

ABSTRACT

Today, the increasingly serious lack of resources and the obsolescence of the plants present on the whole planet led to develop new ways that go beyond “traditional” chemical engineering. The research is now focusing on novel equipment and techniques that potentially could change the concept of chemical plants and lead to compact, safe, energy-efficient, and environment-friendly sustainable processes. These developments share a common focus on “process intensification” — an approach that has truly emerged in the past few years as a special and interesting discipline of chemical engineering, because of the reasons enounced above. Process intensification tends its aim to the reduction of the total costs (fixed and operating) in an industrial plant. This “saving” in economic terms is possible not only by making a minimization of the equipment’s volume, but it’s also related to both chemical and physical aspects of one industrial process.

The principle targets of a process intensification are:

1. Improved control of reactor kinetics giving higher selectivity/reduced waste products.
2. Higher energy efficiency.
3. Reduced capital costs.
4. Reduced inventory/improved intrinsic safety/fast response times.

In order to reach all of these targets, it must be considered that transport phenomena play a very important role for the process intensification of an industrial reactor. Also improvements in environmental impact is another aspect that is constantly faced today, regarding all the processes in which there is the need of eliminating one dangerous chemical species. Taking into accounts all these reasons, one possible candidate for process intensification is represented by the Water Gas Shift process (WGS). It is the first purification stage of a hydrogen production plant, and involves the conversion of CO in CO₂, while at the same time there is an increase in H₂ yield in syngas. It also provides a H₂/N₂ mixtures with the appropriate ratio for the production of an important chemical product, such as ammonia.

The WGS is an exothermic reaction, thermodynamically favored at low temperature, however kinetic limitations make it convenient to work with a two-stage process, i.e. two different catalytic systems: a first stage (HTS), carried out in the temperature range 350-600°C, where the most of the CO conversion is obtained (but thermodynamic limitations effect the theoretically reachable conversion); a second stage (LTS) carried out in the temperature range of 180-350°C, with slow kinetics (the thermodynamic conditions allow to obtain very low CO concentration, less than 10 ppm).

Although this type of configuration is very effective, it shows several disadvantages: as a first, the global system kinetics is very slow, requiring a high mass of catalyst, that in turn results in long activation time; moreover, the presence of the inter-cooling unit increases not only the energy requirements of the process, but also the plant cost itself; furthermore, the LTS catalyst shows pyrophoricity, resulting not able to sustain frequent start up and shut down stages, and then not suitable for mobile fuel cell applications.

Definitely, the actual WGS plant configuration would be of course the biggest unity of an integrated fuel processor. For these reasons, a process intensification is needed. Considering a conventional adiabatic reactor, the exothermicity and the equilibrium characteristics of the WGS reaction, together with the catalysts performances, reflects negatively on the CO conversion, disfavoring the reaction rate at the inlet of the catalytic bed, where the temperature is low, and limiting the very high conversion values at the outlet, where the temperature is high. So, a process intensification for this type of process should accounts for a modification both of the catalytic phase and the catalyst bed thermal profile. In order to reach the first target, it is necessary to find a good catalytic formulation that is able to be efficient in the low temperature range. Moreover, by considering the influence of the heat transport on the whole system, the use of a high conductive catalyst could play a crucial role, with the possibility of redistributing the heat of reaction along the catalytic bed to obtain a flatter thermal profile with a lower outlet temperature and, consequently, a higher CO conversion.

The aim of this PhD thesis was to investigate the influence of the catalyst thermal properties on the Water Gas Shift (WGS) process, by using a structured carrier with high thermal conductivity. The research line was followed in order to verify if it is possible to increase the backdiffusion of the reaction heat throughout the structured catalyst bed, modifying the adiabatic temperature profile, obtaining, with respect to a typical packed bed reactor, a higher temperature at the inlet section and a lowered temperature at the outlet bed section, overcoming respectively, the kinetic and thermodynamic limits, achieving so an increased CO conversion. Accordingly, this approach would ensure that a conventional double staged WGS reactors with

intermediate heat exchange could be replaced with a single WGS reactor, characterized by a "quasi isothermal" temperature profile.

