Applied Catalysis A: General 476 (2014) 78–90

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Review

Fiber based structured materials for catalytic applications

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ARTICLE INFO

Article history:
Received 8 November 2013
Received in revised form 22 January 2014
Accepted 12 February 2014
Available online 19 February 2014

Keywords:
Catalyst support
Fiber based structured materials
Glass fiber
Metal fiber
Ceramic fiber
Trade-off index

ABSTRACT

This review summarizes the resent research on fiber based structured materials for catalytic application. This material class comprises a wide range of differently structured supports made from ceramic, metal or glass. Within the last decades due to their flexibility fiber based catalysts were applied to several reactions ranging from pollutant control to fuel processing and showed significant advantages in mass and heat transfer, pressure drop and productivity. The review focusses on mass transfer and pressure drop characteristics and the published correlations for them. A classification in comparison to established support structures is done not only showing superior properties but also the demand for further studies in hydrodynamics and transfer processes.

Contents

1. Introduction

With regard to the aim of process intensification in chemical industry several new concepts for catalyst support structures besides established ones like pellets, honeycombs and even wire meshes were developed in the last decades, the best known probably being foams and in the broadest sense microreactors. Also many of the new structures are based on fibers made from different materials. Beneficial for catalytic applications could be the high surface to volume ratio and the high void fractions offered by these structures. Based on the preparation method the fibrous substrates can be fitted to various geometries. Also they exhibit lower costs and a better coatability compared to microchannel reactors. The variety of different fiber based catalyst supports is very large and in dependence of the chosen fiber material and manufacturing process all of them show different advantages and also disadvantages. The scope of this review is to summarize the research of the last decades within the field of fibrous catalyst support structures made from ceramic, metal or glass. A focus will be laid on the mass transfer and pressure drop characteristics and on the comparison

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http://dx.doi.org/10.1016/j.apcata.2014.02.021
0926-860X/

Nomenclature

Symbols

d	characteristic length [m]
D	diffusion coefficient [m^2/s]
f	Fanning friction factor
k_m	mass transfer coefficient [m/s]
L	bed length [m]
p	pressure [Pa/m^2]
$Re = u_s d/\nu$	Reynolds number
$Re_s = u_s/S_V \nu$	Reynolds number based on external surface area per bed volume S_V
$Sc = \nu/D$	Schmidt number
$Sh = k_m d/D$	Sherwood number
$Sh_s = k_m/S_V D$	Sherwood number based on external surface area per bed volume S_V
S_{BET}	specific total surface area [m^2/g]
S_V	external surface area per bed volume [m^2/m^3]
t	time [s]
u_s	superficial velocity [m/s]
w	mass fraction

Greek symbols

ε	void fraction
θ	angle between direction of flow inside the bed and perpendicular direction
ϑ	temperature [°C]
ν	kinematic viscosity [m^2/s]
ρ	density [kg/m^3]
τ	tortuosity
ϕ	volume fraction
χ	trade-off index

Subscripts

f	fiber
h	hydraulic
p	pellet
st	strut
w	wire

to established catalyst support structures. It is demonstrated that due to their properties fiber based structured materials offer a promising trade-off between mass transfer and pressure drop.

A comprehensive review on catalytic fibers and cloths was given by Matatov-Meytal and Sheintuch [1]. However, since the publication of their work numerous papers with several new structures were published, so a current overview on this topic seemed to be valuable.

2. Fibrous materials

2.1. Metal fibers

Metal fiber based materials have attracted increasing interest as catalytic support structures within the last decade. Basically two fiber based substrates are applied, unordered sintered metal fiber sheets that are industrially used for filter applications and ordered knitted or woven wire mesh structures. Bulk metal wires have been applied as catalysts for several decades e.g. for the production of nitric and hydrocyanic acid and formaldehyde [2,3]. However, the application of bulk noble metal wires is limited by costs and by their low active surface, making them only relevant catalysts for very fast reactions. In order to benefit from the advantageous properties of metallic substrates, namely good heat and mass transfer properties, low pressure drop and low costs in case of utilization of base metals, the metal structures need to be coated by a layer of high surface area material. Unfortunately coating of metal substrates is a challenging task. Dip coating procedures generally applied for coating of ceramic supports do not lead to well adhered washcoats [4–6]. So in recent years different techniques were applied for the coating of metallic structures.

Ahlström-Silversand and Odenbrand [7,8] used thermal spray deposition for coating of wire meshes. By plasma spraying of a mixture of alumina and polyamide a thin ceramic layer with low surface area ($S_{BET} < 1\ m^2/g$) can be produced. By subsequent wash-coating, repeated sol treatment or in situ precipitation the surface area was significantly enhanced. The same technique was applied in Ref. [9].

Coating of wire mesh structures by electrophoretic deposition was applied first by Vorob'eva et al. [10]. By the deposition of alumina from a sol in an electric field surface areas up to $S_{BET} = 40\ m^2/g$ were reached. This technique was later applied in several works [6,11–20], where in some cases [6,11,16–20] the structure was coated with metal powder (Al, Ti) and the resulting layer was oxidized in a subsequent step.

Several other procedures were applied for coating of metallic fibers with oxidic layers or directly with an active component such as non-equilibrium plasma deposition [21–23], Langmuir–Blodgett method [23,24], spray coating [25], anodic oxidation [26], spray pyrolysis [27,28], atomic layer deposition [29], electroless plating [30], autocatalytic plating [31], galvanic deposition [32–34] and coating with carbon nanotubes by catalytic chemical decomposition of methane [35]. Coating with different zeolites was also investigated [36–43]. Yuranov et al. used Ni fibers and created a Raney-type porous layer to increase the surface area of the metal fibers [44].

As mentioned another important metallic substrate is sintered metal fiber filter sheets. This structure differs from wire meshes by the unordered packing of the fibers and the smaller diameters ($d_f < 50\ \mu m$). Such fiber sheets were often applied for catalytic combustion and therefore the structures were coated for instance with perovskites [27,28,45–49]. Moreover these structures were coated e.g. with carbon nanofibers [50,51], zeolites [42,43] and ionic liquid-phase [52]. But generally coating of this structures is difficult, because conventional coating procedures lead to pore blocking due to the small fibers and pores [53]. Therefore often a technique is applied that is based on the properties of the FeCrAl steel that is used as fiber material. Treated at high temperature in oxidizing atmosphere Al diffuses toward the surface building an α-Al_2O_3 layer that can be coated by conventional procedures [54]. It was demonstrated that the adhesion of the subsequent coating is dependent of the treatment temperature. Ugues et al. showed that the morphology of the α-Al_2O_3 layer changes with temperature and O_2 content in the atmosphere. The best adhesion was achieved with at a treatment temperature of $\vartheta = 1200\ °C$ and an atmosphere containing $\phi = 0.5\%$vol.% oxygen. Samples subsequently coated by spray pyrolysis and conventional washcoating resulted in well adhered layers with mass losses <1% in a mechanical stress test [28].

The metal fiber based structures were applied to several reactions that are summarized in Table 1. The most common form of metallic support structures is wire meshes and gauzes. Among the mentioned advantages a drawback is their two-dimensional shape allowing no axial heat conduction. In contrast common ceramic honeycombs allow no radial mass transfer and possess only limited radial heat transfer. A structure combining the advantages of honeycombs and wire meshes resulting in improved axial and radial heat and mass transfer is the wire mesh honeycomb (WMH) proposed by Chung et al. [4]. The WMH consists of alternatively packed corrugated and flat wire mesh sheets. This structure and its advantages are comparable to the ones of open cellular foams. A review