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New catalytic reactors prepared from symmetric and asymmetric ceramic hollow fibres

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ABSTRACT

In this study, asymmetric and symmetric Al_2O_3 hollow fibres were employed as a support of a 10% CuO/CeO_2 catalyst in the development of an asymmetric hollow fibre reactor (AHFR) and a symmetric hollow fibre reactor (SHFR), respectively. The 10% CuO/CeO_2 catalyst was successfully deposited in both Al_2O_3 hollow fibre substrates by the sol–gel Pechini method. The impregnated fibres were characterized by Ar permeability, Hg porosimetry, X-ray diffraction, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and high-resolution optical microscopy. The water gas shift (WGS) reaction was chosen as a sample reaction to compare the performances of both AHFR and SHFR with a traditional fixed bed reactor (FBR). The catalytic activity tests in the FBR were carried out using the powder ground from either the asymmetric or symmetric Al_2O_3 hollow fibre impregnated with 10% CuO/CeO_2. Two different configurations, "dead-end" and "open-end", were studied in the AHFR and SHFR. The experimental results show that, despite the differences observed between the AHFR and SHFR, both reactors offer important advantages over conventional FBRs including high catalytic activity along with a better selectivity.

1. Introduction

The concept of multifunctional reactors allows the integration of multi-processes in a single reactor device [1–3]. The use of the multifunctional reactors, rather than the traditional technology, enables the intensification of most of today's industrial processes making them safer, cleaner, smaller and cheaper. Thus, the development and design of different approaches for process intensification such as flow through reactors [4,5], micro reactors [6–8], sorption enhanced reactors [9–11], membrane reactors [12–14] and sorption enhanced membrane reactors [15–17] are increasingly gaining the interest of the scientific community.

Although the concept of multifunctional reactors is not new [18], until now the development of multifunctional reactor approaches has not been fully explored due to the difficulty of combining chemistry, material science and engineering knowledge in a single device. In this respect, the use of ceramic hollow fibres as a support of either catalysts, selective membranes or both simultaneously, provides an attractive alternative in the development of novel hollow fibre reactors for gas phase reactions [19].

In our previous study, asymmetric Al_2O_3 hollow fibres were successfully employed as a catalyst support in the development of an asymmetric hollow fibre reactor (AHFR). It has been demonstrated that deposition of catalysts inside the finger-like region of the asymmetric Al_2O_3 hollow fibres increases its catalytic efficiency. This behaviour can be explained by the micro-channelled structure of the finger-like region, which improves the heat and mass transfer during the reactions [20–23]. It has been observed that deposition of the catalyst depends on the physical and chemical properties of the Al_2O_3 hollow fibre surface. Three different methods to deposit the catalyst inside the finger-like region have been tested: (1) infiltration [24]; (2) wet impregnation [25]; and (3) sol–gel [19–21]. Among these methods, infiltration allows the development of AHFR using commercial catalysts. However, in order to avoid the obstruction of the main entrance to the finger-like channels during the catalyst deposition, the catalyst particle size must be at least three times smaller than that of the entrance. Alternatively, wet impregnation and sol gel methods can be used, which do not present this problem and allow catalyst deposition even if the pores of the outer surface of the Al_2O_3 hollow fibre is closed by either a glaze layer or a dense membrane.

In addition, a new symmetric hollow fibre reactor can also be fabricated using symmetric Al_2O_3 hollow fibres as a catalyst support. It consists of an unselective porous membrane where an active catalyst is deposited. According to Westermann and Melin [4], this

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type of the reactors operated in a flow through mode presents the advantage of providing intensive contact between reactants and catalysts, combined with a short residence time, allowing for a high selectivity and catalytic activity.

The tubular geometry of both asymmetric and symmetric Al_2O_3 hollow fibre substrates with an outer diameter smaller than 2 mm easily allows the scaling up of the catalytic process by bundling the fibres into a module. Furthermore, either large-scale or small-scale applications can be achieved, since Al_2O_3 hollow fibre lengths as long as 40–50 cm and as short as 1–2 cm can be employed while maintaining their unique structures along with their chemical and physical stabilities. In addition, the Al_2O_3 hollow fibre substrates are synthesized by a phase-inversion and sintering method, which is a low-cost and easy fabrication technique [26]. Based on the advantages mentioned above, Al_2O_3 hollow fibre substrates may be an attractive alternative for new and promising applications, which have been difficult to achieve due to expensive production procedures and the complex set-up process of current technologies.

Although different aspects in the development of the AHFR have been considered [19–21], the effect of finger-like and sponge-like macrostructures in the catalyst particle size deposited have not been studied. Furthermore, to the best of our knowledge, no symmetric Al_2O_3 hollow fibres have even been employed as a support of catalysts in the development of a symmetric hollow fibre reactor (SHFR). Therefore, in this study, both asymmetric and symmetric Al_2O_3 hollow fibres were used as a support of a 10% CuO/CeO_2 catalyst in the development of the AHFR and SHFR, respectively. The sol–gel Pechini method was used to deposit the catalyst either in the finger-like or in the sponge-like regions of the asymmetric and symmetric Al_2O_3 hollow fibres, respectively. The water gas shift (WGS) reaction [27] was chosen as a sample reaction to compare the performances of both AHFR and SHFR with a conventional fixed bed reactor (FBR).

