



## Polymer-Derived Ceramics with engineered mesoporosity: From design to application in catalysis



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### ABSTRACT

The scientific and technological challenges of energy-related fields are mainly associated with the emergence of new, advanced knowledge and fundamental understanding of materials. In the different categories of materials, ceramics offer a unique combination of physical and chemical properties making them key contributors for energy production/conversion and storage applications. The Polymer-Derived Ceramics (PDC) route enables the synthesis of such materials with an excellent control of the porosity at mesoscopic length scale offering potentialities as support materials to anchor and disperse active metals or for a direct use as catalysts. This review proposes an overview of the works related to the design of mesoporous PDC in the last 15 years. A particular focus is made on the forming methods which have been associated with the PDC route to engineer the mesoporosity and the shape of ceramics derived from preceramic polymers. The main topics reviewed are related to the processing of tailor-made polymeric precursors to mesoporous components, and to the characterization of the material properties. The two strategies adopted for the development of the catalytic activity of mesoporous PDC, i.e., deposition of metal nanoparticles on the mesoporous network or in-situ generation of the catalytically active phase in the mesoporous PDC matrix, are presented. Their recent application in various catalyst-assisted reactions is then discussed. Additionally, we outline the current challenges on the field of mesoporous PDC and provide perspectives on the need for further advances in mesoporous PDC.

### 1. Introduction

Porous solids represent a class of materials that have highly developed internal surface area to perform specific functions for a large variety of applications; especially for energy and environment-related fields. The relative performance of porous solids in these fields depends on the class of materials they belong, i.e., polymers, metals, ceramics. Once an appropriate selection of the class is done, their performance is governed by their composition, their shape and their internal pore structure; thereby the porosity characteristics. Although it is difficult to give a consistent classification of the porous structure in solid materials, the porosity can be reasonably determined by three parameters: The specific surface area (SSA), the total pore volume and the pore size distribution (PSD) as reported in Fig. 1.

The classification of the pore size is a property of major importance in practical applications of porous solids although it has a better

meaning when the geometrical shape of the pores is well defined and known (e.g. cylindrical, ink-bottled, slit-shaped, cone-shaped) [1, 2]. A well convenient classification based on the investigations made by Dubinin [3] and adopted by Everett [4] then Sing et al. [5] consist to classify pores as macropores (> 50 nm, sintered ceramics, foams, ...), mesopores in the range of 2–50 nm (mesoporous silica, activated carbon, ...) while micropores are < 2 nm (zeolite, activated carbon, metal organic framework, membranes, ...) (Fig. 1). In general, the macropores reduce flow resistance, allowing improvement of the mass transfer into and out of the pore network, whereas the large surface area of the micro-/mesopores provides selectivity and active sites to be effectively accessed for catalysis and separation for examples and more generally for environmental and energy applications [6, 7].

Since the discovery of mesoporous materials with uniform porous dimensions, i.e., MS41S family of silicate/aluminosilicate mesoporous molecular sieves, by Mobil Corporation in 1992 [8, 9], research in the

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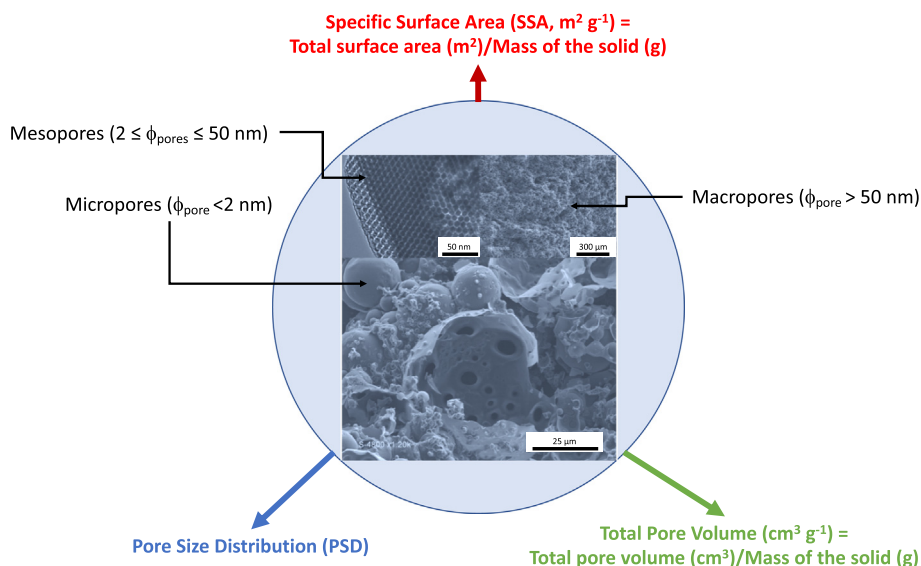


