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Synthesis and characterization of polymeric activated carbon-supported vanadium and magnesium catalysts for ethylbenzene dehydrogenation

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ABSTRACT

The preparation and characterization of activated carbon obtained from the sulfonated styrene-divinylbenzene copolymer and the effect of vanadium and magnesium on its catalytic activity and selectivity to styrene were described. These new catalysts were evaluated in ethylbenzene dehydrogenation without steam to produce styrene, an important intermediate for petrochemical industries. It was found that the activated carbon is active and selective to styrene, a fact which was related to the presence of quinone groups on the surface. The addition of vanadium increased the activity even more and this was assigned to the activity of vanadium in dehydrogenation reactions as well as to an increase of the amount of oxygen groups on the surface. However, no significant effect of vanadium on the selectivity to styrene was found. Magnesium increased the quinone groups on surface leading to an increase of the initial activity of activated carbon-supported vanadium depending on its amount, but the catalysts deactivated during reaction, a fact which was related to coke deposition; at the end of reaction no effect of magnesium on the activity and selectivity was found. The catalysts were more active than a commercial hematite-based one, evaluated in the presence and in the absence of steam. The catalyst with 5% of vanadium was the most promising sample, showing the highest ethylbenzene conversion which was three times the value obtained with the commercial catalyst in the presence of steam. This result is especially advantageous for the economy of the process, since the addition of superheated steam can be avoided during reaction, saving energy for the process.

1. Introduction

Styrene is one of the most important monomers of the modern petrochemical industry, being used for the production of polystyrene, acrylonitrile-butadiene-styrene (ABS) and for the manufacture of a great variety of other polymers [1,2]. It is usually produced by two processes: (i) ethylbenzene dehydrogenation in the presence of steam and (ii) as sub-product of the propene epoxidation with ethylbenzene hydroperoxide on a catalyst based on a molybdenum complex. The first process is the main commercial route to produce the monomer and is responsible for more than 90% of the worldwide styrene production [3,4].

The ethylbenzene dehydrogenation is industrially carried out on catalysts based on iron oxide (hematite, α-Fe_2O_3) containing potassium, chromium and cerium oxides. The commercial catalyst shows several advantages such as low cost and resistance against impurities, but it deactivates very fast due mainly to potassium loss; potassium usually migrates to the pellet centre or to the gas outlet from the reactor, during industrial processes [5]. Besides, this system contains chromium, which can cause health injuries to human beings as well as environmental problems [6]. Another disadvantage is that the process consumes a high amount of energy and is conducted with excess of superheated steam [7,8]. There is thus a demand for a long life and free potassium catalysts, which show high activity and selectivity and which can be easily handled and discarded with no damages to human beings or to the environment.

Several catalysts have been tested for this reaction in the presence or in the absence of steam [1–13]. Zirconium, lanthanum and niobium oxides, copper and vanadium ferrites, copper, iron and vanadium oxides supported on different solids was evaluated and showed high activities in ethylbenzene dehydrogenation and high selectivity to styrene. Activated carbon was also evaluated and seemed to be particularly attractive [14–16]. This material has been

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widely studied as catalyst for the ethylbenzene dehydrogenation in the presence of oxygen, due to its textural properties and its surface functional groups, especially quinones, responsible for the catalytic activity [15].

Activated carbons have been prepared from different kinds of materials such as coconut shells, wood, lignin, petroleum, turf, coke, bones, seeds, sawdust, rice shells, fertilizer residues, rubber and others [17,18]. Among them, the most used raw materials for the production of activated carbon are: wood (130,000 t/year), mineral carbon (100,000 t/year), lignin (50,000 t/year), coconut shell (35,000 t/year) and turf (35,000 t/year) [18].

The activated carbon prepared from natural materials has a higher amount of ashes when compared to those prepared from synthetic polymers, which also has higher mechanical resistance against abrasion and compression. Regardless the source, the carbon adsorption properties are always affected by the chemical structure of the surface. This property is the most important one for most applications of the activated carbon as adsorbent as well as catalyst [19].

Among the carbonaceous materials, the spherical polymeric activated carbon, obtained by the polymer pyrolysis at high temperatures in a non-oxidative atmosphere, is particularly attractive. In this case, regular spheres with high specific surface area are obtained. They also show high adsorption capacity and suitable mechanical properties, besides regular granulometry and resistance against abrasion [20]. Other advantages of the activated carbons include their acid–base properties and low diffusional resistance to liquids and gases, when used in fix bed reactors. Furthermore, these solids allow an easy incorporation of metals in their surface as well as on the surface of the precursor resin [16,21].

