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## Selective catalytic oxidation reaction of *p*-xylene on manganese–iron mixed oxide materials

*Réaction d'oxydation catalytique sélective du p-xylène sur des matériaux constitués d'oxydes mixtes de manganèse et de fer*

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### ABSTRACT

Mixed manganese iron oxides (Mn/Fe/O) as heterogeneous catalysts were prepared by hydrothermal treatment and citrate methods to be tested in the oxidation of *p*-xylene (PX) using as oxidation agent molecular oxygen, hydrogen peroxide, and *tert*-butyl hydroperoxide. Preparation of mixed Mn–Fe oxide by the citrate method releases materials with smaller particle size and lower degree of crystallinity as compared with the hydrothermal one, which further leads to a higher activity toward the oxidation of PX. A conversion of PX of 98% and a yield in *p*-toluic acid of 93% were obtained in the presence of Mn/Fe/O prepared by the citrate method using *tert*-butyl hydroperoxide as an oxidizing agent.

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### RÉSUMÉ

Des oxydes mixtes de manganèse et de fer destinés à être utilisés comme catalyseurs hétérogènes ont été préparés par traitement hydrothermal et par la méthode citrate pour être testés dans l'oxydation du *p*-xylène, en utilisant comme agent d'oxydation l'oxygène moléculaire, le peroxyde d'hydrogène et l'hydroperoxyde de *tert*-butyle. La préparation de l'oxyde mixte de Mn–Fe par la méthode citrate conduit à des matériaux ayant une taille de particules plus petite et une cristallinité moins importante en comparaison de ceux synthétisés selon l'autre méthode, ce qui a entraîné une activité élevée dans l'oxydation du *p*-xylène. Une conversion du *p*-xylène de 85% et une sélectivité vis-à-vis de l'acide *p*-toluique de 72% ont été obtenues en présence du catalyseur Mn/Fe/O préparé par la méthode citrate, en utilisant comme agent d'oxydation l'hydroperoxyde de *tert*-butyle.

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## 1. Introduction

Nowadays, the production of chemicals avoiding waste through nonpolluting processes is still a challenge for researchers [1]. Unlike the pharmaceutical sector,

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involving low quantity chemical fabrication, the chemical industry, widely based on selective oxidation processes, implies large-scale production of chemicals; for example, 25 Mtonnes of terephthalic acid (TPA) is produced yearly from oxidation of *p*-xylene (PX) [2]. This process has a major industrial impact because TPA is the raw material for production of polyethylene terephthalate (starting material for bottles and textiles), polyester fibers, paint, and adhesives [3]. The commercial route implies the use of the acetic acid at 200 °C and 15–30 atm in the presence of the homogeneous catalytic system Co/Mn and Br as promoter. The process, known as AMOCO process, achieves 98% conversion of PX and 95 mol % yield of TPA, which is highly corrosive and polluting for the environment [4–9]. In addition, the crude TPA obtained at the end of reaction contains 3000 ppm 4-carboxybenzaldehyde (4-CBA) and 500 ppm *p*-toluic acid (TA) as major impurities [10].

Heterogeneous catalytic liquid phase oxidation of PX revealed the first encouraging results in 2001 [11] by Chavan et al. with a hybrid material  $\mu_3$ -oxo-bridged Co/Mn cluster complexes encapsulated in Y-zeolites. They have obtained a 99% selectivity of TPA for 100% conversion in only 2 h. Consequently, other heterogeneous systems were developed for PX oxidation, such as manganese oxide modified with Co or Cu [3] or Pd/Sb/Mo–TiO<sub>2</sub> catalytic system [12]. Unfortunately, they suffer a few drawbacks deriving from the use of NaBr as coactivator, acetic acid as solvent, and harsh reaction conditions (high temperatures or pressures). Several studies have focused on the green aspect of the reaction and tried to develop systems that work in mild conditions even if this involves obtaining intermediate oxidation products, such as TA. Usually, AuPd alloy nanoparticles on different supports are able to oxidize the *o*-, *p*- and *m*-xylene to tolualdehyde, toluyl alcohol, and toluic acid in mild conditions [13–17]. Recently, different phases of CeO<sub>2</sub> nanoparticles demonstrate their ability to oxidize with moderate yield the PX to TA (25%–35%) with the advantage of using very friendly reaction conditions [18,19]. Nevertheless, the data obtained in heterogeneous catalysis are not outstanding and further studies are needed.

