Applied Catalysis A: General 458 (2013) 155–161

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

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

Preparation of nitrogen-containing carbon nanotubes and study of their performance as basic catalysts

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ARTICLE INFO

Article history:
Received 24 January 2013
Received in revised form 27 March 2013
Accepted 29 March 2013
Available online 6 April 2013

Keywords:
Doped carbon nanotubes
Aldol condensation
Decarboxylative condensation
Biomass upgrading
Pyridinic species
Ketonization

ABSTRACT

Nitrogen-containing carbon nanotubes were prepared, characterized and used as catalysts for two reactions of interest in the biomass upgrading processes: acetone aldol and acetic acid decarboxylative condensations. N-CNT were synthesized in a fluidized bed reactor by catalytic chemical vapor decomposition of acetonitrile on iron-, cobalt- and nickel-supported catalysts. Ni-N-CNT catalyst exhibits the highest activity, attributed to the surface concentration of basic sites, particularly the pyridinic species detected by X-ray photoelectron spectra (XPS). Likewise, the selectivity toward the final products of the reaction pathway is related both to the strength of basic sites (Ni-N-CNT) and to the morphology and chemical environment of the active sites (Fe-N-CNT). Synthesized catalysts show high stability for acetone condensation, whereas for ketonic condensation the catalyst stability decreases, mainly due to acic–base interactions with the active sites.

1. Introduction

Carbon nanotubes (CNTs) and nanofibers have been largely used as catalytic materials [1]. For these applications, their physicochemical properties, in particular the surface active sites, can be tuned by incorporating heteroatoms in their structures. Nitrogen ad-atoms are incorporated [2] when the scope is the development of materials with enhanced basic properties. The preparation of carbon nanomaterials with nitrogen functionalities is usually accomplished by two methods: insertion of nitrogen functional groups on the CNTs surface, and synthesis of the carbon material from a nitrogen-containing reactant. In the first case, the incorporation of nitrogen ad-atoms is usually very low, but concentrated on material surface, for example by treatments with ammonia at high temperature [3] or by amination of previously oxidized materials [4]. Alternatively, the second procedure conduces to carbon materials with higher nitrogen content. This target can be achieved by the incorporation of ammonia in the reaction mixture, added to the carbon source [5], or by the use of acetonitrile vapor [6] or other nitrogen precursors [7] and their subsequent catalytic pyrolysis.

Significantly, the basic character of the nitrogen surface species can be tailored depending on the chemical character and bond of the incorporated nitrogen ad-atoms [8]. In this way, the basic character of the nitrogen doped CNTs is mainly attributed to the presence of pyridinic-like nitrogen, located at the edges of the graphene layers [9,10]. Although there are other nitrogen types, quaternary nitrogen, pyrrolic nitrogen and oxidized pyridinic nitrogen [11–13], their role in catalysis by basic sites has been scarcely studied, but it is expected to be rather limited. Concerning to the catalytic applications, N-doped CNTs have been proposed as supports for metal catalysts such as, for instance, Pd for cinnamaldehyde hydrogenation reactions [14]. Furthermore, these materials, as a kind of novel metal-free catalysts, have been used for the selective oxidation of H_2S reaction [15] and oxygen reduction reaction [16]. However, and despite of the obvious relationship between nitrogen-doping and basic properties, only few studies have applied this kind of materials for base-catalyzed reactions such as the Knoevenagel condensation [10] or the transesterification of triglycerides [17].

Among the most important applications of the base catalysis are reactions leading to the formation of new carbon–carbon bonds from oxygenated molecules which can be obtained from biomass-derived platform chemicals (short carbon-chain functionalized organics). Aldol condensation (condensation of molecules with two carbonyl groups yielding hydroxyl-ketones or unsaturated

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http://dx.doi.org/10.1016/j.apcata.2013.03.041

ketones) and ketonic condensations (reaction of two carboxylic acids yielding a ketone, CO_2 and water) are key reactions in the upgrading of biomass processing streams [18]. Usually these gas-phase reactions are catalyzed by inorganic basic materials, but these materials present important deactivation rates because of the successive condensation reactions [19]. The use of a catalyst with lower basic strength will overcome this problem.

In this contribution, the acetonitrile vapor decomposition method was used to synthesize nitrogen-containing CNTs with different basic sites depending on the metallic catalytic surface (Fe/SiO_2, Co/SiO_2 and Ni/SiO_2) on where they were grown. The chemical properties of these nitrogen species have been evaluated for two reactions catalyzed by basic sites: acetone aldol condensation and acetic acid decarboxylative condensation. These reactions were chosen due to their interest in the preparation of chemical products from biomass-derived platform chemicals. In this way, the concurrent carbon chain growth and oxygen removal of oxygenates is a major challenge. Furthermore, these reactions have been often considered as model base-catalyzed reactions and they have not been studied yet using these materials as catalysts.

The acetone aldol condensation, catalyzed by strong basic sites, allows the formation of bonds between the carbonyl groups of the molecules, forming C_6 and C_9 chemicals. In the case of the acetic acid decarboxylative condensation, basic sites of lower strength are necessary, and the carboxylic acids are converted into ketones.

