

Influence of precipitating agents on the performance of iron catalysts on ethylbenzene dehydrogenation

Influência de agentes precipitantes no desempenho de catalisadores de ferro na desidrogenação do etilbenzeno

Influencia de los agentes precipitantes sobre el desempeño de los catalizadores de hierro en la deshidrogenación del etilbenceno

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Abstract

Catalytic dehydrogenation of ethylbenzene with steam is the dominant technology for the industrial production of styrene, which is a raw material extensively used in the manufacture of plastics. The commercial catalyst consists of iron oxide doped with potassium and chromium and has a low specific surface area, in addition to being susceptible to deactivation. In order to obtain more efficient catalysts than those available commercially, the effect of the precipitating agent on the performance of iron catalysts, based on hematite, was studied in this work. The samples were prepared by the sol-gel method, using ammonium hydroxide, potassium hydroxide and potassium carbonate as precipitating agents and evaluated in the dehydrogenation of ethylbenzene at 480, 530, 580 and 630 °C. It was observed that the most suitable precipitating agent was potassium carbonate, which produced the most active catalyst, with the highest specific surface area and resistance to reduction. At the temperature of industrial processes (530 °C), this catalyst was four times more active than a commercial sample.

Keywords: Styrene; Ethylbenzene; Iron catalysts; Hematite; Iron oxide.

Resumo

A desidrogenação catalítica do etilbenzeno, com vapor de água, é a tecnologia dominante para a produção industrial de estireno, que é uma matéria-prima extensivamente usada na manufatura de plásticos. O catalisador comercial é constituído de óxido de ferro dopado com potássio e cromo e apresenta baixa área superficial específica, além de ser susceptível à desativação. Visando à obter catalisadores mais eficientes que aqueles disponíveis comercialmente estudou-se, neste trabalho, o efeito do agente precipitante sobre o desempenho de catalisadores de ferro, baseados em hematita. As amostras foram preparadas pelo método sol-gel, usando hidróxido de amônio, hidróxido de potássio e carbonato de potássio como agentes precipitantes e avaliadas na desidrogenação do etilbenzeno a 480, 530, 580 e 630 °C. Observou-se que o agente precipitante mais adequado foi o carbonato de potássio, que produziu o catalisador mais ativo, com área superficial específica e resistência à redução mais elevadas. Na temperatura dos processos industriais (530 °C), esse catalisador foi quatro vezes mais ativo que uma amostra comercial.

Palavras-chave: Estireno; Etilbenzeno; Catalisadores de ferro; Hematita; Óxido de ferro.

Resumen

La deshidrogenación catalítica del etilbenceno, con vapor de agua, es la tecnología dominante para la producción industrial de estireno, que es una materia prima muy utilizada en la fabricación de plásticos. El catalizador comercial consiste en óxido de hierro dopado con potasio y cromo y tiene una superficie específica baja, además de ser

susceptible de desactivación. Con el fin de obtener catalizadores más eficientes que los disponibles comercialmente, este trabajo estudió el efecto del agente precipitante sobre el desempeño de los catalizadores de hierro, basados en hematita. Las muestras se prepararon por el método sol-gel, utilizando hidróxido de amonio, hidróxido de potasio y carbonato de potasio como agentes precipitantes y se evaluaron en la deshidrogenación de etilbenceno a 480, 530, 580 y 630 °C. Se observó que el agente precipitante más adecuado era el carbonato de potasio, que producía el catalizador más activo, con mayor superficie específica y resistencia a la reducción. A la temperatura de los procesos industriales (530 °C), este catalizador era cuatro veces más activo que una muestra comercial.

Palabras clave: Estireno; Etilbenceno; Catalizadores de hierro; Hematita; Óxido de hierro.