This study addresses the problem of corrosive selective oxidation, by substituting the homogeneous system with a heterogeneous system containing mixed oxides of Mn and Fe, and replacing the harsh reaction conditions with more gentle ones. The advantages of this system are the ease in the separation of the catalyst and the reaction products, by filtration and the low waste, eco-friendly reaction conditions. This way the catalyst can be effectively recovered and reused. Manganese oxides are able to promote several oxidation reactions [20,21]. Our recent studies on Mn/Fe oxides emphasize their capabilities to convert the aromatic hydrocarbons in aromatic carboxylic acids [22–24]. Moreover, to achieve materials with specific characteristics, the preparation method should be carefully chosen; therefore, during this work the influence of the preparation method on the properties of the heterogeneous catalysts of Mn/Fe/O was investigated. For this purpose, the materials were prepared by hydrothermal treatment and citrate methods, characterized by several techniques and tested in the

oxidation of PX using hydrogen peroxide, molecular oxygen, and *tert*-butyl hydroperoxide (TBHP) as oxidation agents.

## 2. Experimental section

### 2.1. Material synthesis

All reagents have analytical purity: Mn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (EMSURE, for analysis), Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (Scharlau, extra pure), polyethylene glycol (PEG, Sigma Aldrich), C<sub>6</sub>H<sub>8</sub>O<sub>7</sub> (Sigma Aldrich).

#### 2.1.1. Synthesis of Mn–Fe mixed oxide by hydrothermal treatment

To prepare Mn–Fe mixed oxide (molar ratio Mn/Fe = 1:2), stoichiometric molar amounts of manganese nitrate (2.5 g) [Mn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O] and iron nitrate [Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O] (7 g) were dissolved in 10 mL of water to form a clear solution. While stirring, 10 mL of PEG (a nonionic, polar polymer) was added to the solution to serve as a surfactant to avoid particle agglomeration. The pH was adjusted to 11 by adding 2 M of NaOH dropwise. The mixture was stirred for 1 h to obtain a homogeneous solution, then transferred into an autoclave and kept at 150 °C for 12 h, under autogenous pressure. The product was separated by filtration and washed several times with water, absolute ethanol, and acetone, until pH = 7. The resulted powder was dried at 70 °C overnight and calcined in air at 700 °C for 5 h. This material was denoted as Mn/Fe/O-HT.

#### 2.1.2. Synthesis of Mn–Fe mixed oxide by citrate method

Mn–Fe mixed oxide with the same molar ratio (Mn/Fe = 1:2) was synthesized by complexation with citric acid. Stoichiometric amounts of manganese nitrate (2.5 g) [Mn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O] and iron nitrate [Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O] (7 g) were dissolved in 50 mL of deionized water at 60 °C to form a clear solution. Citric acid was added to this mixture with 20% excess. The solution was stirred for 1 h at 60 °C and then evaporated under vacuum until a gel was formed. The gel was dried under vacuum for 5 h at 60 °C and overnight at 120 °C in air. The obtained powders were calcined in air at 700 °C for 5 h. The material prepared by this method was denoted as Mn/Fe/O-CIT.

### 2.2. Textural and structural characterization

Dried synthesized materials were characterized using differential thermal analysis (DTA) and thermogravimetric (TG) analysis using a TG-DTA analyzer Shimadzu DTA-60 instrument. The experiments were performed in air in a temperature range of room temperature to 900 °C with a heating rate of 10 °C/min, using alumina as reference and 5–10 mg of a sample.

Powder X-ray diffraction (XRD) patterns were recorded using a Shimadzu XRD-7000 diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ , 40 kV, 40 mA) at a scanning speed of 0.10° min<sup>-1</sup>, in the 10°–80° 2 $\theta$  range. XRD served to estimate the crystallite size of catalyst particles. This was calculated using Scherrer's formula ( $D = k\lambda/\beta \cos \theta$ , where

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