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Evaluation of copper supported on polymeric spherical activated carbon in the ethylbenzene dehydrogenation

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Abstract

Activated carbons have found several applications as catalysts and as catalytic supports. They can be useful in the ethylbenzene dehydrogenation to produce styrene, a high value chemical. In order to produce alternative catalysts for this reaction, the preparation of spherical activated carbon-supported copper was studied in this work. Solids with two different amounts of copper were prepared, characterized and evaluated in the ethylbenzene dehydrogenation in the presence of carbon dioxide. It was noted that some copper species were weakly adsorbed on the solid and were removed from the solid during the reaction causing the collapse of the structure. The weakly bonded copper species did not affect the activity but improved the yield to styrene and decreased the production of benzene and toluene. On the other hand, the more strongly bonded species contributed to the activity and to the stability of the catalyst. The solid with the lowest amount of copper was the most promising one, since it showed high activity and resistance against deactivation, being able to work up to 600 °C.

Keywords: Activated carbon; Styrene; Ethylbenzene dehydrogenation

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1. Introduction

Activated carbons have been applied in several fields, including water treatment, chromatography and natural gas storage [1]. Some of these applications do not require a rigorous control of their physical–chemistry properties, regarding purity, particle shapes, mechanic resistance, homogeneity and specific surface area. On the other hand, these properties are required when activated carbon are used as catalytic support or as catalyst. Therefore, extensive research has been carried out in recent years aiming the production of activated carbon from routes which allow the control of these properties. The preparation of activated carbon from synthetic polymers as phenol–formaldehyde [2] resins and styrene–divinylbenzene (Sty–DVB) copolymers [3,4] has been pointed out as a convenient way to get solids with properties suitable to support and catalysts [4]. The principal advantages of these precursors are related to the high purity of the final product as well as to the control of size and shape of the particles. Other advantages include the high specific surface area and the homogeneous structure of the activated carbon obtained. Sulfonated styrene–divinylbenzene copolymer is considered an important precursor due to the acid properties, the homogeneous size distribution of grains and the high physical and chemical resistance of the end product [4,5].

Among the several catalytic applications of the activated carbon, the catalytic dehydrogenation of ethylbenzene (CDE) to produce styrene is one of the most important one. Previous works [6,7] demonstrated that activated carbon prepared by different methods is catalytically active in the ethylbenzene dehydrogenation in the presence of oxygen. However, this reaction presents the inconvenience of producing carbon oxides and oxygenates decreasing the selectivity towards styrene [8,9,10]. This feature has encouraged the research for new

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routes for producing styrene, an important intermediate chemical used in the polymer manufacture, including polystyrene, synthetic rubber, copolymer resins, unsaturated polyesters and elastomers [8,11,12]. As styrene is a high value chemical, there is a demand for the development of processes and catalysts that can reduce the production costs of this monomer [13].

Nowadays, the catalytic dehydrogenation of ethylbenzene in the presence of steam to produce styrene is still the dominant route. This reaction is industrially performed in a catalytic bed of hematite containing cerium, chromium and potassium oxides. Due to the endothermicity of the reaction, large amounts of overheated steam are continuously fed to the reactor, increasing the costs of the process [14,15]. The commercial catalyst presents several advantages, as resistance to impurities and low cost. However, it deactivates with time due to loss of potassium that migrates to the pellet center or to the gaseous effluent [15,16]. Moreover, the catalyst contains chromium that is harmful to the human health and to the environment, making its handling and discarding difficult. Therefore, several processes and catalysts have been proposed to solve these problems [17,18]. One of most promising route to produce styrene is the ethylbenzene dehydrogenation in the presence of carbon dioxide that can act as diluent and as oxidant in the reaction [19]. The steam substitution by carbon dioxide decreases the required energy in the styrene production from 6.3×10^6 to 2.6×10^6 kJ for 1000 kg of styrene, reducing the production costs [20]. In addition, the process allows the consumption of the low cost carbon dioxide, which also contributes to the greenhouse effect.