1. Introduction

Iron-based catalysts have been widely used since their first use in the synthesis of ammonia from nitrogen and hydrogen (Cui, et al., 2018), considered the beginning of catalytic processes. Since that time, these materials have been optimized and their use expanded for several other reactions, giving them great scientific and technological importance. They have been used in several industrial reactions, such as the dehydrogenation of alkanes and alkylbenzenes (Lødeng, Lunder, Lein, Dahl, & Svenum, 2018), the dehydrogenation of ethylbenzene with steam (Medeiros & Rangel, 2010) and the water gas shift reaction (Rangel, et. al, 2017). At the academic level, they have been extensively studied in the removal of pollutants in industrial effluents, through Fenton (Lima, Borges, Rangel, & Marchetti, 2013) or photo-Fenton (Zhang, et al., 2021), among other applications, including its use as a dopant of other catalysts (Brito, Ferreira Júnior, Santos & Simonelli, 2020).

Due to their great economic importance, the processes of dehydrogenation of alkanes and alkylbenzenes have been arousing the interest of the academic and industrial community for several years. In particular, the dehydrogenation of ethylbenzene to produce styrene has motivated many studies, due to the great economic importance of this monomer, as an intermediary in the production of several plastics, including polystyrene, synthetic rubber, copolymeric resins, unsaturated polyesters and elastomers. These derivatives, in turn, are used in countless finished products, such as packaging, parts for appliances, telephones, car accessories, toys, disposable materials and other products, besides their use in the production of biocomposites (Oliveira, de, Souza, Pereira Neto & Lima, 2020) and as environmental catalysts (Silva, et al, 2020). The styrene monomer is one of the main chemical intermediates and its production and importance is only lower than that of polyethylene (Addiego, Liu & Borger, 2001).

In industrial processes, styrene is produced by the catalytic dehydrogenation of ethylbenzene in the presence of steam, over iron oxides (hematite, $\alpha\text{-Fe}_2\text{O}_3$), containing potassium and chromium oxides (Herzog & Raso, 1984). The commercial catalysts have several advantages, such as low cost and resistance to various poisons, but have a rapid deactivation, during industrial processes, mainly due to their low specific surface area and the loss of potassium (Lee, 1974).

Since the implementation of the first industrial process, many attempts have been made to improve the performance of iron oxide-based dehydrogenation catalysts. As industrial units produce millions of pounds of styrene per year, operating at high flow rates, an increase in activity or selectivity can substantially reduce operating costs. For these reasons, these catalysts continue to be extensively studied (Borgna, Sepúlveda, Magni & Apesteguia, 2004; Flego, Cosentino & Tagliabue, 2004; Serra, 2003; Medeiros & Rangel, 2010).

Considering the importance of the styrene monomer, and the need for improvements in the ethylbenzene dehydrogenation catalyst, the influence of the precipitating agent on the activity and selectivity of hematite-based catalysts was studied in this work, in order to obtain more efficient materials, with potential for industrial applications. The catalysts were prepared using different precipitating agents, such as potassium hydroxide, potassium carbonate, which were compared with ammonium hydroxide. The catalysts were evaluated at different reaction temperatures in order to study their deactivation.

2. Methodology

A quantitative methodology was used in this work, in which numerical data were collected, measuring the values of several quantities and obtaining numbers with their respective units. These measurements produced sets of data that were analyzed using mathematical techniques, such as percentages, statistics and probabilities, numerical methods, analytical methods and the use of appropriate mathematical equations and/or formulas (Pereira, Shitsuka, Pareira, & Shitsuka, 2018; Rosário, et. al, 2020).

The precursors were obtained from the sol-gel process. This method is the most convenient alternative for producing catalysts, when compared to the traditional wet mixing technique, as it allows the mixing of components at the molecular level, leading to the formation of more homogeneous solids (Fonseca, et al., 2019).

The samples were prepared by hydrolysis of aqueous Fe^{3+} ion, using solutions (25% w/v) of the following precipitating agents: potassium hydroxide, potassium carbonate and ammonium hydroxide (25% w/v). The sol was prepared by adding 250 ml of a solution of iron nitrate (0.25M) and the precipitating agent to a beaker containing water. This process was performed using a peristaltic pump, under magnetic stirring and at room temperature, reaching a pH of 12, at the end of the process. After the complete addition of the reagents, the system was kept under agitation for 30 min and then it was centrifuged (2000 rpm, 5 min.). The obtained gel was washed with water and centrifuged again. The washing and centrifugation processes were repeated until a total of six washes were completed. The gel was then dried in an oven at 120 °C for 24 h, ground in a roller mill and sieved in 100 mesh. The catalysts were obtained by calcining the precursors at 700 °C, under nitrogen flow (60 mL. min⁻¹), for 2 h.

