



CeFe-Based Bead Nanocomposites as Catalysts for Oxidation of Ethylbenzene Reaction

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Abstract: Oxides with good catalytic performances and more selectivity to valuable chemicals attract numerous research interests for the oxidation of hydrocarbon fuels. Taking advantage of the nanocasting route, CeFe-based nanocomposites were prepared and characterized to achieve superior stability in the oxidation of cyclic compounds. Adding a third metal (Me = Ni²⁺, Mn²⁺/Mn³⁺ or Co²⁺/Co³⁺) to the CeFe-based oxide helped the formation of Ce³⁺/Ce⁴⁺, Fe²⁺/Fe³⁺ and active couples in the ternary nanocomposites. The solids having a spherical morphology and good textural properties enabled the formation of promising ternary oxide catalysts for the oxidation of ethylbenzene compared with those of binary and single monoxide nanocomposites. The close contact among the Ce³⁺/Ce⁴⁺ and Fe²⁺/Fe³⁺ pairs with Ni²⁺ species provided the formation of a highly stable CeFeNi catalyst with enhanced performance in the oxidation of cyclic compounds such as ethylbenzene, styrene and benzyl alcohol substrates.

Keywords: CeFe; nanocomposites; resin beads; catalysts; oxidation reactions; ethylbenzene

1. Introduction

Iron-based catalysts are widely used in many important chemical transformations such as oxidation and dehydrogenation reactions [1,2]. Particularly, the iron monoxides, e.g., α -Fe₂O₃ and γ -Fe₂O₃ appear to be the most interesting materials in terms of availability and widespread redox properties to the previously mentioned reactions [2–4]. Compared to the use of other oxides in catalytic oxidation reactions, the iron-based solids have various advantages including their importance for environmental chemistry, low cost, easy recovery and lower toxicity. In this regard, iron-based oxides are also very attractive from the perspective of replacing liquid catalysts in the selective oxidation of hydrocarbons [1–6].

In this aspect, the selective oxidation of cyclic compounds to their corresponding aldehydes, ketones, or carboxylic acid has gained great interest from both the industrial and academic point of view [7–11].

Depending on the cyclic compounds used as substrate and the reaction conditions, the products obtained are benzaldehyde, acetophenone, styrene epoxide, benzoic acid, 2-phenyl-acetaldehyde, and other valuable compounds [1,3–5]. These products find application in the synthesis of fine chemicals, resins, flavoring agent, plasticizers and agricultural compounds as well as intermediates for biochemical reaction pathways [6–11]. Additionally, the selective oxidation of cyclic compounds such as ethylbenzene, styrene, and benzyl alcohol (Figure 1) selectively produce the above mentioned valuable chemicals using H_2O_2 , tert-butyl hydroperoxide (TBHP) or O_2 as oxidizing agents [4,12–14].



Figure 1. Scheme for ethylbenzene (I), styrene (II), and benzyl alcohol (III) oxidation reactions.

Although the development of a heterogeneous catalyst for these reactions has fast growth in the past few decades, the low resistance against deactivation by leaching as well as the difficulty of the reuse of the Fe-based catalyst remains the major drawback to the development of the process. So far, no comprehensive approaches have been focused on the low stability of the iron-based solids in the selective oxidation of the cyclic compounds. Moreover, the way Fe itself reacts toward the oxidants for achieving the magnitude of this interaction shows a quest to prepare a stable catalyst to the reactions I–III. In this sense, nanocasting has emerged as a new technique for preparing porous metal oxides with tunable properties, endowing oxide surfaces with redox, acidic or organic species [2,15]. Such redox properties especially those occurring between Fe³⁺ sites and other Me³⁺/Me²⁺ centers may provide either the acid-base or redox cycles that impedes the iron phase transformation during the oxidation of hydrocarbons [15,16].

To understand such synergistic effects among the metals, it is a prerequisite to analyze the dependence of both the chemical composition and surface area of that part of the surface, which is accessible to the reactants in the catalytic oxidation of hydrocarbons. Following previously reported porous CeFe catalysts, the surface Fe^{3+}/Fe^{2+} and Ce^{4+}/Ce^{3+} accessible active sites provide a redox cycle during the oxidation reaction. Consequently, the efficient catalysts to hydrocarbon oxidation reactions are obtained [17]. Keeping this idea in mind, the present work aims to develop Fe-based catalysts by the nanocasting technique for ethylbenzene (EB), styrene (St), and benzyl alcohol (BA) oxidations. Therefore, the strategies consist of combining the outstanding properties of the CeFe

catalyst obtained by a nanocasting technique and adding a third metal, e.g., Ni, Mn, or Co to the CeFe to avoid iron reduction and provide the stability of the solid against phase transformation.

2. Results and Discussion

2.1. Structure of the Solids through X-ray Diffraction (XRD) and Raman

Figure 2 depicts a schematic representation of the well-established nanocasting route for the catalyst preparation. In the first step, the carbon bead mold is treated with water to remove the excess of sodium. The following step consisted of applying the nanocasting technique to infiltrate the metal salts in the mold by impregnation, according to a previously developed protocol [2]. Then, the composite is calcined to remove the carbonaceous matrix from the mold. At this step, the metal-resin composite further is calcined once again to produce the inverse replica of the polystyrene resin beads used as a mold.



