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Dehydrogenation of ethylbenzene with CO₂ to produce styrene over Fe-containing ceramic composites

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ABSTRACT

The activity of Fe-containing ceramic composites for the dehydrogenation of ethylbenzene in the presence of CO₂ was studied. Ceramic composites containing Fe, Cu, Cr, Pb and/or Ti were obtained by solid-state reaction method. The materials were characterized by XRD, textural properties, chemical analysis, SEM, Mössbauer spectroscopy, TPR, CO₂-TPD analyses and electrical measurements. A low conversion was obtained using CaTiO₃, due to the loss of the Ca species and coke production. The improvement of styrene selectivity with iron content, as well as the high stability of Cr_{0.75}Fe_{1.25}O₃, resulted in a better activity when using this solid. Fe²⁺ is continuously reoxidized to Fe³⁺ by CO₂ in the Fe–Ti active phase from the Fe_{0.5}Cu_{0.75}Ti_{0.75}O₃ sample. The latter catalyst exhibited high selectivity but limited stability towards styrene production. The ceramic composites appeared to be quite promising candidates for the dehydrogenation of ethylbenzene under CO₂, in comparison with the conventional Fe–K doped catalysts, due to the highly stable Fe³⁺ in a ceramic matrix.

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1. Introduction

Since 1940, the industrial production of styrene has been performed through iron oxide promoted by potassium catalysts, by the dehydrogenation of ethylbenzene (EB) with steam [1,2]. Styrene, one of the most important products in the petrochemical industry, is extensively used as a monomer to produce polystyrene, acrylonitrile–butadiene–styrene terpolymers, styrene–butadiene rubber and styrene–acrylonitrile copolymers [3].

Due to the high endothermicity and volume increase, the dehydrogenation of EB (reaction (I)) is carried out with an excess of superheated steam at temperatures of 550-700 °C.

$$C_6H_5CH_2 - CH_3 \rightarrow C_6H_5CH = CH_2 + H_2, \quad \Delta H = 124.9 \text{ kJ mol}^{-1}$$
 (1)

However, steam-based processes waste a large amount of latent heat through steam condensation and subsequent separation, and they pose thermodynamic limitations [1–5].

Carbon dioxide, a greenhouse gas, has recently been considered a very promising mild oxidant, and its utility in some partial oxidation reactions, such as the CO_2 reforming of methane [6–8], dehydrogenation of propane with CO_2 [9] and the dehydrogenation of EB [10–12] has been reported. CO_2 utilization offers several advantages over steam in the dehydrogenation of ethylbenzene, such as an acceleration of reaction rate, enhancement in styrene selectivity, alleviation of thermodynamic equilibrium limitations, suppression of the total oxidation, prolonging of the catalyst's life, and prevention of hot spots on the catalyst surface [10–15].

Several catalysts or catalystic systems have been tested in the new process [5,11–18], and an iron oxide-based catalyst has been shown to be active and highly selective to styrene, although it also presents disadvantages such as low surface area, lack of stability and easy deactivation of Fe^{3+} catalytically active sites. In the present contribution, we investigate the catalytic performance of Fe-containing ceramic composites in the dehydrogenation of EB in the presence of CO_2 .

Specifically, it is of interest to investigate the activity of ceramic composites for the development of a Fe-based catalyst for the industrial applications of dehydrogenation of EB with CO₂. Ceramic composites represent an attractive class of materials, which, owing to their stability, high surface area, electrical and structural properties [19], exhibit novel abilities that differ from those of the Fe-based catalysts for styrene production by means of the dehydrogenation of EB with CO₂. Therefore, the Fe-containing ceramic compounds can be promising candidates for the improvement of the catalytic parameters required to produce styrene. Few reports study the use of Fe-containing ceramic composite catalysts in dehydrogenation of EB, or the key role played by the ceramics in the process with CO₂ is not

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clear. With this goal in mind, the structural characterization of highly stable Fe-based ceramic composites and their catalytic performance for EB dehydrogenation with CO₂ were studied. The properties of the prepared catalysts, in terms of activity, catalyst stability, and coking resistance are reported and compared to Fe–K catalysts.

2. Experimental

2.1. Synthesis

The solid solutions consisting of $Ti_{1-x}(Fe_{0.5}Cu_{0.5})_xO_3$, $(Cr_{0.5}Fe_{0.5})_{1-x}O_3$, $Pb_{1-x}Fe_{0.5}Nb_{0.5}O_3$, and $CaTi_{1-x}O_3$ (0.1 < x < 0.7), denoted as FCTO, CRFO, PFN and CTO, respectively, were synthesized from powders of CaCO₃, Cr_2O_3 , TiO_2 , Fe_2O_3 , CuO, PbO and Nb₂O₅, using the conventional solid-state reaction method, according to the findings [20]. All oxides were procured from Synth[®].

The oxides and carbonate were weighed according to the compositions of each sample. The mixtures were high-energy ball milled for 4 h in a planetary ball mill (Fritsch Pulverisette 6). The rotation speed of the discs carrying the sealed vials was 400 rpm. This operation was used to improve the homogeneity of the powder. The milled powders were dried and then calcined in conventional controlled furnaces (EDG1800/EDGCON 3P) at 800 °C for 4 h. The calcined powders were mixed with an appropriate amount of glycerine (5 wt.%) as a binder and pressed into cylindrical discs of 10 mm of diameter. The height of the discs was about 3 mm and the pressure used to compact the powders was 600 tonnes cm⁻². These pellets were preheated at 600 °C for 1 h to remove the binder and then sintered at 1100 °C for 3 h.