In order to find new catalysts to the ethylbenzene dehydrogenation in the presence of carbon dioxide, copper supported on spherical polymeric activated carbons were prepared and evaluated in the reaction. Active carbons were prepared by the carbonization of sulfonated styrene–divinylbenzene copolymer (Sulf-Sty–DVB), followed by oxidation and copper incorporation. The polymeric activated carbon allows the easy metal incorporation on its surface as well as on the precursor resin. On the other hand, copper is an active metal in the CDE reaction that also contributes to the increase of the styrene selectivity [21].

2. Experimental

Benzoyl peroxide, toluene, heptane, sodium chloride, hydroxyethylcellulose, gelatin, sulfuric acid, hexahydrated copper nitrate and nitric acid were used without any previous treatment. Styrene and divinylbenzene were given by Nitriflex S.A. and Coremal S.A., respectively and were distilled under vacuum before the use.

2.1. Synthesis of the styrene–divinylbenzene copolymer

The Sty–DVB copolymer was synthesized by suspension polymerization. Heptane and toluene were used as pore forming agents, leading to a macroporous structure type. The copolymer was purified and sieved and only spheres between 250 and 125 μm diameter were used in this work.

2.2. Sty–DVB copolymer sulfonation

The copolymer was sulfonated with sulfuric acid and dichloroethane in the proportion of 1 g/15 mL/3 mL, at 70 °C, under mechanical stirring for 4 h. The copolymer was then filtered and washed with water until neutral pH.

2.3. Thermal treatment and carbon activation

The thermal treatment consisted in heating the sulfonated copolymer at 300 °C, in atmospheric air for 2 h, followed by carbonization at 900 °C, under nitrogen flow, for 3 h. The activation was carried out at 800 °C for 2 h, under ascending steam saturated nitrogen flow, producing the SAC sample. In all cases, the heating was carried out at a rate of 10 °C min^{-1} and the steps were intercalated with cooling until room temperature.

2.4. Oxidation of the polymer activated carbon

In the oxidation process, 1 g of SAC sample went on four successive oxidations at 600, 700 and 800 °C with 5% O_2/N_2 mixture and at 800 °C with 10% O_2/N_2. In each step, the sample was kept at the final temperature for 1 h and then cooled until room temperature before going to the following step. This sample was identified as OSAC.

2.5. Copper adsorption

The OSAC sample (1 g) was dispersed in 19 mL of hexahydrated copper nitrate aqueous solution (0.74 and 1.48 mol L^{-1} of copper) and kept for 3 h, at room temperature. The samples were filtered, washed with water and dried at 100 °C. They were named Cat1 (0.74 mol L^{-1} of copper) and Cat2 (1.48 mol L^{-1} of copper).

2.6. Samples characterization

The amount of copper in the catalysts, before and after the CDE reaction, was determined by atomic absorption spectrometry, in a Perkin-Elmer model 306 equipment. The sample (0.01 g) was dissolved in 2 mL of concentrated hydrochloric acid solution, heated at 100 °C and analyzed.

In order to identify the functional groups of the SAC and OSAC samples, Fourier transform infrared (FTIR) spectrometry was performed, using a Bomem Hartmann & Braun Michelson model MB-Series equipment and potassium bromide discs. The Boehm test was used to confirm the functional acid groups (lactones, phenols and carboxylic acid) generated by the oxidation of the SAC sample. In this test, the SAC and OSAC samples (0.50 g) were dispersed in 25 mL of a sodium hydroxide solution (0.05 mol L^{-1}) and kept at room temperature for 48 h. The system was then filtrated and 10 mL of the remaining solution was titrated with hydrochloric acid (0.05 mol L^{-1}). Each sample was analyzed in duplicate and the solutions used in the Boehm test were previously standardized.

The X-ray diffraction experiments were carried out in a Shimadzu model XRD600 equipment, in a range from $2\theta = 10°$

to 80°, using Cu Kα (λ = 1.54051 Å). The textural properties of the samples, before and after the CDE reaction, were measured by nitrogen adsorption in a Micromeritics model ASAP 2010 equipment. During the analysis, the sample (0.3 g) was heated under vacuum and exposed to gaseous nitrogen for determining the adsorption/desorption isotherms.