Figure 2. Schematic representation for the preparation of the catalysts via a nanocasting route.

XRD patterns of the solids depict broadened diffraction peaks (Figure 3a), which confirm the existence of semi-crystalline structures. This is typical of nanocasted solids that possess the small crystallite sizes and internal strains [2,18,19]. Accordingly, all solids exhibit weak diffraction patterns attributable to the cubic fluorite CeO₂ structure at about 28.7, 34.6, 47.5 and 56.5°, which are indexed to the (111), (200), (220), and (311) planes, respectively (JCPDS card n°. 43-1002). Specifically, CFC has a rhombohedral α -Fe₂O₃ phase at 20 values of 34.1 (104), 36.4 (110) and 48.5° (024), which belongs to the *R*-3*c* space group (JCPDS card n°. 87-1165). The diffraction peaks also match well with those of the inverse spinel γ -Fe₂O₃ at 20 equal to 29.3 (220), 36.7 (311) and 57.3° (511) (JCPDS card n°. 39-1346). Moreover, the peaks at 20 = 36.9°, 44.5°, and 65.0° are also consistent with the (311), (400) and (440) planes, respectively for Co₃O₄ (JCPDS card n°. 42-1467). These phases are all superimposed to those of the fluorite CeO₂.

For CFN, the previously mentioned iron phases arise concomitantly with that of the CeO₂ and cubic NiO (*Fm-3m* space group, JCPDS card n°. 47-1049) as well. Notably, no well-defined peak is detected in CFM by XRD likely due to the nano-sized features of the iron and cerium oxides phases. The MnO_x species may provide the dispersion of the other phases on the solid surface, which is further corroborated by scanning electron microscopy (SEM). Additionally, the MnO_x is a mixture of manganese oxides in the γ -MnO₂ and α -Mn₂O₃ phases [20]. Another explanation could be the

presence of either the smaller particles size of Ce, Fe and mainly Mn species or the formation of an amorphous phase. Such species would not be easily identified with XRD due to either the small size or the amount on the surface, as reported in earlier studies for Ti and Al-containing hydrotalcite based materials [21].



Figure 3. (**a**) X-ray diffraction patterns of the CFC, CFN, and CFM solids. (**b**) Raman spectra of the solids at low wave numbers and (**c**) at higher wave numbers.

Raman spectroscopy measurements were obtained to correlate the structural features of the solids observed by XRD. The Raman spectra are shown in Figure 3b, c. Since it can be observed in Figure 3b, CFC has the vibration modes at around 191 (E_{2g}) and 512 (F_{2g}) cm⁻¹. These vibrational modes are assigned to the spinel Co₃O₄ belonging to the *Fd3m* (O_h^7), which is associated with the CoO₄ tetrahedra in the Co₃O₄ [21]. The A_{1g} mode (670 cm⁻¹) arises from the oxygen atoms vibration in the octahedral CoO₆ units. The typical cation-anion, i.e., Co–O bond lengths from the polyhedral distortion in the spinel lattices is detected, which is found elsewhere [22]. Remarkably, the mode located at 467 cm⁻¹ is attributed to be from the F_{2g} symmetry in a cubic fluorite structure of CeO₂ while the weak one at around 606 cm⁻¹ corresponds to oxygen vacancies [2]. It is noteworthy that the characteristic modes of the iron phases are at about 1100 and 1200 cm⁻¹ (Figure 3c), which are attributed to the α -Fe₂O₃ (R-3c (D^6_{3d}) space group and γ -Fe₂O₃ (Fd3m (O_h^7) space group) are not evident in CFC. Clearly, this might be due to either the substitutional doping into the CeO₂ surface lattice, which increases the oxygen vacancies [2].

On the other hand, the Raman spectrum of CFN displays an intense mode at 462 cm⁻¹ from the F_{2g} mode due to the CeO₂ (Figure 3b). The broadband at around 555 cm⁻¹ originates from the oxygen distortion in the Ce-O lattice probably due to Fe or Ni incorporated into the Ce vacancy. The presence of

other nanometric phases such as α -Fe₂O₃ and γ -Fe₂O₃ exists as an extra framework species that cannot be neglected. Moreover, the broadband at a high-frequency region has vibrations at 830, 1060, 1130 and 1182 cm⁻¹ (Figure 3c). These modes are assigned to be from η^1 superoxide species (η^1 -O₂⁻ species at the one electron defect site) and η^2 peroxide species (η^2 -O₂²⁻), respectively [23,24]. The superimposed mode at 1182 cm⁻¹ corresponds to oxygen vacancies, which is associated with the transverse acoustic mode and the second-order phonon mode in the ceria lattice [23].

The CFM Raman spectrum reveals a feature of the broadband between 550 to 750 cm⁻¹ likely due to the CeO₂ and the α -Fe₂O₃ and γ -Fe₂O₃ iron phases overlap (Figure 3b). The findings state that the main modes of the Fe-O stretching vibration of α -Fe₂O₃ appear at E_g (620 and 658 cm⁻¹). These modes may be overlapped with that at 690 cm⁻¹ from Fe³⁺ in distorted tetrahedral symmetry as well as Fe³⁺/Fe²⁺ in octahedral symmetry from γ -Fe₂O₃ [25]. At a high frequency region (Figure 3c), the modes attributable to the vibrations of α -Fe₂O₃ at 1100 and 1300 cm⁻¹ and the γ -Fe₂O₃ at about 1370 cm⁻¹ are not visible due to CeO₂ covering the previously mentioned iron phases, as observed elsewhere [17]. These results indicate that the semi-crystalline materials have the CeFe as a matrix besides the third oxide existing as NiO, Co₃O₄, or MnO_x appears isolated, respectively, in CFN, CFC, and CFM solids.

