



Short communication

A green methodology for the selective catalytic oxidation of styrene by magnetic metal-transition ferrite nanoparticles

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ARTICLE INFO

Keywords:

Styrene
Oxidation
Ferrite
Magnetic nanoparticles
Microwave irradiation
Solvent-free chemical synthesis

ABSTRACT

A microwave-assisted protocol to selectively produce benzaldehyde from neat styrene was developed by using ferrite magnetic nanoparticles, MFe_2O_4 [$M = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}$ or Zn^{2+}] as catalysts. The $CoFe_2O_4$ nanoparticles revealed the best catalytic performance towards the selective production of benzaldehyde (93% selectivity at 86% styrene conversion) in 3 h at 80 °C using *t*-BuOOH as oxidant. The catalyst can be readily isolated by using an external magnet, and no significant loss of activity is observed when reused up to 5 consecutive runs. The low *E*-factor (mass ratio of waste to desired product) value (2.5) is indicative of the eco-friendly nature of the present catalytic system.

1. Introduction

One of the most important and versatile organic chemicals in the chemical industry is benzaldehyde. It serves as synthetic intermediate for agrochemicals, dyes, perfumery and pharmaceuticals. It appears as the second most important aromatic molecule (after vanillin) used in the cosmetics and flavour industries [1, 2]. One way to produce benzaldehyde is through the catalytic oxidation of styrene at the side chain. Heterogeneous catalysts are in general more favourable than traditional homogeneous ones due to their promising easy separation and potential recycling.

As a class of chemically and thermally stable materials, transition-metal ferrites constitute a type of monodispersed nanomaterials of great technological interest. Spinel ferrites, with the standard formula MFe_2O_4 ($M =$ divalent metal cation) are versatile materials that exhibit several interesting properties, such as optical, electronic, magnetic and catalytic [3, 4]. Especially due to the redox and magnetic recycling features of the nanosized spinel ferrites, these materials have been applied in catalysis with better results than their corresponding single component metal oxides [5]. In particular, their use as catalysts in liquid phase reactions with industrial relevance has been investigated, for instance, in volatile organic compounds treatment [6], decomposition of H_2O_2 [7], alkylation reactions [8], oxidation of chlorobenzene [9], thiols [10], alcohols [11–15] and hydrocarbons [16]. Moreover, magnesium- [17], magnesium/copper- [18], calcium- [19], strontium- [20], cobalt- [21], cerium/cobalt- [22], nickel- [23], zinc- [23] and nickel/gadolinium-based ferrites [24] are among the investigated

spinel ferrite types explored as catalysts for the selective oxidation of styrene.

Despite the considerable progress already achieved, the selective oxidation of a terminal olefin, like styrene, still remains a challenge. Main limitations concern the controlled conversion of styrene into one desired oxygenated product (selectivity issue), the harsh reaction conditions and complex and expensive methodologies implemented.

We have previously reported the preparation of a series of first-row transition-metal ferrites magnetic nanoparticles (NPs) and their applications as efficient magnetically separable catalysts for the oxidation of alcohols [25]. In pursuit of our interest in exploiting magnetic spinel ferrites as catalysts, herein we report for the first time a microwave (MW)-assisted selective oxidation of styrene towards benzaldehyde in a solvent-free medium in the presence of a series of transition-metal (Mn to Zn) ferrite NPs with *tert*-butyl hydroperoxide (*t*-BuOOH) as oxidant. The applied styrene oxidation methodology constitutes an alternative towards more economical and eco-friendlier industrial chemical processes.