2.7. Catalysts evaluation

In the catalysts evaluation, the sample (0.3 g) was placed in a fixed bed microreactor and the system was heated under nitrogen flow (20 mL min^{-1}) up to the reaction temperature (400, 500 or 600 °C). The nitrogen flow was then interrupted and a gaseous mixture containing ethylbenzene and nitrogen (coming from a saturator with ethylbenzene at 77 °C) was mixed with a carbon dioxide stream in a chamber and fed to the reactor. The experiments were performed at atmospheric pressure, using a carbon dioxide to ethylbenzene molar ratio of 10. The gaseous effluent was monitored continuously by a Varian model 3600-X chromatograph with ionization flame detection system, in injection intervals of 30 min. The reaction conditions was adjusted to eliminate the diffusion limitations and to get stable values of 10% of conversion with a commercial catalyst at 600 °C.

3. Results and discussion

Table 1 shows the copper amounts in the samples before and after the ethylbenzene dehydrogenation. It can be noted that the Cat2 sample lost copper during the catalytic reaction while the copper content of Cat1 sample did not change. It means that some copper was not strongly adsorbed on the support. On the other hand, all copper was strongly adsorbed in the Cat1 sample.

The X-ray diffractograms of the fresh and spent catalysts (after the ethylbenzene dehydrogenation) showed no peak, probably due to the low concentration of adsorbed copper (Table 1) or due the production of non-crystalline copper aggregates or even the formation of nanoparticles too small to be detected by this technique.

The infrared spectra of the activated carbon before (SAC sample) and after (OSAC sample) the oxidation are shown in Fig. 1. It can be noted that only the spectrum of OSAC sample showed bands of oxygenated groups, confirming the oxidation.

Table 1
Copper concentration of the activated carbon before and after CDE reaction at 400 °C (Cat1-400, Cat2-400), 500 °C (Cat1-500, Cat2-500) and 600 °C (Cat1-600)

Samples	Copper concentration (mg g^{-1})
Cat1	2.69
Cat1-400	2.67
Cat1-500	2.59
Cat1-600	2.63
Cat2	6.00
Cat2-400	5.70
Cat2-500	2.55

Cat1 and Cat2: activated carbon-supported cooper prepared with 0.74 and 1.48 mol L^{-1} copper nitrate solutions, respectively.

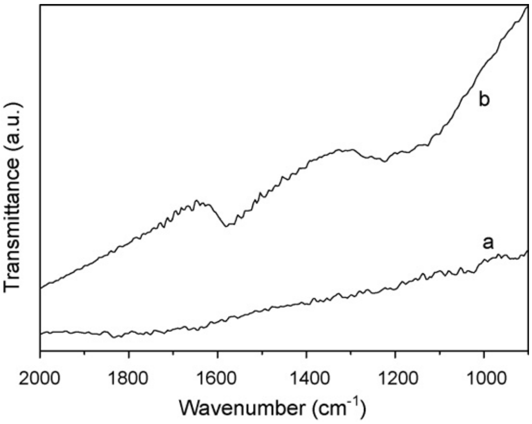

Fig. 1. FTIR spectra of activated carbon (a) before (SAC sample) and (b) after (OSAC sample) the oxidation.

The presence of ketone and quinone groups was confirmed by the absorptions between 1550 and 1680 cm^{-1}. One can also see bands between 1200 and 1350 cm^{-1}, attributed to the stretching vibration of C–O bond related to ethers, lactones, phenols and carboxylic anhydrides [22]. The selective neutralization test, Bohem test, resulted in the following values—SAC: 0.035 mmolH^+ g^{-1} of sample and OSAC: 0.236 mmolH^+ g^{-1} of sample. These results showed that the functional groups (lactones, phenols and carboxylic) were significantly developed on the surface of OSAC sample, after the thermal oxidation of the SAC sample, in accordance with FTIR results.