Additionally, specific amount of CRFO (66%, 83%, 90%), together with FCTO (34%, 17%, 10%) were used to obtain the CRFO66, CRFO83 and CRFO90 samples, respectively, by adopting the methodology described above. The aim of adding FCTO to CRFO100 is to enhance the regeneration of Fe ions of CRFO phase by oxidation with CO₂. It could be achieved by increasing the amount of Fe–Ti active phase due to its well-known ability of regeneration in oxidant atmospheres [20].

2.2. Characterization

All solids were characterized by X-ray diffraction (XRD), textural properties (BET surface area, pore volume and diameter), thermoprogrammed reduction experiments (TPR), thermoprogrammed desorption of CO₂ (CO₂-TPD), electrical measurements, thermogravimetric analysis (TGA), scanning electronic microscopy coupled to EDX analyses (SEM–EDX), Mössbauer spectroscopy, and chemical analysis.

2.2.1. X-ray diffraction (XRD)

The X-ray powder diffraction profiles of the samples were acquired by means of a powder X-ray diffractometer system Rigaku D/max-B model. The system is composed of an X-ray generator, X-ray optics, goniometer, X-ray detector and counting system, and a recorder for data recording/storing [20]. Powdered samples were fixed on a silicon plate with silicon paste. Patterns were collected at 21 °C with Cu K α radiation. The diffractometer was operated at 40 kV and 25 mA in Bragg-Brentano geometry, with 0.02° (2 s count time) and 2 θ ranging from 20° to 90°.

2.2.2. Textural properties

The BET method, from the N₂ adsorption–desorption isotherm, was used to examine the porous properties of the samples by using nitrogen as the adsorbent at a liquid nitrogen temperature. The measurements were carried out in a Micromeritics ASAP 2002 instrument. Before the analysis, all samples were treated under vacuum at 100 °C for 12 h.

2.2.3. Scanning electron microscopy (SEM)

Scanning electron microscopy coupled with the energy dispersive analysis–EDX was used to obtain information about the morphology and surface composition of the as-sintered cylindrical ceramic composites. Previously, the samples were covered with a thin layer of carbon. The analyses were carried out using a Phillips XL-30 machine which was equipped with EDX detector (EDAX-CDU Leap Detector).

2.2.4. Thermoprogrammed reduction (TPR)

The TPR analysis was obtained in a home-made equipment from 25 °C to 1000 °C at a heating rate of 10 °C min⁻¹. N₂ gas containing 5% H₂ was used to reduce catalysts with a flow rate of 10 mL min⁻¹ for 0.35 g of fresh catalyst.

2.2.5. ⁵⁷Fe Mössbauer spectroscopy

Mössbauer spectra were obtained by standard transmission geometry, using a constant acceleration spectrometer with a radioactive source of ⁵⁷Co in Rh matrix. Measurements on powdered samples were obtained at 21 °C. The spectra were evaluated using the Normos fitting routine, which makes use of a set of Lorentzian curves to compute the contribution of each curve to the total absorption spectrum, through the least squares procedure. All isomer shifts (δ) refer to metallic iron (α -Fe).

2.2.6. Electrical conductivity measurements

For these experiments, the samples under investigation were used in the form of discs (ca. 0.5 g) and a diameter and thickness of 11 mm and 12 mm, respectively. Then, the discs were covered by silver conductive paste (Joint Metal, PFT type 9045). Finally, they were dried at 117 °C for 20 min. Electrical measurements were led in an evacuated dielectric cell. The dielectric characterization was carried out by the complex impedance. The measurements at different temperatures for different signal frequencies range from 100 Hz to 10 MHz, using Hewlett-Packard 4192A impedance equipment. A parallel equivalent circuit model was adopted to analyze the data [19,20]. A Eurothermo 2024 model thermocontroller was used to measure the temperature of the sample. The conductivity measurements were determined by checking the sink of the thermoelectric (Seeback coefficient potential (α)) using a D.C. microvoltmeter, given the dimension of the discs [19,20].

2.2.7. CO₂-TPD analyses

CO₂ temperature-programmed desorption (CO₂-TPD) of selected samples was performed on a home-made system. The samples (ca. 200 mg) were charged into a quartz reactor and heated at 550 °C under a helium flow (10 °C min⁻¹, 30 mL min⁻¹) for 1 h. The samples were then exposed to CO₂ (30 mL min⁻¹) at room temperature for 30 min. The desorbed CO₂ was detected by an online thermal conductivity detector (TCD) after passing by a trap (-20 °C) to remove any trace water.

2.2.8. TGA analysis of spent catalysts

TGA experiments for spent catalysts were carried out using Netzsch STA 409 PC/PG equipment coupled to a Bruker Tensor 27 IR instrument. The measurements were performed on spent catalysts to find the coking degree of the spent samples from room temperature to 1000 °C at 10 °C min⁻¹, under air flow, by placing approximately 15 mg of the sample in an aluminium pan.

2.3. Catalytic performance in dehydrogenation of ethylbenzene with $\ensuremath{\mathsf{CO}}_2$

The catalytic tests were carried out in an isothermal fixed tubular bed flow reactor using 100 mg catalyst at 550 °C under atmospheric pressure. Previously, the catalysts were treated in a

Table 1				
Chemical	compositions	of the	samples	obtained.

