Materials Research Bulletin 59 (2014) 131–136

Contents lists available at ScienceDirect

Materials Research Bulletin

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

Synthesis, characterization, and catalytic application of ordered mesoporous carbon–niobium oxide composites

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ARTICLE INFO

Article history:
Received 14 November 2013
Received in revised form 23 June 2014
Accepted 8 July 2014
Available online 9 July 2014

Keywords:
Chemical synthesis
Electron microscopy
X-ray diffraction
Catalytic properties

ABSTRACT

Ordered mesoporous carbon–niobium oxide composites have been synthesized by a multi-component co-assembly method associated with a carbonization process using phenolic resol as carbon source, niobium chloride as precursor and amphiphilic triblock copolymer Pluronic F127 as template. The resulting materials were characterized using a combination of techniques including differential scanning calorimetry–thermogravimetric analysis, N_2 physical adsorption, X-ray diffraction, transmission electron microscopy, and X-ray photoelectron spectroscopy. The results show that with increasing the content of Nb_2O_5 from 38 to 75% the specific surface area decreases from 306.4 to 124.5 $m^2 g^{-1}$, while the ordered mesoporous structure is remained. Niobium species is well dispersed in the amorphous carbon framework. The mesoporous carbon–niobium oxide composites exhibit high catalytic activity in the dehydration of fructose to 5-hydroxymethylfurfural. A 100% conversion of fructose and a 76.5% selectivity of 5-hydroxymethylfurfural were obtained over the carbon–niobium oxide composite containing 75% Nb_2O_5 under the investigated reaction conditions.

1. Introduction

Recently, ordered mesoporous carbon-based nanocomposites have attracted much attention for their possible applications as adsorbents for large and small biomolecules, catalysts, catalytic supports, electrode materials, and etc., [1–4]. The uniform pore size, large surface area, and the unique features derived from combining two or more components together on the nanoscale offer many possibilities for tuning the catalytic activity and selectivity when the composites are used as catalysts or catalyst supports [5–8]. Particularly, the mesoporous carbon materials modified by acidic and alkali oxides might provide many special applications [9–11]. So far, various ordered mesoporous carbon-based nanocomposites including MgO/C, TiO_2/C, ZrO_2/C, SiO_2/C and Al_2O_3/C have been synthesized using a multi-component co-assembly followed by a direct carbonization process [12–18].

Niobium compounds and materials such as niobium pentoxide (Nb_2O_5), niobic acid ($Nb_2O_5 \cdot nH_2O$), niobium phosphate ($NbOPO_4$), niobium layer compounds ($K_4Nb_6O_{17}$ and $HCa_2Nb_3O_{10}$), and mixed oxides containing niobia (Nb_2O_5–SiO_2, Nb_2O_5–Al_2O_5, Nb_2O_5–TiO_2, and Nb_2O_5–V_2O_5) are shown to be very useful as promoters and supports of catalysts and as promising solid acid catalysts, selective oxidation catalysts, and photosensitive catalysts [19,20]. Mesoporous niobium oxides with highly ordered porous structures and amorphous pore walls exhibit a pronounced effect as supports of metal and metal oxide catalysts [21,22]. In addition, mesoporous niobium oxides are also expected to be applicable in electronic and magnetic devices, biotechnology, and nanotechnology [23–25]. Very recently, niobia/carbon composites have been synthesized using a deposition–precipitation–carbonization method, and the niobia/carbon composites show improved hydrothermal stability and higher reactivity for butanol dehydration compared with the commercially available amorphous niobia [26]. This makes these oxide/carbon composites as promising alternatives to carbon supports for aqueous-phase reactions.

In the present work, ordered mesoporous carbon–niobium oxide composites were synthesized via a multi-component co-assembly method using resol as carbon source, niobium chloride as niobium source and F127 as template. The carbon–niobium oxide composites had adjustable Nb_2O_5 content from 38 to 75%, and niobium species was highly dispersed in the amorphous carbon frameworks. The resulting carbon–niobium oxide

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http://dx.doi.org/10.1016/j.materresbull.2014.07.007
0025-5408/

composites exhibited high catalytic activity for the dehydration of fructose to 5-hydroxymethylfurfural.

2. Experimental

2.1. Chemicals

Pluronic F127 ($EO_{106}PO_{70}EO_{106}$, M_{av} = 12,600) was purchased from Aldrich. HCl solution (36–38%), NaOH, C_2H_5OH, and $NbCl_5$ were obtained from Sinopharm Chemical Reagent Co., Ltd., (Shanghai, China). Phenol and formalin solution (37%) were purchased from Fuchen Chemical Reagent Company (Tianjin, China). Fructose was purchased from Tianjin Chemical Reagents Company. All chemicals were of analytical grade unless otherwise stated and used without further purification.

2.2. Preparation of resol precursors

The resol precursor solution was prepared according to the following procedure. Typical preparation procedure could be described as follows: 61 g of phenol was mixed with 13 g of 20 wt% NaOH aqueous solution under stirring at 75 °C. Then 105 g of formaldehyde solution (37 wt%) was slowly dropped to this solution. The mixture solution was kept on stirring for 1 h. The solution was then cooled to room temperature, and the pH of the solution was adjusted to about 7.0 by addition of 2.0 M HCl. Subsequently, the solution was vacuum evaporated at 70 °C to remove water, and the resultant product was mixed with ethanol to separate NaCl by filtration. The obtained resol was dissolved in 400 g ethanol (20 wt%) for further use.

