



## Catalytic conversion of glycerol to acrolein over modified molecular sieves: Activity and deactivation studies

Aldenor S. de Oliveira<sup>a</sup>, Santiago J.S. Vasconcelos<sup>a</sup>, Jackson R. de Sousa<sup>b</sup>, Francisco F. de Sousa<sup>c,d</sup>, Josué M. Filho<sup>c</sup>, Alcineia C. Oliveira<sup>a,\*</sup>

<sup>a</sup> University Federal of Ceará, Campus do Pici-Bloco 940, Departamento de Química Analítica e Físico-Química, Langmur Lab de Adsorção e Catálise, Fortaleza, Ceará, Brazil<sup>1</sup>

<sup>b</sup> University Federal of Ceará, Campus do Pici-Bloco 940, Departamento de Química Orgânica e Inorgânica, Fortaleza, Ceará, Brazil<sup>2</sup>

<sup>c</sup> University Federal of Ceará, Campus do Pici-Bloco 922, Departamento de Física, Fortaleza, Ceará, Brazil<sup>3</sup>

<sup>d</sup> University Federal of Pará, Campus Universitário de Marabá, Nova Marabá, Cep 68505-080, Marabá Pará, Brazil<sup>4</sup>

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### ABSTRACT

The catalytic conversion of glycerol to acrolein by liquid-phase dehydration over molecular sieves catalysts was studied. In order to understand the role of the acidity, structure and porosity, five structures were synthesized and evaluated. The lower the Si/Al ratio, the higher the activity; large pore molecular sieves, as HY showed high performance (conversion = 89.0%; selectivity to acrolein = 99.5%), while siliceous molecular sieves such as SBA-15 possessing weak acidity, exhibited low conversion (40.6%) and decreased selectivity to acrolein (84.0%). The structure and the acidity govern the selectivity to acrolein and hydroxyacetone, the latter being a by-product mainly dependent on the amount of weak and medium strengths acidic sites, as in the case of H $\beta$ . The activity has almost the same order of the acidity: HY > H $\beta$  > Mor > SBA-15 > ZSM-23. Modifications of the most acidic and active catalysts by silanation (CVD) or Pt incorporation did not result in an enhanced conversion. The studies of reusability and the nature of the coke deposits indicated that heavy polycondensed and cyclic C<sub>6</sub> compounds resulting from the reaction between glycerol and acrolein block the pores and the acidic sites. The blockage was the main cause of deactivation, whereas acidic site poisoning led to a less extensive deactivation of the surface active sites. From these results, it was possible to establish acidity–activity–deactivation relationships that allow to explain the behaviour of the catalysts.

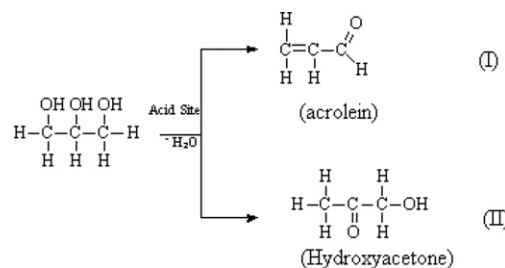
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### 1. Introduction

In recent years, the increased demand for renewable energy sources that produce clean fuels and chemicals has led to intensive research to develop industrial applications of biomass. Biodiesel production is an example of this process, and glycerol is its main by-product [1]. Therefore, glycerol is an important renewable resource derived from biomass, which is currently used in pharmaceutical, food and cosmetics applications [1–5].

However, unrefined glycerol purification is costly to industries and small biodiesel plants [2]. Hence, the development of an economical follow-up chemistry of glycerol is foreseen due to the technological advancements in the biodiesel indus-

try. Indeed, there is a need to develop new, innovative, and greener catalytic processes to transform glycerol into high-added value products. The direct transformation of glycerol attends to these demands and has received much attention as an economical and environmental friendly simple process. Other economical and environmental benefits include the use of crude glycerol thus avoiding its purification and the sharp reduction of industrial water consumption. A promising way to convert the crude glycerol aqueous solution is to produce chemicals of high value by dehydration of glycerol, according to the following reactions:



\* Corresponding author. Tel.: +55 85 3366 99 82; fax: +55 85 3366 99 82.

