A Comparative Study of Al_2O_3 Fluka, Al_2O_3-69, Al_2O_3-33 and MIL-53Ga, MIL-53Al in Catalytic Epoxidation of Licarin A

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Resumo/Abstract

RESUMO: O presente trabalho concentrou-se na avaliação das eficiências catalíticas de diferentes catalisadores heterogêneos, incluindo três tipos de óxidos de alumínio (Al_2O_3 Fluka, Al_2O_3-169 e Al_2O_3-33) e dois redes metal-orgânicas (MOFs) (MIL-53(Ga) e MIL-53(Al)) na epoxidação da Licarina A com peróxido de hidrogênio (H_2O_2), sendo as reações monitoradas por HPLC. Altas conversões de 95,7% e 95,6% foram obtidas na presença de MIL-53(Ga) e MIL-53(Al), respectivamente, enquanto os experimentos utilizando óxidos de alumínio (Al_2O_3 Fluka, Al_2O_3-169 e Al_2O_3-33) alcançaram conversões de 65,5%, 68,3% e 69,8%, respectivamente. Esse desempenho foi atribuído à geometria de coordenação específica dos sítios ativos catalíticos presentes nos MOFs.

ABSTRACT: The present work focused on the of catalytic efficiencies of different heterogenous catalysts including three types of Aluminum oxides; Al_2O_3 Fluka, Al_2O_3-169 and Al_2O_3-33 and two Metal-Organic Frameworks (MOFs); MIL-53Ga and MIL-53Al) in the epoxidation of Licarin A with hydrogen peroxide H_2O_2 and the reactions were monitored by HPLC. High conversions reached 95.7% and 95.6% were obtained in the presence of MIL-53Ga and MIL-53Al respectively, while experiments using Aluminum oxides; (Al_2O_3 Fluka, Al_2O_3-69 and Al_2O_3-33) achieved conversions of 65.5, 68.3 and 69.8%, respectively. This was attributed to the specific coordination geometry of the catalytically active MOFs sites within these metals.

Keywords: Licarin A, Aluminum oxides, Metal-Organic Frameworks Epoxidation Reaction,

Introduction

Olefines epoxidation is a very useful reaction in industrial organic synthesis. Epoxides are key raw materials for a wide variety of products and much effort is devoted to the development of new active and selective epoxidation catalysts for processes that avoid the formation of large amounts of byproducts (1). Hydrogen peroxide (H_2O_2) offers several advantages as an oxidant in epoxidation, including its powerful oxidizing capabilities, relatively non-toxic nature, and ability to break down into water and oxygen, leaving no harmful residues (2). Licarin A is a naturally occurring compound, belong to group of neolignane. This compound displays a wide range of biological activities including antiparasitic particularly, antitrypanosomal, anthelmintic, and antischistosomal (3). However, the yield from these plants is relatively low; therefore, necessitates chemical transformation for increased availability (4). Aluminum oxides and Metal-Organic Frameworks (MOF) have been reported as an efficient heterogeneous catalyst for epoxidation of alkenes, including terpenes, in the presence of H_2O_2 as an oxidant (5). In the present study, we aim to evaluate catalytic potential of different heterogenous catalysts, applying three Aluminum oxides types and Metal-Organic Frameworks (MOFs) for epoxidation of Licarin A.

Experimental

1. *Materials and Equipment*

EtOAc, isoeugenol, H_2O_2 (Peróxidos do Brasil, 60%) and Aluminum oxides were purchased from Sigma Aldrich, MOFs; MIL-53Ga and MIL-53Al were provide by Gabriela Xavier MOFs research group, UFABC. The NMR Spectra were recorded on a Bruker Avance DRX-500-spectrometer (^{1}H NMR at 500, MHz, and ^{13}C NMR at 100, 125, or 150 MHz), Hexane and ethyl acetate were distilled prior to use. CC was performed using 300-400 mesh silica gel, TLC was carried out on silica gel GF_{254} (Merck). HPLC (1220 infinity from the Lab 506 UFABC

2. *Licarin A preparation and epoxidation reaction*

Licarin A was obtained by oxidative coupling of isoeugenol method reported by Leopold, 195(6); The epoxidation reaction was carried out in 5 vials containing screw caps. (0.083mol, 8.6mg) Licarin A (substrate), was weighed and transferred in to each vial then solubilized by 3mL EtOAc

(solvent), and 13.4g of each catalyst were separately added. 6.66 mmol (0.3775mL) of hydrogen peroxide H_2O_2 as oxidant and 1.0 mmol(0.0536mL) of CH_3NO_2 as internal standard were added in each vial. Reaction mixtures were stirred in constant temperature 80 °C, over a period of 24h. Samples (50 µL) were taken from the reaction mixture through the septum via syringe after 0, 3 and 24 h of reaction. Aliquots of the samples (50 µL) were diluted in 1mL MeOH and analyzed by high performance liquid chromatography (HPLC) XDB-C-18 (4.5×250mm, 5-Micron), Using a mixture of double-distilled water and acetonitrile (73:27) as mobile phase. Flow rate was set at 1 mL/min. The UV detector was set at 282 nm