Samples	Compositio	Formulation						
	Cr ₂ O ₃	CuO	PbO	Nb ₂ O ₅	TiO ₂	Fe ₂ O ₃	CaCO ₃	
Cr	74.3 ^a	-	-	-	-	-	-	Cr ₂ O ₃
Cu	-	71.0 ^a	-	-	-	-	-	CuO
Pb	-	-	69.4 ^a	-	-	-	-	РЬО
Nb	-	-	-	66.5 ^a	-	-	-	Nb ₂ O ₅
Ti	-	-	-	-	71.7 ^x	-	-	TiO
Fe	-	-	-	-		70.9 ^a	-	Fe ₂ O ₃
CRFO100	36.4	-	-	-		63.6	-	Cr _{0.75} Fe _{1.25} O ₃
CRFO90	32.8	3.75			3.75	59.7		Cr _{0.65} Fe _{1.19} Ti _{0.08} Cu _{0.08} O ₃
CRFO83	30.2	6.37	-	-	6.38	57.0	-	Cr _{0.60} Fe _{1.14} Ti _{0.13} Cu _{0.13} O ₃
CRFO66	34.0	12.75	-	-	12.75	66.0	-	Cr _{0.48} FeTi _{0.26} Cu _{0.26} O ₃
FCTO	-	37.4	-	-	37.5	25.0	-	Fe _{0.5} Cu _{0.75} Ti _{0.75} O ₃
CTO	-	-	-	-	52.9	-	41.5	CaTiO ₃
PFN	-	-	67.7	20.2	-	12.1	-	PbFe _{0.5} Nb _{0.5} O ₃

^a Values refer to the metal composition.

gas flow containing nitrogen (10 mL min⁻¹, AGA 99%) at the stated temperature for 1 h at a heating rate of 5 °C min⁻¹. After this period was passed, the reaction was started by introducing a gas mixture of CO₂ (58.7 mmol h⁻¹, AGA 99%), N₂ (11.7 mmol h⁻¹, AGA 99%) and EB (1.9 mmol h⁻¹) to the reactor. Ethylbenzene was fed by bubbling the N₂ and CO₂ gases through a glass evaporator filled with liquid ethylbenzene maintained at 30 °C. The weight hourly space velocity (WHSV) was 0.15 h⁻¹, CO₂:EB molar ratio was 30. All liquids were procured from Aldrich, having 99.99% of purity.

The reaction was also conducted at 550 °C using 100 mg of catalyst in the absence of CO_2 , by flowing N₂ through ethylbenzene.

The products were analyzed by gas chromatography (CG) with FID, Model Simple Chrom Ciola. The EB conversion (C), styrene selectivity (S) and CO₂ conversion (C_{CO₂}) are expressed as mol.% on the basis of carbon atoms.

3. Results and discussion

3.1. Chemical analysis, morphological and structural characterizations

The chemical compositions of the solids are similar to theoretical ones measured by ICP-OES (Table 1).

The chemical reactions that describe the formation of the mixed oxides are represented by Eqs. (II)–(V).

$$5/2Fe_2O_3 + 3/2Cr_2O_3 \rightarrow 4Fe_{1.25}Cr_{0.75}O_3 \tag{II}$$

 $Fe_2O_3 + CuO \ + \ 3TiO \ \rightarrow \ 4Fe_{0.5}Cu_{0.75}Ti_{0.75}O_3 \eqno(III)$

 $Fe_{2}O_{3} + 4PbO \ + \ 3Nb_{2}O_{5} \ \rightarrow \ 4PbFe_{0.25}Nb_{0.25}O_{3} \eqno(IV)$

$$CaCO_3 + TiO_2 \rightarrow CaTiO_3 + CO_2$$
 (V)

3.1.1. XRD analysis

Fig. 1 shows the XRD patterns of the samples. All solids are highly crystalline materials and the pure oxides are identified as Cr_2O_3 , CuO, Fe_2O_3 , PbO, Nb_2O_5 , and TiO_2 , respectively for Cr, Cu, Fe, Pb, Nb and Ti samples (Fig. 1a). Indeed, the rutile structure is observed on the Ti sample. The diffractograms of the mixed oxides are in Fig. 1b.

In the case of the FCTO ceramic composite, a cubic symmetry belonging to Ia3 spatial group was observed [21]. In this structure iron, copper as well as titanium are distributed in 8b and 24d Wyckoff position, while the oxygen occupies the 48e site.

The Rietveld refinement analysis on the X-ray diffraction of FCTO found a solid solution, whose composition is $Fe_{2x-}Cu_{1-x}Ti_{1-x}O_3$ [20], in accordance with the chemical analysis of

the solid. Large amounts of $Cu^{2+}-Ti^{4+}$ pairs typically cause a lack of stabilization of the structure; however, this was not observed here and both CuO and TiO₂ phases produced FCTO sample.

For the CRFO100 ceramic composite, a trigonal symmetry belonging to the R3c group was found. In this structure Fe and Cr are the 12c Wyckoff positions while oxygen occupies the 18e site. The diffactogram of CRFO100 is similar to that of Fe_2O_3 and any Cr_2O_3 oxide, is observed. As the mixture of the FCTO and CRFO proceeds in the CRFO90, CRFO83 and CRFO66 samples, peaks assigned to the FCTO phase appear and they coexist with those of purely CRFO100.

For PFN ceramic composite, both the PbFe_{0.5}Nb_{0.5}O₃ tetrahedral Perovskite structure (ICDD PDF: 88356) and the "pyrochloride" Pb₂Nb_{0.5}Fe_{1.5}O_{6.5} structure are found, the latter being a cubic structure. The Perovskite phase represents 90.8% of the solids; no other isolated oxides were found. The Perovskite Pb(B'_{1-x}B''_x)O₃ are highly stable systems, in which the B' site has cations of low charge-to-radius ratio whereas the B'' has the highest ones. Indeed, both Pb₂Nb₂O₇ and Pb₃Nb₄O₁₃ phases are the so-called "pyrochloride" [20]; these phases are mixed with Fe₂O₃ and Nb₂O₅, resulting in the FeNbO₄ (wolframite) structure as an isolated phase. However, only a pure PbFe_{0.5}Nb_{0.5}O₃ ceramic composite was observed, because of reaction (IV) occurrence.

