



## Studies on styrene selective oxidation over iron-based catalysts: Reaction parameters effects



Antonio de Brito S. Neto<sup>a,1</sup>, Ludimila G. Pinheiro<sup>a,1</sup>, Josue M. Filho<sup>b,2</sup>, Alcineia C. Oliveira<sup>a,\*</sup>

<sup>a</sup> Universidade Federal do Ceará, Campus do Pici-Bloco 940, Departamento de Química Analítica e Físico Química, Fortaleza, Ceará, Brazil

<sup>b</sup> Universidade Federal do Ceará, Campus do Pici-Bloco 922, Departamento de Física, Fortaleza, Ceará, Brazil

### HIGHLIGHTS

- Mesoporous MnFe is active for styrene oxidation with outstanding reusability along 72 h.
- Catalyst screening, effect of temperature and efficiency of the H<sub>2</sub>O<sub>2</sub> were deeply studied.
- Synergistic effect of Fe with Co and Mn promoters to produce benzaldehyde and styrene oxide.
- Using acetone, good performances due to oxidation of MnFe<sub>2</sub>O<sub>4</sub> phase.
- Partial loss of catalyst structure of CoFe showed by Raman and ATR-FTIR.

### ARTICLE INFO

#### Article history:

Received 6 September 2014

Received in revised form 20 January 2015

Accepted 21 January 2015

Available online 17 February 2015

#### Keywords:

Porous materials  
Styrene oxidation  
Iron oxide  
ATR-FTIR  
Raman

### ABSTRACT

Iron-based hydrotalcite catalysts such as MnFe, CoFe, CeFe, NiFe and MgFe as well as their single monoxides were screened for selective oxidation of styrene to obtain benzaldehyde and styrene epoxide. The catalysts were characterized by X-ray diffraction, ATR-FTIR and Raman spectroscopy, chemical analyses, scanning electron microscopy coupled to EDX and N<sub>2</sub> adsorption–desorption measurements, before and after the catalytic evaluation. The influence of the reaction conditions such as temperature, reactant compositions as well as the presence of solvents was also evaluated. Best performances were reached by MnFe due to the presence of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> phases together with the stable MnFe<sub>2</sub>O<sub>4</sub> one. These species allowed reaching 17% of styrene conversion and selectively produced benzaldehyde and styrene epoxide, after 72 h of reaction. Under these conditions, MnFe can be recycled by 3 times with a very low deactivation rate due to the partial loss of catalyst structure, after being characterized by Raman and ATR-FTIR.

© 2015 Elsevier Ltd. All rights reserved.

## 1. Introduction

The oxidative conversion of styrene to aldehyde and epoxide is of great interest to chemical industry (Fig. 1).

Benzaldehyde is a versatile chemical intermediate widely used for the production of agrochemicals, pharmaceuticals, perfumes, resin additives, flavors and dyestuffs [1,2]. Whereas carbonyl compounds such as styrene epoxides are important raw material in the manufacture of bulk chemicals, cosmetics, surface coatings, epoxy resins as well as perfumery to obtain chemical phenylethyl alcohol, organic synthesis intermediate for styrene glycol and its derivatives production [3 (and references herewith)]. Benzaldehyde can

be also commercially produced as a by-product of the gas phase or through liquid phase oxidation of toluene to benzoic acid [4]. Other routes consist of benzyl alcohol oxidation and hydrolysis of benzalchloride, as well. However, these processes suffer from drawbacks such as presence of chlorine free benzaldehyde, which is not acceptable in perfumes and pharmaceuticals and a very significant carbon loss in the form of carbon oxides [2]. In case of styrene oxide, it is a derived from epoxidation of styrene with peroxybenzoic acid via Prilezhaev reaction [4,5]. Nevertheless, this reaction gives a variety of by-products of oxidative cleavage of C–C or C–O bonds [4].

Therefore, oxidation of styrene with environmentally benign oxidants is a highly desirable reaction for benzaldehyde and styrene epoxide production with regard to the selectivity to the products and an alternative to traditional processes that use expensive inorganic oxidants [6–11]. Due to environmental concerns, the use of traditional oxidizing agents in styrene oxidation such as KMnO<sub>4</sub>,

\* Corresponding author. Tel./fax: +55 85 3366 9051.

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

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

<sup>2</sup> Tel./fax: +55 85 3366 9900.

$K_2Cr_2O_7$ ,  $CrO_3^{2-}$ ,  $HNO_3$  and tert-butyl peroxide has been reduced or substituted by environmentally and economically significant oxidants such as molecular oxygen or  $H_2O_2$  [12–15].

In addition, several catalysts such as heteropolyacids, cationic metalloporphyrins, mesoporous metal silicates, transition metal Schiff-base complexes, perovskites, molecular sieves, spinel oxides, zeolites, titania, molybdena, bulk or supported iron, vanadium, nickel, uranium, gold, silver, calcium, copper, manganese, uranium, yttrium, zirconium, tungsten, chromium, lanthanum and cobalt-based oxides have been successfully employed for this purpose [1–15]. Owing to its excellent selectivity to the main products of the reaction as well as its environmentally benign character, Fe-based oxide catalysts have outstanding redox properties in the reaction. Many attempts have been made to improve the catalytic activity of these catalysts. One of the strategies is by supporting or anchoring the  $Fe^{3+}$  active phase on stable supports [9,11,13]. Other methods, like using promoters such as Zn, Cr, Cu, Mn to the iron oxides in the form of spinel ferrites and hydrotalcites have also been successfully applied in oxidation of hydrocarbons resulting in elevated conversions [7,11,16]. Even though several attempts have been made to enhance the catalytic activity of iron-based catalysts, the low selectivity of the products obtained remains the main problem associated with the reaction. Besides, the majority of the solids cannot be reused and suffer leaching during the reaction.

