Contents lists available at SciVerse ScienceDirect







journal homepage: www.elsevier.com/locate/apcata

Mesoporous carbon as an efficient catalyst for alcoholysis and aminolysis of epoxides

Inês Matos^{a,*}, Paulo Duarte Neves^a, José Eduardo Castanheiro^b, Elena Perez-Mayoral^c, Rosa Martin-Aranda^c, Carlos Duran-Valle^d, Joaquim Vital^a, Ana M. Botelho do Rego^e, Isabel M. Fonseca^{a,*}

^a REQUIMTE/CQFB, Faculdade de Ciências e Tecnologia, Universidade Nova de, Lisboa, 2829-516 Caparica, Portugal

^b Centro de Química de Évora, Departamento de Química, Universidade de Évora, 7000-671 Évora, Portugal

^c Departamento de Química Inorgánica y Química Técnica, Facultad de Ciencias, UNED, Paseo Senda del Rey 9, 28040 Madrid, Spain

^d Departamento de Química Orgânica e Inorgánica, Universidad de Extremadura, Avda de Elvas, s/n, E-06006 Badajoz, Spain

^e CQFM and IN, Technical University of Lisbon, IST, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

ARTICLE INFO

Article history: Received 2 March 2012 Received in revised form 28 May 2012 Accepted 21 June 2012 Available online 30 June 2012

Keywords: Ring opening Mesoporous carbon Alcoholysis of epoxides Aminolysis of epoxides

ABSTRACT

The ring opening reaction of epoxides by alcohols and amines using mesoporous activated carbon as efficient and environmentally friendly heterogeneous catalyst is reported. Carbon xerogels were synthesized by polymerization of resorcinol and formaldehyde. The surface of the activated carbon was oxidized in liquid phase with HNO₃ and then functionalized with H_2SO_4 .

Chemical and textural characterization by elemental analysis, pH_{PZC} , TPD, BET and XPS indicates that oxidation in liquid phase is effective in the introduction of strong acid groups in the carbon surface. The functionalization with H_2SO_4 led to more acid functional groups, as expected. The activated carbons were tested in alcoholysis and aminolysis of epoxides, having been obtained excellent results of conversion and selectivity, both over 95%.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

For the sustainability of our ever evolving modern world it is necessary to keep looking for new and diverse ways to optimize the available resources. In this sense the development of new and less expensive heterogeneous catalysts and their application in reactions with synthetic interest such as the ring opening of epoxides is an important challenge with industrial repercussions.

Epoxides are versatile and valuable intermediates in organic synthesis. These oxygen heterocycles are significantly more reactive than other ethers due to the strain induced by the presence of the three-membered ring; thus, epoxides undergo ring-opening reactions with alcohols to give β -alkoxy alcohols [1,2], which may result in valuable organic solvents or be used as a synthetic route for the synthesis of relevant compounds such as antitumorals or immunosuppressives [3].

It is also possible to synthesize amino alcohols by the amination of epoxides, where the cleavage of the C–O bond occurs in the presence of an amine. β -Amino alcohols are of growing importance for the pharmaceutical industry for their role as treatment agents of several human disorders [4–6].

Among the possible synthetic approaches yielding these products, the ring opening reaction appears as a very attractive method due to its simplicity leading to the corresponding β -substituted alcohols in high yields.

Suitable epoxide ring opening catalysts include Lewis acids and bases, Brönsted acids, porphyrin complexes [1], triflates [7] and perchlorates [8] in homogeneous phase. Heterogeneous catalysts have also been reported among them polymer supported ferric chloride [9], aluminumdodecatungstophosphate [10] and AlKIT-5 [11].

Other methods used include electrochemical reaction with triorganylborane [12] and microwave assisted synthesis [13–15].

All these catalysts used in the alcoholysis or aminolysis of epoxides show some disadvantages such as high reaction temperature, prolonged reaction time, non-catalytic nature of the reagent, low conversion and low regioselectivity. Furthermore, some of them may become explosive, are expensive, need special conditions for their preparation and, in homogenous phase, have some problems for the separation, isolation and purification of the product. Thus, the development of new catalytic methods for the reaction under study is highly desirable.

^{*} Corresponding authors. Tel.: +351 212948385; fax: +351 212948385. E-mail addresses: ines.matos@fct.unl.pt (I. Matos), blo@fct.unl.pt (I.M. Fonseca).

⁰⁹²⁶⁻⁸⁶⁰X/\$ - see front matter © 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.apcata.2012.06.036