Journal of Membrane Science 501 (2016) 79–92

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Silicon carbide-based membranes with high soot particle filtration efficiency, durability and catalytic activity for CO/HC oxidation and soot combustion

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ARTICLE INFO

Article history:
Received 13 August 2015
Received in revised form
4 November 2015
Accepted 5 December 2015
Available online 9 December 2015

Keywords:
Silicon carbide
Membranes
Diesel particulate filter
Ceria-based catalysts
Soot cmbustion

ABSTRACT

We report here the solution coatings of Diesel Particulate Filter (DPF) with allylhydridopolycarbosilane (AHPCS)-based polymers leading to supported silicon carbide (SiC)-based membranes with high temperature soot particle filtration efficiency, durability and catalytic activity. In a first part of the present study, our objective was to reduce the pore size of DPF to filtrate finer particles without altering filtration efficiency by coating DPF with an additional fine porous AHPCS-derived SiC membrane. The latter is produced by dip-coating AHPCS on DPF following by a pyrolysis of the AHPCS membrane-modified DPF at 1000 °C under argon. We investigated the influence of dip-coating parameters and viscosity of different AHPCS solutions on the SiC membrane-coated DPF by SEM, mercury porosimetry, XRD and high-temperature thermogravimetric analysis. The evolution of the filtration capacity has been determined with a synthetic gas bench. An additional fine SiC membrane (~150 nm in thickness) prepared from a 10 vol% of AHPCS in THF deposited on DPF allowed maintaining filtration efficiency as high as the virgin DPF while the pore size of the SiC membrane coated-DPF decreased to filter finer particles. Results are confirmed using a commercially-available polysiloxane (Si–C–O precursor). Furthermore, the SiC membrane acted as a thermal barrier coating and provided a better durability to the DPF by preventing apparition of cracks after heat-treatment to 1500 °C under argon. The use of mixed oxide and metallic phases formed *in-situ* in SiC constitutes one of the solutions to generate new and effective catalytic performances to membranes. Within this context, in a second part of the study, we applied a reverse AHPCS-based microemulsion to combine SiC and oxide phases in the same additional porous membrane. As a proof of concept, we have prepared catalytically active Ce–O–Fe–Pt/SiC membrane coated DPF after dip-coating and pyrolysis under argon. These materials have been characterized and tested with regard to CO/HC oxidation and soot combustion. Ce–O–Fe–Pt/SiC membrane coated DPF showed an activity for CO conversion reaching a light-off temperature T_{50}=270 °C and the presence of the catalytic phase allowed burning soot at 486 °C.

1. Introduction

Recently, the impact of technical membrane technology has exponentially increased in research settings and industrial applications mainly due to the chemical and petrochemical industries [1]. A technical membrane can be defined as a barrier that permits selective mass transport between two phases [2]. It is selective because some components can pass the membrane more easily than others according to their porosity. Technical membranes offer nowadays the greatest industrial potential in fluid separation technologies in terms of low capital investment, overall energy savings, low weight, required facility foot-print, space requirement

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http://dx.doi.org/10.1016/j.memsci.2015.12.015
0376-7388/

and high process flexibility [3].

The exhaust emissions from Diesel engines include important contaminants, nitrogen oxides (NO_x), carbon monoxide (CO) with a significant level of particulate matter (PM) that consists mostly of carbonaceous soot and soluble hydrocarbons (HC) condensed on the soot [4,5]. Since 2009 and the 'Euro 5' standard, Diesel cars have required fitment of a Diesel Particulate Filter (DPF) to filtrate the contaminants [6]. It represents a honeycomb monolith, usually made of silicon carbide (SiC) which is now considered as a state-of-the-art system for the safe and effective reduction of Diesel engine exhaust gases.

The constant filtration of the exhaust gases generates a progressive accumulation of soot which requires the filter regeneration by combustion of the retained soot [7,8]. Active regeneration of the DPFs involves fuel post-injection, which is used for increasing the exhaust temperature up to the soot ignition, via exothermic oxidations of unburnt hydrocarbons in the Diesel Oxidation Catalyst (DOC) placed up-stream the DPF. To limit the fuel overconsumption induced by post-injections, catalysts are either added in the combustion chamber as liquid additives [9–11] or deposited in the DPF channels by solution combustion synthesis [12], impregnation [13], washcoating [14] and combination methods [15]. A large number of catalyst formulations have been reported for soot combustion. Cerium-based compounds have been mainly investigated as the catalytically active phases because of their ability to release and store oxygen [16–20].

Due to the tighter emission standards, the demand for more energy efficient vehicles and the severe operating conditions of the exhausts pipe such as high flows, high corrosive atmospheres, thermal shocks and vibrations, it is essential to have future developments of particle filters. One of the most desirable ways for increasing the filtration efficiency (future emission standards) would be to use an additional fine porous filtration membrane (=coating) on the filter wall. Preferentially, the composition of this membrane would be SiC to match the thermal expansion coefficient of DPF and satisfy the severe operating conditions. In addition, the SiC membrane is expected to display high temperature catalytic activity in order to offer in the same materials both soot particulate filtration efficiency, durability and activity for CO/HC oxidation and soot combustion. This is the double objective we have fixed in our study: on the one hand, the feasibility to coat a commercial lab-scale DPF with a thin SiC membrane and on the other hand to render catalytically active this membrane using ceria-based catalysts formed *in-situ* during the SiC membrane elaboration.