2.2. Valence States by Electron Paramagnetic Resonance (EPR)

In an attempt to determine the possible oxidation states of the Fe species present in the samples, EPR measurements were recorded at room temperature (Figure 4). Noteworthy, all samples have broad resonance linewidth with magnetic field values in the 3400 to 3700 G range. The significant similarities observed for the resonance signals among the spectra suggest that they display similar surface structures in agreement with the Fe phases shown by XRD and Raman measurements. Particularly, the intensities of the asymmetric lines decrease and their widths broaden in the following sequence comparatively: CFM (Figure 4a), CFN (Figure 4b) and CFC (Figure 4c). The corresponding EPR signals for the CFM, CFN and CFC samples have hyperfine structures at *g* values at \approx 5.60–5.61, 2.28–2.29 and 4.9–5.4, respectively [4].

A low magnetic field with the *g* value close to 4.3 revels that the Fe species belongs to d^5 configuration, which has the samples of a paramagnetic Fe³⁺ ion [26]. The first signal is attributed to either the isolated tetrahedral FeO₄ or the distorted rhombic octahedral FeO₆ entities [27]. Because the signals in the CFM and CFN samples (included Figure 4a,b) are narrower than that of CFC (included Figure 4c), the Fe ions are present in various oxidation states in the former samples. In line with these observations, the high magnetic field signal has an expected *g* value very much greater than 2.0, which is due to the ferromagnetic resonance of Fe species in all solids. As found elsewhere, it can also be related to Fe²⁺ and Fe³⁺ dimers or their clusters in interstitial defects of the structure, which suggests the presence of the α -Fe₂O₃ and γ -Fe₂O₃. This is in line with the findings [17,27]. This confirms the XRD and Raman results that detected these phases in CFC and CFN. Although the XRD results do not detect the phases in CFM, the EPR spectrum of the sample is characterized by a broad and asymmetric signal of the previously mentioned species. Thus, all samples studied possess Fe²⁺ and Fe³⁺ species associated with the α -Fe₂O₃ and γ -Fe₂O₃ phases.

Additionally, the CFM has a typical well resolved Mn^{2+} signal observed at *g* values of 2.0 while a poorly resolved one has a *g* value of 4.3 [28,29]. The MnO₂ species has a *g* value at around 3.99 from the Mn⁴⁺ ion signals [30]. Based on these assumptions, the signal CFM might be due to Mn⁴⁺ and Mn²⁺ from the MnO_x entity. Most likely, this slightly resembles the ones obtained for Fe since the lines are in similar positions in the EPR spectrum. In the case of CFN, the Ni signal appears broader and asymmetrical (Figure 4b). Due to the presence of high spin configuration and Ni²⁺ in the octahedral environment, the *g* value varies from 2.28 to 2.29 in accordance with the literature results [31,32]. A complete assignation of the NiO presence in the solid by EPR is not possible because of the superimposition with Fe lines. For the CFC sample, a weak low-symmetrical field of tetrahedrally coordinated Co²⁺ ions signal can be an overlapping of the previously mentioned species with that of the strong Fe ones. Thereby, the divalent Co has a *g* value close to 4.9–5.4, which is comparable to those previously found for Co-containing samples with only a small fraction of Co^{2+} being oxidized to Co^{3+} [32–34]. This confirms the findings by XRD and Raman that suggested the presence of the Co_2O_3 phase in the CFC sample.



Figure 4. EPR spectra recorded at room temperature: (**a**) CFM, (**b**) CFN and (**c**) CFC catalysts. The inset shows the signal amplification in a specific magnetic field value for each sample.

Importantly, the EPR resonance linewidths of CeFe-based catalysts has been widely studied elsewhere [35]. Accordingly, signals at g = 1.96 are attributed to the presence of Ce³⁺ located at two different sites in the CeO₂ lattice whereas a g = 2.10 is assigned to the surface superoxide species [23,35]. In addition, the substitution of Fe³⁺ by Ce³⁺ ions in the CeO₂ lattice as well as the Fe³⁺ ions occupying the network Ce⁴⁺ sites indicate the formation of the Fe-O-Ce bond at g = 2.61 [23]. All of these attributions cannot be ruled out since the EPR signals of the present samples are in a magnetic field position similar as those of the reported CeFe solids.

2.3. Morphology Characteristics and Textural Properties

The starting XAD-16 resin beads are composed of polystyrene-divinylbenzene resin with a high hydrophobic character, which is illustrated by the picture of the resin swollen in water (Figure 5a). When dried (Figure 5a, included), the beads seem to be uniform in terms of their sizes. The scanning electron microscopy image (Figure 5b) reveals that the bead mould is spherical with particles possessing 0.45 to 0.70 mm in size. The spherical beads have a flat surface composed essentially by carbon as exposed by SEM-EDS (scanning electron microscopy and energy-dispersive X-ray spectroscopy) mapping image (Figure 5c).