2. Experimental

2.1. Materials and instrumentation

All the chemicals were obtained from commercial sources (Aldrich) and used as received. The catalytic tests under MW irradiation were performed in a focused microwave Anton Paar Monowave 300 reactor (10 W), using a 10-mL capacity reaction tube with a 13-mm internal

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diameter, fitted with a rotational system and an IR temperature detector. Gas chromatographic (GC) measurements were carried out using a FISONs Instruments GC 8000 series gas chromatograph with a DB-624 (J&W) capillary column (FID detector) and the Jasco-Borwin v.1.50 software. The temperature of injection was 240 °C. The initial temperature was maintained at 100 °C for 1 min, then raised 10 °C/min to 180 °C and held at this temperature for 1 min. Helium was used as the carrier gas. Reaction products were identified by comparison of their retention times with known reference compounds and quantified by an internal standard method. GC–MS analyses were performed in a Perkin Elmer Clarus 600C GC–MS instrument (Shelton, Connecticut, USA) equipped with two 30 m × 0.22 mm × 25 μm BPX5 (SGE) capillary columns, one having an EI-MS (electron impact) detector and the other one with a FID detector. Helium was used as the carrier gas.

2.2. Catalyst preparation

Ferrite and magnetite nanoparticles were synthesized by a co-precipitation method as reported in our previous work [25]. Anhydrous FeCl₃ (0.32 g, 2.0 mmol) and MnCl₂·4H₂O (0.20 g, 1 mmol) were dissolved in 50 mL deionized water. Ammonia (30% v/v aq. sol.) was added dropwise until the solution reach pH = 12, while stirring at 80 °C. The black turned mixture was then cooled to room temperature and stirred for additional 2 h. The precipitate was isolated with an external magnet, washed three times with deionized water, and then dried at 60 °C for 6 h. The above procedure was extended to the synthesis of MFe₂O₄ [M = Mn²⁺ (1), Fe²⁺ (2), Co²⁺ (3), Ni²⁺ (4), Cu²⁺ (5) or Zn²⁺ (6)] NPs by co-precipitation of M(II) and Fe(III) chlorides (M²⁺/Fe³⁺ = 0.5).

3. Results and discussion

3.1. Catalysts characterization

The MFe₂O₄ (M = 1–6) solid NPs characterization results and the accompanied discussion was previously reported [25]. Briefly, by Transmission Electron Microscopy and Scanning Electron Microscopy, MFe₂O₄ (M = 1–6) solid NPs showed an agglomerated nanocrystalline irregular spherical shape with a broad particle size distribution (ca. 5 to 50 nm). From powder X-Ray Diffraction, MFe₂O₄ (M = 2) NPs exhibited a cubic spinel crystalline structure that can be easily indexed to synthetic magnetite (JCPDS 79-0417). On the other hand, MFe₂O₄ (M = 1, 3–6) NPs revealed a non-crystalline nature. This difference in the crystal structure largely influences the magnetic properties, namely: 6.4 emu/g (MFe₂O₄ (M = 1)) vs. 63.5 emu/g (MFe₂O₄ (M = 2)) according to the Vibrating Sample Magnetometry studies. Therefore, MFe₂O₄ (M = 2) NPs have a higher response in the presence of an external magnet, thus allowing their easy separation and recycling from the reaction medium. Despite the fact that MFe₂O₄ (M = 1) has a lower saturation magnetization than MFe₂O₄ (M = 2), this is considered enough to allow also the magnetic separation of the former NPs.

3.2. Styrene oxidation

In order to evaluate the catalytic activity of the prepared magnetic ferrites for the styrene oxidation in added solvent free-medium, MnFe₂O₄ (M = 1) was selected as a model catalyst to pursue optimal reaction parameters. Firstly, the presence and absence of the MnFe₂O₄ catalyst or/and *tert*-butyl hydroperoxide (*t*-BuOOH) were compared (see entries 1–3, Table 1). The results show that the presence of oxidant is mandatory for the reaction to occur. On the other hand, in the absence of the catalyst, the oxygenated products can still be formed although in a low yield (see entry 2, Table 1). This is indicative of a free radical-based mechanism, in which the radical species are produced from the interaction of the peroxide agent (oxidant) with the magnetic ferrite NPs. At the surface of the prepared NPs, the Fe³⁺ cation from the

octahedral sites reacts with the organic peroxide molecule to form a metal-oxyl radical (Fe⁴⁺-O·) [19] or a free-radical peroxy species (*t*-BuOO· and/or *t*-BuO·) [25]. This radical species will initiate the catalytic cycle by its further interaction with the alkene substrate in a similar way to that proposed for the alcohol oxidation with the same prepared catalysts as previously reported [25].