2.3. Preparation of ordered mesoporous carbon–niobium oxide composites

The ordered mesoporous carbon–niobium oxide (OMCN) composites were synthesized via the co-assembly of resol, $NbCl_5$, and copolymer Pluronic F127. In a typical procedure, 1.57 g of F127 was dissolved in 30 g of ethanol to afford a clear solution. Then, 0.27 g of $NbCl_5$ was added to the above solution, and the mixture solution was stirred for 1 h. 1.5 g of 20 wt% resol solution was added in sequence. After being stirred for 2 h, the solution was transferred into dishes and then put into an oven for evaporation-induced self-assembly (EISA) at 40 °C for 24 h and 100 °C for 24 h. The as-made products were collected from the dishes and then heated in a tubular furnace under flowing nitrogen using a ramping rate of 1 °C min^{-1} from room temperature to 500 °C unless otherwise stated, and remaining at this temperature for 4 h. The OMCN composites with different Nb_2O_5 contents from 38 to 75 wt % were synthesized by varying the mass ratio of the two precursors and the amount of F127. The content of Nb_2O_5 in the composites was determined by thermogravimetric analysis.

2.4. Catalyst characterization

X-ray diffraction (XRD) patterns of the composites were collected on a Bruker D8 Advance X-ray diffractometer using Cu Kα radiation. Transmission electron microscopy (TEM) and the corresponding selected area diffraction (SAED) were performed on a JEOL, JEM2010 electronic microscope. Prior to imaging, the samples were ground into powder and dispersed in ethanol, and then dropped onto a holey carbon film on a Cu grid. X-ray photoelectron spectroscopy (XPS) measurements were performed on an Axis Ultra, Kratos (UK) spectrometer with an Al Kα source (1486.6 eV). The binding energy was calibrated relative to the C1s peak (284.8 eV) of the contaminant carbon. Nitrogen adsorption–desorption isotherms were obtained on a Micromeritics ASAP 2020M system. Prior to measurements, the samples were degassed at 250 °C for 6 h. The Brunauer–Emmett–Teller (BET) method was used to calculate the specific surface area. The micropore surface area S_{mi} was obtained using the *t*-plot method. The mesoporous surface area (S_{meso}) was determined by subtracting S_{mi} from S_{BET}. The pore size distributions were derived from the desorption branches of the isotherms based on the Barrett–Joyner–Halanda (BJH) model. The total pore volume was estimated from the adsorption branches at a relative pressure (P/P_0) of 0.998. The average pore diameter (D_p) was estimated from the surface area and the total pore volume ($D_p = 4V_p/S_{BET}$). Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on a TA-Q600SDT TGA analyzer. The samples were heated at a heating rate of 10 °C min^{-1} under a flow of Air or N_2, respectively.

2.5. Catalytic test and product analysis

The batch catalytic experiments were conducted in a 10-mL thick-walled glass vessel equipped with a reflux condenser. 100 mg (0.56 mmol) of fructose as substrate and 5 g (64.1 mmol) of DMSO as solvent were firstly added to the reactor, and then 10 mg of catalyst was added into the mixture. The reaction mixture was heated to 120 °C with an oil bath under strong stirring at 500 rpm. After the reaction, the reactor was cooled to room temperature. The catalyst was separated by centrifugation and the post-reaction sample was diluted with mobile phase solution prior to analysis.

Sample analyzes were performed on a Shimadzu LC-20AT HPLC system equipped with a RID-10A detector and a Bio-Rad Aminex HPX-87H ion exclusion column (300 mm × 7.8 mm) using 0.005 M H_2SO_4 as the mobile phase at a flow rate of 0.55 mL min^{-1}. The column temperature was 50 °C, and the detector temperature was set to 45 °C. The amount of fructose and HMF was determined by using calibration curves.

3. Results and discussions

3.1. Structure characterization of the OMCN composites

TG analyzes of the OMCN composites in air were performed and the results are shown in Fig. 1. The initial weight loss below 150 °C could be attributed to the adsorbed water. The sharp weight loss in the temperature range of 400–475 °C was attributed to the burn of carbon in the OMCN composites. After the TG measurements, the

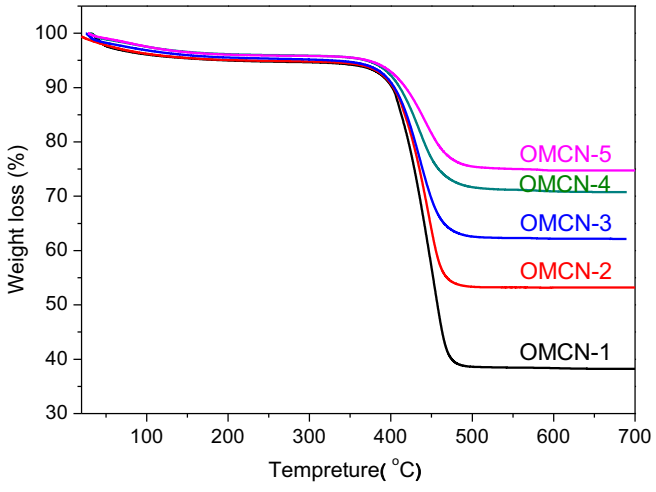

Fig. 1. TG curves for the mesoporous carbon–niobium oxide composites in air.