Figure 5. (a) The XAD-16 resin beads immersed in water. The included figure is the dry resin beads. (b) An overview image by SEM and (c) an EDS mapping image for C-K α of a resin bead.

Even with the impregnation of metals, the solids exhibit the spherical-like morphology, which is shown in Figure 6. Additionally, it confirms that the impregnating solutions are successfully introduced into the pores of the matrix. It is assumed that such a morphological feature is a result of the maintenance of the structure of the solid, as an inverse replica of the mould [2]. The high magnification images depict the presence of rough surfaces with and without particle accumulation on it.



Figure 6. SEM images and EDS mappings of the catalysts: (a) CFC, (b) CFN and (c) CFM.

The element mapping of the CFC sample shows that the Ce, Fe, Co, and O are located around the spherical particle and also in the inner sphere region. Sometimes the beam of the microscope can occasionally cause the heating of the particle and, thereby, the spheres may be distorted [36], as shown in the SEM image (Figure 6a). The low magnification image of CFC depicts small roles on the particle surface. On the other hand, the higher magnification image shows a rough surface, which is presumably attributable to the CeO₂ deposition on the solid surface.

In the case of CFN (Figure 6b), the SEM-EDS mapping shows the Ce, Fe, Ni and O elements with the Ni randomly distributed on the solid surface. Moreover, some CFN spheres have large holes and collapse, which forms leaf-like structures and is likely due to the exposure to air during the calcination. Regardless of the used Ni impregnating solution, the amount of Ni impregnated turned out to be insufficient to infiltrate into the sphere to obtain the isolated particles.

The SEM image of CFM (Figure 6c) reveals the presence of rigid spheres with a less rough surface texture and smaller particles agglomeration on it, which is seen in the higher magnification image. Additionally, many of the CFM spheres appear to be broken and present distinct morphologies including particles located apart from each other. This may occur because of the magnetic interaction between the particles so as to minimize their energy. According to the findings, the magnetic phases such as those based on Fe species can provoke the previously mentioned effects [37]. Moreover, the Mn species are found finely dispersed on the solid surface. This is in accordance with the XRD results that suggest nanometric sizes of the MnO_x species (small volumes to diffract) or a high dispersion of them on the solid surface.

All solids exhibit type IV isotherms with similar hysteresis loop shapes with CFM having the largest one (Figure 7a). Both CFC and CFN have a capillary condensation step together with a hysteresis loop occurring at P/P_0 between 0.60–0.95. On the contrary, CFM has a hysteresis loop in the 0.20–0.99 range, which is larger than that of the CFC and CFN counterparts. Judging from their morphologies, all the spherical nanocasted materials display a mesoporosity. Additionally, the higher magnification SEM images from CFC and CFN suggest a rough surface with void spaces between the particles. Meanwhile, it may indicate that these samples also display mesopores and micro-pores. Differently, CFM possesses loosely packed spherical with some aggregated particles on the sphere (Figure 6c) that can promote the formation of micropores besides the mesopores. It is noteworthy that these results are reflected in their corresponding Barrett-Joyner-Halenda (BJH) pore size distribution curves (Figure 7b). Accordingly, CFC and CFN exhibit a broad distribution, which implies the existence of a porous structure with micropores, mesopores, and macropores. In contrast, CFM has a narrower curve, which further confirms the presence of mesopores originating from the void space between the aggregated and spherical particles whereas the micropores are also included within the distribution. The textual parameters are obtained based on the adsorption-desorption isotherms and the results summarized in Table 1.

For comparison purposes, the spherical mold has a relatively high textural porosity with a surface area of 800 m²·g⁻¹ and pore volume of 0.55 cm³·g⁻¹ and pores with a diameter of 200 Å. which can be verified in Table 1. The composites oxides have different BET surface areas and pore volumes. The areas are lower than that of the mold due to the semi-crystallinity of the oxides through the calcination process when compared to that of the amorphous mold.

Table 1. Textural properties obtained by the nitrogen adsorption-desorption isotherms of the investigated solids.

Sample	^a S _{gBET} (m ² ·g ⁻¹)	<i>t</i> -plot External Surface Area (m ² ·g ⁻¹)	^b Pore Volume (cm ³ ·g ⁻¹)	^b Mesopore Diameter (Å)
CFC	70	68	0.29	150
CFN	49	53	0.17	117
CFM	14	14	0.031	83

^a From Brunauer-Emmet-Teller (BET) method. ^b From Barrett-Joyner-Halenda (BJH) method.



Figure 7. Physisorption measurements of the solids: (**a**) Nitrogen adsorption-desorption isotherms and (**b**) pore size distributions.

It is found that the CFC has the highest BET surface area (70 m²·g⁻¹) and pore volume (0.29 cm³·g⁻¹), which is most likely influenced by its morphological feature as well as the smaller particle sizes. Similarly to the CFC counterparts, the CFN also exhibits high textural properties ($S_g = 49 \text{ m}^2 \cdot \text{g}^{-1}$, pore volume = 0.17 cm³·g⁻¹) due to the previously mentioned characteristics. However, the CFM possesses the lowest textural properties due to the accumulation of particles on its surface and also in the pores. Moreover, all samples possess micro-pores, as indicated by the *t*-plot values with CFC and CFN having the major values for this kind of pores. In agreement, the *t*-plot external surface area varies from 14–68 m²·g⁻¹ and these areas correspond to the micro-pore ones. Additionally, the CFC and CFN samples exhibit a pore size centered at a 117–150 Å range as a result of their hollow spherical interiors porous structure comprising of micro, meso and macropores. In the case of CFM, pores with diameters of ca. 83 Å correspond to the mesopores. All these results are in agreement with the SEM observations.