The aim of this study was to investigate the oxidation of styrene in the presence of hydrogen peroxide over Fe-based hydrotalcites. The latter are layered with anionic species e.g., hydroxide and carbonate located in the interlayer, which have been reported to be used in oxidation reactions due to the high efficiency of their derived oxides [7]. Promoters such as Ni, Mg, Co and Mn are expected to improve catalytic performance of the iron oxides. The reusability and leaching studies on the oxidation of styrene are carried out over the most active solids.

To the best of our knowledge, it is the first time that different approaches have been proposed simultaneously to solve the problem of low stability of Fe-based oxides in the titled reaction such as screening of the best promoters, effects of the temperature, types of solvent, styrene/ $H_2O_2$  molar ratio, efficiency of the  $H_2O_2$  as well as leaching and recyclability studies through the investigation of the structural properties of the spent catalysts, among others. Notably, the improved performance of MnFe catalyst is motivated by the effect of Mn promoter on the structural and textural properties of the mixed oxide, comparing with the traditional molecular sieves used in the reaction.

## 2. Experimental

### 2.1. Catalyst preparation

Catalysts were prepared via co-precipitation, according to the method described in the literature [17]. In a typical synthesis of hydrotalcites, about 200 mL of a mixed aqueous solution of magnesium nitrate and iron nitrate into a 200 mL of sodium hydroxide and carbonate mixed solution were added dropwise to a beaker, under vigorous mechanical stirring. Then, the suspension was

stirred for additional 30 min at room temperature and pH was 11. Afterward, the product was filtered off, thoroughly washed with distilled water until pH equal to 7. Finally, the solid was dried at 60 °C overnight and the solids were crushed and then calcined at 700 °C for 6 h in air. The catalyst having magnesium-to-iron molar ratio of 2 was represented as MgFe.

The same methodology was followed using cobalt or nickel nitrate with iron nitrate as hydrotalcite precursors, in this case. The molar ratios of the calcined catalysts were 2:1 for NiFe, CoFe and MnFe. Also, a reference catalyst based on ceria (CeFe) possessing a Fe/Ce molar ratio of 2:1 was used for catalytic activity comparison purposes [18]. Magnesium, cobalt, iron, nickel, cerium and manganese monoxides were prepared by using appropriated methodologies [17,18] and used for catalytic evaluation comparisons.

### 2.2. Characterization of the catalysts

X-ray diffraction (XRD) patterns were collected on a DMAXB Rigaku diffractometer using  $Cu K\alpha$  radiation at 40 kV and 25 mA. The experiments were performed at high diffraction angles (from 10 to 80°).

BET measurements were recorded on a Belsorp mini Japan instrument. The samples were degasified at 150 °C and the textural features were studied via nitrogen adsorption at 77 K. The pore sizes were obtained from the analysis of the adsorption isotherms, according to the BJH method (Barrett–Joyner–Halenda).

Inductively coupled plasma optical emission spectroscopy (ICP-OES) was used to determine the concentration of metals in the catalysts. The analyses were conducted on a Perkin Elmer, Cary AA spectrometer. The samples were previously dissolved in a mixture of hydrochloric and nitric acid, and were heated in a sand bath at 200 °C. The solvent was evaporated, and nitric acid and water were added to the resulting precipitate.

The composition of the samples was determined by energy dispersive X-ray spectroscopy EDX analysis using a FEI, Quanta 200 FEG electron microscope equipped with an EDX system coupled to an SEM microscope with an acceleration voltage of 2 kV.

Raman spectroscopy was used to study the structural features of the fresh and spent catalysts through their vibrational properties. The measurements were obtained using a LabRam HR Raman spectrometer (from Horiba). An Ar laser (514.5 nm) operated at 2 mW was used as the excitation source. The laser was focused on powdered samples, which were placed on a microscope slide, to produce a spot with a diameter of approximately 8 mm. An air-refrigerated charge-coupled device (CCD) was used as the detector.

### 2.3. Catalytic measurements in oxidation of styrene

The oxidation of styrene with hydrogen peroxide was carried out in a batch glass reactor equipped with a thermocouple. The reactor was equipped with a reflux condenser and a gas inlet. In a typical experiment, nitrogen was bubbled through the reactor under room pressure, and 0.1 g of the catalysts was introduced

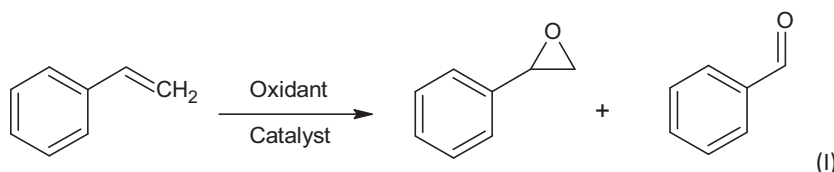


Fig. 1. Schematic representation of the reaction.

Download English Version:

<https://daneshyari.com/en/article/205714>

Download Persian Version:

<https://daneshyari.com/article/205714>

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