Intensification of catalytic processes with structured catalysts and reactors

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Highlights

- Process intensification is characterized by high mass and heat transfer coefficients.
- Structured catalysts allow reducing both external and internal diffusion limitations.
- Metallic substrates allow producing catalytic systems with high thermal conductivity.

1. Introduction

Intensification of catalytic processes requires catalysts with high activity per unit of reactor volume. For this to be practiced, a suitable catalyst arrangement is also required in the reactor to ensure sufficient flow of reagents and products and heat transfer in the proper direction. These flows are controlled by the external diffusion processes (from the bulk fluid phase to the catalyst surface or the inverse), internal diffusion (in the porous network of the catalyst) and by the heat transfer within the catalytic bed. Such processes depend on both the properties of the fluid and the operating conditions as well as on the characteristics of the catalyst, the substrate in the case of structured catalysts, and the reactor itself in the case of structured reactors such as microreactors. To enhance the external diffusion rate it is convenient to increase the linear velocity of the fluid and the turbulence, but looking for a trade-off with pressure drop that is favored by the same conditions [1]. As for the internal diffusion in the porous network of the catalyst, we were able to enhance it by increasing the diameter of the pores and reducing the diffusion path which is usually achieved by reducing the catalyst particle size. However, this reduction in particle size also leads to an increase in pressure drop in fixed-beds. Finally, heat transfer requirements are usually solved in fixed-bed reactors adopting multitubular configurations which provide higher surface-to-volume ratios. In response to the opposite effects of the process variables on diffusion limitations and pressure drop, structured catalysts and reactors have been developed, and particularly the monoliths with parallel longitudinal channels that have reached their highest degree of development in the catalytic converters for exhaust gas emissions control. But it is known that conventional ceramic monolithic catalysts operate under a quasi-adiabatic regime which is not suitable for chemical reactions with large thermal effect.

The purpose of this communication is to show several examples of the work developed in our laboratories that demonstrate the advantages offered by structured catalysts and reactors for the intensification of catalytic reactions with high thermal effect involved in fuel conversion processes as well as energy and environmental applications.

2. Results and discussion

External diffusion. Its effects have been studied by comparing the performance of monoliths with longitudinal parallel channels, stacked wire mesh monoliths and foams on different reactions: VOC removal, selective butadiene hydrogenation and Fischer-Tropsch synthesis (FTS). In the case of meshes for VOCs removal, kinetic analyses explained their greater activity compared to longitudinal channel monoliths which was due to enhanced turbulence [2]. Metallic foams applied to the above-mentioned reactions have always shown improvements compared to the longitudinal channel monoliths both in activity and selectivity due to the increased turbulence produced. The fundamental role of turbulence is also evidenced by the improvement obtained with the increase of the linear pore density (dpi) of the foams or the decrease of the mesh opening.

Internal diffusion. Studies performed with both monoliths and foams in the FTS showed that thicknesses of the catalytic film exceeding 50 microns produced a significant decrease of the selectivity to C5+ and a slight CO conversion decrease. Therefore, the best strategy for the intensification of this reaction is the use of monoliths with very high cell densities, thus allowing to increase the geometric surface area exposed by the substrates and therefore reducing the thickness of the catalytic film for a given catalyst loading [3]. Another strategy to reduce the limitations of internal diffusion is to increase the porosity of the catalytic layer. Studies done incorporating macroporosity to the catalytic layer (hierarchical porosity) showed a paradoxical effect. Macroporosity resulted in a decrease of the catalytic coating density which produced an increase of the layer thickness for the same amount of catalyst. This led to an increased diffusion path that produced so negative effects that rendered irrelevant the incorporation of macroporosity [3].

Thermal conductivity effects. According to Tronconi et al. [4], the effective thermal conductivity of a structured catalysts depends fundamentally on the conductivity of the substrate and that of the solid deposited on the substrate. Our studies on methanol steam reforming with metallic monoliths of different cell density showed an a priori unexpected result: the methanol conversion increased as the cell density of the monolith decreased. Accurate temperature measurements showed marked temperature profiles for the same core monolith temperature depending on the cell density of the substrate. This caused the average temperature to increase as the cell density decreased due to the lower effective thermal conductivity. These results were confirmed through CFD simulations thus explaining the experimentally observed methanol conversion evolution [5].

The FTS is very exothermic, so temperature control is critical and a high thermal conductivity is necessary to avoid hot spots that produce temperature runaway leading to the sole and undesired production of CH_4 and CO_2. Conventional metallic monoliths fabricated by corrugation exhibited high thermal conductivity when manufactured with a very high cell density (> 2000cpsi) or with a highly conductive alloy (such as aluminum instead of steel), which allowed a good control of the FTS temperature [6]. In these circumstances a remarkable intensification of the process is possible since by increasing the temperature a high volumetric productivity of C5+ can be obtained, much higher than that presented in the literature and very close to that of the much more sophisticated and expensive monoliths obtained by extrusion [6].

4. Conclusions

Structured catalytic systems with metallic substrates offer substantial improvements over conventional catalytic reactors for reactions presenting high thermal effects. By properly selecting geometry and materials, the turbulence and the thermal conductivity can be enhanced thus avoiding important limitations associated to transport phenomena of reactants and products together with a better control of the reaction temperature.

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