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Metallic monoliths of AISI 304 stainless steel, aluminum, FeCrAlloy® and brass, coated by Mo and W oxides for thiophene hydrodesulfurization

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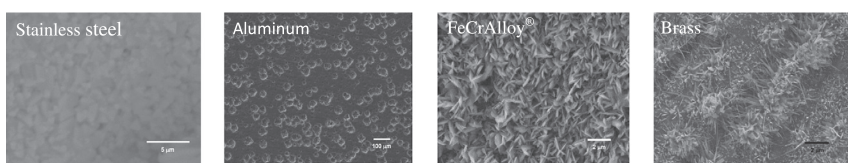
HIGHLIGHTS

- ▶ SS, Al, FA and B were shown to be good for the manufacturing of metal monoliths.
- ▶ Oxides on the surfaces of sheets facilitated attachment of the catalytic slurries.
- ▶ Coated monolithic structures have the potential to be used for HDS.

GRAPHICAL ABSTRACT

Metal sheets of AISI 304 stainless steel, aluminum, FeCrAlloy® and brass were employed in the manufacture of metallic monoliths to provide a support for catalysts based on Mo and W oxides; these solids were tested in the thiophene hydrodesulfuration reaction. Oxidic phases generated on the surfaces of the metal sheets after the pretreatments applied not only facilitated attachment of the slurries of Mo and W, but also contributed to the activity of the monoliths in C_4H_4S HDS. These sheets presented good characteristics for the manufacturing of metallic monoliths.



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ABSTRACT

Metal sheets of AISI 304 stainless steel (SS), aluminum (Al), FeCrAlloy® (FA) and brass (B) were employed in the manufacture of metallic monoliths to provide a support for catalysts based on Mo and W oxides. These materials were characterized by XRD, N_2 physisorption (BET), adherence test and SEM-EDS. The catalytic performance of the uncoated and coated metallic monoliths was studied using thiophene hydrodesulfuration (HDS) at 400 °C and $P = 1$ atm as model reaction. With the purpose of generating a high rugosity interface appropriate for anchoring the catalytic slurry, thermal treatments were applied under a stream of synthetic air to the sheet of SS, FA and B, while an anodizing process (chemical treatment) was used for Al. The XRD patterns showed oxidic phases of Cr_3O_8, Al_2O_3 type boehmite, α-Al_2O_3 and θ-Al_2O_3 and ZnO type wurtzite formed on the surfaces after thermal or anodizing treatments, as well as MoO_3 or WO_3 phases when coated. SEM of the SS, Al, FA and B sheets treated and coated with Mo or W allowed visualization of the homogeneously rough surface formed by whiskers for SS, FA and B, and the pores on the surface of Al. Incorporation of Mo and W in the structure is evidenced from the EDS analyses, detecting contents of 7–10 wt% of these metals. The textural analysis by BET showed values between 5 and 16 m^2/g, while the adherence test reported mass loss below 5% where metal monoliths showed that the slurry of Mo has more grip than the slurry of W. Finally, the evaluations of the catalytic systems showed that the monoliths of Mo-FeCrAlloy® and Mo-brass were the most active in HDS with activities above 0.27 mmol-C_4H_4S/g × min, showing that the monoliths coated with slurry of Mo presented higher catalytic activity than those coated with slurry of W.

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1. Introduction

Since the early decades of the 20th century, petroleum has played a decisive role in the history of our nations. Nevertheless, most of the remaining hydrocarbon reserves are composed of heavy and extra-heavy crude oils, which due to their elevated contents of N, S, O and metals, are hugely polluting. These substances are cause of environmental problems, deactivate catalysts and corrode pipelines and equipment of production, forcing the oil industry to take corrective actions to reduce these effects. On the other hand, the growing increase in greenhouse gas emissions into the atmosphere is causing the establishment of a series of increasingly stringent regulations, for example, the measures imposed by agencies such as the Environmental Protection Agency (EPA) of the United Stated, which has ordered to gradually reduce the content sulfur in gasoline to 15 ppm for the period 2008–2015. Similar values have been established in Europe and Japan [1].

To remove contaminants in petroleum derivatives and maintain profitability in the oil market, the refineries commonly use the hydrotreating process. The hydrodesulfurization (HDS) is the reaction with more commercial interest, because it allows removal of sulfur heteroatom content in the crude using active and selective catalysts in the presence of hydrogen [2]. The main characteristics of this reaction type are: (i) HDS is strongly exothermic; (ii) hot points are usually generate in the reactor walls and, (iii) high pressure drops commonly occur in the conventional beds conformed by catalysts in the shape of spheres and/or extrudates, due to bed plugging with coke. For these reasons it is desirable to decrease the exothermicity of the system seeking to favor the phenomena of heat and mass transfer within the fluid away from the catalyst surfaces to avoid the formation of hot points which deactivate quickly the catalysts during the reaction.