The catalyst precursors were analyzed by Fourier transform infrared spectroscopy to detect nitrate and carbonate ions in solids. The catalysts were characterized by elemental analysis, specific surface area measurements, thermoprogrammed reduction and X-ray diffraction.

Fourier transform infrared spectroscopy analyzes were performed in a Spectra IV model Perkim-Elmer equipment, in the range of 4000 to 400 cm⁻¹, using samples diluted in potassium bromide. The iron content of the catalysts was determined using a 3410 model ARL sequentially coupled plasma atomic emission spectrometer (ICP/AES) with mini torch. In this analysis, about 0.1 g of the sample was dissolved in 10 ml of concentrated hydrochloric acid and completed to 250 ml.

The specific surface area measurements, as well as the temperature programmed reduction experiments were carried out in a TPD/TPO 2900 model Micrometrics equipment. In the specific surface area measurements, a mass of about 0.15 g was used in a glass cell, which was heated, under nitrogen flow (60 mL.min⁻¹), to 160 °C. The sample remained at this temperature for 1 h and then was analyzed using a 30% N₂/He mixture (60 mL.min⁻¹). In the temperature programmed reduction experiments, about 0.35 g of the sample was heated (10 °C.min⁻¹), following the consumption of hydrogen in a 5% H₂/N₂ mixture, from the temperature up to 1000 °C.

The X-ray diffractograms were obtained using a Shimadzu instrument, model XD3A, using CuK α radiation, generated at 30 KV and 20 mA and a nickel filter. The samples were ground in an agate mortar and then placed in the sample holder of the equipment for the measurements.

The activity of the catalysts was evaluated in the dehydrogenation of ethylbenzene, in a microreactor, operating at 1 atm, using a steam to ethylbenzene molar ratio of 10 (industrial ratio) and temperatures of 480, 530, 580 and 630 °C. The conditions of reaction were adjusted to obtain 10% conversion (to eliminate diffusion effects), over a commercial catalyst, at 530 °C. During the measurements, a stream of nitrogen (60 mL.min⁻¹) was bubbled into a saturator containing ethylbenzene, at 77 °C. The resulting stream was conducted to a mixing chamber, where it was mixed with steam, from a peristaltic pump, whose outlet was coupled to a heated tube. Then, the mixture was introduced into the reactor containing the powdered catalyst (0.3 g), previously ground and sieved in 100 mesh. The products from the reactor outlet were collected at 30 min intervals,

condensed and the organic layer was separated and analyzed by gas chromatography, in a Varian 3400 chromatograph equipped with a Petro 50 column and flame ionization detector. At the end of the experiments, the nitrogen and steam flows were stopped, and the reactor was cooled to room temperature, under nitrogen flow. After the reaction, the spent catalysts were characterized by X-ray diffraction and specific surface area measurements.

3. Results and Discussion

Table 1 shows the results of elementary analysis of the catalysts. It is observed that, when ammonium hydroxide or potassium carbonate was used, the iron content was close to the stoichiometric content in hematite (70%). This indicates that these precipitating agents provided the appropriate experimental conditions for the formation of the catalyst precursors. In the case of the solid precipitated with potassium hydroxide, the content was lower than the stoichiometric one, indicating that the precipitation of iron compounds was inhibited.

Table 1. Results of elementary analysis of the samples obtained. Sample F, FK and FKC: precipitated with ammonium hydroxide, potassium hydroxide and potassium carbonate.