E-mail address: [alcineia@ufc.br](mailto:alcineia@ufc.br) (A.C. Oliveira).

<sup>1</sup> Tel.: +55 85 3366 9051; fax: +55 8533669982.

<sup>2</sup> Tel.: +55 85 3366 9938; fax: +55 853366 9938.

<sup>3</sup> Tel.: +55 85 3366 9483; fax: +55 853366 9450.

<sup>4</sup> Tel.: +55 94 21015900/5901; fax: +55 94 2101 5900.

From these processes, acrolein can be used as a raw material to produce acrylic acid and its derivatives, whereas hydroxyacetone is an intermediate for the production of propanediols [3,5]. Moreover, the process can either be conducted in the liquid or gas phase. While the dehydration of glycerol in the gas phase is a widely investigated technique to obtain the referred chemicals, only a few recent investigations have been published on the dehydration of glycerol in the liquid phase [6–9,10–14].

Among the various catalysts that have been used in the production of acrolein and other compounds, solid acids appear to be more viable than liquid acids for environmental reasons [1,4–9,10–18]. Furthermore, it was pointed out that ion-exchange resins, sulphates, phosphates [12], heteropolyacids supported on silica, alumina, or active carbon [6,13] and zeolites [9,15,17] were successfully employed to transform glycerol. Most of the research in catalysis has been focused on the latter catalysts due to their versatility. Indeed, they are non-corrosive and they have a tuneable acidic character and different selectivity properties. Examples of such catalysts include acidic ZSM-5, Beta, SAPO and Faujasite supported on heteropolyacids or mineral acids that were used in the dehydration of glycerol in water and that led to high yields of acrolein [9,14–19].

However, under the conditions mentioned in the literature, water itself induces the deactivation of acidic zeolites by leaching of the acid sites or heteropolyacids used [9,19]. The major drawbacks for the production of acrolein and hydroxyacetone over zeolite-based catalysts were the significant mass transport limitations to the active sites located in the micropores and the carbonaceous deposits blocking the catalytic surface.

In this study, we have investigated in more detail the role of the acidic sites of molecular sieves on the catalytic behaviour in the dehydration of glycerol. For this purpose, we aimed to get insights into the preparation and characterization of acidic molecular sieves to identify the effects of the acidity, structure and porosity on the reaction pathways. Modifications of the acidic sites in the most active molecular sieves studied were performed by chemical vapour deposition (silanation) or platinum incorporation in order to achieve superior activity and shape selectivity with bi-functional catalysts.

Strategies to overcome the transport limitations on the microporous zeolites and zeolites analogues were the use of mesoporous materials and noble metal incorporations. These strategies resulted in excellent catalytic properties as compared to conventional zeolites for glycerol transformations [12,15,17–21]. However, no investigations on the dehydration of glycerol to acrolein and other compounds that could give a deeper understanding on the effect of the molecular sieves properties (topology, acidity) on the catalytic performance of the reaction have previously been published. The nature of coke deposits on a deactivated catalyst was also studied in this work.

## 2. Experimental

### 2.1. Catalyst preparation

All the protonic molecular sieves studied (ZSM-23, HY, Mor, H $\beta$  and SBA-15) were synthesized by the following procedures and were similar to the ones described in the literature [22–24].

A surface modified, silylated molecular sieve was prepared by chemical vapor deposition of silica (CVD) on HY, based on Chen et al. procedure [25] in order to control the acidity of this solid. 1.0 g of the sample was placed in a tubular cell and heated in air flow (rate = 100 mL min<sup>-1</sup>) for 5 h, under nitrogen flow (rate = 100 mL min<sup>-1</sup>). Silanation treatment of HY zeolite was carried out by passing a mixture of 4 wt.% TEOS in toluene through the

catalyst at 150 °C under nitrogen in a flow rate of 10 mL h<sup>-1</sup> for 1 h of deposition time; the solid was calcined under air flow at 500 °C for 4 h and it was denoted as HY CVD.

