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Letter to the Editor

# Mesophase pitch-derived graphite foams with selective distribution of TiC nanoparticles for catalytic applications

ABSTRACT

TiC-supported metals are systems of great importance in catalysis science and technology. Albeit their interest, catalysts based on monoliths consisting of TiC-containing carbonaceous foams have not yet been fabricated. This work aims to present a route for fabrication of mesophase pitch-derived open-pore graphite foams with TiC nanoparticles selectively distributed in two locations: at the surface of the pore cells, able for metal-support, and in the bulk, essential to achieve high degree of graphitization for enhancement of thermal conductivity. The double distinctive effect of the nanoparticles in the monoliths makes these materials interesting to be checked in catalytic applications.



Titanium carbide (TiC) and other simple transition metal carbides are considered to be excellent supports for metallic nanoparticles able to act as catalysts in different reactions of technological importance such as molecular dissociation of oxygen and hydrogen, desulfurization, hydrogenation of $CO_2$ to methanol and the water-gas shift reaction, among others [1]. Fundamental insight into key features that influence the activity, selectivity, and lifetime of these nanocatalysts is nowadays under development. In spite of its current importance, there has been yet no attempt to fabricate porous TiC-containing ceramic monoliths for those catalytic applications. In the present contribution the author presents a fabrication route to obtain mesophase pitch-derived open-pore graphite foams with TiC nanoparticles selectively distributed in two locations. A fraction of particles is located in the bulk of the foam structure and serves to catalyse the conversion of the mesophase pitch into graphite, in order to increase the thermal conductivity of the foam (something that insures that the heat of any reaction is properly lead off from or supplied to the reactor). Another fraction of particles is at the surface of the pore cells and can serve as support for transition metallic nanoparticles for catalytic purposes.

Fabrication of the carbonaceous foams was achieved by the replication process [2]. Slight variations to the process presented in [2] were introduced in order to incorporate the TiC nanoparticles. In general terms, the process consists of infiltrating a liquid mesophase pitch (graphite precursor) doped with TiC nanoparticles into preforms of packed particles of NaCl supporting TiC nanoparticles on its surface. The NaCl particles are afterwards leached by water dissolution and the mesophase-pitch foams are subsequently subjected to stabilization at 170 °C under air atmosphere for 40 h, carbonization at 1450 °C under Ar gas flow using the following thermal profile: room temperature to 450 °C at 2 °C/min, 450–1450 °C at 4 °C/min and 1450–25 °C at 4 °C/min and graphitization at 2500 °C or 2750 °C under inert Ar atmosphere for 30 min each.

NaCl particles of analytical quality (99.5% purity) were purchased from Sigma–Aldrich Chemie GmbH (Steinheim, Germany). These particles, originally of 30–400 μm, were grinded and sieved in order to obtain fractions of narrower particle size distributions from which those in the range 100–150 μm were selected. TiC nanoparticles were purchased from Sigma–Aldrich Chemie GmbH (Steinheim, Germany) as titanium (IV) carbide (TiC) nanopowder <200 nm of high purity (>95%), with a nominal specific surface of 19 $m^2/g$ (provided by the supplier). The graphite precursor was the Mistsubishi AR24 naphthalene-based synthetic mesophase pitch, kindly supplied as pellets by Mitsubishi Gas Chemical Company Inc. (Tokyo, Japan).

Doping of mesophase pitch with TiC nanoparticles was achieved by dispersion with toluene following the next procedure: (i) TiC nanoparticles are mixed with the mesophase pitch in desired proportions in a reactor flask; (ii) toluene is added in 25:75 weight proportion of mesophase pitch:toluene; (iii) the mixture is homogenized by a mechanical blade-stirring system for 1 h: (iv) ultrasounds are applied to the reactor during 1 h while mechanical stirring is maintained; and (v) toluene is evaporated by magnetic stirring until dried mixture is attained. In order to obtain a complete toluene-free mixture, an extra final step is added: the TiC-doped mesophase pitch is molten and mechanically blade-stirred during 1 h, after which it is solidified and subsequently ball milled.

TiC nanoparticles supported on the NaCl particles were prepared by mechanically mixing the right proportion of TiC and NaCl particles during 30 min. The TiC nanoparticles stuck to the surface of NaCl by particle interactions (mainly of electrostatic nature)