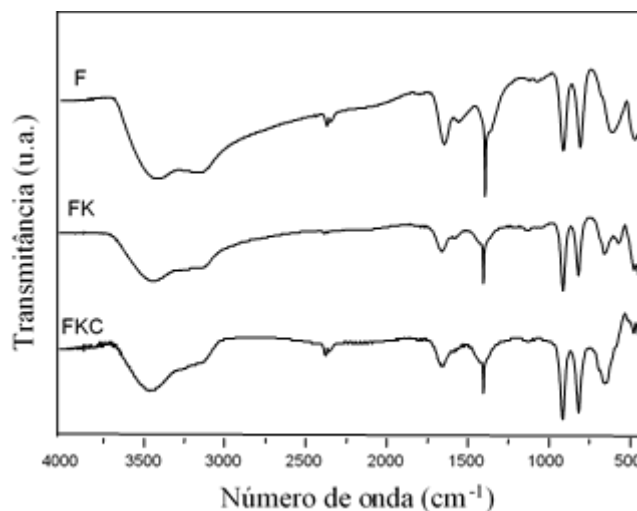
Samples	Precipitating agente	%Fe (+/- 0,05)
F	NH ₄ OH	70,51
FK	KOH	67,23
FKC	K ₂ CO ₃	69,22

Source: Authors.

Results of chemical analysis showing that the iron contents did not vary with the use of ammonium hydroxide but decreased with the use of potassium hydroxide.

The Fourier transform infrared spectra of the catalyst precursors (Figure 1) showed a wide band at 3400 cm⁻¹, assigned to the stretching vibrations of hydroxyl groups in water in the solids, in addition to an absorption at 1638 cm⁻¹, referring to the angular deformation of water molecules (Miller & Wilkins, 1952; Nyquist & Kagel, 1971). The characteristic band of the nitrate species at 1384 cm⁻¹ was also noted (Schertmann & Fischer, 1973). Below 800 cm⁻¹, bands corresponding to metal-oxygen bonds were observed in iron hydroxides (McDevitt & Baun, 1964).

Figure 1. Fourier transform infrared spectra of catalyst precursors. F, FK and FKC samples: precipitated with ammonium hydroxide, potassium hydroxide and potassium carbonate, respectively.

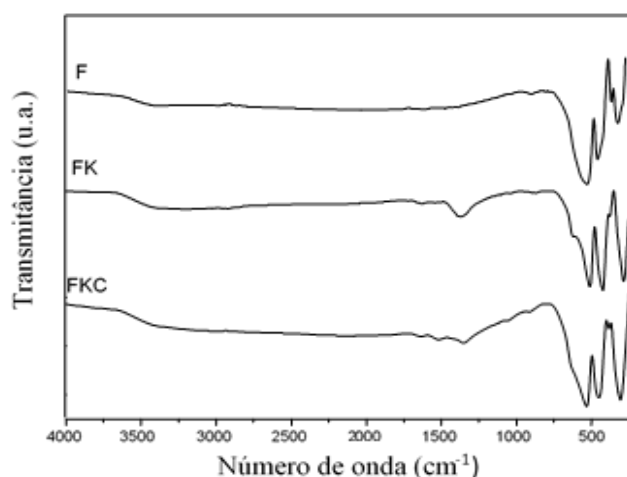


Source: Authors.

Infrared spectra (Figure 1) showing the identification of the functional groups in the catalyst precursors: hydroxyl groups in water, nitrate species and iron hydroxides.

After calcination of the precursors, the band referring to the nitrate species disappeared, in the case of the solid prepared with ammonium hydroxide and decreased markedly in the other cases (Figure 2). These results suggest that, in the latter cases, nitrate species were stabilized in the solids by sodium and potassium ions. The spectra also showed narrow bands below 600 cm⁻¹, typical of hematite (McDevitt & Baun, 1964).

Figure 2. Fourier transform infrared spectra of the catalysts. F, FK and FKC samples: precipitated with ammonium hydroxide, potassium hydroxide and potassium carbonate, respectively.



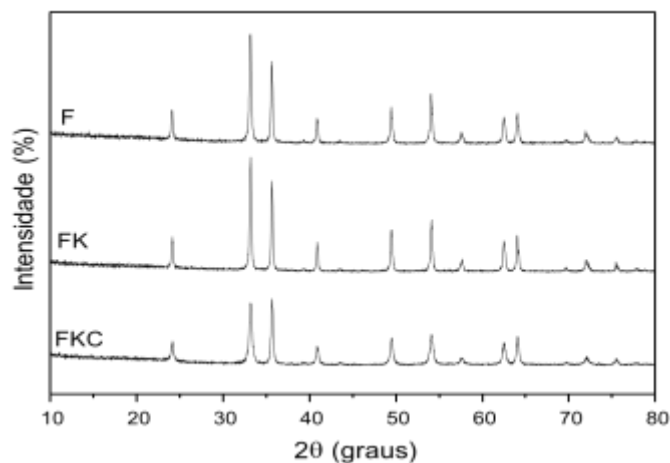
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Infrared spectra (Figure 2) showing the elimination of nitrate in the sample prepared with ammonium hydroxide (F) and the decrease in quantities in those obtained with potassium hydroxide (FK) and potassium carbonate (FKC).

