C. R. Chimie xxx (2016) 1–17

Contents lists available at ScienceDirect

Comptes Rendus Chimie

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Hierarchical porous silica monoliths: A novel class of microreactors for process intensification in catalysis and adsorption

Les monolithes siliciques à porosité hiérarchique: une nouvelle classe de microréacteurs pour l'Intensification des procédés en catalyse et en adsorption

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A R T I C L E I N F O

Article history:
Received 6 March 2015
Accepted 28 May 2015
Available online xxxx

Keywords:
Synthesis design
Microreactors
Macroporous materials
Mesoporous materials
Microporous materials
Zeolites
Liquid-phase reactions

Mots clés:
Design de synthèse
Microréacteurs
Matériaux macroporeux
Matériaux mésoporeux
Matériaux microporeux
Zéolithes
Réactions en phase liquide

A B S T R A C T

Silica monoliths with hierarchical porosity (macro-/mesoporous), prepared by a combination of phase separation (spinodal decomposition) and sol–gel process, have demonstrated remarkable potential as supports for catalysts and adsorbents with improved efficiency and productivity of a number of applications. This is due to perfect homogeneous interconnected porous networks enabling an exceptional mass transfer and a fine control of contact times. Silica monoliths have been functionalized by an important variety of moities and techniques, such as grafting with versatile species (acidic, basic), by alumina coating, immobilization of ionic liquids, *in-situ* synthesis of nanoparticles of Pd, MOF, and $NiMoS_2$, pseudomorphic transformation of the skeleton into MCM-41 or zeolites (SOD, LTA). These functional materials reveal great opportunities for process intensification.

R É S U M É

Les monolithes siliciques à porosité hiérarchique (macro-/mésoporeux) synthétisés par une combinaison de séparation de phase (décomposition spinodale) et de procédé sol–gel sont des supports remarquables pour des catalyseurs et des adsorbants. ls ont permis d'améliorer l'efficacité et la productivité d'un grand nombre d'applications, grâce à a un réseau de pores homogenes rendant possibles un transfert de matiere exceptionnel et une parfaite maîtrise du temps de contact. Les monolithes de silice ont été fonctionnalisés par greffage de différentes espèces (acides, basiques), par recouvrement d'alumine, par dépôt de liquide ionique, par synthèse in situ de nanoparticules de Pd, de MOF (CuBTC), de

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http://dx.doi.org/10.1016/j.crci.2015.05.017
1631-0748/

$NiMoS_2$ et par transformation pseudomorphique du squelette silicique en MCM-41 et en zéolithes (SOD, LTA). Tous ces nouveaux catalyseurs et adsorbants ainsi mis en forme ont révélé de grandes potentialités pour l'intensification de divers procédés.

1. Introduction

The development of nanostructured materials has been receiving increasing attention in recent years in various fields of applications and especially in catalysis and adsorption. Such materials include for example: zeolites, carbons, clays, MoS_2, graphene, carbon nitrides, Layered Double Hydroxides (LDHs), Metal Organic Frameworks (MOFs), carbon nanotubes, mesostructured materials (carbons and oxides), hybrid materials, bioinspired materials, nanoparticles, etc. Yet, industrial needs are rather focused on optimizing properties of existing catalysts and adsorbents. These can be achieved by creating hierarchical porosity in micro- or mesoporous systems by controlling the macroporous network to improve heat and mass transfer which enhances the accessibility to the active sites and diffusion issues. These materials also allow for controlling the contact time, which is a key parameter for increasing selectivity and limiting the occurrence of secondary reaction. The macroscopic shaping has to be designed for the integration of the material in processes where the lifetime and the selectivity of the material will be improved. Moreover, economic and environmental issues push towards implementation of catalytic and separation processes in continuous flow mode, with the advantages associated with easier phase separation and product recovery, safety and easier operation. Consideration of cost and environmental impact (eco-design) has also become indispensable in new materials synthesis. Innovative synthetic strategies such as the creation of porosity on different length scales, microporous/mesoporous/macroporous (so-called hierarchical porous materials) [1], or the development of synthesis routes permitting the achievement of nanocrystals and their immobilization in shaped bodies adapted for their integration into processes are needed. For example, in the field of zeolites, several approaches can be followed to improve their efficiency. Mesopores can be introduced in the micron-sized crystals by dealumination/dessilication, by the association of nanocrystals or nanosheets of zeolites or by partial delamination of the zeolites followed by a different reconstruction [2,3]. Similarly, it is important to optimize the stability of the materials (for example, in zeolite synthesis, silanol defects should be avoided and the dispersion of heteroatoms (Al, Ti, Ge) has to be controlled) to increase their durability and enable a detailed understanding of their properties.

Most of the materials, which are active in catalysis and in adsorption, are produced in the form of micron-sized powders and are used as millimetric particles (extrudated) or washcoats (after grinding) on ceramic monoliths to be used industrially. The shaping expertise relies mostly on industrial knowledge while few academic groups have made research effort in formulations. The implementation of new material formulation methodologies must be accompanied by a scientific approach. For example, preparation of extrudates or washcoats can rarely be made without the use of binders (clays, silica, alumina, polymers,⋯) or additives. It is therefore necessary to understand the interactions between binders and additives with the active phase that can affect the properties of the materials, which can be quite different between the lab scale and the industrial use [4]. The design of catalytic bodies that do not rely on the use of binders is of prime importance.

Promising emerging materials, such as hybrid materials (MOFs, bioinspired materials, biocatalysts, etc.), can also help to solve some of the challenges in the areas of catalysis, adsorption and separation. If their extraordinary variability is a major asset, the challenge ahead lies in their shaping and improvement of their mechanical, chemical and hydrothermal stability. Similarly, process improvement can be achieved with well-known zeolites used on an industrial scale (FAU-Y, FAU-X, LTA, SAPO-34, ZSM-5, MOR, *BEA, TS-1) by improving secondary porosity and shaping. Other zeolite structures also appear increasingly important as partially delaminated zeolites (FER, MWW, MCM-22), the so-called 2D zeolites. Besides zeolites, other lamellar materials could also be optimized by shaping them as nanoparticles or by creating mesoporosity, as for example $NiMoS_2$ for hydrotreatment catalysis or MoS_2 to replace noble metals like Pt. The formulation of the catalysts and adsorbents is a key point for the improvement and intensification of existing processes.

The objective of our research in adsorbent and catalyst synthesis is to improve mass and heat transfer, to control the contact time between the reactants and the host material, and to increase mechanical and hydrothermal stability of materials. Each of these aspects contributes to the improvement of catalyst's lifetime and selectivity. For this purpose we have demonstrated that the rigorous control of shape into monolithic bodies with well-defined homogeneous hierarchical porosity brings novel and great potential to improve process efficiency in catalysis and adsorption. In this presentation, we will review the most efficient monolithic catalysts and adsorbents we have achieved [5–20] and some new opportunities.

2. Materials synthesis

2.1. Silica monolith synthesis

A very precise amount of tetraethylorthosilicate (TEOS, Aldrich) (20 g) is weighed and left at −19 °C for 1 h. In a 100 mL Erlenmeyer, water (24.560 g) is precisely weighed and then (2.313 g) nitric acid (68%) is added. The mixture is

Please cite this article in press as: A. Galarneau, et al., Hierarchical porous silica monoliths: A novel class of microreactors for process intensification in catalysis and adsorption, Comptes Rendus Chimie (2016), http://dx.doi.org/10.1016/j.crci.2015.05.017