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Catalytic performance of MnFeSi composite in selective oxidation of styrene, ethylbenzene and benzyl alcohol

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This paper is dedicated to the memory of Professor Josue Mendes Filho.

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ABSTRACT

FeMnSi composite was synthesized from a mecanosynthesis method using SiO_2 nanopowder and FeMn hydrotalcite. The composite was tested in styrene, ethylbenzene and benzyl alcohol oxidations in the presence of H_2O_2. The solid was characterized before and after the oxidation reactions through XRD, chemical analyses, textural properties, HRTEM, SEM-EDS, Raman and EPR measurements. Effects of catalyst mass, substrate/H_2O_2 molar ratios and catalyst' recyclability were investigated to explore the relationship between the physicochemical properties of the solid and the catalytic performance. Results revealed that FeMnSi catalyst exhibited much higher activity for styrene oxidation compared with ethylbenzene and benzyl alcohol counterparts due to Si providing a relatively stability on the Fe^{3+} and Mn^{4+}/Mn^{3+} sites. The Si was responsible for improving the texture, structure and morphology of the catalyst in styrene oxidation. Best reaction conditions were achieved at temperature of 50 °C, H_2O_2 to styrene molar ratio of 1, using 100 mg of catalyst.

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1. Introduction

The oxidation of olefins represents a step of major importance to produce valuable chemical intermediates such as epoxides and acetophenone as well as fine chemical products i.e.,benzaldehyde and its derivatives for pharmaceuticals, resins, drugs and perfumes production. Importantly, epoxides are used as a solvent for cellulose ethers and esters in the manufacture of alcohol-soluble resins while the acetophenone find application in resins, pharmaceuticals, plastics and adhesives [1–4].

Currently, oxidation of styrene is one of the most studied processes for converting hydrocarbons into other useful products such as benzaldehyde, styrene epoxide and formaldehyde, among other chemical commodities [1–5]. The production of these useful products by styrene oxidation with H_2O_2 is of major importance due the low cost of the heterogeneous catalysts employed in the reaction, which make chemical processing more appropriate in terms of saving energy and money demands [1,6,7]. Also, the separation and purification steps are avoided using solids as catalysts and the process became more advantageous in comparison with the traditional uses of homogenous catalysts [1–3,7]. In addition, H_2O_2 is an environmental benign oxidant as compared with the traditional organic compounds used during the reaction [1,3,7].

Iron-based catalysts are the preferred choice as catalysts for the liquid phase selective oxidations due to the low cost and easy availability of Fe sites [6–9], when compared with Ru, Co and Ti based-catalysts. On the contrary, the main disadvantage of Fe-supported catalysts compared with the massic Fe ones is the lower structural stability of the formers with respect to the phase transformation occurring during the reactions. Many attempts have been made to improve the stability of Fe-based catalysts in selective oxidation of aromatic hydrocarbons, including using promoters, varying the synthetic routes, increasing the dispersion of iron sites on supports and so far [7,8].

In this sense, the effective catalysts comprising of Fe-containing zeolites and mesoporous materials, immobilized or encapsulated iron complexes, iron-doped metal oxides such as Fe^{3+}-doped silicates, iron-containing compounds with isolated iron sites typified

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by iron phosphate, physical mixtures of Fe with other metals, phosphates alloys, among other catalysts have demonstrated great potential as catalysts for selective oxidation of styrene in the presence of environmentally benign and economically attractive oxidants such as hydrogen peroxide and oxygen [7–11].

Also, it has been well established the catalytic properties of iron for selective oxidation of hydrocarbons such as styrene is not only determined by its redox mechanism during the reaction, but also the particle size and the surfaces properties [7,12], which in turn, determines the requirements of the active iron sites in target-selective oxidation.

From a prior study, it has been demonstrated that iron-based hydrotalcites i.e., MnFe, CoFe, CeFe, NiFe and MgFe are active catalysts to styrene oxidation, having MnFe a great catalytic performance [12]. Using appropriate physicochemical characterizations tools, a redox cycle of Fe^{3+}/Fe^{2+} and Mn^{4+} /Mn^{3+} during the reaction seems to be closely associated with the nature of the Fe and Mn sites, respectively. However, the solid lacks of stability and the selectivity to the products in styrene oxidation are considered low.

In the present work, we systematically investigate the role played by Si in Fe-based hydrotalcite catalyst adding silica to the composition of the solid to enhance its performance in the reaction. In addition, using different experimental setups, structural and spectroscopic characterizations, we tentatively try to improve the catalytic performance of the solid. This is an attempt to elucidate the performance of MnFeSi catalyst in oxidation reactions with different substrates to better understand the reasons for what Si circumvents the deactivation of the catalyst during the selective oxidation of styrene.