Both HY and SBA-15 were also used as carriers for preparing the supported catalysts. The incipient impregnation wetness method with aqueous solutions of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (Aldrich) was used to obtain 1 wt.% of Pt on the molecular sieves support. Following the impregnation, the catalysts were dried at 100 °C for 3 h and calcined at 550 °C for 3 h in air flow and the bifunctional solids were designated as Pt/HY and Pt/SBA-15.

For determination of coke composition, the most active catalysts used in 24 h of reaction were treated with hydrofluoric acid solution (Synth, 40%) at room temperature to remove the aluminosilicate matrix. Subsequently, the soluble carbon components were extracted with dichloromethane (Merck, 99%) and analyzed by GC–MS. The carbonaceous compounds, which are insoluble were recovered and analyzed by TG in oxidative atmosphere, FTIR and Raman measurements.

### 2.2. Catalysts characterization

X-ray diffraction analyses of fresh and spent catalysts were performed in the  $2\theta$  range of 10°–80° and also in 1°–9° for Al-containing SBA-15 in a Rigaku D-Max 240 diffractometer, using Cu K $\alpha$  radiation at 30 V and 40 mA.

The textural properties were examined from N<sub>2</sub> adsorption isotherms in a ASAP2000 Micromeritics equipment. Prior to analysis, all samples were degassed for 4 h at 150 °C in an oven. The experiment was performed by nitrogen adsorption at –196 °C. The surface areas were taken from the isotherms in the  $P/P_0$  relative pressure range of 0.1–0.4. Pore volumes were determined at  $P/P_0$  of 0.99.

The Si/Al ratio was measured in a Varian ICP-OES instrument. Previously, the samples were treated in a sand bath at 200 °C with hydrofluoric acid and the subsequent dissolution with a 1 wt.% nitric acid solution.

FTIR spectra of the samples were collected in a JASCO-4200 equipment in the range of 4000–400 cm<sup>-1</sup>. Approximately, 1 wt.% of each sample was dissolved in KBr, prior recording the curves.

The scanning electron microscopy (SEM) images were obtained from a Hitachi SEM equipment at 15 kV. Transmission electron microscopy (TEM) micrographs were obtained with a JEOL-1200 TEM microscope operation at 200 kV. The samples were dispersed in acetone by ultrasonic process and a drop of the suspension was placed in a carbon coated grid to perform the analysis.

Spectroscopic investigations by Raman analysis were carried out for spent catalysts by using a T64000 Jobin Ivon spectrometer equipped with a N<sub>2</sub>-cooled charge and a coupled device to detect the scattered light. Approximately, 50 mg of samples was used with an argon laser of 5141 Å.

The acidity of the samples was evaluated by means of TPD of ammonia. 50 mg of each solid was flushed with He (20 mL min<sup>-1</sup>) from room temperature to 150 °C in a Shimadzu TG/DSC-50 model. The solids were subsequently desorbed in the 150–600 °C range. In the same equipment, the spent samples were burnt in order to determine the carbon content, by using a flow of nitrogen from room temperature to 1000 °C, with a heating rate of 5 °C min<sup>-1</sup>.

The acidity measurements were also performed by FTIR spectra of adsorbed and desorbed pyridine. The self-supported wafers were degassed in a vacuum of 10<sup>-7</sup> atm. at 300 °C overnight. After cooling down to room temperature, the samples were exposed to the vapour of pyridine, and thus pyridine IR spectra were recorded in a Shimadzu instrument. The desorption procedure for the pyridine probe was monitored stepwise by evacuating the sample at increasing temperatures of 150 and 250 °C.

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