2.4. Catalytic Activity Studies

2.4.1. Screening of the Catalysts

The catalytic activity of the solids in the ethylbenzene liquid oxidation was examined in short-term catalytic runs at 50 °C with ethylbenzene to the H₂O₂ molar ratio of 1:1 and using 50 mg of catalysts (Table 2). In the absence of the catalysts, a null conversion of ethylbenzene is achieved. Table 2 illustrates that all the nanocasted monoxides, i.e., Fe (α -Fe₂O₃), Ce (CeO₂), Mn (MnO_x), Co (Co₃O₄) and Mn (MnO₂), convert a negligible amount of ethylbenzene, e.g., lesser than 5.9% in 1 hour of the reaction being highly selective to others. By comparison, the binary nanocasted oxides (CeFe, CeCo, CeMn, and CeNi) have also been used in the reaction under the same reaction conditions and their conversions are superior to those of the monoxides during the first hour of the reaction. The selectivity to others remains high in the case of the binary oxides.

Catalyst	Ethylbenzene Conversion (%)	Selectivity (%)				
		Benzaldehyde	Acetophenone	Benzoic Acid	^a Others	
Ce	2.8	12.0	7.1	18.0	62.9	
Fe	5.9	16.8	14.3	17.4	51.5	
Со	3.3	6.1	4.0	10.1	79.8	
Ni	0.3	-	-	-	-	
Mn	3.7	9.6	6.8	13.0	70.6	
CeFe	10.7	18.3	15.7	23.5	42.5	
CeNi	6.4	5.2	9.7	8.6	76.5	
CeMn	8.2	7.8	6.3	9.0	76.8	
CeCo	7.6	2.5	4.3	7.5	85.7	
CFC	49.2	24.9	22.8	29.4	22.9	
CFN	85.2	32.4	23.3	18.6	25.7	
CFM	47.9	14.5	4.6	7.8	73.1	

Table 2. Catalytic performances of the solids in the ethylbenzene oxidation. Reaction conditions: temperature of 50 °C, ethylbenzene to H_2O_2 molar ratio of 1:1 with 50 mg of catalyst during 1 h of the reaction time.

^a Others include 1-phenyl ethanol, 2-phenyl ethanol, 2-phenyl acetic acid, 2-phenyl acetaldehyde, and heavy byproducts of polymerization.

Studies on styrene oxidation in the presence of H_2O_2 reveals that Fe, Ni, and Ce species show a better performance in the reaction at a short reaction time when compared with other solids [25,38,39]. To our knowledge, a reason for the catalytic activity of the solids can be anticipated by noticing that the binary CeFe catalyst offers the acid-base and redox species to accentuate this effect [25]. This supports the idea that the reactivity of the binary nanocasted oxides under study is thanks to the transition metals Fe^{3+}/Fe^{2+} and Ce^{4+}/Ce^{3+} pairs having predominant Lewis acid sites, which is demonstrated by using transition metals and which act as catalysts for oxidation reactions [17,39,40]. The ethylbenzene oxidation reaction over the monoxides may follow similar approaches for mechanistic considerations as those of gold nanoparticles-catalyzed epoxidation of stilbene by involving a formation of a reactive oxygen species through the metal nanoparticles surface, which induces the decomposition of the peroxyl radical intermediate [41,42]. On the contrary, adding a third metal to the binary oxides further improves the reactivity of CFC, CFN, and CFM composites with CFN holding the best conversion among the ternary oxides studied. The desired products such as benzaldehyde, acetophenone, and benzoic acid are selectively formed in higher amounts than those of the monoxides and the binary oxides. Thus, the performance of the ternary nanocasted oxides is investigated in detail.

2.4.2. Catalytic Performance of the Ternary Oxides Catalysts

The ethylbenzene conversion over the ternary oxides as a function of time is depicted in Figure 8a. Both CFC and CFM catalysts experience a decline in their performances while CFN exhibits a very small decrease in the ethylbenzene (EB) conversion. It is known that the NiO oxide has greater Brønsted acidity than the Co oxides [43]. Therefore, H_2O_2 oxidant adsorbs on the surface of the CFN easier than in the CFC and CFM in reason of the Brønsted acidic nature of the nickel. Concomitantly, the oxygen from the H_2O_2 desorbs to the Fe and Mn or Ce sites due to the Lewis acidic nature in these species. This can explain the elevated conversions of CFN when compared with CFC and CFM. Meanwhile, the CFN gives high selectivities of 30.7, 21.3, and 16.9% for benzaldehyde, acetophenone, and benzyl alcohol, respectively. Others are found to be 31.1% of the products formed when the reaction is allowed to run for 6 h (Table 3).