By considering these aspects, the aim of this work is to describe the synthesis of activated carbon obtained by pyrolysis of a sulfonated styrene-divinylbenzene copolymer and the effect of vanadium and magnesium on its properties. This study intends to get free potassium and chromium catalysts for producing styrene through ethylbenzene dehydrogenation, which can work in the absence of steam. This route is particularly attractive, since it can minimize the high production costs related to the use of superheated steam. Several studies about the reaction of ethylbenzene dehydrogenation in the presence of carbon dioxide show that magnesia-supported vanadium catalysts are highly active for this reaction, showing high selectivity to styrene [22].

2. Experimental

2.1. Catalysts preparation

The styrene and divinylbenzene copolymer was synthesized through polymerization in aqueous solution. Inert diluents were used (heptane and toluene) to form pores, leading to a porous structure. For the preparation of the aqueous phase, a mixture of gelatin and hydroxiethilcelulose was used as a suspension agent. Sodium chloride (0.6% of the aqueous phase) was used to reduce the solubility of monomers in the aqueous phase. The gelatin (0.12% of the aqueous phase) was dissolved at 50 °C, under stirring. A clear solution of hydroxiethilcelulose (0.45% of the aqueous phase) was obtained in about 24 h, after adding the polymer to water at room temperature, under stirring. After the dissolution of both suspension agents, these solutions were mixed and sodium chloride was added to the resulting solution, completing the reaction medium volume up to 1326 mL. The aqueous phase/organic phase ratio was maintained at 4:1 (v/v) through the synthesis.

In the preparation of the organic phase, 1% of the polymerization initiator (benzoic peroxide) was used, calculated considering the total number of moles of the monomers. At first, benzoic peroxide was dissolved in the styrene and divinylbenzene mixture using a molar ratio of 15/85 (organic phase) at 25 °C, under stirring. Then, the diluents mixture (toluene and heptane) was added under stirring.

The organic phase was added to the aqueous phase in a three neck flask equipped with a magnetic agitator, a reflux condenser, a nitrogen bubbler and a thermometer and the mixture was kept under stirring at 25 °C. The emulsion was maintained under continuous agitation at room temperature for 10 min, before increasing temperature. Then, the reaction mixture was heated at 60 °C under stirring (500 rpm) for 24 h. The reaction mixture was cooled and the copolymer pearls formed were isolated by reduced pressure filtration.

The synthetized copolymer was transfered to a beaker containing distilled water. The mixture was stirred and heated at 50 °C, for 1 h and filtered while still hot. Then, the polymer was transferred to a beaker containing ethanol (ethanol volume was two times the polymer volume). The mixture was heated at 50 °C, for 1 h and then it was filtered while still hot. This operation was repeated until the filtrate was completely solubilized in water, i.e., it was free of residual monomers and diluents. After purification, the resin was dried in an oven at 70 °C, for 24 h and then it was sieved. In this work, only spheres within the granulometric range between 125 μm and 250 μm were used.

During the sulfonation of the copolymer, the dried resin was dispersed in a concentrated sulfuric acid solution, its volume was fifteen times the resin mass. Then, the mixture was heated up to 70 °C and it was kept at this temperature for 30 min. After this period of time, dicloroethane (solvent) was added to the mixture, using a volume of three times the resin mass. The temperature (70 °C) was kept constant during reaction time. After 4 h of reaction, the resin was washed with the reaction mixture diluted with 2% of distilled water. The dilution proportion was gradually increased, starting with 2%, followed by 5%, 10%, 20%, 30% until reaching 100% of dilution, in order to avoid the rupture of the spheres by osmotic shock.

The thermal treatment consisted on heating the sulfonated copolymer at 300 °C, under air atmosphere 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 ascendant flow of nitrogen saturated with steam, thus obtaining the AC sample. All the heating procedures were conducted at a rate of 10 °C min^{-1}, intercalated with cooling processes until reaching room temperature.

For vanadium adsorption, 5 g of the activated carbon were dispersed in 50 mL and 100 mL of aqueous solution of ammonium metavanadate in oxalic acid (0.098 mol L^{-1} of vanadium), generating the V/AC 5 and V/AC 10 samples, respectively. For vanadium and magnesium adsorption, 50 mL and 100 mL of ammonium metavanadate solution with 0.269 g and 0.538 g of magnesium nitrate was used to get the V-Mg/AC 5-05 and V-Mg/AC 10-05 samples, respectively. All suspensions were kept under stirring for 24 h at room temperature. Then, the samples were heated at 60 °C, under vacuum. The solids obtained were calcined at 600 °C under nitrogen flow, for 1 h, using a heating rate of 10 °C min^{-1}.

2.2. Samples characterization

The thermal stability of the solids was evaluated by thermogravimetric analysis carried out on the activated carbon (AC sample), in a TGA/SDTA851E equipment from Mettler Toledo. The experiments were carried out under air flow (50 mL min^{-1}), using a heating rate of 10 °C min^{-1}, from room temperature up to 1000 °C. The amount of vanadium and magnesium in the catalysts