Results and Discussion

The oxidation reactions of isoeugenol **1**was carried out in a system of $FeCl_3$ in 45% ethanol at 4 °C for 48 h to give Licarin A **2** in yield of 36.3%. the structure Licarin A was confirmed by ^1H and ^{13}C-NMR. We modified the alkenyl side chain of Licarin A to obtain Licarin A epoxide **3**, Fig **1.**

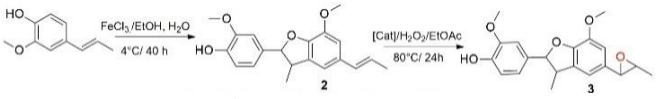

Fig. 1: Synthesis of Licarin A and its epoxidation reaction.

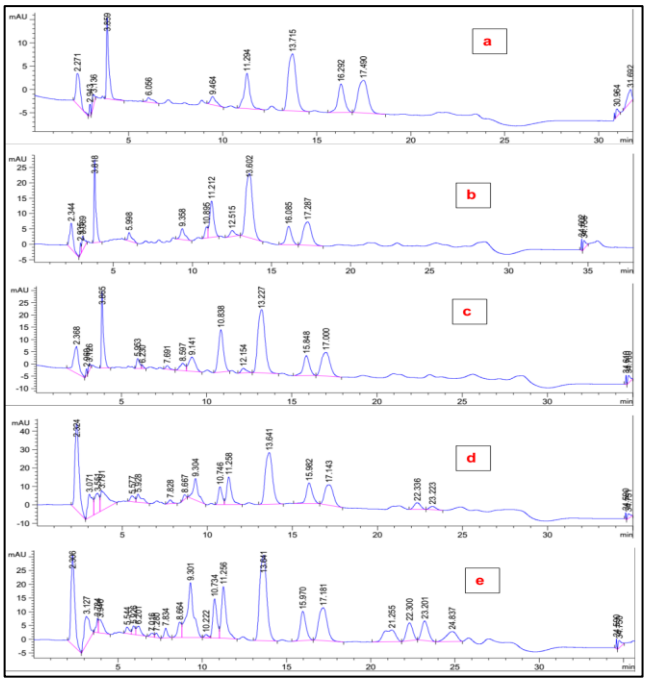

Fig.2: Chromatogram at 282 nm obtained by HPLC from the reaction with catalysts (a) Al_2O_3 Fluka, (b) Al_2O_3-69, (c) Al_2O_3-33, (d) MIL-53Ga and (e) MIL-53Al, EtOAc and H_2O_2 (24 h).

Reaction mixtures were analyzed by HPL at 0, 3 and 24 h Fig. 2. The conversion of Licarin A with H2O2 over catalysts in function of reaction time shown in Fig:3. After 24 h of reaction 95.7% and 95.6% Licarin A are convertedover MIL-53Ga and MIL-53Al respectively, while the conversion of the substrate over Al_2O_3 Fluka, Al_2O_3-69 and Al_2O_3-33 achieved values of 65.5, 68.3 and 69.8%, respectively. In comparison, the results for the Licarin A conversion over MIL-53Ga and MIL-53Al showed high conversion than those of Aluminum oxides

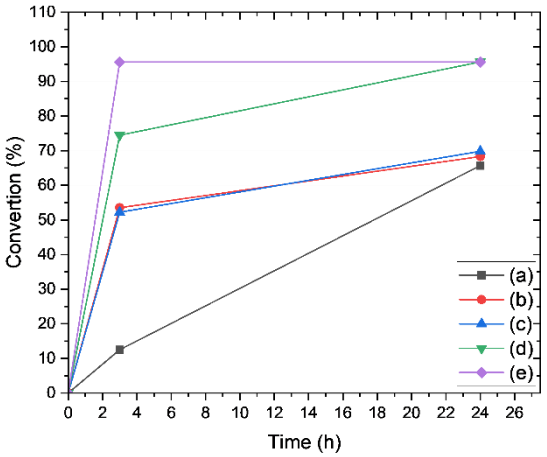

Fig. 3: Licarin A conversion in the oxidation reaction over (a) Al_2O_3 Fluka, (b) Al_2O_3-69, (c) Al_2O_3-33, (d) MIL-53Ga and (e) MIL-53Al, as a function of time of reaction (Oxidant: H_2O_2 6.66mmol (0.3775mL), EtOAc 3.0mL, , Licarin A 0.083mmol (81.6mg), CH_3NO_2 1.0mmol (0.0536mL).

catalysts.

Conclusion

All five catalysts were showed to be efficient catalysts in the conversion of Licarin A. The best results were obtained with the MIL-53Ga and MIL-53Al, however, their selectivity's are lower, they produce a wider range of byproducts. While the conversion of Licarin A over Aluminum oxides comparatively low, but they show less reaction products.

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