Ceramic monoliths have been implemented in various gas-phase catalytic reactions, such as three-way catalytic converters, selective reduction of NO_x, destruction of volatile organic compounds, catalytic combustion, and other emerging applications such as generation of hydrogen for fuel cells, steam reforming of hydrocarbons, preferential oxidation of CO, H_2O_2 production, among others [3]. However, the essence of the use of a structured reactor is that it enables the dissociation of the intrinsic reaction kinetics, transport phenomena and hydrodynamics [4]. It has been reported performance comparisons between conventional monolithic reactors, finding that the monolithic reactors are hydrodynamically superior to conventional multiphase reactors and industrial reactors [5]. Besides presenting favorable properties with respect to practicality, high rates, high selectivity and low power consumption [6]. Moreover, computational models [7,8] have been developed in the search for evaluating monolithic reactors advantages compared to packed bed reactors.

In the search of new technologies, metallic monoliths have become one of the most relevant and economically viable for their application to catalytic reactors in engineering and environmental catalysis. These materials have a lofty durability at high temperatures, excellent mechanical strength and flexibility of design to promote turbulence and high geometric surface area which allows incorporation of the most of the active catalysts by the adhesion of a thin layer to the walls [9].

The possibility of incorporating the active phase into the surface of metallic structures of various geometries and materials has prompted the development of design and fabrication of monolithic catalysts [10] for potential use in various applications [11–15]. In the literature it has been used AISI 304 stainless steel [16–19], aluminum [20,21], FeCrAlloy® [22–24] and brass [25–27] as materials for the manufacture of metallic monoliths. However, there are few published studies regarding their use in hydrotreatment reactions [6,7,28–31].

Highly exothermic reactions, including several large-scale processes such as HDS, are attractive options for monolithic systems [28]. The monolith is most suitable for processes that are (1) stable enough for packed-bed operation and (2) need better mass transfer than can be obtained in any conventional reactor, including the trickle bed and the stirred tank reactor [29]. Higher productivity can be achieved in combination with safer operation, and its main advantage is a high cell density monolith that creates a high geometric surface area identical to the external surface of the catalyst particles. In this regard, a comparison of their geometric surface areas shows that the monolithic catalysts in the diffusion distance and the pressure drop are lower by approximately one order of magnitude, see Fig. 6 of Ref. [30]. It has also been modeled the hydrodesulfurization of a vacuum gas oil in liquid phase [7] using reactors with three-levels-of-porosity (TLP) and internally finned monoliths (MFI) as compared to conventional trickle-bed reactor (TBR), showing a significant increase in conversion in countercurrent mode and mass transfer properties sufficient to efficiently remove H_2S produced in monolithic reactors [31].

This investigation proposes the use of AISI 304 stainless steel, aluminum, FeCrAlloy® and brass as precursor materials for preparation of structured catalysts based on alumina-supported Mo and W oxides catalysts, in order to favor the mass and heat transfer phenomena in thiophene hydrodesulfurization.

2. Materials and methods

The choice of metal alloys used as catalytic substrate was based on desired properties related to the use of the catalyst at operating conditions of the catalytic test, those related to the catalytic coating adhesion and those related to the manufacturing process. In this sense, we choose two iron based alloys, FeCrAlloy® and steel, which are two of the most widely used alloys in this context, being capable of producing oxides on their surfaces with excellent properties for anchoring the catalytic coating. This is especially so in the case of FeCrAlloy® given its relatively high Al content. Another selected material was aluminum, which has good mechanical and thermal properties, and may be anodized to produce highly adherent alumina layers with suitable texture to be used as catalyst support. Finally, brass (of not so common use) was included for its potential to form zinc oxide layer on its surface with good characteristics to adequately tolerate the coating. Commercial metal sheets of AISI 304 stainless steel (SS), aluminum (Al), FeCrAlloy® (FA) and brass (B) supplied by Goodfellow and OHIO were employed. These materials have the following compositions in weight%: **SS:** 70.480 Fe; 18.400 Cr; 8.110 Ni; 0.440 Si; 1.450 Mn; 0.057 N; 0.064 C; 0.230 Cu; 0.250 Mo; 0.030 P; 0.001 S; 0.200 Co; 0.130 V and 0.150 W. **FA:** 72.500 Fe; 20.300 Cr; 5.400 Al; 0.084 Ti; 0.080 Zr; 0.045 Y and 0.310 Hf. **B:** 71.200 Cu; 27.350 Zn; 1.270 Sn; 0.070 Pb; 0.030 Fe; 0.030 As; 0.010 Si; 0.010 Mn; 0.010 Al; 0.010 Sb and 0.004 Ni.

2.1. Pretreatments of metal supports

The pretreatment conditions of the surface of a metallic support are determined by the nature of the chemical composition of the sheet. Depending on the type of material, either thermal or electrochemical methods can be applied. In the cases of stainless steel, Fecralloy® and brass thermal methods (i.e., calcination processes) are the best procedures for obtaining rough surfaces, while aluminum is best suited for electrochemical generation of the oxidic layer. This stage seeks to provide roughness or porosity to the surface in order to ensure proper diffusion of the catalytic slurry and to favor its subsequent attachment to the monolithic structure in the process of washcoating [10]. The morphological and textural