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Selective hydrogenation of 1,3-butadiene in the presence of 1-butene under liquid phase conditions using structured catalysts

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ABSTRACT

Different aluminium structured substrates (monoliths of 350 and 1100 cpsi; foams of 10, 20 and 40 ppi) have been loaded with NiPd/(CeO_2-Al_2O_3) catalyst by washcoating. To improve the adherence between catalyst particles and metallic surface, aluminium substrates were previously anodized to produce a rough (cracked) surface. Catalytic layers of different thickness have been deposited onto aluminium substrates. The catalytic coatings were characterized measuring their textural properties, adhesion and morphology. These structured catalysts have been tested in the selective hydrogenation of 1,3-butadiene in presence of 1-butene under liquid-phase conditions. The effects of some design parameters over the catalytic performance were studied: catalyst loading (125, 250 or 500 mg), geometry of the structured substrate (monoliths or foams), and porosity (cpsi or ppi). The catalytic results show that foams present better activity than the monoliths. This can be related to better mass and heat transfer in the case of foams. In addition, the catalytic coating thickness influence directly the reaction selectivity; thicker layers produce undesired products (BA and isomers) due to diffusion limitations. However, it seems that the mass transfer of reactants to the surface of the catalyst layer plays a major role than the diffusion of reactants inside the catalyst layer.

1. Introduction

The selective hydrogenation processes are the most important reactions used for the purification of products from cracking units, being one such reactions is the elimination of 1,3-butadiene (BD) present in 1-butene (BE) rich stream. This process serves to obtain high-quality reactants for petrochemical application, *e.g.*, highly purified BE cut is used as co-monomer in the production of linear-low-density polyethylene [1,2]. Currently, this technology employs catalytic fixed beds with co-current flow of the liquid hydrocarbons and gaseous hydrogen, operating temperatures ranging from ambient temperature up to around 60–70 °C and total pressure up to about 1.38 MPa for maintaining the hydrocarbon stream in liquid phase while allowing the desired level of hydrogen partial pressure [2,3]. Industrially, M-Pd/Al_2O_3 (M = Cu, Co, Tl, Fe, Ag, Au, Sn, Ni and Pb) bimetallic catalysts with *egg-shell* distribution of the active components are used to carry out such reactions [4]. In a previous work [5] we have observed that the addition of Ni to the Pd-based catalysts suppressed n-butane (BA) formation and increases recovery of BE due to the formation of Ni-Pd bimetallic phase [6]. It has been reported that Pd overlayered on the surface of Ni or Ni-rich Pd_8Ni_{92} alloy showed much higher activity in the partial hydrogenation of BD than palladium single crystal [7] some theories have been proposed to explain these performances that most importantly indicate that: (1) a favorable geometrical arrangement of surface atoms could occur during annealing of Pd atom deposit on Ni(111), favoring the adsorption of the reactants during hydrogenation [8], (2) a strain relaxation effect of the Ni-Pd surfaces of a Pd monolayer on Ni(110) also could contribute to alkene hydrogenation [9] or (3) self-poisoning or competitive adsorption between BEs and oligomers when $Pd_2Ni_{50}Nb_{48}$ ribbon is used as catalysts has also been reported [10].

The hydrogenation reactions are characterized by their exothermic nature, with ΔH_F −30.3 and −57.1 Kcal/mol for BE and BD, respectively [11]. This characteristic imposes special catalysts or

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reactors to avoid local hot spots and loss of selectivity. In addition to this, the catalyst systems currently used suffer the disadvantage of needing catalytic and physical properties in the same material [12] such as showing poor control of the reactivity/selectivity ratio, non-homogeneous access to the catalytic surface and very high pressure drops. BD hydrogenation reaction proceed under strong diffusion limitations inside the active shell of the catalyst particles, causing significant losses of the substance to be purified [13]. Although the use of slurry reactors with sufficiently small catalyst pellets can reduce diffusional limitations, the industrial application is inappropriate due to costly filtration steps that would be necessary. The development of structured catalysts, such as monoliths, foams or membranes, has been stimulated by the search for other types of catalytic systems that may avoid some of these problems [12,14,15], for reactions of commercial interest, as *e.g.*, volatile organic compounds total oxidation [16–18], hydrogenation of sunflower oil [19]. Fischer-Tropsch synthesis [20], methanol steam reforming [21], among others. The structured catalysts are systems that allow separate catalytic functions and physical ones, since they comprise a material which gives the necessary physical properties (structured substrate) and a layer of a catalytic support where the active species are placed [22]. Structured substrates are stiff, three-dimensional structures with channels or macropores that lead to a very low pressure drop and which exhibit high lateral surface where a thin layer of catalyst can be applied. Benefits of the monolithic catalyst comparing with conventional three-phase reactors are the short internal diffusion lengths due to thin catalyst layer (less than 20 μm) and the high external mass transfer values due to the bubble train flow inside the channels [23].

