Applied Catalysis B: Environmental 144 (2014) 216–222

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

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

Preparation of smart nano-engineered electrospun membranes for methanol gas-phase photoxidation

Michele Modesti*, Martina Roso, Carlo Boaretti, Stefano Besco, Denis Hrelja, Paolo Sgarbossa, Alessandra Lorenzetti

University of Padova, Department of Industrial Engineering, Via Marzolo, 9, 35131 Padova, Italy

ARTICLE INFO

Article history:
Received 27 March 2013
Received in revised form 4 July 2013
Accepted 8 July 2013
Available online 17 July 2013

Keywords:
Multistructured membranes
VOCs removal
Nanofibers
Electro-hydrodynamic technologies

ABSTRACT

Nano-engineered membranes obtained by electro-hydrodynamic technologies have been proposed as a good candidate for active filtration. The present work reports some results on the development, production and characterization of three different nanostructured membranes based on: electrospun TiO_2 inorganic nanofibers, nanocomposite structures of polymer nanofibers with TiO_2 embedded nanoparticles and multilayered structures of polymer nanofibers and electrosprayed TiO_2 nanoparticles. Their catalytic activity on volatile organic compounds (VOCs) decomposition has been explored in a photoreactor properly design for this purpose and a comparison among their performance will be extensively discussed. Multilayered membranes showed a complete degradation of methanol in gas phase and the photo-catalytic activity has been found to be affected from the catalyst content and morphology, by means that there is a critical concentration of catalyst over which its increase results on worse photo-oxidation performance. Inorganic TiO_2 based membranes revealed the same activity as the nanocomposite membranes, in terms of methanol reacted per gram of catalyst, but their poor mechanical properties makes them not suitable for a potential scale up.

1. Introduction

In the last decade many efforts have been done in the nanotechnology fields thanks to the awareness that most of major disciplines, from chemistry, physics, medicine to engineering tend to converge at the nanoscale toward some basic structures, principles and tools of investigation. Based on this multidisciplinary perspective, new challenges appear, offering a unimagined tasks for scientific discovery and technological applications.

The development of new solutions in pollution sensing and prevention by using adequate nanostructures with unique properties has gained more interest according to a pressing need for new advanced solutions both for indoor and outdoor pollution. At this regard, polymer nanofiber technology starts its evolution in 90s [1] and is still growing rapidly as the usefulness of nanofibers became apparent in the scientific and business communities [2]. Nanofiber filter media have enabled new levels of filtration and environmental clean up performances in a broad range of applications since they have proven to be a good candidate for promoting a significant increase in filter efficiency and more contaminate holding capacity [3].

According to the United States Environmental Protection Agency (EPA), the concentrations of many VOCs are consistently higher indoors (up to ten times higher) than outdoors. VOCs are emitted by a wide array of products numbering in the thousands (paints and lacquers, paint strippers, cleaning supplies, pesticides, building materials and furnishings, to cite just few examples) and the Indoor Air Quality (IAQ) has become an important community concern due to the increased amount of personal time spent in indoor environment. The ability of organic chemicals to cause health effects varies greatly from those that are highly toxic, to those with no known health effect. Among the methods suggested to improve the indoor air quality, traditional pollution control method such as adsorption by activated carbon merely transfers pollutants from gaseous phase to solid phase [4]. Consequently, advanced oxidation processes (AOP) such as thermal oxidation destruction [5–7] and photocatalytic oxidation (PCO) [8,9] are promising technologies for air purification because the pollutants can be oxidized to H_2O and CO_2.

Within this scenario this work represents an important step within the broad research on the development of an "active" filter media which couple both the physical action, for particulates removal, and chemical action, for VOC decomposition.

Recently, numerous studies have concentrated on the degradation of volatile organic compounds via photocatalysis of various semiconductors. Among the photocatalysts, TiO_2 with anatase

* Corresponding author. Tel.: +39 0498275541.
E-mail address: michele.modesti@unipd.it (M. Modesti).

0926-3373/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apcatb.2013.07.021

phase has been most widely investigated due to its good photocatalytic activity and chemical stability, non-environmental effect and low cost [10]. Looking at the state of the art of PCO in gas phase, the research mainly focus on the the gas-solid heterogeneous photocatalytic oxidation of several chemicals such as CO, acetone, ethanol, organic sulfides, and dimethyl methylphosphonate [11] and also aromatic compounds like benzene, toluene, ethylbenzene and m-xylene [12]. As regards methanol photo-oxidation, metal-modified TiO_2 [13], Ti Silicalite Molecular Sieve [14] as well as titanium(IV)oxide [15] have been tested as a thin film catalyst or as nanoparticles. Moreover, several scientific papers refers to the development of photocatalytic TiO_2 inorganic nanofibers by electrospinning (ES) method [16,17]. To improve the photocatalytic performance of TiO_2, many researchers try to combine TiO_2 fibers with metal, semiconductor or organic materials with the aim of improving charge separation during photocatalysis or increasing the response of TiO_2 to visible light [18]. The photocatalytic performances of electrospun inorganic TiO_2 have been tested for the degradation of organic molecules such as methylene blue and methyl orange [19] while other systems, such as Pt/TiO_2, and WO_3/TiO_2, have been tested, in the form of film deposited within a photoreactor, toward several VOCs degradation in vapor phase [20–23].