Figure 3 shows the X-ray diffraction pattern of the obtained catalysts. The presence of hematite (ASTM Card 13534) is noted in all cases, indicating that the use of different precipitating agents did not affect the nature of the formed iron oxide

phases. During the dehydrogenation of ethylbenzene, these solids underwent a phase change, producing magnetite, Fe_3O_4 , regardless of the nature of the precipitating agent, as shown in the diffractograms in Figure 4.

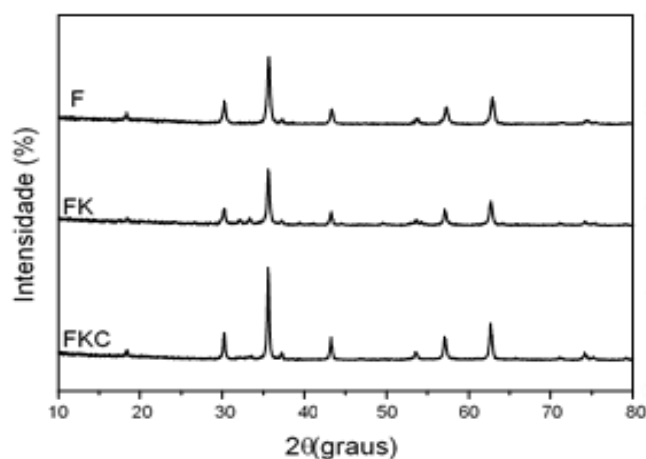
Figure 3. X-ray diffractograms of the obtained catalysts. F, FK and FKC samples: precipitated with ammonium hydroxide, potassium hydroxide and potassium carbonate, respectively.



Source: Authors.

X-ray diffractograms (Figure 3) showing that hematite ($\alpha\text{-Fe}_2\text{O}_3$) was formed in all catalysts.

Figure 4. X-ray diffractograms of the catalysts used in the dehydrogenation of ethylbenzene, prepared from iron nitrate using ammonium hydroxide (F), potassium hydroxide (FK), potassium carbonate (FKC) as precipitating agents.



Source: Authors.

X-ray diffractograms (Figure 4) showing that all catalysts were converted to magnetite (Fe_3O_4) in all samples.

The specific surface areas of the catalysts, before and after the reaction, are shown in Table 2. In general, the solids showed low specific surface areas, due to the high value of the calcination temperature (700 °C), which caused the sintering of the materials. Significant differences were observed between the samples, indicating that the use of different precipitating agents is relevant in determining their textural properties. An increase in the specific surface area in the order $F < FK < FKC$ was observed, showing that the presence of potassium ions leads to the production of smaller particles, during the precipitation

and calcination of the materials, resulting in a low specific surface area.

Table 2. Specific surface areas before (S_g) and after (S_g^*) the dehydrogenation of ethylbenzene in the presence of water vapor, conducted at different temperatures. F, FK and FKC samples: precipitated with ammonium hydroxide, potassium hydroxide and potassium carbonate.

Samples	S_g ($m^2.g^{-1}$)	S_g^* ($m^2.g^{-1}$)			
		480 °C	530 °C	580 °C	630 °C
F	5,4	5,3	5,0	4,9	5,0
FK	9,9	8,6	8,0	7,8	8,0
FKC	20	18	12	11	12

Source: Authors.

