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Potential for metal foams to act as structured catalyst supports in fixed-bed reactors

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ABSTRACT

Experiments were performed in which the benefits of flow through the large interconnecting cavities in structured metal foams (acting as catalyst supports) could be better understood. For example, using tablet shaped ($8 \text{ mm} \times 8 \text{ mm} \times 3 \text{ mm}$) metal foam pellets ($1200 \mu \text{m}$ cavity size), at a pressure drop of 0.5 bar across a 2 m long packed bed (i.d. = 71.7 mm, flow = 0.039 kg/s), the forced convective bulk flow through the foam pellets was found to represent 38% of the total flow, thereby demonstrating the ease with which reactants could access the internal cavities of the metal foam pellet and hence the catalyst layer.

In another example it is shown how a metal foam structure could be exploited in a high temperature fixed bed application (e.g. for endothermic reactions). Experiments were performed in a 74 mm i.d. column, which contained different forms of catalyst supports, such that the depth of the fixed bed was 600 mm. To represent a gaseous mixture in a process application, compressed air (e.g. 0.008 kg/s) was electrically pre-heated (e.g. up to 500 °C), and then fed into the fixed-bed which was surrounded by an electrical furnace (e.g. tube surface 650–950 °C). From these experiments it was shown that, depending on the application, the metal foam structure could: (a) completely fill the channel as a continuous structure; (b) be used in the form of catalyst foam pellets; and (c) be installed with gaps between segments to exploit heat transfer by radiation (from the walls of the channel).

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1. Introduction

Over the last two decades there has been much interest in the use of metal foams as structured catalyst supports, though it is relatively recently that such structures have attracted the interest of commercial organisations willing to invest in the manufacturing techniques that are necessary to make large quantities of such a structured catalyst support for the market. Without such a commitment end users are unlikely to take such technical advances seriously. The product must be available in large quantities, to a satisfactory standard and at a competitive price. To illustrate the advance of this technology, a number of examples are provided

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http://dx.doi.org/10.1016/j.cattod.2016.03.047 0920-5861/© 2016 Elsevier B.V. All rights reserved. from different recent experimental trials in which the features of the use of metal foams as structured catalyst supports are explored in an applied manner.

The metal foam structure is completely porous (see Fig. 1) and consists of a homogeneous and reproducible morphology with thin struts (Bohm et al. [1]; Walther et al. [2]). The struts exhibit an extremely rough surface making it especially suitable for coating with a catalytically active wash-coat. The metal foam structures can be made with a pore size ranging from 450 to 6000 μ m and various alloy compositions, e.g. NiFeCrAl, NiCrAl, FeCrAl or as pure metals, e.g. Ni, Cu, Ag.

To illustrate the advances that have been made, information is presented on the following three key questions, which when answered, should help to stimulate interest in the use of metal foams as catalyst supports:

- Can metal foams be coated with a washcoat and a catalyst, such that they can act as an adequate catalyst support? This in turn will require information on the geometric surface area, and the







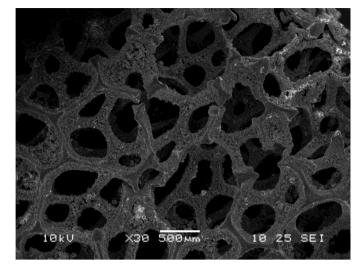


Fig. 1. Example of a scanning electron micrograph showing a 1200 μ m metal foam structure consisting of large cavities with thin struts. Image supplied courtesy of Kolaczkowski (University of Bath).

way in which the metal foam can be coated with washcoat and catalyst.

- Can the large pores in metal foam provide additional easy access to the internal structure and catalytic sites? If they can, then in applications in which (a) the catalyst effectiveness factor for a pellet is low, and (b) pellets are formed with large holes in them (e.g. Raschig ring type of design), opportunities exist to consider replacing such ceramic pellets, with metal foam structures.
- In what form should metal foams be used as structured supports? They could for example, be in the form of foam pellets, or a solid metal foam structure which occupies the space in the reactor, or configured in special layers with gaps between them so as to promote heat transfer by radiation and forced convection, or other variations on these themes.

In the subsections that follow, information is provided in this paper to help answer these three key questions.