CTO ceramic composites have an orthorhombic symmetry corresponding to CaTiO₃ Peroviskite [22]. The $Cu_{1-x}Ti_{1-x}Fe_{2x}O_3$ composition belongs to the bixbyite family, in which Cu^{2+} , Cu^+ , Fe^{3+} and Ti^{4+} cations are likely [23].

3.1.2. SEM measurements

The morphology of the samples was evidenced by SEM (Fig. 2). CRFO100 morphology is composed of spherical and polygonal aggregates, possessing a large range of particles (Fig. 2a).

By contrast, the FCTO morphology (Fig. 2b) is characterized by irregular prismatic crystals which are smaller than those of CRFO100. EDX analysis shows that both samples have almost no isolated Fe and Cr (e.g., CRFO100), and Fe, Cu, and Ti (e.g., FCTO) oxides on the solids surfaces. The mixtures of CRFO and FCTO (e.g., CRFO90, CRFO83 and CRFO66) produce aggregates of particles of approximately 100 Å, and their morphologies are quite similar to those of CRFO100. Over the solid surface, EDX analysis identified a large amount of Fe_{0.5}Cu_{0.75}Ti_{0.75}O₃ oxide, as previously described by XRD.

PFN has plate morphology due to the FeNbO₄ precursor presence, and it results in a stable duplex morphology of a ceramic [22]. CTO morphology (not shown) is typical of CaTiO₃ structure. The Perovskites are a large group of crystalline ceramics that have a general ABO₃ formula, in which A^{2+} and B^{4+} atoms are located in distinct positions [24,25]. The A atoms that are equally in



Fig. 1. XRD diffractograms of the samples studied: (a) the pure oxides and (b) the ceramic composites.



Fig. 2. SEM images of (a) CRFO100, (b) FCTO, and (c) PFN.

the vertices of the cubic or octahedral symmetry are on the face of the cube, whereas B atoms are located in the centre of the structure. A typical member of this family is CaTiO₃.

The system α -Fe₂O₃ (hematite) and Cr₂O₃ (eskolaite) are isostructural with the corundum group. These oxides are completely miscible, resulting in thermodynamically solid-state solutions [25,26]. In a Fe_{2-2x}Cr_{2x}O₃ structure, both Fe³⁺ and Cr³⁺ are well-distributed due to the similarity of the ionic radii of the referred cations, in a good agreement with XRD analysis of CRFO series of ceramics composites.

3.1.3. Mössbauer analysis

The Mössbauer spectra of the samples obtained are shown in Fig. 3.

The average width of the Lorentizan is in the range of 0.17–0.40 mm s⁻¹ (FWHM), characteristic of metallic iron [22]. The isomer shift values in the range of 0.35–0.55 mm s⁻¹, referenced to metallic iron, indicates that the iron is in an octahedral coordination [27,28] for the Fe-containing ceramic composites.

The spectra of the CRFO100, CRFO90, CRFO83 and CRFO66 are formed by four sets of sextets, which is indicative of magnetic ordering in the iron matrix (antiferromagnetism). In contrast, FCTO and PFN are composed of doublets that are characteristic of paramagnetic materials [29]. These results suggest that Fe³⁺ species are present in all samples studied. Indeed, the multiplets observed in CRFO90, CRFO83 and CRFO66 give insight into any side reactions from the solid-state mixture of the oxides, and hence, the



Fig. 3. Mössbauer spectra of the Fe-containing ceramic composites.

Table 2

Quadrupole splitting (Δ), isomer shift (δ) and hyperfine magnetic field (BHF) parameters of the samples.

Samples	Average of qua over the distril	drupole (Δ) oution	Average of BHF over the distribution		
	$\Delta (\mathrm{mms^{-1}}) \qquad \delta (\mathrm{mms^{-1}})$		BHF (T)	$\delta ({ m mms^{-1}})$	
CRFO100	-	-	49.8 (±0.3)	0.45	
CRFO90	1.0 (±0.6)	0.42	47.7 (±0.1)	0.39	
CRFO83	1.0 (±0.6)	0.41	47.6 (±0.1)	0.39	
CRFO66	1.0 (±0.1)	0.43	47.7 (±0.1)	0.39	
FCTO	1.0 (±0.1)	0.35	-	-	
PFN	$0.40~(\pm 0.0)$	0.31	-	-	

formation of these ceramic composites can be achieved. The Mössbauer parameter obtained from the spectra are presented in Table 2.

The quadrupole splitting of 1.0 (±0.6) is typical of α -Fe₂O₃, confirming the predominance of Fe³⁺ in the octahedral sites. For the CRFO series, the quadrupole splitting distribution is relatively large; this is probably due the imperfect crystal lattice, as observed earlier for Fe-based materials [5]. In this case, Cr presence can contribute to the deformation of Fe³⁺ octahedral sites.

High spin Fe³⁺ is found in case of the PFN sample and it is characterized by a quadrupole splitting between 0.2 mm s⁻¹ and 0.6 mm s⁻¹, in agreement with the findings [30]. The magnetic splitting of 47.2–45.5 T is attributed to tetrahedral Fe³⁺, as in the case of CRFO series. Therefore, the Fe³⁺ species can be located in both octahedral and tetrahedral sites over these samples. Specifically, CRFO100 has the largest magnetic hyperfine field, e.g., 49.8 T (±0.3) that is characteristic of α -Fe₂O₃. It implies that the excess of addition of FCTO phase in CRFO66, CRFO83 and CRFO90 inhibits the α -Fe₂O₃ interaction with Cr₂O₃ to form the mixed Fe_{1.25}Cr_{0.75}O₃ composite.

Apart from the above results, Fe^{3+} ion appears to be the only specie of iron present in the samples. In addition, the literature reports show the ability of Fe^{3+} to convert EB [2,9], thus, the ceramic composites obtained can be considered as potential candidates to produce styrene.