Despite the good photocatalytic performances, the well-known trouble with inorganic nanofibers regards their mechanical resistance, which makes the final membrane very hard to handle.

According to this and to the state of art of our knowledge, there are no published papers on the photocatalytic degradation of VOCs, such as methanol, evaluated in gas phase and on polymer based membranes obtained by electrospinning (ES) and electrospraying (EHDA).

In the present study we report the results of the development, characterization and catalytic performances of three different kinds of membranes:

- Membranes based on TiO_2 inorganic electrospun nanofibers (Type1).
- Nanocomposites membranes based on polymer nanofibers and TiO_2 nanoparticles embedded within the organic scaffold (Type2).
- Multilayered membranes based on polymer nanofibers and TiO_2 electrosprayed nanoparticles (Type3).

A comparison among their photocatalytic activity on methanol degradation has been carried out in a properly designed photoreactor and experiments have been run in discontinuous mode.

2. Experimental

2.1. Materials

Poly(vinyl pyrrolidone) (PVP, *Mw* = 1,300,000 g/mol), titanium (IV) isopropoxide ($Ti(OCH(CH_3)_2)_4$), poly(methyl methacrylate-co-methacrylic acid) (PMMAcoMAA, *Mw* = 34,000 g/mol), polyacrilonitrile (PAN, *Mw* = 150,000 g/mol) were all purchased from Sigma–Aldrich, USA, as well as the solvents ethanol, acetic acid (99 wt%), *N*,*N*-dimethylformamide (used as a solvent after dehydration by storage over molecular sieves). Aeroxide® P25, TiO_2 was purchased from Evonik industries.

2.2. Membrane production and characterization

2.2.1. Titanium dioxide nanofibers production

A solution containing 2 mL of titanium(IV) isopropoxide (TIP) and 2 mL of glacial acetic acid was prepared. This solution was added to 4 mL of a 10 wt.% PVP solution in ethanol. The homogeneously mixed colloid was transferred into a 5 ml syringe fitted with a metallic needle of 0.4 mm of inner diameter. The syringe was fixed horizontally on the syringe pump (NE-300 single syringe pump, NewEra Pump System Inc.) and the positive electrode of the high voltage power supply (Gamma High Voltage Inc. (Ormond Beach, FL)), capable of generating voltages up to 60 kV, was clamped to the metal needle tip. The flow rate of polymer solution was kept at 2.5 ml/h, the applied voltage was 12.5 kV and the tip-to-collector distance was kept at 12 cm. All experiments were conducted at room temperature. The obtained nanofiber mats were initially dried for 24 h at 50 °C under vacuum and then calcined in oven at 500 °C in air for 1 h, with a heating rate of 10 °C/min. The temperature of thermal treatment has been chosen in order to get final nanofibers based on TiO_2-anatase crystals phase rather than rutile, according to the literature [19].

Table 1
Process conditions optimized for both electrospinning (ES) and electrospraying (EHDA).

Process	Voltage (kV)	Flow rate (ml/h)	Electrodes distance (cm)	Needle i.d. (mm)
PAN ES	15	2	25	0.4
TiO_2 EHDA	15	8	12	1.2

2.2.2. Nanocomposite membranes preparation

PMMAcoMAA has been chosen because of the presence of –COOH pendent groups, which are able to interact with the –OH groups on the TiO_2 surface under atmospheric conditions. A solution in *N*,*N*-dimethylformamide was prepared at a concentration in polymer of 23% weight by weight and subsequently a concentration of 12% (w/w on the polymer) of Aeroxide® P25, TiO_2 was added as a catalyst. The final suspension was mixed by ultrasonic mixer (VibraCell VC 505 (500 watts), Sonics&Material, Inc.) and then electrospun at a voltage of 17 kV and a 1.5 ml/h flow rate, with a distance electrode-collector of 15 cm.

2.2.3. Multistructured membranes preparation

According to the methodology previously published [24], polyacrylonitrile solutions in *N*,*N*-dimethylformamide were prepared at a concentration of 5% in polymer weight by weight and then electrospun (ES) on a plate collector. After a suitable amount of fibers had been collected, electrospinning was stopped and electrospraying (EHDA) of nanoparticles suspension (TiO_2, 5%, w/w in ethanol, 40 min ultrasonication at 40% amplitude and dispersant agent addition, according to [24]) was performed in order to spread the nanoparticles over the nanofibers surface. The optimized conditions for both processes are shown in Table 1. Subsequently, one more electrospinning stage was carried out to obtain the final membranes. The membranes were stored overnight in a vacuum chamber for drying and solvent stripping. The amount of catalyst has been express in terms of mg of catalyst per cm^2 of membrane surface.

Different concentrations of TiO_2 were tested, 2.56 mg/cm^2, 1.2 mg/cm^2 and 0.69 mg/cm^2, respectively.

2.2.4. Characterization techniques

All the produced membranes were characterized in terms of morphological analysis by Scanning Electron Microscopy (Obducat CamScan MX2500; Cambridge, UK). Further investigation on nanocomposites membranes has been carried by Transmission Electron Microscopy TEM (FEI Tecnai G12) in order to have a better understanding of the TiO_2 nanoparticles dispersion within the nanofibers.