Table 2 shows that the specific surface area (S_{BET}), the micropore area (S_{MIC}), the pore volume (V) and the average pore diameter (D) of copper-impregnated carbons (Cat1 and Cat2 samples) were almost the same. These results show that the presence and the amount of adsorbed copper in our experimental conditions did not influence the catalyst textural properties. However, a decrease of the surface area, pore volume and of the mesoporous area during the CDE reaction was noted (samples Cat1-500 and Cat2-500). This decrease is sharp in the sample with the highest copper concentration, as we can infer by comparing Tables 1 and 2. This is assigned to the sintering and collapse of the porous structure, due to the presence of copper. It is well-known that active carbons are amorphous with a porous structure that is easily collapsed. If this structure losses a metal, for instance, this process is very slow so that the metal remains in the structure for a period long enough to collapse the porous structure by the migration of the weakly bounded copper.

Table 2
Textural properties of copper-based samples before (Cat1 and Cat2) and after the CDE reaction at 500 °C (Cat1-500 and Cat2-500)

Samples	S_{BET} (m^2 g^{-1})	S_{MIC} (m^2 g^{-1})	V (cm^3 g^{-1})	D (nm)
Cat1	824	533	0.913	12.6
Cat2	810	518	0.897	12.4
Cat1-500	471	230	0.736	12.9
Cat2-500	41	9	0.114	13.6

Cat1 and Cat2: activated carbon-supported copper prepared with 0.74 and 1.48 mol L^{-1} copper nitrate solutions, respectively.

The nitrogen adsorption and desorption curves of the catalysts before the reaction are shown in Fig. 2. The profiles are typical of macro and mesoporous materials (Type II). The volumes of adsorbed nitrogen were smaller for used catalysts (Fig. 3), mainly for the Cat2-500 sample, in agreement with the substantial loss of specific surface area during the reaction.

The pore size distribution curves, presented in Fig. 4, show mesoporous domains between 10 and 40 nm, in the fresh and spent catalysts. It means that the catalysts did not change during reaction in the range of mesoporous. However, a sharp reduction of pore volume was noted for Cat2, during reaction, as a consequence of the pore collapse by metal loss.

The ethylbenzene conversion after 6 h of reaction is shown in Table 3. It can be seen that Cat1 and Cat2 samples showed the same conversion at 400 °C (10%) while the commercial catalyst was not active in this condition. Increasing the reaction temperature up to 500 °C, the conversion of both catalysts strongly increased and the commercial catalyst became active. In this condition, the catalyst with lower copper content was the most active (Cat1). At higher temperature (600 °C) all samples led to lower values of conversion, and the Cat2 became inactive, indicating the catalyst deactivation. Cat1 sample was still the most active, showing that it is also the most resistant against deactivation. Fig. 5 illustrated the behavior of ethylbenzene conversion as a function of time at different temperatures on the catalyst with the lowest copper amount (Cat1).

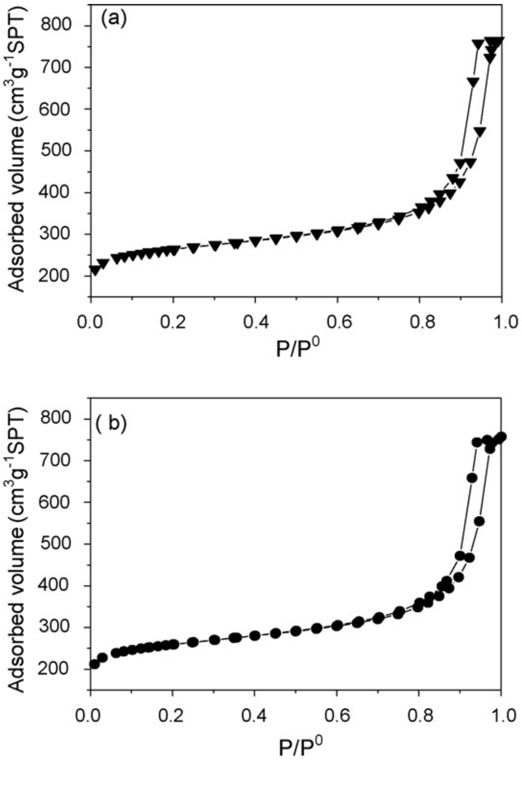

Fig. 2. Nitrogen adsorption and desorption curves of (a) Cat1 sample (activated carbon-supported copper prepared with 0.74 mol L^{-1} copper nitrate solution) and of (b) Cat2 sample (activated carbon-supported copper prepared with 1.48 mol L^{-1} copper nitrate solution).