Fig. 4. TPR profiles of the ceramic composites.

3.2. TPR measurements

TPR curves (Fig. 4) display similar profiles for CRFO100 sample with peaks at 300 °C and 400 °C related to the Fe³⁺ to Fe²⁺ and Cr³⁺ to Cr²⁺ reduction, respectively. A broad peak at approximately 650 °C, which is due to Fe⁰ reduction [4] is also found.

CRFO90, CRFO83 and CRFO66 reduction peaks are shifted to high temperatures due to the behaviour of Cu and Ti as structural promoters in avoiding the iron reduction, and it increases as the FCTO phase comes into the sample. By contrast, for FCTO sample Ti acts promoting the reduction of iron for lower temperatures, e.g., $250 \degree C (Fe^{3+} to Fe^{2+}) and 590 \degree C (Fe^{2+} to Fe^{0})$, in comparison with a TPR profile of pure α -Fe₂O₃ [4]. The presence of Pb or Nb in the PFN sample has an interesting effect in Fe reduction: neither Nb nor Pb reduction was found, however, the temperatures of 690 °C and 710 °C are attributed to the abovementioned steps of Fe reduction. CTO has no reduction peaks.

3.3. Textural characterization

The physico-chemical properties of the samples studied in the dehydrogenation of EB are shown in Table 3.

The textural parameters decrease upon Ca presence (e.g., surface area of CTO is $67 \text{ m}^2 \text{ g}^{-1}$ and its pore volume is $0.11 \text{ cm}^3 \text{ g}^{-1}$). This phenomenon was also observed for other alkali metals present in catalysts for EB dehydrogenation [4,10,31–34]. For PFN catalyst, these parameters became too low in the presence of Pb and Nb together and it is observed a decrease of the surface area and pore volume to respectively $52 \text{ m}^2 \text{ g}^{-1}$ and $0.09 \text{ cm}^3 \text{ g}^{-1}$. Moreover, all samples display a unimodal distribution of pores, which is rather narrow for PFN and it justifies the smaller pore volume found for this sample.

CRF0100 and FCTO catalysts have the highest values of the textural parameters. The surface phenomenon on the samples is explained by the fact that chromium as well as copper may act as structural promoters, keeping the particles apart from each other. Thus, these metals are spacers and cause strains in the lattice, shifting the equilibrium particle size toward smaller particles, since the ratio of strain to surface effects becomes greater for larger particles. However, the highest particle sizes exhibited by the CRF0100 and FCTO samples (respectively, 104 Å and 109.7 Å) indicates that a sintering effect is likely. Indeed, as the FCTO phase increases in the CRFO catalyst, the textural parameter slightly decreases because of FCTO agglomeration on the solid surface, as

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υ	υ	

Table 3

Physico-chemicals and catalytic properties of the samples studied in dehydrogenation of ethylbenzene with CO2.

Samples	Chemical composition	Sg (m^2g^{-1})	$V_{ m micro}$ (cm ³ g ⁻¹)	$R_{\rm p} ({\rm \AA})^{\rm a}$	D (Å) ^b	% Initial conversion		% Selectivity to styrene	Coke ^c content (wt.%)
						EB	CO_2		
CRFO100	Cr _{0.75} Fe _{1.25} O ₃	85	0.13	9.8	104.3	33	16	98.2	5.0
CRFO90	Cr _{0.65} Fe _{1.19} Ti _{0.08} Cu _{0.08} O ₃	82	0.12	9.0	101.8	30	14	99.1	9.6
CRFO83	Cr _{0.60} Fe _{1.14} Ti _{0.13} Cu _{0.13} O ₃	79	0.11	9.1	101.2	28	16	97.0	10.9
CRFO66	Cr _{0.48} FeTi _{0.26} Cu _{0.26} O ₃	80	0.11	9.2	101.7	15	12	98.0	15.5
FCTO	Fe _{0.5} Cu _{0.75} Ti _{0.75} O ₃	107	0.14	10.5	109.7	21	10	82.5	20.0
PFN	PbFe _{0.5} Nb _{0.5} O ₃	52	0.09	6.7	105.6	12	5	100.0	13.8
СТО	CaTiO ₃	67	0.11	9.1	83.9	4	27	-	1.7

^a Average pore size derived from the desorption branch of the isotherm using the BJH method.

^b From XRD analysis.

^c From TGA measurements of spent catalysts.

Table 4

Seeback coefficient (α), activation energy (E_{α}), type of semiconductor, and structural properties of the samples.

Samples	$lpha$ ($ imes 10^4 \Omega^{-1} cm^{-1}$)	$E_{\alpha} (\mathrm{eV})^{\mathrm{a}}$	Type of semiconductor	$I_{2\ 0\ 0}/I_{4\ 0\ 0}{}^{\rm b}$	lons at tetrahedral sites	Ions at octahedral sites
CRFO100	0.42	0.66	n	2.80	Cr ³⁺	Fe ³⁺
CRFO90	0.50	0.31	n	2.78	Cr ³⁺	Fe ³⁺
CRFO83	0.67	0.30	n	2.44	Cr ³⁺ , Fe ³⁺	Fe ³⁺
CRFO66	1.18	0.16	n	2.53	Cr ³⁺ , Fe ³⁺	Fe ³⁺
FCTO	0.94	0.43	n	2.60	Cu, Fe ³⁺	Fe ³⁺ , Ti ⁴⁺
PFN	1.50	-	р	2.86	Pb, Fe ³⁺	Fe ³⁺ , Nb ⁷⁺
СТО	0.31	-	-	-	Ca	Ti ⁴⁺

^a From Arrhenius equation ($k = 8.61 \times 10^{-5} \text{ eV K}^{-1}$).

