CATALYTIC REUTILIZATION OF Cr(VI) BIOSORPTION SUPPORTS

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Introduction

This work presents the usage of zeolites as supports for a biofilm of *Arthrobacter viscosus.* The combined zeolite-biomass system showed capacity for the treatment of Cr(VI) solutions *via* reduction of the Cr(VI) ions to Cr(III) species, which are able to be ion-exchanged by the zeolite (Cr(VI) is unable to be directly ion-exchanged by zeolites).

The Cr-laden zeolites can be recovered and thermally treated to yield a purely inorganic Cr-containing inorganic matrix. This matrix was tested as catalysts for gas and liquid-phase oxidation reactions. However, liquid-phase catalysts require that the metal ions are immobilized on the surface to avoid leaching. Therefore, the Cr-containing zeolites were treated with chelating agents to form complex structures within the zeolite pores, in a process known as *ship-in-a-bottle synthesis.* The prepared catalysts were tested in the oxidation reaction of cyclohexene and cyclohexanol.

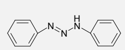
Experimental Section

a) Biotreatment of Cr(VI) solutions

Work was carried out in batch reactors, in either single-step or sequencing batch reactor (SBR) operation. All reactors were started with:

150.0 mL of $K_2Cr_2O_7$ (100 mg_{Cr}/L); Biomass concentration: 5.0 g/L, 1.0 g of zeolite (HY or NaY) and pH kept at 4.0

b) Immobilization of metal complex



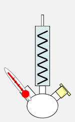
Diphenyltriazene ligand (ligand L)

1.0 g of Cr-zeolite (host) is refluxed with 2.8 mmol of ligand L in 100 mL ethanol for 24 h.

Soxhlet extraction was carried out for 6 h with 50 mL of dichloromethane.

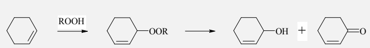
Finally, the solid is stabilised in 50 mL of $NaNO_3$ 0.01 M for 24 h.

c) Catalytic oxidation reactions



Reactions were carried or in batch conditions, in 23 hours cycles, using *tert*-buthylhydroperoxide as oxidant. Reaction pathways are:

Cyclohexene:

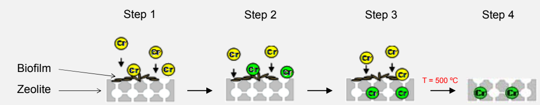


Cyclohexanol:

Process Overview

1. Biotreatment of aqueous Cr(VI)

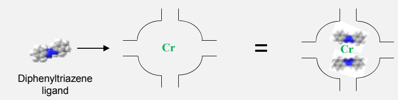
Cr(VI) species are negatively-charged and therefore, direct removal of these with zeolites is not possible.



The combination of the *Arthrobacter viscosus* bacterium and FAU zeolites (step 1) results in a system that performs the bioreduction of Cr(VI) (yellow) into Cr(III) (green), which can be ion-exchanged by the zeolite (steps 2 and 3). Thermal treatment is applied to remove biomass, yielding a Cr-containing inorganic support which is used for the preparation of Cr catalysts (step 4).

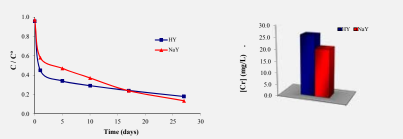
2. Immobilization of Cr by the flexible ligand method

The FAU zeolite structure possesses cavities interconnected by pores. These allow *in-situ* formation of metal complexes by diffusing a ligand molecule through the pores, which will ultimately coordinate with the Cr(III) ions, immobilising them in the zeolite cavity.



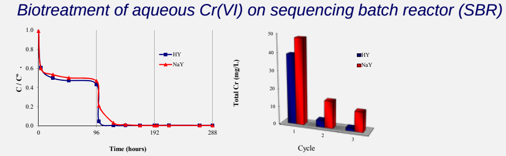
Experimental Results

Biotreatment of aqueous Cr(VI) on single-batch



Cr(VI) evolution and final total Cr concentration for systems based on HY and NaY zeolites.

Biotreatment of aqueous Cr(VI) on sequencing batch reactor (SBR)

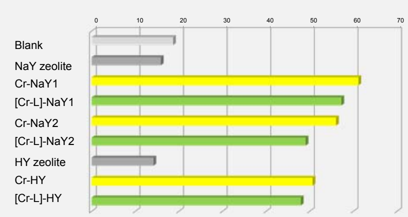


Cr(VI) evolution and final total Cr concentration for systems based on HY and NaY zeolites.

The operation of the *Arthrobacter viscosus*-zeolite system in SBR mode allows overcoming the limitation on Cr(VI) reduction witnessed after 24 hours (best illustrated by the single batch results).

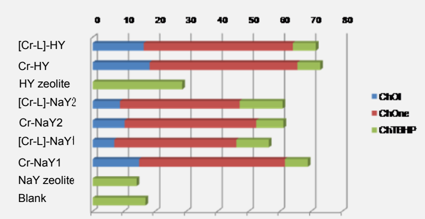
HY zeolite proved to be the best support for assisting the initial Cr(VI) reduction, which explains the better comparative results using this zeolite in SBR mode. NaY zeolite proved to be the best support for the subsequential Cr(III) removal, which explains the better performance of this support in single-batch experiments.

Oxidation of cyclohexanol



Conversion of cyclohexanol for the different catalysts. Immobilized supports are marked with "[Cr-L]" as reference to the complex.

Oxidation of cyclohexene



Conversion of cyclohexene for the different catalysts and respective selectivity to 2-cyclohexene-1-one (ChOne), 2-cyclohexene-1-ol (ChOl) and 2-cyclohexene-1-*tert*-buthylhydroperoxide (ChTBHP).

The presence of Cr on the zeolite matrix promotes a drastic increase in overall conversion, for both reactions.

The catalysts with immobilized complexes (marked with [Cr-L] prefix) present comparable conversion and selectivity to the respective inorganic matrix, used on its preparation.

Acknoledgements

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