The manufacturing process of SiC was initiated by Acheson in 1892 [21,22] and is still today applied to produce the commercially available SiC (α-SiC). This process is not adapted to the preparation of fine porous filtration membrane coatings and does not allow to generate *in-situ* the catalytic phase within the SiC matrix. Chemistry is clearly the way to achieve this goal. Gas phase coating methods allow producing thin non-oxide ceramic coatings [23,24]. However, such processes are relatively expensive and time consuming and the generation of single or mixed oxide and metallic phases in the SiC matrix is extremely complex to achieve. Liquid phase coating methods are more appropriate. An easy approach is the Polymer-Derived Ceramics (PDCs) route [25–40].

The PDCs route is making an increasingly important contribution to the research development and manufacture of non-oxide ceramics from preceramic polymers and may find many applications in environment [38] and energy [39,40]. The processing of coatings based on the PDCs route can be divided into three steps: 1) Synthesis of a preceramic polymer; 2) dip-coating followed by cross-linking of the precursor into an infusible network; 3) conversion into ceramic coatings by pyrolysis [41–47].

In polymer-derived SiC, amorphous structures are formed at relatively low temperature (800–1000 °C). They exhibit atomically homogenous elemental distributions and they have demonstrated excellent creep, corrosion, chemical, and oxidation resistance [34]. These properties are complimented by temperature stability of the amorphous network. Novel properties are also expected to emerge through the modification of the SiC precursor with other low molecular weight precursors leading to the precipitation of secondary phases inside the PDC matrix during the pyrolysis [25–31,48–51].

Herein, we investigate the PDCs route using organosilicon precursors to coat DPF with an additional SiC-based membrane. Supported SiC membranes have been already developed for H_2 permeselectivity [52–57]. To our knowledge, SiC membranes coated on DPF have never been reported for high temperature soot particle filtration efficiency. Here, the materials are prepared from organosilicon polymers (allylhydridopolycarbosilane (AHPCS), SiC precursor [58,59]) by dip-coating and pyrolysis. Complete characterization is done at different length scales using complementary characterization tools. It is demonstrated, by means of reproducible soot loading experiments on a special laboratory test bench, that the additional fine porous SiC membrane (~150 nm in thickness) allowed decreasing the pore size diameter of DPF to filter fine particles without altering filtration efficiency while improving the durability at high temperature in comparison to the virgin DPF.

Combining filtration efficiency, durability and catalytic activity in a same membrane is a great challenge. To reach this objective, we investigated as a proof of concept a microemulsion method coupled with the PDCs route.

Microemulsions are isotropic, macroscopically homogeneous, and thermodynamically stable solutions containing at least three components, namely a polar phase (usually water), a nonpolar phase (usually oil) and a surfactant. On a microscopic level the surfactant molecules form an interfacial film separating the polar and the non-polar domains. This interfacial layer forms three basic types of microemulsions ranging from droplets of oil dispersed in a continuous water phase (O/W-direct microemulsion) over a bicontinuous phase to water droplets dispersed in a continuous oil phase (W/O-reverse microemulsion). Depending on the proportion of various components and the hydrophilic-lipophilic balance value of the surfactant used, the formation of microdroplets can be in the form of oil-swollen micelles dispersed in water as oil-in-water (O/W) microemulsion or water swollen micelles dispersed in oil as for water–in-oil (W/O) microemulsion, also called reverse microemulsion. Here, a reverse microemulsion coupled with the PDCs was investigated to allow single-step synthesis of nanocomposite membranes with mixed oxide and metallic phases *in situ* generated during the AHPCS-to-SiC conversion. This combination was already explored by Kaskel et al. to generate CeO_2 nanoparticles inside SiC powders [49,50]. As mentioned before, CeO_2 is an important oxidation catalyst for burning the carbon combustion residues from Diesel engine exhaust [16–19]. The combination of CeO_2 with metal oxides such as ZrO_2, CuO, Fe_2O_3 strongly improves the activity and stability of CeO_2-based catalysts according to the fact that they usually exhibit high surface reducibility. In particular Fe-doped CeO_2 catalysts were demonstrated as very active for soot combustion due to the strong Ce–O–Fe interactions [20, 60–65]. If these nanocatalysts are dispersed in a SiC matrix, we expect to keep the filtration efficiency and durability of the membrane while minimizing or even preventing the sintering and agglomeration of the nanocatalysts during operating conditions and as a consequence improving the catalytic activity of SiC for HC/CO oxidation and soot combustion. Thus, we apply a reverse AHPCS-based microemulsion to generate new Ce–O–Fe–Pt (mixed oxide and metallic phases)/SiC membranes coated on DPF after dip-coating and pyrolysis under argon. These materials are tested with regard to CO/HC oxidation and soot combustion. The