^b From XRD data.

evidenced by EDX analysis. However, the surface area values of CRFO series are all within 10% and these values are statistically equivalent.

3.4. Electrical conductivity analysis

The conductivity mechanism in Perovskite-type oxides depends on the arrangement of ions in different sites [19,20,34]. The influence of both conductivity and temperature on the arrangement of ions in the ceramic composites might give valuable information on the stability of the solids. These measurements can be important for the dehydrogenation of EB led in different temperatures [34].

Table 4 shows that the conductivity has no linear correlation with the perceptual content of the phases in the ceramic composites.

CTO conductivity is particularly interesting because of the values of conductivity as a function of the frequency obtained, which can be justified by the Ca oxides as a dielectric isolator. The average electrical conductivity value varies from $10^{-2} \Omega^{-1} \text{cm}^{-1}$ to $10^{-4} \Omega^{-1} \text{cm}^{-1}$ (Table 4).

Moreover, the activation energy conduction (E_{α}) was obtained from the slope of the plot of log α versus 1/T (as mentioned in Section 2), from the Arrhenius equation, and the values obtained were calculated varying the temperature from 25 °C to 100 °C. There exists a tendency of decreasing the activation energy of conduction as the FCTO phase is increased in the composite (Table 4). In other words, the FCTO phase leads to a decrease in the dielectric relaxation energy due to the drift mobility of electric charge carriers. Hence, the activation energy decreases with an increase in the FCTO phase, indicating that the pairs (Cu²⁺ \Rightarrow Cu⁰, Ti⁴⁺ \Rightarrow Ti³⁺) require comparatively higher energy (with respect to Fe³⁺ \Rightarrow Fe²⁺) to exchange electrons. PFN and CTO activation energies were not evaluated due to the lack of dielectric relaxation.

As dielectrics have a conductive band filled with electrons, with a gap and an empty band following, the bands of conduction are not completely filled by the d orbital, which permits a high

conduction by charge transferring. It results in a high mobility of the Fe, Pb, and Nb ions in PFN, which result in the highest conductivity ($15 \times 10^{-2} \Omega^{-1} cm^{-1}$). Thus, the exchange of electron pairs (Fe³⁺ \rightleftharpoons Fe²⁺) and (Nb⁵⁺ \rightleftharpoons Nb⁴⁺) are responsible for electrical conduction of PFN.

In addition, the intensity for the planes (2 2 0) and (4 0 0) from XRD data is used to estimate the locations of cations [34]. It is seen that the A^{2+} cations preferentially occupy the tetrahedral sites over the B^{4+}/B^{3+} ions, by comparing the experimental values of $I_{2 2 0}/I_{4 0 0}$ with respect to the theoretical ones. The CRFO series is an exception that suggests the Fe³⁺ location in both tetrahedral or octahedral sites, and this tendency makes the electrons more mobile than in the pure CRFO100 phase, in which Cr³⁺ and Fe³⁺ ions are arrested in the tetrahedral and octahedral sites, respectively. The major values of E_{α} for the latter sample confirm these results, which are in accordance with Mössbauer and TPR measurements.

3.5. CO₂-TPD analysis

The surface basicity of the ceramic compounds is measured by the CO_2 -TPD (Fig. 5).

According to the findings, there are two modes of CO₂ adsorption on Fe-based catalysts, i.e., weak (desorption occurred in the 50–200 °C range) and strong (desorption occurred in the 190–400 °C range) [31]. The amount of weak and strong basic sites that coexist in CRFO100 sample ($Cr_{0.75}Fe_{1.25}O_3$) is larger than the other samples. This result suggests that the high amount of Cr apparently could enhance the amounts of strong basic sites (the board peak at 250–350 °C range in the CRFO100 curve), and it could improve the CO₂ conversion for the dehydrogenation of ethylbenzene.

As the amount of FCTO phase ($Fe_{0.5}Cu_{0.75} Ti_{0.75}O_3$) increases in the samples, the intensity of the CO₂ desorption peaks decreases and the samples are exclusively composed of weak basic sites (e.g., CRFO66). This fact evidences that the CO₂ preferentially interacts with CRFO phase in the composites by forming $Fe_2O_2CO_3$ or



Fig. 5. CO₂-TPD curves of the ceramic composites.

 $Cr_2O_2CO_3$ and the basicity of the samples is diminished after addition of appropriate amounts of FCTO.

Over the CTO sample (CaTiO₃), a single desorption peak is observed at approximately 200 °C, which is assigned to weak basic sites due to CO₂ adsorption by Ca ions. Indeed, CO₂ adsorption over FCTO and PFN gives peaks with a very low intensity, suggesting that these samples are primarily acids.

3.6. Catalytic dehydrogenation of ethylbenzene (EB) with CO₂

Table 3 gives the results of converting a CO_2/EB molar ratio of 30 with ceramic composites. It is observed that all Fe-containing samples are actives in the reaction. It is well-known that potassium-promoted iron oxide catalyst in the form of Fe₂O₃ (hematite) undergoes significant catalytic activity for styrene synthesis through dehydrogenation of EB [10,12,34]. The Fe³⁺ ability of activating the molecule of EB through the dissociation of the C–H bond explains the activity of the Fe-based ceramic compounds. The pure Cr, Fe, Ti, Cu, Pb and Nb oxides have conversion values lower than 2%, because of their inactivity and/or ease reducibility of these oxides in the reaction media.