1.1. Metal foam as a catalyst support

It is well recognized that a multichannel monolith can act as a structured support for a catalyst, providing a large number of channels through which the reactants in the fluid can flow. Such structures and their use is well known and described in many references (e.g. Hayes & Kolaczkowski [3]; Cybulski and Moulijn [4]). The monolith structure when made from a ceramic (e.g. cordierite), can be coated with a thin layer of washcoat (e.g. γ -alumina), which can then be impregnated with catalyst. Metals can also be used and formed into a monolith type of support (Twigg and Webster [5]). In that case, Fecralloy® and other Fe-Cr-Al steels (which may contain Y and Zr) can be used, which when oxidized provides an outer layer of alumina to which a washcoat may be attached, and then impregnated with catalyst. So, returning to the metal foam structure, this consists of relatively large pores (e.g. see Fig. 1) which are similar to the channels in a monolith (e.g. 1 mm), and these we will call 'mm-scale-pores'. These can be coated in a similar manner (as monoliths) with washcoat and then impregnated with catalyst. The metal foam structure does not in itself have a high surface area, so in many applications it will be necessary to deposit a high surface area washcoat which is then impregnated with catalyst in a two step procedure. First, an oxidic high surface material, e.g. SiO_2 , Al_2O_3 or zeolite (Seiger et al. [6]) is deposited on the foam by washcoating or sol-gel techniques. In a second step, the active material

is added by incipient wetness impregnation, precipitation or ion exchange (Catillon et al. [7]).

In comparison with a catalytic monolith, because of the more tortuous nature of the pathways in a metal foam, greater care needs to be taken to drain or to blow-out excess slurry from the structure during the coating process.

In the literature, there are many examples of researchers taking an interest in the viability of using metal foams as catalyst supports. For example, Giani et al. [8] studied the heat transfer characteristics of metal foams. They were motivated by the possibility of using them as catalyst supports in gas-solid catalytic processes with short contact times and high reaction rates (typically controlled by diffusional mass transport). Their studies were performed in a flow rig, using porous metal foam cylinders in a fixed bed that was 75 mm in diameter, and their lengths varied from 25 to 50 mm, with some of the experiments being performed with multiple lengths. The air into the metal foam was directly heated by the catalytic combustion of hydrogen (in a catalytic pre-heater), then when steady-state conditions were reached (e.g. $T_{in} = 300 \degree C$), the supply of hydrogen was turned off, and as the gas inlet temperature to the metal foam dropped, the transient thermal response was monitored from which heat transfer coefficients were evaluated (with the aid of a mathematical model). In their analysis, radiation effects were not considered as they maintained temperatures below 300 °C in all of their tests. However, the correlations obtained provide a useful insight into how such correlations for flow through metal foams may be formulated.

Another example of work on metal foams, is by Zhao et al. [9], who took an interest in the temperature dependence of the effective thermal conductivity, ke, performing experiments across the 300–800 K range (27–527 °C), under both vacuum and atmospheric conditions. Their experiments were performed on foam discs, approximately 100 mm in diameter and 25 mm thick. These were mounted in a guarded-hot-plate apparatus, with the foam disc being sandwiched between a heated surface and a cold surface. This type of equipment is used for thermal conductivity measurements, and gas does not flow through the foam sample. By performing experiments with the sample maintained at vacuum condition, they were able to eliminate natural convection effects, and just study the combination of conduction and radiation between the struts in the metal foam. They concluded that ke values increase rapidly with temperature in the 500-800 K (227-527 °C) range, and at 800 K can be three times higher than at room temperature (300 K). In experiments with the sample at atmospheric pressure (no vacuum), they found that the contribution by natural convection to the value of ke can be very significant.

1.2. Exploiting the large cavities

In catalytic monolith support structures (ceramic or metals), the presence of the large open void fraction for the flow of reactants is exploited, to provide access to the thin layer of catalytically active material on the large geometric surface area of the support. Such catalytic systems are used, for example in catalytic converters, for the control of emissions from diesel and gasoline engines. In that type of application, reactions are exothermic overall, and the heat is retained within the monolith structure, so as to raise the temperature of the exhaust stream, which in turn increases the rates of desirable reactions.

However, in an application such as the steam reforming of methane, which occurs for example in long tubes, the reactions are highly endothermic, and heat needs to be transferred from the walls of the tube to the reactants as they flow through catalyst pellets inside the tube. It would not be possible to replace the catalyst pellets with a continuous monolith structure. Therefore, as the catalyst effectiveness factor is known to be low, pellets have been produced Download English Version:

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