Advanced Powder Technology xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Advanced Powder Technology

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

Original Research Paper

Microwave synthesis of titanium-containing carbon nanosheet over mesostructured cellular foam and the catalytic application

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ARTICLE INFO

Article history:
Received 10 April 2017
Received in revised form 7 October 2017
Accepted 9 November 2017
Available online xxxx

Keywords:
Microwave synthesis
Carbon nanosheet
Mesostructured cellular foam
Catalysis

ABSTRACT

Titanium-containing carbon nanosheets have been prepared from graphite powder, titanocene dichloride, pyrrole and other components by using mesostructured cellular foam (MCF) as template under microwave irradiation. Characterizations reveal the present nanosheets have similar composition, functional group and thickness as classical graphene oxide, but they are probably formed by stitching of tiny carbon fibers those grown from pores of MCF. Meanwhile, titanium oxides appear on nanosheets, making a new catalytic system. In oxidation of alkenes, synthetic materials provide satisfactory conversions and promising stereoselectivities. Moreover, various oxidized products are obtained as key intermediates for synthesis of high-value-added chemicals. On the other hand, encouraging conversions and chiral inductions are realized in diethylzinc addition to benzaldehyde. Catalytic results also propose the synergy of MCF with attached chiral additive in chiral induction. This work not only provides a new method to produce two-dimensional carbon materials, but also shows their potentials for catalytic transformation of hydrocarbons, which would contribute to the design of new heterogeneous catalysts.

1. Introduction

Carbon materials have been used extensively in many academic and industrial applications, including electrodes for batteries [1], fuel cells [2], supercapacitors [3], as well as supports for catalytic processes [4]. The applications are mainly originated from their excellent physical and chemical properties, like electric conductivity, thermal conductivity, plasticity and chemical stability [5]. So far, there are several typical series of nanostructured carbon materials, like zero-dimensional (fullerene) [6], one-dimensional (nanotube) [7] and two-dimensional (graphene) [8]. In catalysis, most of them behave like electron-deficient alkenes featuring electrophilicity of π electrons, which would stabilize intermediate free radicals, leading to higher conversions [9]. Currently, this unique character is greatly promoting carbon materials, and there is a big room for the new advancements of carbon-based nanocatalysts.

However, preparations of nanostructured carbon materials are not very easy. For example, synthesis of graphene could only be accomplished in small quantities by using some unusual techniques, such as chemical vapor deposition [10] and epitaxial growth [11]. Large-scale manufacture could be realized through reduction of graphene oxide (GO), which is obtained through oxidation of graphite and intercalated by ultrasonication [12]. At the same time, carbon mesoporous materials are prepared by employing templates, where carbonization and template removal are involved [13]. Nowadays, preparation of nanostructured carbon materials has aroused continuous interests in many fields.

Oxidation of alkenes provides a lot of valuable oxygenated compounds for fine chemistry and pharmaceutical production [14]. The present catalysts of this transformation include metal complexes [15], oxides [16], or metal-doped silicates [17]. In particular, TS-1, a titanium-incorporated silicate, has been industrialized [18], which approves the exploration of titanium catalysts to achieve nontoxic, efficient and low cost processes. On the other hand, catalytic addition of dialkylzinc to aldehydes may produce chiral secondary alcohols, which have aroused attentions in pharmaceutical design [19]. In view of reaction rate, scale, and waste disposal,

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https://doi.org/10.1016/j.apt.2017.11.016
0921-8831/

developing efficient and eco-friendly titanium catalysts have become a popular option for concerns of many areas.

In this work, a new mesoporous silicate, belonging to mesostructured cellular foam (MCF) [20], is prepared in sol-gel, which is further used as template for construction of carbon nanomaterials. Furthermore, MCF, carbon source, pyrrole, titanocene dichloride, oxidant, or chiral sulfonyl chloride are combined into *n*-hexane under microwave irradiation, which aims to produce functional carbon-based nanomaterials. The resulting materials would then be used as catalysts for both oxidation and reduction catalysis. Once this strategy does work, new carbon-based nanocatalysts would be obtained in large quantity, which might bring out new frontiers for heterogeneous catalysis.