2. Experimental

2.1. Catalysts preparation and characterization

Three silica-supported transition metal catalysts were prepared for further N-CNTs synthesis. The silica (Kiesegel 60, Fluka) was impregnated with a metal loading of 5 wt%, using aqueous solutions of $Fe(NO_3)_3 \cdot 9H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ (Sigma–Aldrich) as metal precursors. After impregnation, the samples were dried in air at 393 K overnight. Metal loading was selected in order to obtain metal crystallites small enough for proper growth of carbon nanotubes, according to the procedures optimized in previous works [20].

Carbon nanotubes doped with nitrogen groups (N-CNTs) were synthesized in a fluidized-bed reactor, over the Fe/SiO_2, Co/SiO_2 and Ni/SiO_2 catalysts, by catalytic chemical vapor decomposition of acetonitrile vapor. After loading the dried catalysts in the reactor, the samples were treated in H_2/N_2 (50/700 $cm^3\,min^{-1}$) by increasing the temperature from ambient to 1123 K at 10 $K\,min^{-1}$. Subsequently, the reactant mixture was saturated in acetonitrile at 285 K, and introduced into the reaction media. The reactor was kept at 1123 K during 4 h. After the reaction, N_2 gas flow was continued till the furnace was cooled to room temperature. This method can be considered as a modification of that previously described [20].

The obtained materials were purified by a method consisted of metal and silica removal in an excess of hydrofluoric acid at room temperature, resulting materials being washed with distilled water in a Soxhlet extractor up to obtain a neutral pH of the leachate. Finally, the samples, denoted as Fe-N-CNT, Co-N-CNT and Ni-N-CNT, were dried at 393 K for 10 h in a vacuum oven. The yields of the overall processes, expressed as grams of carbon per gram of metal in the initial SiO_2 supported catalysts, are 6.1, 4.6 and 4.5 for Fe/SiO_2, Co/SiO_2 and Ni/SiO_2, respectively. For comparison purpose, a commercial sample of multiwall carbon nanotubes without nitrogen functionalities, which was provided by Dropsens company (DRP-MWCNT), was studied in the catalytic tests. These commercial nanotubes have a surface area of –307 m^2/g and 0.33 cc/g of mesopore volume. The three samples were characterized by transmission electron microscopy (TEM), N_2 adsorption isotherm determination (BET-N_2-77 K), X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis. Likewise, elemental analysis of carbon, hydrogen and nitrogen was carried out in a LECO CHNS-932 instrument. TEM studies of the samples were performed in a JEOL TEM-2000 FX microscope at 200 kV, the samples were prepared by grinding and ultrasonic dispersal in an acetone solution. A Micromeritics ASAP 2010 system was used to obtain the corresponding nitrogen adsorption isotherms in order to calculate the specific surface areas and porosity features of the samples. X-ray photoelectron spectra were recorded with an Omicron spectrometer equipped with an EA-125 hemispherical electron multichannel analyzer and an unmonochromatized Mg Kα X-ray source having radiation energy of 1253.6 eV at 150 W and a pass energy of 50 eV. The samples (0.2 mg) were slightly pressed into a small pellet of 15 mm diameter and then mounted on the sample holder. Every sample was introduced into the chamber where they were degassed for 6–8 h, in order to achieve a dynamic vacuum below 10^{-8} Pa prior to analysis. Spectra were analyzed with CasaXPS software and RSF database by fitting after Shirley background correction. Thermogravimetric analysis was carried out using a $SDTQ_{600}$ 5200 TA System. Samples of about 10 mg were treated at room temperature for 10 min under helium (flow rate 100 $mL\,min^{-1}$). Then, the system was heated up to 1273 K, with a heating rate of 5 $K\,min^{-1}$.

2.2. Catalytic activity measurements

Two reaction studies were carried out: acetone aldol condensation (reaction 1) and acetic acid decarboxylative condensation (reaction 2). Both reactions were carried out in a fixed bed U-shaped quartz reactor (0.4 cm i.d.) placed in a PID-controlled electric furnace. About 200 mg catalysts were placed over a plug of quartz wool and a thermocouple was placed inside the catalyst bed. As reactants, acetone or acetic acid (both supplied by Panreac, 99.5%) were introduced in a nitrogen flow of 50 $cm^3\,min^{-1}$, at a mole fraction of 0.035. Products were collected in a cold trap (mixture of liquid nitrogen and isopropanol) and analyzed by gas chromatography equipped with a FID (Shimadzu QP-2010). Product identification was confirmed by analysis in a GC–MS (Shimadzu QP-2010), using the same column and conditions that in the gas chromatograph. Conversion was calculated based on reactant peak areas. Mass balance closures (considering the stoichiometry of the studied reactions) were always higher than 95%, discarding the presence of side reaction leading to non-condensable carbon-containing molecules. Reported experiments were twice duplicated, with less than 5% error (even lower for the case of acetone condensation).

In order to discard the presence of intraparticle diffusional effects, several experiments (Ni-N-CNT for aldol condensation) were replicated with the catalyst pelletized, crushed and sieved with different particle sizes (50, 100 and 250 μm). Similar conversions and selectivities were obtained in these cases (±5%), suggesting the absence of these effects.

3. Results and discussion

3.1. Catalysts characterization

Fig 1 shows representative TEM images of the three carbon nanotube materials, as well as the histograms with the outer and inner diameter distribution. More than 100 nanotubes where measured for each material in order to obtain representative statistical data. In all cases, the observed carbon nanotubes are the main component, exhibiting features of multiwall periodical bamboo-like carbon nanotubes [5]. Such periodically capped microstructure has