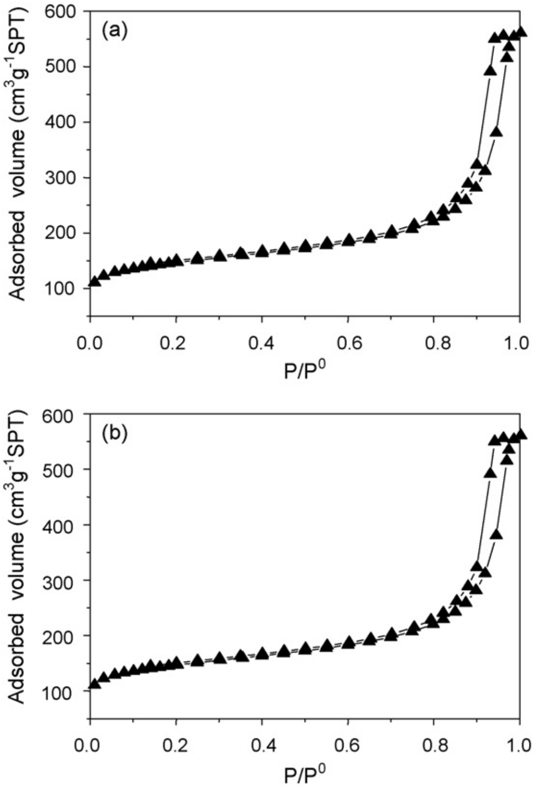

Fig. 3. Nitrogen adsorption and desorption curves of the (a) Cat1-500 sample (activated carbon-supported copper prepared with 0.74 mol L^{-1} copper nitrate solution) and of (b) Cat2-500 sample (activated carbon-supported copper prepared with 1.48 mol L^{-1} copper nitrate solution) after evaluation in the CDE reaction at 500 °C.

Fig. 6 shows the ethylbenzene conversion as a function of time at 500 °C. One can see that the sample with less copper (Cat1) showed a slight increase of activity after 2 h of reaction and then achieved stable values. On the other hand, the sample richer in copper (Cat2) showed an opposite behavior, with a continuous decrease of activity in the beginning of reaction, reaching steady values after this time. The commercial catalyst showed a continuous decrease of activity as a function of time. These results show that the catalyst with low amount of copper (Cat1) is more active, a fact which can be related to its higher specific surface area and pore volume, as compared to the other

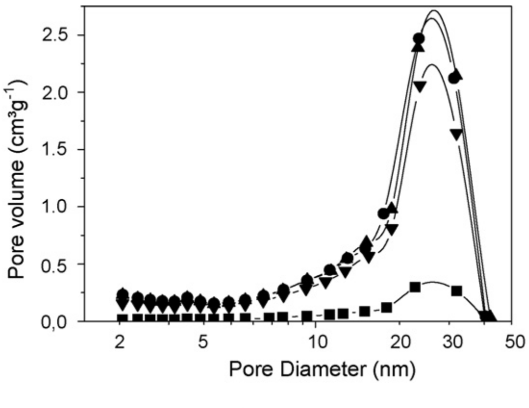

Fig. 4. Pore distribution curves of the samples. Cat1 (▼) and Cat2 (●): activated carbon-supported copper prepared with 0.74 and 1.48 mol L^{-1} copper nitrate solution, respectively; Cat1-500 (▲) and Cat2-500 (■): Cat1 and Cat2 after the reaction at 500 °C.

Table 3
Ethylbenzene conversion and styrene selectivity after 6 h of the CDE reaction at 400, 500 and 600 °C

Samples	Conversion (%)			Styrene selectivity (%)		
	400 °C	500 °C	600 °C	400 °C	500 °C	600 °C
Cat1	10	82	58	39	65	45
Cat2	10	49	–	33	66	–
Commercial	–	26	8.5	–	88	97

Cat1 and Cat2: activated carbon-supported copper, prepared with 0.74 and 1.48 mol L^{-1} copper nitrate solutions.