Catalyst	Ethylbenzene Conversion (%)		H ₂ O ₂			
		Benzaldehyde	Acetophenone	Benzoic Acid	^a Others	Efficiency (%)
CFC	30.8	24.0	23.1	26.9	26.0	10
CFN	70.0	30.7	21.3	16.9	31.1	15
CFM	37.8	12.0	5.0	3.0	80.0	28

Table 3. Ethylbenzene conversion, selectivity of the products obtained, and H_2O_2 efficiency for the ternary compounds. Reaction conditions: temperature of 50 °C, ethylbenzene to H_2O_2 molar ratio of 1:1 with 50 mg of catalysts in 6 h of a reaction time.

^a Others include, 2-phenyl ethanol, 2-phenyl acetic acid, 2-phenyl acetaldehyde and heavy by products of polymerization.

As can be observed in Figure 8a, EB conversion over CFC has a declining activity over the course of 6 h of reaction and by-products, i.e., others are predominant in addition to small amounts of benzaldehyde, 2-phenylacetaldehyde and benzoic acid products. Thus, the ternary catalysts may prevent, to some extent, the EB approaches to the active catalyst sites, e.g., Fe, Ce, or Co, most likely due to the steric hindrance of the aromatic ring. On the contrary, the ethyl group of EB promotes the side chain oxidation mechanism at primary and secondary carbon atoms by forming the carbinols entities [40], which further undergo oxidation to the respective aldehyde and ketone obtained.

The nature of the third metal added to Fe^{2+}/Fe^{3+} and Ce^{3+}/Ce^{4+} active sites could improve significantly the catalytic property of solids, which is found elsewhere [17]. In particular, Co existing as Co^{2+} species has been recently reported to be effective for styrene oxidation due to the intra-lattice cobalt ions being stable, which avoids the Co^{2+} oxidation to Co_3O_4 and Co_2O_3 phases [24,43]. Another point is that the structural Co^{2+} present in the porous of the solids such as Co-containing molecular sieves could be oxidized to structural Co^{3+} to produce sites for oxidation redox reactions [44]. Although Co may participate as a promoter to transfer electrons to CeFe, the poor stability of the CFC catalyst is caused by the inner Co^{2+}/Co^{3+} species encapsulation in the spherical particles, which is shown by SEM-EDS, EPR, and Raman results. As a consequence, the electron transfer of the previously mentioned Co species to avoid the Fe and Ce reduction may not occur and, thereby, the CFC catalyst undergoes a low performance in 6 h of reaction time. Moreover, the selectivity for acetophenone, benzaldehyde and benzyl alcohol are 24.0, 23.1 and 26.9%, respectively (Table 3). In addition, the by-products named as others correspond to 26.0% of the total amount of the compounds formed over CFC.

Interestingly, the CFM shows a great performance at the beginning of the reaction with conversions above 40% (Figure 8a). The reason for this behavior is that the active sites possessing positive charges defects, high oxidation potential from the Fe^{2+}/Fe^{3+} and Mn^{3+}/Mn^{2+} entities, and oxygen vacancies from CeO₂ that might facilitate the oxidation of the ethylbenzene. Additionally, it is feasible to speculate that the good individual dispersion of MnO_x particles participates in the EB conversion at short reaction times. Bearing with this argument in mind, the Mn^{4+} ions changes to Mn^{2+} in Mn-containing molecular sieves that are acting as an excellent oxidant for selective oxidation of the hydrocarbon process [45]. However, the catalyst experiences a drop in the conversion at the end of the 5-hour reaction period and the solid shows comparable catalytic activity to the corresponding CFC one (Figure 8a). In other words, the presence of the little agglomerates of Ce and Fe on the sphere surface (EPR and SEM-EDS results) has a beneficial effect in the catalytic performance even though it could favor a low accessibility of the reactants to the active sites. For this reason, CFM catalyst suffers a deactivation and the EB conversion decays during 6 h of the reaction time. Moreover, the selectivity to others is of ca. 80% with acetophenone, benzaldehyde, and benzoic acid, which is found in 20% of the total amount.



Figure 8. (a) Ethylbenzene conversion evaluation as a function of time over the catalysts: CFN, CFM, and CFC. (b) Comparison of the oxidation reactions with distinct substrates by using CFN as the catalyst. Reaction conditions: temperature of 50 °C, substrate to H_2O_2 molar ratio of 1:1, and catalyst mass of 50 mg.

Regarding the CFN performance, it is well-known that Ni²⁺ promotes hydrocarbon oxidation when low reaction temperatures are used because of the ability of NiO of either adsorbing or decomposing H₂O₂ to catalyzing oxidation reactions [39,46,47]. Running the reaction for a short time, the CFN catalyst exhibits a conversion superior to 70%, which means that the presence of Ni²⁺ is favorable for the EB oxidation. Thus, it is speculated that Ni may provide a synergistic effect among Fe and Ce playing a vital role in the oxidation reaction, which is reported earlier [47]. After 3 h, a further slight decline in the conversion is observed. This is mostly due to the low potential oxidation of Ni faced to Ce and Fe, which causes the latter species reduction when the reaction proceeds. Both the porosity and the very low agglomeration of NiO particles throughout the surface could favor the EB oxidation during the first stages of the reaction. However, the drop in the conversion is associated with the low availability of active sites, which provides lesser active Ce²⁺/Ce³⁺, Fe²⁺/Fe³⁺, and Ni²⁺ centers for the reaction.