2. Experimental

2.1. Preparation of the Al_2O_3 hollow fibre

Asymmetric and symmetric Al_2O_3 hollow fibre substrates, which have an OD/ID = 2.0/1.0 mm and OD/ID = 1.6/1.0 mm, respectively, were prepared using the phase-inversion technique, followed by sintering at high temperatures. The detailed procedures for fabricating the substrates can be found elsewhere [26].

2.2. Deposition of the 10% CuO/CeO_2 catalyst into the asymmetric and symmetric Al_2O_3 hollow fibre substrates

In our previous work [23], a series of CuO/CeO_2 catalysts with a Cu content ranging from 5 to 40% were studied during the water gas shift (WGS) reaction concluding that 10% CuO/CeO_2 is a very promising catalyst to be used in the development of ceramic hollow fibre reactors. Indeed, 10% CuO/CeO_2 catalyst was very stable; non-deactivation was observed at least for 24 h under the WGS reaction conditions. The high stability of the catalyst could be attributed to the fact that non-crystalline CuO acts to increase the thermal stability of the CeO_2 particles avoiding crystal growth at high temperatures [28–30].

Prior to the deposition of the 10% CuO/CeO_2 catalyst into both Al_2O_3 hollow fibre substrates, the outer surface was wrapped with PTFE tape in order to prevent direct contact with the catalyst solution. A homogeneous precursor catalyst solution as shown in Table 1 was later injected into the lumen of the Al_2O_3 hollow fibre substrates using a glass pipette. The process was repeated several times in order to ensure that the pores of the fibres were filled with the precursor catalyst solution. The Al_2O_3 hollow fibre substrates were then dried in an oven (Salvislab Thermocenter) at 60 °C for 24 h and further dried at 115 °C to complete the polymerization of a polymeric resin precursor. The calcination process was later carried out by flowing 30 ml/min of air into the lumen-side of the fibre at 400 °C for 1 h. The catalyst loading in the Al_2O_3 hollow fibre substrates was obtained by measuring the weight of the fibres (30 cm length) before and after calcination steps and was found to be around 15 mg in all cases.

Table 1
Composition of the sol–gel precursor catalyst solution.

Solution precursor catalyst composition	10% CuO/CeO_2
$Cu(NO_3)_2{\cdot}3H_2O$	2.7 mg
$Ce(NO_3)_3{\cdot}6H_2O$	20.0 mg
Citric acid	22.0 mg
Ethylene glycol	5.8 mg
H_2O	50 ml

2.3. Characterization

A permeation test as a function of transmembrane pressures at different temperatures using pure Ar was carried out on both asymmetric and symmetric Al_2O_3 hollow fibre substrates before catalyst impregnation. The Ar flux can be described either by Eq. (1) or (2).

$$J_{\mathrm{Ar}} = \frac{P}{\delta_M}(p_{\mathrm{Ar2}} - p_{\mathrm{Ar1}}) \tag{1}$$

$$J_{\mathrm{Ar}} = P'(p_{\mathrm{Ar2}} - p_{\mathrm{Ar1}}) \tag{2}$$

where J_{Ar} is the Ar flux, P is the membrane permeability, P' is the membrane permeance, δ_M is the membrane effective thickness and p_{Ar2} and p_{Ar1} are the partial pressure of Ar on the lumen and shell sides of the membrane, respectively. In both asymmetric and symmetric Al_2O_3 hollow fibres the thickness of the sponge-like layer has been considered to be δ_M, which is estimated as 100 and 300 μm, respectively.

The pore size distribution of both symmetric and asymmetric Al_2O_3 hollow fibre substrates was measured using Hg porosimetry before and after the catalyst deposition and after grinding them into a powder. Hg intrusion data were collected at absolute pressures of between 1.38×10^3 Pa and 2.28×10^8 Pa (0.2–33,000 psia) with an equilibrium time of 10 s (Micromeritics Autopore IV). The fibres were broken into sections of approximately 3 mm in length prior to the Hg intrusion analysis.

The morphology and structures of both symmetric and asymmetric Al_2O_3 hollow fibre substrates were observed using different microscopic techniques: scanning electron microscope (SEM, JEOL JSM-5610LV), transmission electron microscope (TEM, JEOL 2000FX) and high-resolution optical microscope (Olympus OLS3100). The Al_2O_3 hollow fibre substrates were studied before and after catalyst deposition and both the surface and cross-section were recorded at different magnifications.

In order to study the crystalline phases (pure or mixed metal oxides) formed after calcination of the CuO/CeO_2 catalysts, X-ray diffraction (XRD) analysis was carried out. XRD measurements were performed with a Bruker AXS D8 ADVANCE diffractometer with $Co_{K\alpha1}$ source ($\lambda = 0.178897$) in a wide-angle range (from 30 to 90 in 2θ).

2.4. Catalytic activity

The catalytic activity measurements of the WGS reaction were tested in the AHFR, SHFR and FBR operated under atmospheric pressure over a temperature range from 200 °C to 500 °C. The feed