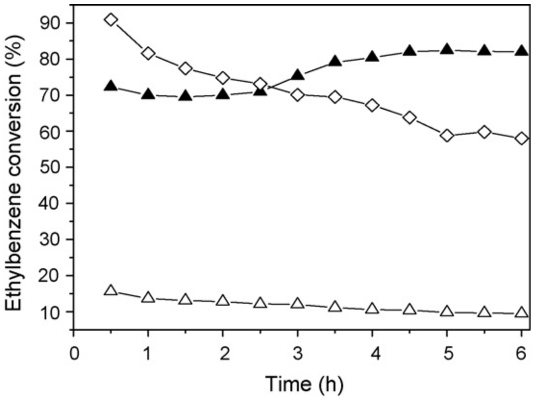

Fig. 5. Ethylbenzene conversion as a function of time on Cat1 sample (activated carbon-supported copper prepared with 0.74 mol L^{-1} copper nitrate solution) at 400 °C (△), 500 °C (▲) and 600 °C (◇).

sample (Cat2), which porous structure was collapsed during reaction.

The styrene selectivities are also shown in Table 3. Small differences were noted between the two samples regardless the reaction temperature. In all cases, the selectivity increased with temperature up to 500 °C; at higher temperature (600 °C) it decreased as the consequence of the catalyst deactivation.

Fig. 7 shows the selectivity of the catalyst with the lowest amount of copper (Cat1) as a function of time at different temperatures. It can be seen that the selectivity achieved stable values after 2 h at 400 and 600 °C, while the selectivity at 500 °C increased continuously with time and tended to stable values only after 5 h.

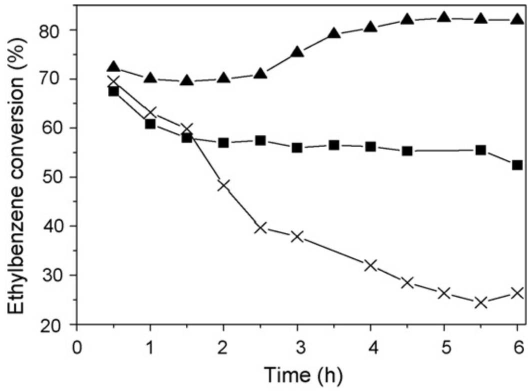

Fig. 6. Ethylbenzene conversion as a function of time on Cat1 (▲) and Cat2 (■) samples and on a commercial catalyst (×) at 500 °C. Cat1 and Cat2 samples: activated carbon-supported copper prepared with 0.74 and 1.48 mol L^{-1} copper nitrate solutions, respectively.

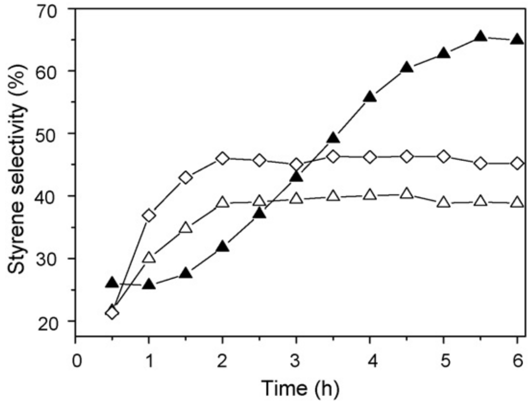

Fig. 7. Ethylbenzene selectivity as a function of time on Cat1 sample (activated carbon-supported copper prepared with 0.74 mol L^{-1} copper nitrate solution) at 400 °C (△), 500 °C (▲) and 600 °C (◇).

