Applied Catalysis A: General 469 (2014) 8–17

Contents lists available at ScienceDirect

Applied Catalysis A: General

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

Partial oxidation of ethanol to acetaldehyde over surface-modified single-walled carbon nanotubes

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ARTICLE INFO

Article history:
Received 15 August 2013
Received in revised form
10 September 2013
Accepted 17 September 2013
Available online 27 September 2013

Keywords:
Ethanol
Partial oxidation
SWCNT
Optical absorption
FTIR
Raman
TPO
TPD
XPS.

ABSTRACT

The catalytic activity of surface-modified single-walled carbon nanotubes (SWCNTs) for partial oxidation processes was tested. A battery of characterization techniques including temperature programmed desorption (TPD) Fourier transform infrared (FTIR), and X-ray photoelectron spectroscopy (XPS) were used to probe the degree and type of oxygen bearing functional groups introduced on the nanotube surface and responsible for catalytic activity. Raman and optical absorption spectroscopy and temperature programmed oxidation (TPO), were used to probe the SWCNTs structure before and after reaction to monitor structural changes that take place during partial oxidation of ethanol to acetaldehyde. The results indicate a strong link between ketonic surface groups (C=O) on the SWCNTs surface and its catalytic activity for partial oxidation processes.

1. Introduction

Carbon nanotubes (CNTs) are finding an increasing number of applications in catalysis, either as supports or catalysts on their own [1–3]. Carbon itself as a catalytic material has significant advantages over the traditional metal-supported systems, owing to the unique controllability of both its surface chemistry and electron density through surface functionalization [4]. Carbon based catalysis is in fact regaining lots of attention due to sustainability issues and recent push for the development of metal free technologies. It is recognized that carbon materials performance in catalysis can be influenced both by their texture and surface chemistry [1,4,5]. In contrast to amorphous carbon materials, CNT materials offer the opportunity of a better control on types and number of active sites. Multi-walled carbon nanotubes (MWCNTs) have been used as active catalysts in oxidative dehydrogenation (ODH) of butane, propane and ethylbenzene [6–9] while graphite nanofibers have also shown a significant activity and selectivity in the oxidation of ethanol to acetaldehyde and ethyl acetate [10]. The nature and concentration of surface functionalities on these carbon materials can be modified by appropriate thermal or chemical treatments. For instance, gas or liquid phase oxidation can be used to increase the concentration of surface oxygen groups while heating under an inert atmosphere may remove some of these functionalities [8,11,12].

Herein, we report single-walled carbon nanotubes (SWCNTs) as an alternative to these carbon-based systems. Contrasting to MWCNTs and carbon nanofibers, SWCNTs offer the opportunity of a careful tailoring of active catalytic sites through well-established surface functionalization protocols [13–15] which can be used to obtain very specific types of catalytic chemical functionalities on the carbon surface. The main objectives of our work are to investigate the effect of SWCNT-based catalyst pretreatment temperatures in the attachment of oxygen functionalities on the carbon surface and its concomitant effect on ethanol partial oxidation activity and reaction selectivity as well as to identify the nature and concentration of the surface functionalities responsible for catalytic activity.

2. Experimental

2.1. Synthesis and purification of SWCNTs

The SWCNTs used for partial oxidation of ethanol were obtained by catalytic decomposition of methane at 800 °C on 2 wt.% Co–MgO

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http://dx.doi.org/10.1016/j.apcata.2013.09.027

catalyst. Full details of the synthesis and purification protocols have been described previously [16].

2.2. SWCNTs characterization

Raman spectra of SWCNTs were obtained to investigate their structure and structural changes during the introduction of surface functionalities and partial oxidation of ethanol. A ReniShaw micro-Raman 2000 system was used. The spectra were obtained using the 632.8 nm excitation laser wavelength (He–Ne laser) in the range of 120–2000 cm^{-1} in micro mode, and the acquisition time was 20 s at 2 mW for each spectra. Six scans were taken at different points of every sample and the average used as the representative spectra.

TPO was used to identify the different carbonaceous species present in the SWCNT material before and after the introduction of surface functionalities and after partial oxidation of ethanol. The TPO experimental procedure has been described elsewhere [16].

TPD experiments were performed using the same experimental setup in a similar fashion, except that, in TPD the heating of the SWCNTs material was conducted in pure helium (Praxair, UHP) instead of O_2/He. The amounts of CO and CO_2 desorbed from the SWCNTs samples under thermal helium treatment were quantitatively converted to methane in a methanator, and the FID used to monitor methane formed.

Optical absorption spectroscopy was used to investigate the diameter distribution and carry chirality assessments of the SWCNT materials before and after the introduction of surface functionalities and after partial oxidation of ethanol. Optical absorption experimental procedure has been described previously [16].

FTIR spectra of as-purified and pretreated samples at different temperatures were recorded on a Vertex 70 FTIR Spectrometer (Bruker, Germany) in the range of 400–4000 cm^{-1} wavenumber range. The samples were analyzed as pellets mixed with ZnSe at a mass ratio of 1:100. A hydraulic press was used to pelletize the sample at 10 MPa for 3 min.