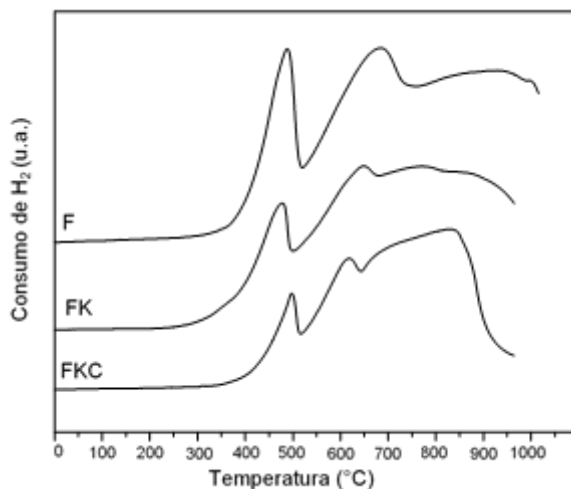
Specific surface areas of the catalysts before and after the reaction (Table 2), showing that the presence of potassium (FK and FKC samples) decreases the specific surface areas and that the values decreased during the reaction.

During the dehydrogenation of ethylbenzene, the samples were sintered, indicating that the transformation of hematite to form magnetite was followed by coalescence of the particles. In the case of the FKC sample, there was a progressive loss of the specific surface area with increasing temperature, up to 530 °C; from this condition, the specific surface areas remained stable. In the other samples, the specific surface areas remained stable, the differences observed being within the experimental error of the measurement (10%). Comparing the specific surface areas of the catalysts used at different temperatures, it is noted that the material prepared with potassium carbonate showed the highest specific surface area and a more pronounced decrease with increasing temperature. Despite this decrease, this solid showed higher values than the other samples, over the entire temperature range studied.

The temperature programmed reduction profiles are shown in Figure 5. The curves were similar, but the peaks were shifted to different temperatures. In all cases, a peak was observed at low temperatures and two others at higher values. The first is associated with the reduction of Fe^{3+} species to produce Fe^{2+} , while the others are attributed to the reduction of Fe^{+2} species to form metallic iron (Araújo & Rangel, 2000). The second peak is related to reduction of species on particles surface and the third to reduction of particles inside the solid (Araújo & Rangel, 2000; Oliveira, Fierro, Valentini, Nobre, & Rangel, 2003). It is noted that the use of potassium carbonate caused the displacement of the first peak to higher temperatures, in relation to the materials obtained with ammonium and potassium hydroxide. This indicates that this precipitant is the most suitable for preparing the catalysts, since it stabilizes the active phase (hematite), making it difficult to reduce it.

The conversions of ethylbenzene at steady state, as a function of temperature, are shown in Table 3. It can be noted that the conversion varied markedly, as a function of the precipitating agent and temperature. In general, the activity increased in the order $F < FK < FKC$, indicating that the most active catalyst was the one prepared with potassium carbonate. However, at 630 °C, the sample obtained with potassium hydroxide led to the highest conversion, followed by that prepared with potassium carbonate and ammonium hydroxide. In all cases, the conversion increased with temperature, except for the solid obtained with potassium carbonate, which showed deactivation at 630 °C. In all cases, the conversions were far from those in equilibrium.

Figure 5. Temperature programmed reduction profiles of catalysts obtained with iron nitrate using precipitating agents as ammonium hydroxide (F), potassium hydroxide (FK), potassium carbonate (FKC).



Source: Authors.

Temperature programmed reduction curves (Figure 5) showing that potassium carbonate led to the production of the most resistant catalyst against reduction (FKC sample).

Table 3. Conversion values in the dehydrogenation of ethylbenzene on catalysts at steady state, as a function of temperature. F, FK and FKC samples: prepared with ammonium hydroxide, potassium hydroxide and potassium carbonate, respectively.

Samples	Conversion (%)			
	480 °C	530 °C	580 °C	630 °C
F	5	3	8	15
FK	15	32	53	62
FKC	18	50	65	50

Source: Authors.

Ethylbenzene conversion values (Table 3) showing that FKC sample led to the highest values.

Table 4 shows the selectivity values for styrene of the catalysts, obtained at steady state. It is observed that this parameter also varied depending on the precipitating agent and temperature. The sample prepared with ammonium hydroxide showed an increase in selectivity with temperature, while the reverse was verified with the material obtained with potassium carbonate. On the other hand, the solid prepared with potassium hydroxide showed values which were independent of temperature. Comparing the effect of the precipitating agent, at each temperature it is observed that, in a general trend, selectivity decreased in the order $F > FK > FKC$.