2. Experimental

2.1. Materials

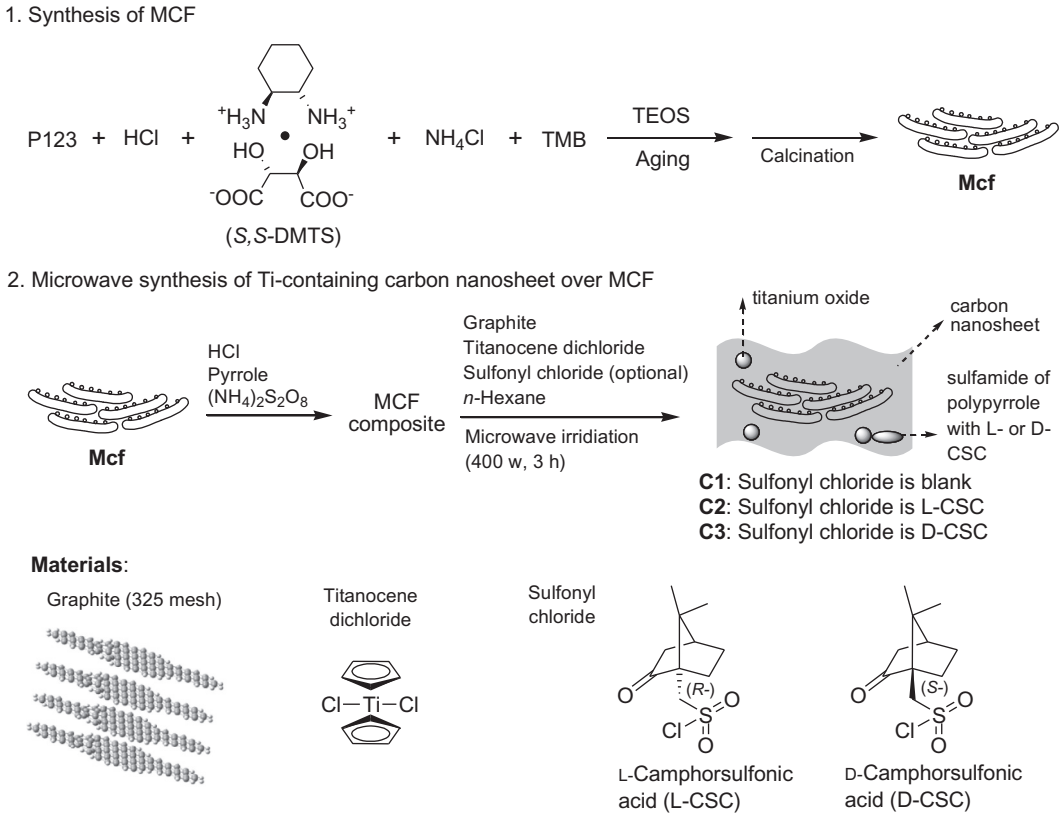
Tetraethyl orthosilicate (TEOS), EO_{20}-PO_{70}-EO_{20} (Pluronic P123; average M_n, 5800), trimethyl benzene (TMB), graphite powder (microcrystalline, 325 mesh), titanocene dichloride (99%), 1,2-diaminocyclohexane (99%), pyrrole (99%), L-(+)-sodium tartrate dihydrate (99%), L-(−)-10-camphorsulfonyl chloride (L-CSC, 98%, Scheme 1), D-(+)-10-camphorsulfonyl chloride (D-CSC, 97%, Scheme 1), iodobenzene diacetate ($PhI(OAc)_2$), *tert*-butyl hydroperoxide (*t*-BuOOH, 70% aqueous solution), diethylzinc (2 mol L^{-1} in toluene), styrene, α-methylstyrene, *R*-(+)-limonene and (−)-α-pinene are purchased from Acros, Accela Aldrich, Adams or Innochem. Ammonium persulfate (99%) and benzaldehyde (98%) are provided by local supplier. Iodosylbenzene (PhIO) [21] and (*S,S*)-1,2-diammoniumcyclohexane mono-(−)-tartrate salt (*S,S*-DMTS, Scheme 1) [22] are prepared according to literatures. Power of microwave oven is 400 watts.

2.2. Instruments

Scanning electron microscopy (SEM) is performed on JEOL JSM-6700F at 20.0 kV (Fig. 1 except for Fig. 1b), or on COXEM-30 (Fig. 1b), without Au coating. Transmission electron microscopy (TEM) is tested on JEOL JEM-200CX at 120 kV. Atomic force microscopy (AFM) is performed on a Veeco Nano Scope IV Multi-Mode AFM system. Low-angle (2θ = 0.5–10°) and wide-angle (2θ = 10–80°) X-ray diffractions (XRD) of powdered samples are collected on Philips X'Pert Pro diffractometer using Cu-Kα radiation (λ = 1.5418 Å), with interval of 0.05° s^{-1}. X-ray photoelectron spectroscopy (XPS) is carried out on Kratos Axis Ultra DLD, using monochromatic Al Kα X-ray (1486.6 eV) as irradiation source, and the binding energy scale is calibrated by using C 1s peak at 284.8 eV. The Gauss-Lorentz peak shapes are used for peak fitting.

BET surface area, pore volume, pore radius and pore size distribution are measured on Micromeritics ASAP 2020, using N_2 adsorption isotherms at 77.35 K. Samples are degassed at 150 °C in vacuum before testing. Surface area is calculated using the multi-point Brunauer-Emmett-Teller (BET) method based on adsorption data with relative pressure P/P_0 of 0.06–0.3. Total pore volume is obtained from N_2 adsorbed at P/P_0 = 0.97. Pore volume and pore radius are determined using Barrett-Joyner-Halenda (BJH) method.

FT-IR spectra are detected in KBr pellets on Bruker Tensor 27, having wave numbers of 400–4000 cm^{-1}. UV–vis spectra are measured in dichloromethane on UV1800, Shimadzu. The static contact angle is measured according to conventional sessile drop method by a charge-coupled device (CCD) camera (Sony XC-ST70CE).



Scheme 1. Synthesis of catalysts.

Please cite this article in press as: B. Huang et al., Microwave synthesis of titanium-containing carbon nanosheet over mesostructured cellular foam and the catalytic application, Advanced Powder Technology (2017), https://doi.org/10.1016/j.apt.2017.11.016