In addition, three different research directions have been proposed for the transformation of hydrocarbons with MnFeSi e.g., styrene oxidation (St), ethylbenzene oxidation (EB) and oxidation of benzyl alcohol (BA).

2. Experimental

2.1. Preparation of the catalyst

The solids were prepared using a co-precipitation method, according to the described procedure by Brito et al. [12], with modifications. Briefly, the hydrotalcites precursors were obtained by mixing 200 mL of an aqueous solution of manganese nitrate and iron nitrate to have a manganese-to-iron molar ratio of 2 into sodium hydroxide and carbonate solutions, under vigorous mechanical stirring.

The suspension was left for precipitation in ambient environment under stirring to reach pH 11. Afterwards, the resulting product was thoroughly washed with deionized water several times to remove any excess of base that may be present and was subsequently dried overnight at 60 °C to obtain the precursor MnFe hydrotalcite. A detailed description about the preparation procedure is given in reference [12].

A mechanosynthesis consisting of the mixture of the MnFe hydrotalcite and nanopowder SiO_2 in a molar ratio of 1:2 was performed to obtain a solid state reaction in a ball-mill with using 18 ml ethanol for 2 h. Subsequently, the resulting mixture was dried overnight. Finally, the powder was calcined under air flow at 500°C for 6 h to give the MnFeSi composite.

2.2. Characterization of the catalysts

X-ray powder diffraction (XRD) measurements were carried out using a DMAXB Rigaku diffractometer using CuKα radiation at 40 kV and 25 mA. The experiments were performed at high diffractions angles from 10 to 80°. The X-ray patterns of the catalysts were compared to that of the standard materials.

Inductively coupled plasma optical emission spectroscopy (ICP-OES) was used to determine the iron and manganese concentrations. 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 subsequently heated in a sand bath at 200 °C. The solvent was evaporated and then, a 1 wt.% of nitric acid solution was added to the resulting precipitate to determine the metal contents.

Nitrogen physisorption isotherms were determined by using a Belsorp mini-II apparatus, after degassing the catalysts at 90 °C for 24 h. The surface areas of the solids were obtained by Brunauer–Emmett–Teller method (BET). The pore sizes were obtained from the adsorption isotherms measurements, according to the Barrett-Joyner-Halenda method (BJH).

Scanning electron microscopy (SEM) images and samples composition were taken on a FEI, Quanta 200 FEG electron microscope equipped with an Energy Dispersive Spectroscopy (EDS) system, which was coupled to an SEM microscope with an acceleration voltage of 2 kV. Before the measurements, the solids were prepared by gold sputtering on their surfaces.

Transmission electron microscopy (TEM) images were taken on a JEOL JEM 2010F electron microscope with an acceleration voltage of 200 kV. The catalysts were prepared by dipping the carbon-coated copper grids into ethanol solutions of the samples and drying at ambient condition.

Raman spectroscopy was carried out on a LabRam spectrometer using an Olympus confocal microscope and an objective lens of 100 times. The laser line of 532 nm was focused on powdered samples for exciting at a power level of 2 mW on the sample and the Raman spectrum was scanned over a range of 50–2200 cm^{-1} with a resolution of 4 cm^{-1}.

Electron paramagnetic resonance (EPR) spectra were recorded for the select samples to determine the valence state of Fe in a Bruker spectrometer working at the X-band microwave frequencies close to 9.5 GHz. The apparatus has a double cavity with high frequency modulation of 100 kHz. Prior to EPR measurements, the samples were placed in quartz tubes of 4 mm inner diameter at room temperature (293 K) under a helium atmosphere. The g factor values were measured by the simultaneous determination of the magnetic field magnitude and the microwave frequency, as well.

2.3. Catalytic testing

Catalytic activity was evaluated using a batch glass reactor equipped with a thermocouple, a reflux condenser and a gas inlet. In short, the reaction was carried out by flowing nitrogen through the reactor system containing 10 mmol of styrene, 10 mmol of dilute H_2O_2 (30%) and acetone at 50 °C for 24 h. At the end of the reaction, the reaction mixture was cooled to room temperature, and the products were analyzed in a GCrom gas cromatograph and identified by gas chromatography coupled to mass spectrometry (GC–MS) device in a Shimadzu GCMSQP5050 equipment.

The starting catalyst mass was 0.1 g with variation in this parameter. The styrene to H_2O_2 molar ratio was also varied. Xylene was used as internal standard. Detailed methods of calculations and analysis were described elsewhere [12].

Recycling tests were conducted by using the MnFeSi catalyst, followed by separation by hot filtration and a subsequent washing with hot solvent and dried. Latter, the catalyst was heated again at 50 °C for 6 h to remove any adsorbed reactant or products and reused in the catalytic reactions. Leaching experiments were carried out in the styrene oxidation reaction using 100 mg of

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