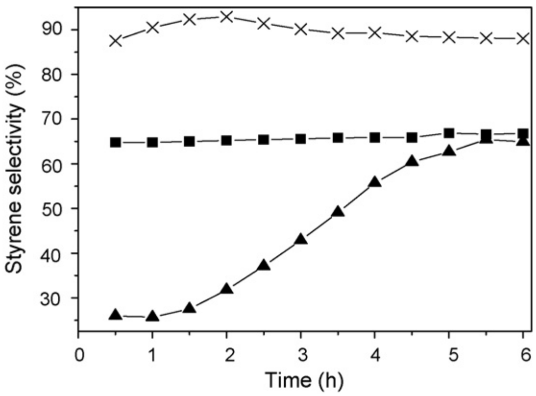

Fig. 8. Ethylbenzene selectivity as a function of time on Cat1 (▲) and Cat2 (■) samples and on a commercial catalyst (×) at 500 °C. Cat1 and Cat2 samples: activated carbon-supported copper prepared with 0.74 and 1.48 mol L^{-1} copper nitrate solutions, respectively.

Fig. 8 shows the selectivity of the catalysts as a function of time reaction at 500 °C. It can be noted that the selectivity for the sample with the highest amount of copper (Cat2) showed stable values since the beginning of reaction while the selectivity for the other sample (Cat1) increased continuously with time. On the other hand, the commercial catalyst showed the highest selectivity which reached stable values after 1 h of reaction.

The styrene yields after 6 h reaction are shown in Table 4. In all cases, this parameter increased with the temperature increase up to 500 °C and decreased at 600 °C, indicating

Table 4
Styrene yield after 6 h of the CDE reaction on the Cat1, Cat2 and the commercial catalyst at 400, 500 and 600 °C

Samples	Yield (%)		
	400 °C	500 °C	600 °C
Cat1	4	53	28
Cat2	3	35	–
Commercial	–	22	8

Cat1 and Cat2: activated carbon-supported copper, prepared with 0.74 and 1.48 mol L^{-1} copper nitrate solutions.

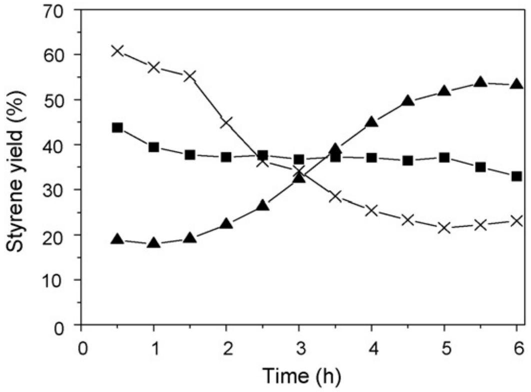

Fig. 9. Styrene yield as a function of time at 500 °C on Cat1 (▲) and Cat2 (■): activated carbon-supported copper, prepared with copper nitrate solutions 0.74 and 1.48 mol L^{-1}, respectively; commercial catalyst (×).

the deactivation of the selective sites to styrene at high temperatures. The Cat2 sample was completely inactive at this temperature. Both catalysts led to a styrene yield higher than the commercial catalyst, regardless the reaction temperature.

Fig. 9 shows the yield of styrene as a function of time for the Cat1 and Cat2 samples and for the commercial catalyst. It can be noted that the catalyst with the lowest copper concentration (Cat1) showed an increase of styrene yield with time, which can be assigned to the reduction of Cu^{2+} species to metallic copper by hydrogen released from the reaction. As the majority of the dehydrogenation reactions is catalyzed by copper, the metallic form is expected to be the active phase in the CDE. On the other hand, the styrene yield of the sample with the highest copper concentration (Cat2) was almost the same throughout the process. This result suggests that when cooper species are present in small amount they are stabilized in the active carbon structure and are slowly reduced with time reaction. However, when there are bigger amounts of copper species they are more easily reduced, because some species are weakly bounded. This effect is favored by the temperature increase, as we can see from Fig. 10. The styrene yield increased sharply in the first hours of reaction at 600 °C but did not increase at 400 °C; this temperature seems to be too low to favor the copper reduction in the activated carbon.