As shown in Table 3, the obtained reaction products are benzaldehyde, acetophenone, and benzyl alcohol from the selective oxidation of C-H bonds from ethylbenzene molecule under mild conditions. The findings state that the acetophenone formation involves the adsorption of both hydrogen peroxide

and ethylbenzene on the surface of the catalyst and the abstraction of an α -hydrogen from the CH₂ group of ethylbenzene to obtain 1-phenylethyl radicals [47]. This step is followed by a reaction with oxygen to produce acetophenone. On the other hand, the benzaldehyde is formed through the decomposition of 1-phenylethoxyl radicals [17,48,49]. In turn, the formation of benzoic acid is believed to occur via double oxidation of the lateral methyl group linked to the ethylbenzene aromatic ring. The others, which include 1-phenyl ethanol, 2-phenyl ethanol, 2-phenyl acetic acid, and 2-phenyl acetaldehyde, are the major products formed over all the catalysts (Table 3).

The assumed mechanism for others entails the oxidation of the C-H bonds from EB activation by H₂O₂ to form phenylethyl radicals and hydrogen atoms [25,47]. As a second step, the oxygen radicals react with phenylethyl radicals to yield 1-phenylethylperoxyl one. Furthermore, these radicals subsequently undertake the proton abstraction from the substrate to give 1-phenyl-ethylhydroperoxide intermediate and the final products are formed, which is shown by the mechanistic considerations [48,49]. Moreover, it is expected the ethylbenzene aromatic ring hydroxylation by-products such as *ortho*-hydroxy-ethylbenzene and *para*-hydroxy-ethylbenzene, respectively, arise from the ethylbenzene hydroxylation in the *ortho* and *para*-positions. However, these products are not detected. Hence, the conversion exhibited with the catalysts is clearly dependent on the nature of the mixed metal oxides.

Taking into account the H_2O_2 efficiency (Table 3), it is expected that the third metal, e.g., Co, Ni, or Mn influences in the H_2O_2 reaction. Accordingly, the EB efficiency parameter follows the same order as that of the EB conversion. For instance, both CFC and CFN have the lowest H_2O_2 efficiency of ca. 10 to 15% whereas the CFM has the highest one of ca. 28%. For this reason, ease coordination of H_2O_2 on metals such as Co and Ni besides Fe and its subsequent decomposition to the OH radical can explain these results. In addition, the low affinity of H_2O_2 by Ce and Ni may not improve the H_2O_2 efficiency [25].

2.4.3. Catalytic Performance of the CFN in the Oxidations of Styrene and Benzyl Alcohol

To provide more evidence on the effectiveness of the CFN toward the oxidation of cyclic compounds, the catalyst was tested with different substrates (Figure 8b). The results consistently suggest that the ternary nanocasted oxide composite is active in the presence of the distinct substrates. This is directly correlated with the role of the Fe³⁺ ions insertion on the CeO₂ interstitial site or on their oxygen vacancies [35] with a further help of Ni²⁺ improving the oxidation ability of CeO₂. The catalytic performance of the CFN in the presence of styrene and benzyl alcohol substrates is lower than that of the ethylbenzene one. However, the CFN catalyst produces selectively benzaldehyde, which is an important chemical intermediate for perfumery industry [49–51], independent on the substrate used (Table 4). It is worth underlining that the addition of a third metal oxide to the CeFe greatly improves the oxidation of the ethylbenzene reaction. In particular, the addition of Ni significantly improves the EB conversion due to the Lewis sites.

Table 4. The oxidation of cyclic substrates in the presence of H_2O_2 using CFN as the catalyst. Reaction conditions: temperature of 50 °C, substrates to H_2O_2 molar ratio of 1:1 with 50 mg of catalysts in 6 h of reaction time.

Substrate	Conversion (%)	Selectivity to the Main Product of the Reactions (%)				
		Styrene Epoxide	Benzaldehyde	Acetophenone	Benzoic Acid	
Ethylbenzene	70.0	-	30.7	21.3	26.0	
Styrene	35.5	29.7	48.2	-	-	
Benzyl alcohol	20.0	-	41.6	-	58.4	

The good selectivities of the main oxidation products and the catalyst stability can be attributed to the synergistic effect regarding the redox Ce^{2+}/Ce^{3+} , Fe^{2+}/Fe^{3+} , and Ni^{2+} pairs such as in the case of CFN. On the contrary, the Co and Mn addition is found to show a lesser performance due

to the structural and textural features of the CFC and CFM catalysts under an optimized condition. Our results indicate that the CFN nanocomposite has potential use for oxidation of cyclic compounds to obtain the desired valuable chemical intermediates.

3. Materials and Methods

3.1. Preparation of the Solids

The XAD-16 polystyrene bead resins (Sigma-Aldrich, St. Louis, MO, USA) was used as a template for the preparation of the solids based on the procedure developed by Marques [2]. Typically, the resin was stirred in deionized water seven times to remove the excess sodium. The metal salts were infiltrated into the resin by an impregnation method. This includes 10 g of resin mixed with iron nitrate solution (Vetec, Sigma-Aldrich, St. Louis, MO, USA) and cerium nitrate (Sigma-Aldrich, St. Louis, MO, USA) under stirring where the solvent evaporated. The resultant solid was then put into the nickel nitrate solution again for another impregnation to load a third metal into the resin, keeping the stirring at room temperature for 2 h. The molar ratio of the metals was selected to be equimolar ratios for Ce, Fe, and Ni. Ultimately, the solid was dried overnight and calcined at 500 °C (heating rate of 2 °C·min⁻¹) for 8 h in air flow to remove the organic constituents. The impregnation procedure was repeated with the previously mentioned metal nitrates precursors and calcined again at 500 °C (heating rate of 2 °C·min⁻¹) for 8 h. The solid was designed as CFN, which represents the Ce, Fe, and Ni metals. The scheme of the solids preparation procedure is summarized in Figure 2.