Figure 6 shows the conversion as a function of temperature over the catalysts. One can note that the samples show different behaviors, depending on the precipitating agent used and the reaction temperature. The catalyst obtained with ammonium hydroxide led to stable conversion values, throughout the reaction, except in the case where the reaction was carried out at low temperatures (480 °C). In this case, the conversion decreased after about 5000 s of reaction, at the end of

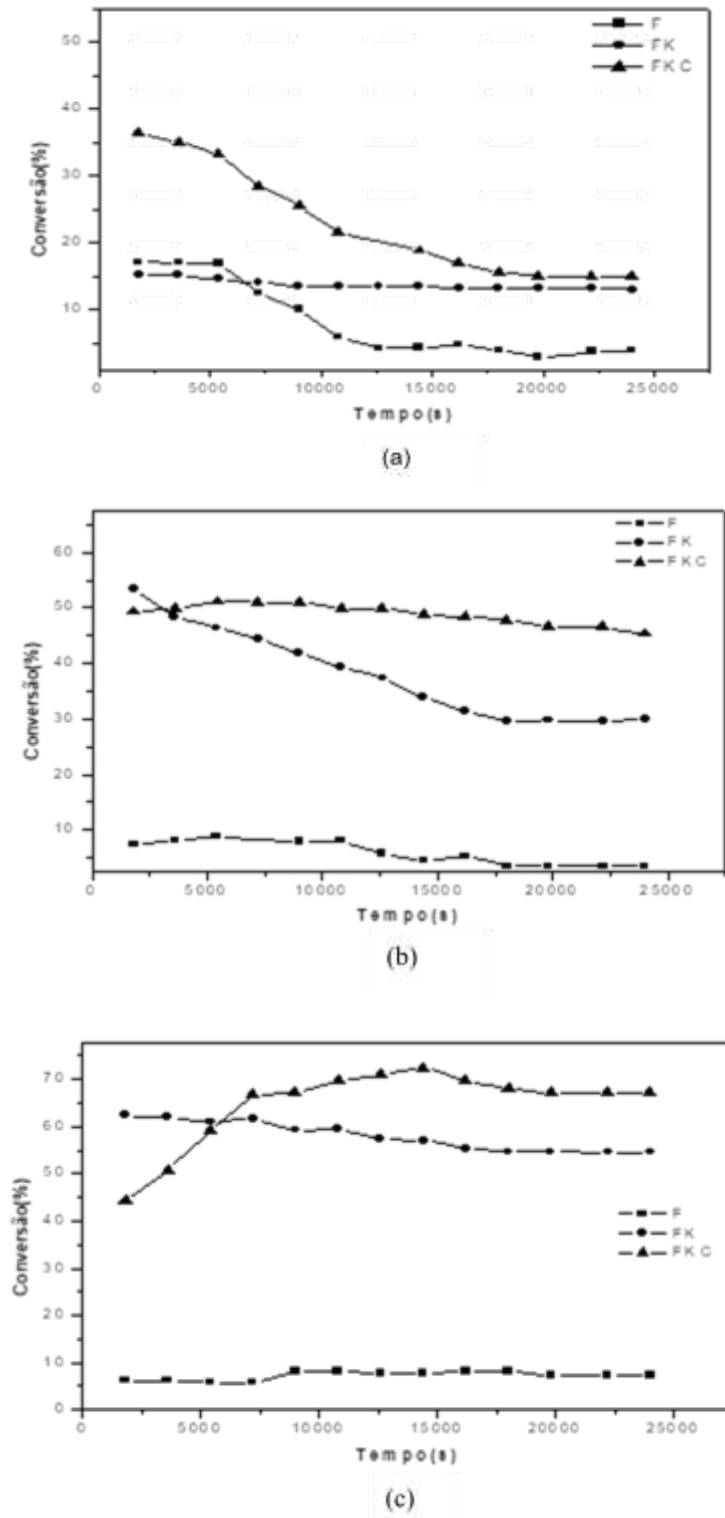
Table 4. Values of selectivity to styrene of catalysts in the dehydrogenation of ethylbenzene, in the presence of steam, as a function of temperature, obtained at steady state. F, FK and FKC samples: precipitated with ammonium hydroxide, potassium hydroxide and potassium carbonate, respectively.