XPS analysis was run on a Thermo Scientific K-Alpha XPS spectrometer (Thermo Fisher, East Grinstead, UK). The samples were run at a take-off angle (relative to the surface) of 90°. A monochromatic Al Kα X-ray source was used, with a spot area (on a 90° sample) of 400 μm. Charge compensation was not needed. Position of the energy scale was adjusted to place the main C 1s feature (C—C) at 284.6 eV. Spectrum parameters were; survey – 200 eV pass energy, low resolution – 150 eV pass energy, 0.2 eV step. Quantification for the high resolution – 25 eV pass energy. The instrument and all data processing was performed using the software (Avantage) provided with the instrument. Modified Scofield parameters were used which were provided with the instrument. The purified SWCNTs material was further characterized by chemical analysis using an ICPMS to determine the amount of impurities remaining after purification.

2.3. Ethanol partial oxidation tests

SWCNTs powder was pelletized to 425 μm size before introduction in the reactor catalyst bed. Steady-state partial oxidation reactions of ethanol were conducted using 17 mg catalyst in a continuous flow fixed bed quartz glass reactor oriented vertically inside an electrically heated furnace at atmospheric pressure. The height of the catalyst in the reactor was approximately 0.2–0.4 cm while the heated length was 32 cm. The reactor was 50 cm long with an inner diameter of ~5 mm. Temperature was measured with a K-type thermocouple inserted into the furnace and positioned within the catalyst bed. To introduce oxygen functionalities before reaction, all catalysts were pretreated in 5% O_2/He gas mixture (Airgas, 88 mL/min) at 200, 250, 300, 350 and 400 °C for 3 h. After pretreatment absolute ethanol (Brampton, Ontario) was introduced into the reactor by vaporizing it into the flowing O_2/He mixture at 150 °C using a microsyringe pump. Reactant conversions were varied by changing the O_2/He flow rate (1.47–0.40 $cm^3\ s^{-1}$) at constant ethanol partial pressures (0.23 kPa) and temperature (200 °C). The different weight hourly space velocity (WHSV) values used are shown in Table 1. The gas flow was regulated through pre-calibrated mass flow controllers with digital read-out units (MKS Instruments). These reaction conditions were selected to ensure ethanol conversions below 30% so that mainly differential conditions can be assumed; similar conditions have been previously reported in the literature [17–19]. Reactant and product concentrations were measured using an online gas chromatograph (Shimadzu gas chromatograph, GC-2014) containing a capillary column (BP-5, 30 m × 0.53 mm, 1.0 μm thickness) connected to a flame ionization detector. Catalytic tests were monitored for at least 8 h time on stream, varying the space velocity. Combustion products (CO and CO_2) were not observed. The total carbon balance on the system was always above 98.0%.

Table 1
Experimental conditions used for partial oxidation of ethanol.

He/O_2 (mL/min)	O_2 (mL/min)	$C_2H_5OH_{(l)}$ (mL/h)	C_2H_5OH/O_2 molar ratio	WHSV ((mol C_2H_5OH/mol C) h^{-1})
88	4.4	0.11	0.16	1.33
64	3.2	0.08	0.16	0.97
48	2.4	0.06	0.16	0.73
24	1.2	0.03	0.16	0.36

The catalyst behavior was evaluated in terms of the following parameters: the conversion of ethanol is defined as the ratio between reacted and fed ethanol.

$$\text{Conversion} = \frac{\text{ethanol(in)} - \text{ethanol(out)}}{\text{ethanol(in)}} \times 100\% \quad (1)$$

Product selectivity is defined as ethanol transformed to each product with respect to the ethanol reacted, thus the percentage selectivity to acetaldehyde is;

$$\text{Selectivity} = \frac{\text{acetaldehyde(out)}}{\text{ethanol(in)} - \text{ethanol(out)}} \times 100\% \quad (2)$$

A set of preliminary experiments were conducted in order to determine that the partial oxidation process is entirely catalytic (i.e. the product, acetaldehyde is not formed by oxidation of ethanol by oxygen functionalities on the nanotube). For this purpose, first a blank experiment (no SWCNT catalyst) was carried out in O_2/He (after exposing the system to the same pretreatment protocols in O_2/He described in the experimental section), we observed zero ethanol conversion at 200 °C at all residence times, which proved that the contribution of homogenous gas-phase reactions was negligible. Another set of experiments were also conducted with the catalyst in O_2/He at 200 °C, but without ethanol feed (after exposing the system to the same pretreatment protocols in O_2/He we described in the experimental section). We did not observed evolution of gas phase carbon bearing molecules under these reaction conditions. Further experiments were conducted with the catalyst in helium alone (without oxygen), in the presence of ethanol feed. Again, we observed zero ethanol conversion at 200 °C at all space velocities. We repeated this experiment at higher temperatures (260 °C) for the case of the catalyst pretreated in O_2/He at 200 and 300 °C. No conversion was observed at all spaces velocities except for 0.36 h^{-1} WHSV which showed (~4%) ethanol conversion with a high selectivity to ethylene (98%) as compared to ethanol conversions around 88% (acetaldehyde selectivity 96%) obtained in the presence of oxygen under the same conditions. This experiment again suggested that direct reaction between oxygen functionalities present in the nanotube surface and the ethanol