Fig. 1. The three parameters that determine the porosity of porous solids.

field of mesoporous solids is steadily growing. This is mainly due to the fact that the pore structure in these materials provides an extremely large surface area within a relatively small volume allowing these materials suitable for a large variety of applications. These mesoporous solids are particularly convenient for catalysis-related applications because the presence of mesopores enhances the diffusion properties of the material and increases the amount of accessible active sites [10]. Therefore, a vast number of solids containing pore size from 2 to 50 nm have been identified to play a significant role in catalysis, in particular in clean energy technologies [11–15], including mesostructured silicas, mesoporous zeolites, alumina and more generally metal oxides.

As mentioned previously, the relative performance of porous solids for catalysis-related applications is also governed by the class of materials they belong and their composition. Ceramics have been extensively used as catalyst carriers and supports [11–16]. Indeed, their thermal and chemical stability and capability of being tailored make them especially attractive for catalytic reactions in harsh environments. Although a wide variety of ceramics have been developed as catalyst supports, mainly of metal oxide type [14, 15], this area of research and development remains well open for new materials as supports or for a direct use as catalysts. Indeed, in reactions involving high temperatures, reducing media (highly alkaline) and/or fast reaction rates, oxide-type supports exhibit stability issues (thermal, chemical and mechanical). For such reactions, non-oxide ceramics represent better alternative materials. In the category of non-oxide ceramics, silicon or transition metal carbides, carbonitrides and nitrides display attractive properties (high thermal and chemical stability, oxidation and corrosion resistance, low bulk density, high thermal conductivity, mechanical reliability) to be used in harsh environment [17, 18]. However, the development of the mesoporosity in these compounds remains a great challenge difficult to reach using conventional ceramic process. One of the ways to design such materials at meso-scale is to control the structure of materials in an early stage of their synthesis and, within this context, chemistry plays a pivotal role. Among the bottom-up approach to design non-oxide ceramics, the Polymer-Derived Ceramics (PDC) route takes advantage of the chemistry of molecular and polymeric precursors and their ability to be coupled with forming methods to form after pyrolysis non-oxide ceramics with tuned mesoporosity. Comprehensive reviews [19–22] have been already published on the topic of porous PDC but the design of mesoporous PDC and their application as catalysts or as catalyst supports has not been covered yet. Therefore, we felt that it was desirable and timely to present a comprehensive, detailed and critical review covering the developments of

mesoporous PDC, especially those which have been applied for catalysis.

In this review, we will describe the polymer-derived ceramics routes and the various approaches to engineer their mesoporosity through appropriate examples of published reports. This will be presented through a comprehensive overview concerning the design and characterization of mesoporous PDC via template-based methods and template-free approaches. Then, we will introduce the application of mesoporous PDC as supports to anchor and disperse a variety of active metallic nanoparticles and as catalysts through direct precipitation of the catalytically active phase in the mesoporous PDC matrix for a variety of catalyst-assisted reactions. The final section will conclude the discussion and summarize the future challenges and additionally address issues that need to be clarified in the near future to extend the application of mesoporous PDC in catalysis.

## 2. The Polymer-Derived Ceramics (PDC) route

The main principle of the PDCs route (Fig. 2) is to form ceramics, in general non-oxide, through the thermo-chemical conversion of inorganic/organometallic precursors denoted as preceramic polymers [23–28].

Preceramic polymers are synthesized from tailor-made molecular precursors, enabling to control and adjust their chemical composition as well as their architecture and degree of crosslinking. The major benefits of the use of preceramic polymers are summarized below:

- 1) the higher purity of the synthesized materials compared with those obtained by traditional powder technology,
- 2) the significant reduction of the processing temperature (also compared with the traditional powder technology),
- 3) the possibility to produce multi-component and hybrid (organic-inorganic) materials via modification of precursors at molecular scale, i.e., with molecular compounds, or at nano-/microscale, i.e., with passive or active fillers,
- 4) the high versatility in terms of processability.

Indeed, because of the high degree of control on the physical state and rheological properties of preceramic polymers, the PDC route also allows polymer shaping before or during the crosslinking to produce by pyrolysis then annealing if required thin ceramic parts or complex architectures such as fibers, coatings or dense monoliths [23–28].

Although the first conversion of molecular precursors into ceramics

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