A similar methodology was adopted to incorporate cobalt and manganese as the third metal to the resin, respectively, using cobalt and manganese nitrate precursors. The obtained solids were labeled as CFC and CFM for CeFeCo and CeFeMn, respectively. In addition, binary oxides were prepared by following the mentioned protocol without the assistance of the third metal and its catalytic activity was compared to that of the ternary solids.

3.2. Characterizations

X-ray diffraction (XRD) patterns were collected on a DMAXB Rigaku diffractometer (Bruker, Karlsruhe, Germany) using Cu-K α radiation at 40 kV and 25 mA. The patterns were compared to that of the JCPDS (Joint Committee of Powder Diffraction Standard). The diffractograms were obtained between 10° and 80° (2 θ range) with a 0.02° step.

Nitrogen adsorption-desorption isotherms were measured at a liquid nitrogen temperature on an ASAP 2420 (Micrometrics, Norcross, GA, USA) after desorbing the samples at 150 °C for 8 h. The surface area and the pore size distribution were calculated by the Brunauer, Emmett and Teller (BET) equation and the Barrett-Joyner-Halenda (BJH) model, respectively.

Scanning electron microscopy (SEM) images were recorded on an FEI, Quanta 200 FEG electron microscope (FEI Quanta, Hillsboro, OR, USA), which was operated at 2 kV and equipped with an energy dispersive X-ray spectroscopy (EDS) system coupled. Prior to the measurements, a thin gold film was sprayed on the sample surfaces.

Micro-Raman scattering spectra were acquired on a LabRAM HR Horiba Scientific spectrophotometer using an $100 \times$ objective lens. The 514.5 nm line of an argon ion laser was used as the excitation source with an average power of 2 mW on the sample surface. The measurements were calibrated by referencing Si at 521 cm⁻¹ with a spectral resolution higher than 4 cm⁻¹. The spectra were obtained in the wavenumber range between 100 and 1600 cm⁻¹.

Electron paramagnetic resonance (EPR) measurements were performed to determine the valence state of the Fe on a Bruker spectrometer (Bruker, Rheinstetten, Germany). The X-band microwave frequencies were used with a field modulation of 9.5 GHz. The samples were flushed with helium at room temperature before measuring. The magnetic field was sweep integrated for X-band spectra to determine the *g* factor.

3.3. Catalytic Evaluation in the Selective Oxidation of the Cyclic Compounds

The selective oxidation of the ethylbenzene was conducted under mild conditions. The catalytic runs were carried out in a batch glass reactor equipped with a thermocouple and a reflux condenser possessing a magnetic stirrer. In a typical procedure, about 50 mg of the catalyst was placed in the reactor under nitrogen flow and using 10 mmol of the substrate, 10 mmol of dilute H_2O_2 (30%) as an oxidant, and acetone as the solvent at 50 °C for 6 h. The reaction aliquots were withdrawn after every hour and, then, analyzed in a GCrom gas chromatograph (GCrom, São Paulo, Brazil) equipped with a flame ionization detector (FID). Reaction products were identified by using a Shimadzu GC-2010 Plus gas chromatograph coupled to mass spectrometry, GC-MS (Shimadzu, Kyoto, Japan).

The selective oxidation of the other cyclic compounds, i.e., styrene and benzyl alcohol was carried out over the most active solid. About 50 mg of the solid was loaded in the reactor with styrene or benzyl alcohol as the substrates. Subsequently, the H_2O_2 oxidant was added to the reaction mixture in the presence of acetone under continuous stirring. Following that, the temperature was raised from room temperature to 50 °C and kept for 6 h. Lastly, the reaction aliquots were withdrawn after every hour and then analyzed in the chromatograph. Xylene was used as an internal standard. The calculations used are in our previous work [17]. The carbon balance was close to 98%.

4. Conclusions

CeFe-based oxide composites were synthesized by a nanocasting route. The addition of a third metal to the composites provided an improvement in the structural stability to the solids when tested in the oxidation of cyclic compounds. The solids possessing interesting spherical-like morphology showed elevated textural properties due to the nanocasted route used. XRD, EPR, and Raman results elucidated the presence of mixed oxides with Ce^{3+}/Ce^{4+} and Fe^{2+}/Fe^{3+} pairs besides the Me active sites (Me = Ni²⁺, Co²⁺/Co³⁺ or Mn³⁺/Mn⁴⁺). Catalytic results demonstrated that the ternary solids had good performance in the oxidation of ethylbenzene when compared with the binary and single monoxide nanocomposites. The combination of CeFe with Ni species significantly enhanced the ethylbenzene conversion, giving useful chemicals compounds, when compared to the styrene and benzyl alcohol substrates. This was due to the synergistic effect of the Ce³⁺/Ce⁴⁺, Fe²⁺/Fe³⁺, and Ni²⁺ active centers.

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