Over the PFN catalysts, only a conversion of 12% is obtained, and the Perovskite phase (XRD, TPR and Mössbauer measurements) is able to interact with the EB molecule over Fe³⁺ and reduce it at relatively low temperatures to Fe^{2+} during the reaction [34]. Neither the surface area of 107 m² g⁻¹ nor the Fe_{0.5}Cu_{0.75}Ti_{0.75}O₃ structure results in substantial improvements in the catalytic activity of FCTO sample. We expected that the molecular dimension of EB of 61 Å [35], which is larger than the FCTO pore size (9.2 Å), would cause diffusion limitations on the ions during the reaction. However, the mobility of the Cu²⁺ and Ti⁴⁺, being the latter mostly distributed in octahedral sites, as well as the easy electrical changes of these chemical entities during the reaction, caused a high degree of carbon deposition on the FCTO surface, and 20% of carbon is detected by TGA analysis. Thus, it negatively influenced the accessibility for reagents, and consequently, 21% of EB conversion for the FCTO ceramic composite was obtained; the activity is restricted to the Fe³⁺ site.

Activity of the CTO sample is the lowest among the solids studied (4%) due to CaTiO₃ phase physical degradation. This result is in accordance with XRD and TPR analyses of the CTO sample that previously identified these phenomena.

CRFO series exhibits the highest EB conversion for styrene production among the solids studied. The slight differences in terms of conversion suggest that the catalytic performance follows the order: CRFO100 > CRFO90 > CRFO83 > CRFO66, which is in the inverse order of FCTO loading. This may be due to the effect of substitution of Fe³⁺ and Cr³⁺ for Cu²⁺and Ti⁴⁺, from FCTO, in the CRFO matrix. The inherent phase change of Fe³⁺ under reaction conditions toward Fe²⁺ is avoided due to the synergistic effects between Fe³⁺ and Cr³⁺ in the octahedral sites in CRFO100 sample; as a result, the further reduction of Fe²⁺ is inhibited. The redox cycle involving the Fe³⁺ \Rightarrow Fe²⁺ active sites for the

The redox cycle involving the $Fe^{3+} \rightleftharpoons Fe^{2+}$ active sites for the reaction remains during the catalytic test. By contrast, the increase of the FCTO phase as in CRFO90, CRFO83 and CRFO66 produces coking, as explained before for FCTO sample and the overall effect is the lowest performance of the solids. Moreover, the 27% of CO₂ conversion (Table 3) shows the affinity of Ca to this gas; CTO displays the highest CO₂ conversion, which is an indication of the reverse shift reaction (VI) occurrence parallel to the dehydrogenation governing the overall reaction (VII).

$$CO_2 + H_2O \rightarrow CO + H_2$$
 (VI)

$$C_6H_5CH_2 - CH_3 + CO_2 \rightarrow C_6H_5CH = CH_2 + H_2O + CO$$
(VII)

As the Ca sites are saturated, the TiO_3 matrix experiences degradation, as pointed out before. Indeed, CO degradation could also give the coking of this sample, according to the findings [8,10,13], however this is not observed over CTO catalyst, regarding its coke content of 1.7 wt.%.

The conversion of CO₂ over CRFO series is pronounced and decreases as the FCTO phase increases. The thermodynamic properties of Fe–Cr were considered elsewhere [34,36], suggesting that the conversion of EB in the presence of oxidants such as O₂, H₂O and CO₂ is highly favourable upon chromium-promoted iron oxide catalysts, because the Fe³⁺ and O⁻ attached to Cr³⁺, and the acid–base pairs are responsible for adsorption of EB and α -hydrogen abstraction, respectively.

Upon an increase in the FCTO load over the CRFO catalysts, the catalytic function decreases, as seen in the case of CRFO90, CRFO83, CRFO66 and FCTO due to the inefficacy of Cu^{2+} and Ti^{4+} species in the reaction. Hence, the activity is mainly due to Cr^{3+} together with Fe³⁺ species found on the related samples. Indeed, in the case of CRFO100, the CO₂ gas may furnish the oxygen vacant in the Fe₂O₃ framework as the reaction proceeds. It agrees with the conversion of CO₂ observed on this sample as well as the Mössbauer analyses that detected only Fe³⁺ species after the reaction. Indeed, CO₂ adsorption is favourable as the CRFO loading increases on the samples (CO₂-TPD analysis); thus, CO₂ interaction with Fe₂O₃ is a plausible result.

 CO_2 conversion for PFN Perovskite is too low, which demonstrates increased resistance of Pb and Nb ions against CO_2 chemisorption (CO_2 -TPD results). These metals probably enhance the Fe³⁺ stability in a Perovskite matrix due to the difficulty of the diffusion of styrene in the pores of PFN (i.e., average pore size of 6.7 Å), in one hand. On the other hand, the styrene oligomerization to coke can occur, as seen from the 13.8 wt.% of carbon found over this sample.

All catalysts are selective to styrene. However, the CTO selectivity is not meaningful due to the low conversion observed with using this sample. The high selectivity to styrene is justified, according to the mechanistic considerations [34]. First, an anion vacancy adjacent to an Fe^{3+} site and an adsorbed oxygen ion react with EB by forming the complex $(C_8H_9Fe)^{3+}$. Then, the lattice

Table	5	

Samples	% C	% Selectivitie	Coke ^a content (wt.%)					
		Styrene	Toluene	Benzene	Ethane	Methane	Others	
CRFO100	16	70.1	10.4	1.5	7.9	0.3	10.1	7.4
CRFO90	11	65.2	12.6	1.1	8.4	0.9	11.8	11.3
CRFO83	10	66.4	13.0	1.6	5.9	0.4	12.7	12.5
CRFO66	8	69.7	11.6	1.2	7.3	0.8	10.8	19.8
FCTO	14	68.3	10.8	1.8	11.7	0.2	7.4	25.6
PFN	3	100	-	-	-	-	-	17.4
СТО	1	-	-	-	-	-	-	3.1

Catalytic performance of the solids in the dehydrogenation of ethylbenzene in the absence of CO₂.