In this context, during the PhD project different phases have been followed to reach the intended objective.

1. CHOICE OF THE STRUCTURED CARRIER

In order to reach the desired heat transfer properties, metal foams were chosen as structured carriers. They are open-cell structures that may be fabricated in a variety of shapes from a wide range of materials, and they exhibit very high porosities with good interconnectivity. These characteristics result in a lower pressure drop than that observed with packed beds and high convection in the tortuous megapores, which, in turn, enhances mass and heat transfer. Moreover, they are also easily coated with high-surface-area catalytic components, using well-established techniques.

In general, mainly two parameters effect on overall heat transfer coefficient: the void fraction (or porosity) and the pore density (PPI), in addition to the bulk thermal conductivity. The first two parameters can highly influence the third one, because the first one is related to the amount of solid material and the second one to the way in which the solid material is distributed in the structured carrier. Moreover, the conventionally applicable foams for a catalytic process must be highly porous, otherwise pressure drops can increase dramatically.

In order to find an efficient open cell foam for the purposes of this PhD project, the heat transfer through different structured metal foams was investigated. The thermal properties, in particular the thermal conductivity and the gas phase heat transfer coefficient of the structured supports were estimated by means of a mathematical model, developed on the basis of other similar heat transfer models accounted for honeycomb monoliths. An experimental set up was built, including an oven for heating the whole system at different temperatures, a quartz tube in which the metal foam was inserted, and a set of thermocouples to measure temperature in different points of the carrier. The experimental results were used to optimize the mathematical model and validate it, and the thermal properties estimated were used as basis for a comparison between the carriers and the choice of the best one in terms of heat transfer.

2. CHOICE OF THE CATALYTIC PHASES

The literature research revealed that reducible oxides supported platinum based catalysts are today the best choice for obtaining a highly active and efficient catalytic system for the WGS reaction. These types of catalysts, instead of gold ones, are more stable and, if high dispersed on a reducible oxide, can prevent phenomena such as sintering of the active metal particles. On the basis of this review, different platinum based catalysts, supported on ceria, ceria-zirconia and ceria-alumina were prepared, through the wet impregnation method, followed by drying at 120°C and calcination in muffle. A wide characterization of the samples was done, including the specific surface area estimation (BET method), the XRF and XRD analysis, the use of the Raman shift and the study on the reducibility properties of the samples, through the technique of the temperature programmed reduction (TPR). The Water Gas Shift tests were made by fixing the operative conditions, in order to have a benchmark for this initial screening. The CO concentration was set to 5%, water at 25% and helium balance, as inert component. These activity and selectivity tests were made at atmospheric pressure, in a range of temperature between 150°C and 400°C, with a gas hourly space velocity of 5000 h⁻¹. All the samples were reduced to particles with a size between 180 and 355 nm. the aim of this experimental campaign was to find a good and efficient catalytic formulation, active in a very low temperature range.

The best catalyst, from those investigated, was also tested by increasing the space velocity of one order of magnitude and by verifying its durability, in order to investigate about possible critical issue to be corrected.

3. DEPOSITION OF THE CATALYTIC PHASES ON THE STRUCTURED CARRIER

In order to anchor the catalytic phases to the structured carrier, it is necessary to formulate a good washcoat. A washcoat is a chemical species that in catalysis is used to disperse the materials over a large surface area. Washcoat materials must form a rough surface, which greatly increases the surface area compared to the smooth surface of the bare structured carrier. This in turn maximizes the catalytically active surface available to react.