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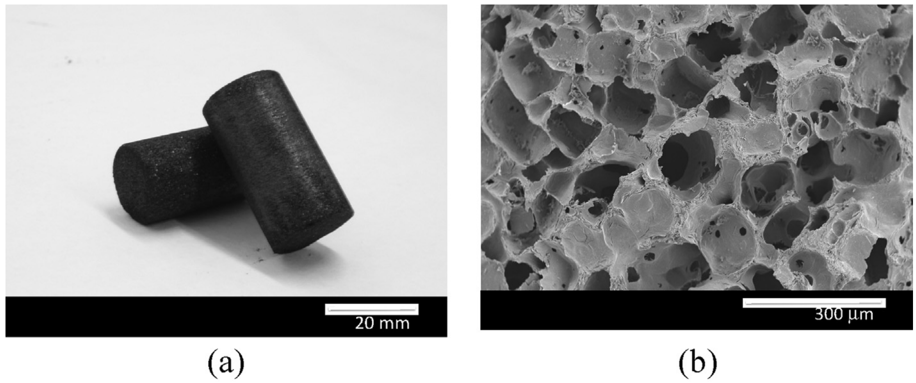


**Fig. 1.** Images of mesophase pitch-derived graphite foams with selective distribution of TiC nanoparticles: (a) photograph of cylindrical samples; (b) SEM image of the fracture surface.

generated during the mechanical mixing. The TiC–NaCl particulate system was delicately packed in glass containers consisting of tubes (17 mm inner diameter) closed on one side and afterwards infiltrated with the TiC-doped mesophase pitch at a temperature of 300 °C and pressure of 0.5 MPa (for infiltration and subsequent dissolution of NaCl particles please see [2]). Immediately after

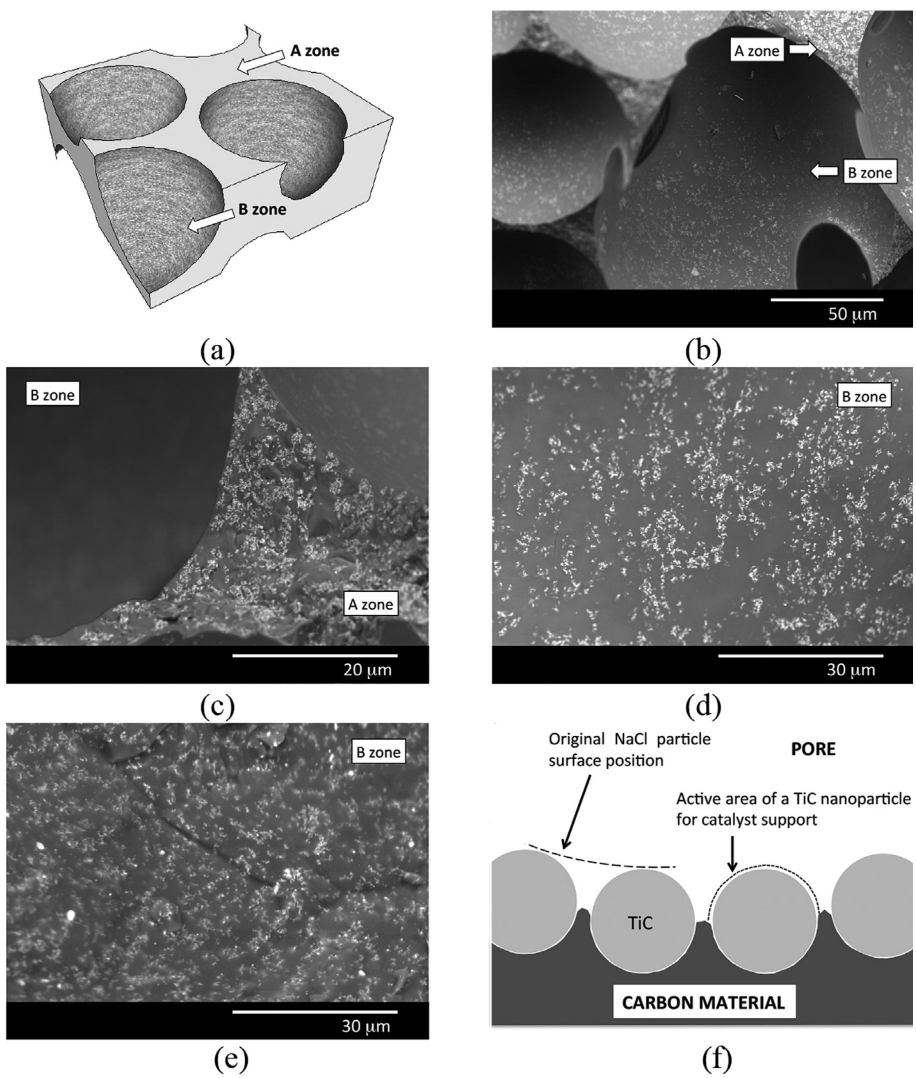


**Fig. 2.** Schematic drawings (a and f) and SEM images (b–e) showing the location of TiC nanoparticles in the bulk (A zones) and at the pore cell surfaces (B zones) of mesophase pitch-derived foams. (b–d) correspond to sample G1-15-15 while (e) corresponds to sample G1-15-45. (f) is a representation of TiC nanoparticles at the pore cell surface, which are not completely embedded in the carbon material.