^a From TGA analysis.

oxygen (O^{2-}) reacts with the complex to give styrene (C_8H_8) and form Fe²⁺ and OH⁻ ions. Two molecules of the later specie are necessary to form water, and regenerate the O²⁻ and also to obtain a vacant site. Finally, Fe²⁺ is oxidized to Fe³⁺ by CO₂ and also to O_a⁻ species, according to reactions (IIX)–(XII).

$$\varDelta + C_8 H_{10} + F e^{3+} + O_a^- \rightarrow (C_8 H_9 F e)^3 + O H^- \tag{IIX}$$

$$(C_8H_9Fe)^{3+} + O^{2-} \rightarrow C_8H_{10} + Fe^2 + OH^-$$
(X)

 $20H^- \rightarrow \varDelta + H_2 0 \ + \ 0^{2-} \eqno(XI)$

$$Fe^{2+} + CO_2 \rightarrow Fe^{3+} + O_a^{-} \tag{XII}$$

FCTO and CRFO83 have the lowest values of selectivity to styrene, 82.5% and 97.0%, respectively. The side reactions of toluene, benzene, ethane and methane production took place over these catalysts.

The catalysts are also tested in the absence of CO_2 (Table 5) and a drastic decrease in the conversion is observed.

The values of conversion are inferior to 16% for all catalysts studied. In addition, the selectivities to styrene decline in the absence of CO_2 (<70%) whereas the production of benzene and ethane has no substantial decline. Toluene and methane are the main byproducts which are obtained as a result of the cracking of the ethylbenzene molecule. The amount of coke on the catalysts is higher in the absence of CO_2 than that in presence of the referred gas. These results suggest that CO_2 does work as the oxidant on Fe species in the dehydrogenation of ethylbenzene in the presence of CO_2 and also it helps to remove the carbonaceous deposits [10,13].

Fig. 6 gives the comparative EB conversion and selected results with time-on-stream for a period for 6 h.

As expected, the conversion of ethylbenzene and the formation of styrene are high over CRFO series whereas the performance



Moreover, over CRFO100 and CRFO90, the strong basic sites could be responsible for the activation of CO_2 (as evidenced by CO_2 -TPD analysis). This result is in accordance with the findings that shows over the Fe supported catalyst with Cr as promoter, the strong basic sites may play an important role in improving the activity of the dehydrogenation of ethylbenzene in the presence of CO_2 [32]. In case of CRFO83 and CRFO66 with few strong basic sites, CO_2 can be activated through either the basic sites or the redox sites on the catalysts.

The effect of reaction temperature on catalytic performance (Fig. 7) is led to CRFO100.

An increase in the temperature, which was varied from $530 \degree C$ to $590 \degree C$, provides the activity increase from $2 \times 10^{-4} \mod g^{-1} h^{-1}$ to $23 \times 10^{-4} \mod g^{-1} h^{-1}$. The thermodynamic considerations state that the dehydrogenation of EB to produce styrene is an endothermic reaction [4,9,34]; thus, the higher the temperature is, the higher the level of styrene produced. Higher reaction temperatures did indeed facilitate the catalytic activity and correspondingly cause a decrease in styrene selectivity, as expected for an endothermic process. The activation energy is approximately 22.79 kJ mol⁻¹, according to the Arrhenius equation, a value that is lower than that of the oxidative process with



Fig. 6. Ethylbenzene conversion and selectivity in function of the time-on-stream.



Fig. 7. Effect of the temperature in function of the catalytic activity for CRFO100 catalyst.

oxygen (e.g., $26.5 \pm 7.0 \text{ kJ mol}^{-1}$) and is much lower as compared with the process with steam (e.g., $103.1 \pm 5.1 \text{ kJ mol}^{-1}$), which uses Fe-based catalysts [37,38]. Although Fe-based ceramic composites studied are effective for dehydrogenation of EB with CO₂, they are not effective for industrial applications, which require catalysts possessing excellent activity. The Fe-containing ceramic composite stability also influences the activities for EB dehydrogenation. Further investigations to improve the stability of the solids are in progress.

4. Conclusions

A series of ceramic composites comprising of $Cr_{0.75}Fe_{1.25}O_3$, $Fe_{0.5}Cu_{0.75}Ti_{0.75}O_3$, $CaTiO_3$ and $PbFe_{0.5}Nb_{0.5}O_3$ were synthesized by a solid-state reaction method. XRD analysis showed the Perovskite phase ($PbFe_{0.5}Nb_{0.5}O_3$), rutile structure ($CaTiO_3$), and cubic and trigonal structures, respectively $Cr_{0.75}Fe_{1.25}O_3$, $Fe_{0.5}Cu_{0.75}Ti_{0.75}O_3$. On the latter, the Fe^{3+} species are detected with a large number of defects, as shown by Mössbauer spectroscopy and XRD. TPR curves show that Cr stabilizes Fe^{3+} in a complex matrix of $Cr_{0.75}Fe_{1.25}O_3$ while Cu in $Fe_{0.5}Cu_{0.75}Ti_{0.75}O_3$ enhances the Fe reduction. The textural properties show that the ceramic composites possess low surface area and pore volume, characteristic of microporous oxides.

The conversion of CaTiO₃ and PbFe_{0.5}Nb_{0.5}O₃ toward styrene production was modest due to the physical degradation of the catalyst. Fe_{0.5}Cu_{0.75}Ti_{0.75}O₃ was more active than the latter, but both coke production and Fe³⁺ reduction were responsible for decreased catalytic activity of the solid. The high catalytic activity of Cr_{0.75}Fe_{1.25}O₃ was a result of the optimal balance between Fe²⁺ and Fe³⁺, which are continuously oxidized by the CO₂ participation in the reverse shift reaction, as compared to a Fe–K catalyst.

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