So, the washcoat was formulated on the basis of what enounced above. The catalyst preparation was divided into three stages. All these stages were followed by drying at 120°C and calcination at 450°C for 3 hours. Firstly, the washcoat was anchored to the foam surface by using the dip-coating procedure. Then, chemical support was added to the washcoat by the wet impregnation method. Finally, the sample was impregnated

with a solution of the platinum precursor. The same catalyst formulation was also prepared in powder form, and employed as reference. The stability of the washcoat on the foam surface was tested via sonication, to verify the adhesion of the chemical species on the structured support. The specific surface area (SSA) was determined by the BET method. The Scanning Electron Microscope (SEM) was used to study the morphology of the foams and to check the washcoat on the surface of the foam. It was possible to estimate the pores average diameter and the fibers diameter, and it was also verified that the washcoating procedure led to a homogeneous deposition on the surface of the structured carrier. The temperature programmed reduction (TPR) was performed in a stainless steel tube with an internal diameter of 22 mm. A 5% H₂/N₂ gas mixture (flow rate: 1000 Ncm³/min) was fed to the reactor, and temperature was raised up to 400°C with a heating rate of 10°C/min. The WGS catalytic tests were performed at atmospheric pressure, in typical conditions for the LTS process (a temperature range of 200-400°C). The reacting mixture consisted of 8% CO, 30% H₂O and N₂ balance. The catalysts activity was tested in the same reactor as the TPR. The gas hourly space velocity (GHSV) was set up to 10000 h⁻¹.

4. DEVELOPMENT OF A “QUASI” ADIABATIC SYSTEM: COMPARISON BETWEEN PACKED BED AND STRUCTURED FOAM CATALYST

An important phase of the PhD was dedicated to the development of a “quasi” adiabatic system, in order to exploit the high conduction of the structured catalyst, prepared in the previous phase, with respect to a conventional packed bed catalyst.

In order to evaluate the influence of the thermal transport properties of the foams on the WGS reaction, a laboratory system able to avoid thermal dispersions was set up. This target was reached by increasing the total flow rate, keeping constant the L/D ratio of the structured foam catalyst. The experimental set up was used to drive a WGS reaction in the following conditions: inlet T = 260 °C, P = 1 atm, CO molar fraction = 8 vol%, H₂O molar fraction = 30 vol%, N₂ balance, WHSV = 2.4 gCO/gcat-1/h-1, linear flow velocity = 18.2 cm/s-1. In order to compare the performances of the different samples, two thermocouples were installed, one at the inlet section of the catalyst and the other one at the outlet section, while the CO conversion was continuously monitored with the aid of an ABB detector.

After making a comparison between the performances of a foam catalyst with those of a packed bed catalyst, the developed experimental set up was used to perform different WGS tests on different types of foam. The aim of these tests was to investigate how the void fraction and the pore density can influence the heat transfer, and so the performances of the structured catalyst.

5. MODELING OF THE WGS ADIABATIC REACTOR

In order to validate the results obtained by the tests made with the “quasi” adiabatic system, the model of the adiabatic reactor was developed with the aid of the finite element software COMSOL Multiphysics 5.0 (License number: No.13073437,00-0f-fe-0a-73-34). The comparison has been done between the structured foam catalyst and a conventional packed bed adiabatic reactor. The process has been modeled coupling transport phenomena and reaction kinetics. The reactor model was implemented exclusively with the CFD.

A simplified geometry of the real system was built. By assuming no dependence of the transport parameters with the tangential coordinate, it was possible to reduce the volume domain to ¼ of the real one. In particular, the simulated geometry was built as follows. The gas stream flows axially, along the z-coordinate, through the reactor (internal diameter of 22 mm, thickness of 2.5 mm). The catalytic zone was put in the middle of the reactor (catalyst diameter of 16.5 mm). The length of the catalytic zone was set to 88 mm, while the total length of the reactor was 400 mm.

The use of COMSOL allowed to simulate the packed bed adiabatic reactor and the structured foam catalyst, in order to exploit the high thermal properties of the latter in view of an intensification of the Water Gas Shift process. The developed model will be the basis for the design of an industrial reactor, where the catalyzed structured foam technology is applied.