



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,*}

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

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

^c Instituto 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

Download English Version:

<https://daneshyari.com/en/article/147531>

Download Persian Version:

<https://daneshyari.com/article/147531>

[Daneshyari.com](https://daneshyari.com)