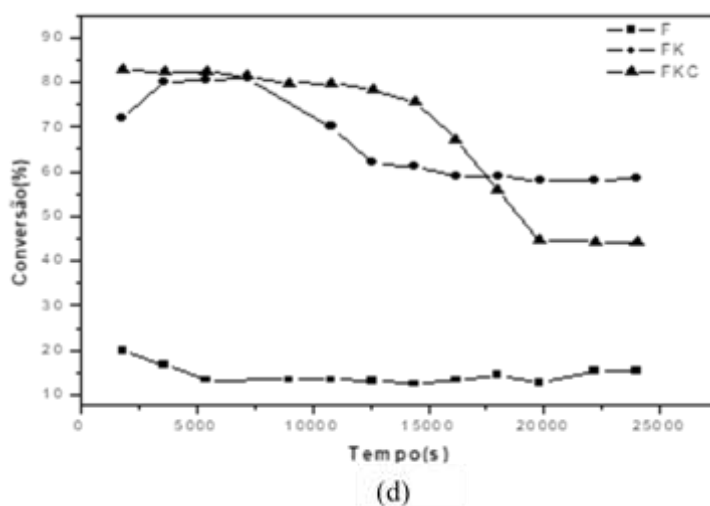
Samples	Selectivity (%)			
	480 °C	530 °C	580 °C	630 °C
F	92	97	96	98
FK	96	96	97	97
FKC	97	93	90	89

Source: Authors.

Styrene selectivity of the catalysts (Table 4), showing that the F sample was the most selective. Which it decreases continuously until about 12000 s, in which it reaches stationary values. However, the values were low, over the entire temperature range studied. On the other hand, the sample prepared with potassium hydroxide led to stable conversion values, since the beginning of the reaction performed at 480 and 580 °C, but showed a drop in conversion after 1200 min, when the reaction was conducted at 530 and 630 °C. The catalyst obtained with potassium carbonate was stable in the experiment conducted at 530 °C. However, there was a loss of conversion in the reactions conducted at 480 and 630 °C, after about 2000 s of reaction. At 580 °C, the catalyst showed a unique behavior when compared to the other samples, showing an initial increase in conversion, followed by the stabilization of these values after about 15000 s of reaction.

Figure 6. Conversion curves as a function of time, at different temperatures, obtained over the catalysts. F, FK and FK C samples: prepared with ammonium hydroxide (F), potassium hydroxide (FK), potassium carbonate (FKC). (a) 480 °C; (b) 530 °C; (c) 580 °C and (d) 630 °C.





Source: Authors.

Conversion as a function of time during the dehydrogenation of ethylbenzene performed over the catalysts at different temperatures (Figure 6) showing that the one prepared with potassium carbonate (FKC) is the most active and most stable.

From these results, it can be concluded that the catalyst prepared with potassium carbonate is the most promising for industrial applications, presenting an activity four times higher than a commercial sample, at the temperature of industrial processes (530 °C). Its superior performance can be associated with its higher specific surface area, as well as with the stability of the active phase (hematite) under reducing conditions.

4. Conclusion

The use of different precipitating agents in the preparation of iron oxides, in the form of hematite, produces catalysts with different specific surface areas and resistance to reduction, which lead to different values of conversion and selectivity. The most suitable precipitating agent to prepare these materials is potassium carbonate, which produces solids with higher specific surface areas and greater resistance to deactivation due to destruction of the active phase, being the most active in the dehydrogenation of ethylbenzene, at the temperature used in commercial processes (530 °C). This solid can be used in the temperature range of 480 to 630 °C, without undergoing appreciable deactivation at the highest temperature. It is four times more active than a commercial sample, at the temperature of industrial processes, which makes it promising for the reaction. As future work, it can be suggested the study of the effect of dopants (aluminum, zinc, vanadium and others) on the performance of the catalysts prepared from potassium carbonate, in order to obtain even more efficient systems.

Acknowledgments

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