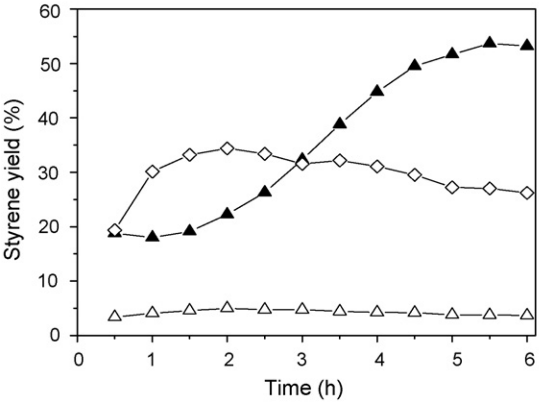

Fig. 10. Styrene yield as a function of time on Cat1 sample (activated carbon-supported copper prepared with copper nitrate solutions 0.74 mol L^{-1}) at 400 °C (△), 500 °C (▲) and 600 °C (◇).

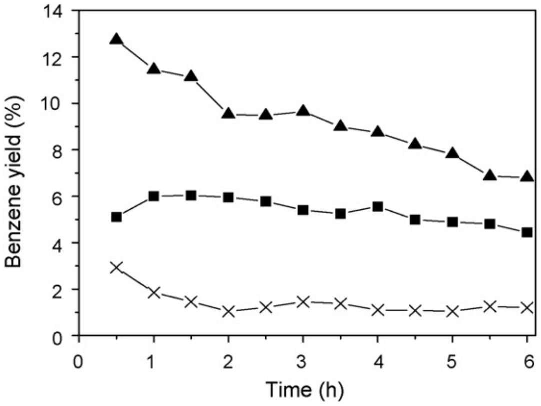

Fig. 11. Benzene yield as a function of time at 500 °C on Cat1 (▲) and Cat2 (■): activated carbon-supported copper, prepared with copper nitrate solutions 0.74 and 1.48 mol L^{-1}, respectively; commercial catalyst (×).

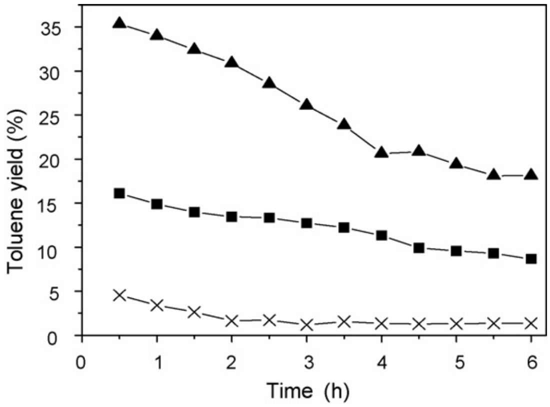

Fig. 12. Toluene yield as a function of time at 500 °C on Cat1 (▲) and Cat2 (■): activated carbon-supported copper, prepared with copper nitrate solutions 0.74 and 1.48 mol L^{-1}, respectively; commercial catalyst (×).

Figs. 11 and 12 show the yield to benzene and toluene as a function of time reaction, respectively. One can notice that, in the case of the catalyst with low copper concentration (Cat1), the yield to benzene and toluene decreased with time, since the sites were becoming more selective to styrene, as more metallic copper was being produced. On the other hand, the material with higher copper concentration showed a profile similar to the commercial catalyst showing low yield to these products, from the beginning of the reaction, since metallic copper was already formed.

4. Conclusions

Spherical activated carbon-supported copper catalysts with different metal loads were obtained from carbonization and activation of sulfonated styrene–divinylbenzene copolymer, followed by oxidation and copper incorporation. These solids were active in the ethylbenzene dehydrogenation to produce styrene. Some copper species were strong adsorbed on the solid, while another part was weakly adsorbed. The species weakly adsorbed were leached from the catalysts, during the reaction and caused the collapse of the activated carbon structure, decreasing the specific surface area and the pore volume. The catalyst containing less copper did not loose metal during reaction, indicating that the copper species were strongly adsorbed on the solid. The species weakly adsorbed did not affect the activity, but they contribute to increase the styrene yield and to decrease the benzene and toluene yield, by-products of the reaction. This catalyst showed high values of conversion since the beginning of the reaction due to its porous structure stability even at 600 °C. It is also highly selective to styrene and then it is the most promising catalyst.

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