spooen, R.A. Schoonheydt, A quantitative diffuse reflectance spectroscopy study of chromium-containing zeolites, *Zeolites*. 14 (1994) 450–457.
- [38] Y. Huang, R.M. Paroli, A.H. Delgado, T.A. Richardson, An FT-Raman study of solid-state ion exchange in zeolites, *Spectrochim Acta Part A Mol. Biomol. Spectrosc.* 54 (1998) 1347–1354.
- [39] B. Kwiecinska, I. Suárez-Ruiz, C. Paluszkiwicz, S. Rodrigues, Raman spectroscopy of selected carbonaceous samples, *Int. J. Coal Geol.* 84 (2010) 206–212.
- [40] P.-P. Knops-Gerrits, D. De Vos, E.J.P. Feijen, P.A. Jacobs, Raman spectroscopy on zeolites, *Microporous Mater.* 8 (1997) 3–17.
- [41] S. Morin, P. Ayrault, N.S. Gnep, M. Guisnet, Influence of the framework composition of commercial HFAU zeolites on their activity and selectivity in m-xylene transformation, *Appl. Catal. A Gen.* 166 (1998) 281–292.
- [42] K. Tanaka, C.-K. Choo, Y. Komatsu, K. Hamaguchi, M. Yamaki, T. Itoh, T. Nishigaya, R. Nakata, K. Morimoto, Characterization and preparation of chained Si species in zeolite supercages, *J. Phys. Chem. B.* 108 (2004) 2501–2508.
- [43] C. Sedlmair, B. Gil, K. Seshan, A. Jentys, J.A. Lercher, An in situ IR study of the NO_x adsorption/reduction mechanism on modified Y zeolites, *Phys. Chem. Chem. Phys.* 5 (2003) 1897–1905.
- [44] B. Dutta, S. Jana, R. Bera, P.K. Saha, S. Koner, Immobilization of copper Schiff base complexes in zeolite matrix: preparation, characterization and catalytic study, *Appl. Catal. A Gen.* 318 (2007) 89–94.
- [45] M. Álvaro, B. Ferrer, H. García, A. Sanjuán, Heterogeneous Gif oxidation of cyclohexane using Fe³⁺-picolinate complex encapsulated within zeolites, *Tetrahedron*. 55 (1999) 11895–11902.
- [46] M. Salavati-Niasari, Host (nanopores of zeolite-Y)/guest [manganese(II) with 12-membered tetradentate N₂O₂, N₂S₂ and N₄ donor macrocyclic ligands] nanocatalysts: flexible ligand synthesis, characterization and catalytic activity, *Transition Met. Chem.* 33 (2008) 443–452.
- [47] H.S. Abbo, S.J.J. Titinchi, Synthesis and catalytic activity of Cu(II), Fe(III) and Bi(III) complexes of Thio-Schiff base encapsulated in zeolite-Y for hydroxylation of phenol, *Top. Catal.* 53 (2010) 254–264.
- [48] I. Kuźniarska-Biernacka, K. Biernacki, A.L. Magalhães, A.M. Fonseca, I.C. Neves, Catalytic behavior of 1-(2-pyridylazo)-2-naphthol transition metal complexes encapsulated in Y zeolite, *J. Catal.* 278 (2011) 102–110.
- [49] C.T. Dalton, K.M. Ryan, I.J. Langan, É.J. Coyne, D.G. Gilheany, Asymmetric alkene epoxidation with chromium oxo salen complexes: effect of π-rich and other types of additives, *J. Mol. Catal. A Chem.* 187 (2002) 179–187.
- [50] G. Rothenberg, H. Wiener, Y. Sasson, Pyridines as bifunctional co-catalysts in the CrO₃-catalyzed oxygenation of olefins by t-butyl hydroperoxide, *J. Mol. Catal. A Chem.* 136 (1998) 253–262.
- [51] B. Liu, Y. Fang, M. Terano, High resolution X-ray photoelectron spectroscopic analysis of transformation of surface chromium species on Phillips CrO_x/SiO₂ catalysts isothermally calcined at various temperatures, *J. Mol. Catal. A Chem.* 219 (2004) 165–173.
- [52] A. Gaspar, J.L. Brito, L. Dieguez, Characterization of chromium species in catalysts for dehydrogenation and polymerization, *J. Mol. Catal. A Chem.* 203 (2003) 251–266.
- [53] P.B. Samnani, P.K. Bhattacharya, P.A. Ganeshpure, V.J. Koshy, S. Satish, Mixed ligand complexes of chromium(III) and iron(III): synthesis and evaluation as catalysts for oxidation of olefins, *J. Mol. Catal. A Chem.* 110 (1996) 89–94.
- [54] A. Sakthivel, S.E. Dapurkar, P. Selvam, Allylic oxidation of cyclohexene over chromium containing mesoporous molecular sieves, *Appl. Catal. A Gen.* 246 (2003) 283–293.