Benzaldehyde was the main product, followed by styrene epoxide. Other products, such as phenylacetaldehyde, acetophenone, benzoic 1-phenyl ethane-1,2-diol and benzoic acid, were also observed in residual amounts. Those observations are in harmony with the literature [21, 22, 26]. Carbonyl compounds are obtained in larger yields, most of them conceivably from the further oxidation of styrene epoxide (see Scheme 1). A reason for these observations can rely on the conjugation of the aromatic ring with the carbonyl group that confers extra stability to the carbonyl products [21].

Envisaging the use of alternative eco-friendly oxygen sources, hydrogen peroxide and dioxygen gas were also tested as oxidants (see entries 4–5, Table 1). The yield and selectivity of benzaldehyde highly decreased when H₂O₂ was used instead of *t*-BuOOH. In accord, H₂O₂ tends to rapidly decompose in the presence of transition-metal ferrites [21, 25]. No reaction occurred using atmospheric O₂. This points out the difference between the O₂ and a peroxide-type oxidant ability to form radical species able to initiate the catalytic oxidation of styrene.

Possible reaction pathways for the production of detected products from the present oxidation of styrene are shown in Scheme 1 [2, 27–30]: A) oxidative C=C cleavage of the styrene side chain double bond giving benzaldehyde; B) Epoxidation of the C=C bond of styrene giving styrene epoxide, and; C) Conversion of styrene epoxide to benzaldehyde, through hydrolysis and ring opening. A high selectivity towards benzaldehyde was observed in the present catalytic system, suggesting that the reaction proceeds preferably by direct oxidative cleavage of the C=C bond of styrene (pathway A) rather than via styrene epoxide (pathway C) as previous reported.

Some control experiments that could be useful for the elucidation of the reaction mechanism might be:

- i) starting from styrene epoxide reaction with *t*-BuOOH or H₂O₂ in order to evaluate the following oxidized products and finally disclose if benzaldehyde conversion is possible from styrene epoxide, and
- ii) performing the oxidation of styrene through isotopic labelling experiments, using ¹⁸O₂ and/or H₂¹⁸O₂, to identify the ¹⁸O-labelled products and, therefore, find out the oxygen true source.

After *t*-BuOOH has been proved to be the best studied oxidant, the oxidant-styrene molar ratio influence on the selective production of benzaldehyde was investigated. As shown in Fig. 1, *t*-BuOOH: styrene molar ratios of 3:1 and 4:1 exhibit the best conversions of styrene, 42.9 and 45.1%, respectively. However, the selectivity of benzaldehyde was higher for the 3:1 (86.3%) than 4:1 (80.4%) molar ratio of *t*-BuOOH: styrene. Increasing the latter ratio from 3:1 to 4:1 marginally increases the conversion of styrene but decreases the selectivity of benzaldehyde, while the total selectivity towards other oxygenated by-products increases. According to these results, taking into account the compromise between conversion of styrene and selectivity of benzaldehyde, the 3:1 molar ratio was considered as optimal.

The influence of the reaction temperature on the styrene oxidation reaction was evaluated in the range of 40 to 100 °C after 3 h of reaction and the obtained results are depicted in Fig. 2. It is seen that conversion of styrene increases with increasing temperature, whereas the epoxide selectivity decreases, suggesting that at higher temperatures, the C=C bond cleavage (pathway A, Scheme 1) is more favourable than the epoxidation route (pathway B–C, Scheme 1). However, at 100 °C, the selectivity to benzaldehyde decreases in comparison with the case of 60 or 80 °C reaction temperature, showing that at higher temperatures, more deeply oxidized by-products are formed (see Scheme 1). Taking

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