Most of the studies for selective hydrogenation have been focused on some aspects of the catalysts, *i.e.*, active phase [24–26] and promoter or co-metal nature [4] or additives in the process stream [27–31]. However, in the literature only a few studies have dealt with the utilization of structured catalysts for similar reactions to those studied in this research. García Colli et al. [32] compared the catalytic activity of 2.3 mm *egg-shell* pellets and multi-layer microreactor in the hydrogenation of 1-butyne. They concluded that pellets show a strong diffusional resistance inside the active shell that are avoided using microchannel reactor producing a significant increment in catalytic activity and selectivity. Nagamoto and Inoue [33] showed that the hydrogenation reaction of BD using commercial membrane-supported Pd catalysts was limited by the hydrogen adsorption, the reaction rate was affected by the presence of BD, and that reaction proceeded much faster for a permeation system that for a mixture system. Similar results were reported by Lambert and Gonzalez [34] when the membrane-supported Pd catalysts were tested in the partial hydrogenation of BD and 1-butyne. Furthermore, these authors showed that the hydrogenation reactions carried out by flowing a premixed feed through a membrane resulted in the highest selectivity to the partially hydrogenated products while maintaining a high conversion without any loss of hydrocarbon species. Ciebien et al. [35] showed that Pd nanoclusters synthesized within diblock copolymer films could also be active and selective catalysts for this reaction, even though the clusters are completely surrounded by a bulk polymer matrix and that it could not be avoided some systematic increases in cluster diameter. Liu et al. [36] showed that PVP-Pd/CA monometallic catalytic hollow fibers (PVP = Poly(*N*-vinyl-2-pyrrolidone) and CA = cellulose acetate) is an efficient structured catalyst for the selective hydrogenation of BD in BE, because content of BD can be reduced to <10 ppm and the simultaneous loss of BE is only about 2% by adjusting the reaction parameters. However, the isomerization of BE only is avoided when a Co-Pd bimetallic catalytic hollow fibers were used. Another type of structured catalysts, metal sponge-like packing, has also been used. Galiasso-Tailleur et al. [37,38] used a NiPdCe(x)/Si-Al catalyst coated onto two commercial structured packings: a Sulzer BX gauze and a compressed 3 M stainless steel sponge. The main results showed an important diffusion control of the reaction only at the inlet of the reactor where BD is 10 times faster than BE hydrogenation. At high BD conversion, mass transfer did not affect the selectivity.

In the present work, the trace removal of BD from BE feedstock through selective hydrogenation reaction in a recirculation system with external fixed-bed reactor was studied using anodized aluminium structured catalysts. The anodization treatment of the alumina substrate produces a cracked alumina layer on the structured substrate. This layer has a dual function. On the one hand, increases the chemical compatibility between the catalyst and the metallic substrate that favors the adhesion. Furthemore, promotes the mechanical anchoring between the catalyst particles and the surface roughness of the substrate offered by the cracked alumina, which also improves adhesion [20,21,39,40]. The washcoating method was used to incorporate a NiPd/(CeO_2-Al_2O_3) formulation over these aluminium structured substrates. The effect of some specific characteristics of the structured substrates, such as the catalyst loading, geometry, and cell density for monoliths or pore density for foams, over the catalytic performance were analyzed.

2. Experimental

The preparation of the structured catalysts was carried out in three steps: powder catalysts synthesis, aluminium surface modification by anodization using oxalic acid as electrolyte and coating of the substrates by washcoating using catalyst slurry.

2.1. Catalyst preparation

Powder NiPd/(CeO_2-Al_2O_3) catalyst (0.5% and 3.0% wt.% of Pd and CeO_2, respectively; Ni/Pd atomic ratio = 1.0) was prepared using two impregnation steps. In the first impregnation step, CeO_2-Al_2O_3 was obtained by addition of an aqueous solution containing ammonium cerium (IV) nitrate to γ-Al_2O_3 (Alfa Aesar, ground to <150 μm, pre-treated at 120 °C for 12 h). Then, pH was adjusted to ~8.0 with NH_4OH (4 M) and the suspension was maintained under stirring. In order to remove most of the solvent, suspensions were treated in a rotary evaporator at 60 °C and 60 rpm whereas pore-retained moisture was eliminated at 150 °C for 12 h in N_2 (100 mL/min). The fresh support was obtained with a linear heating rate of 5 °C/min to the final temperature of 500 °C, which was held for 4 h under a flow of synthetic air (100 mL/min). In the second impregnation step, simultaneous incorporation of Ni and Pd over CeO_2-Al_2O_3 was realized following the same synthetic procedure using tetraamminepalladium (II) chloride monohydrate and nickel (II) nitrate hexahydrate as metallic precursors. However, retained moisture was eliminated at 60 °C for 12 h under N_2 flow (100 mL/min).

2.2. Aluminium surface modification

Aluminium foils were supplied by INASA S.A., while aluminium foam blocks were manufactured by ERG AEROSPACE CORPORATION through the DUOCEL® process. The chemical compositions of both materials are shown in Table 1. For monoliths manufacture, aluminium foils (120 μm) were corrugated using two home-made machines with nylon indentations to obtain two cell densities, 350 or 1100 cpsi (channel per square inch). The aluminium foam cylinders were cut from slabs of 40 mm of thickness using a hollow drill with a diamond saw of 16 mm of internal diameter. Foams of 10, 20 and 40 ppi (pores per inch) were used. Both types of materials were washed successively with a detergent-water mixture and acetone, afterward dried with a flow of compressed air.

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