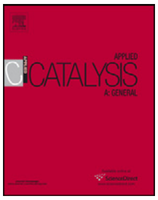
Applied Catalysis A: General 348 (2008) 251–256

Contents lists available at ScienceDirect

Applied Catalysis A: General

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



Characteristics of iron oxide/activated carbon nanocomposites prepared using supercritical water

Chunbao Xu, Amyn S. Teja *

School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, 311 Ferst Drive NW, Atlanta, GA 30332-0100, United States

ARTICLE INFO

Article history:
Received 13 March 2008
Received in revised form 30 June 2008
Accepted 2 July 2008
Available online 10 July 2008

Keywords:
Supercritical water
Activated carbon
Iron oxide
Nanocomposite

ABSTRACT

The properties of nanocomposites obtained by depositing iron oxide nanoparticles in the pores of two types of commercial activated carbon pellets using supercritical water were studied as a function of process variables. The loading of iron oxide nanoparticles in the nanocomposites increased with precursor concentration and immersion time, but was apparently unaffected by the temperature. The specific surface area and pore volume of the nanocomposites decreased with increased loading of the nanoparticles, possibly due to pore blockage and/or pore destruction resulting from acid attack during processing. The results suggest that an optimum loading of nanoparticles in the nanocomposites can be achieved by manipulating pellet dimensions, precursor concentration, and immersion time.

1. Introduction

There is increasing interest in highly dispersed metal or metal oxide catalysts on solid supports for the oxidation of volatile organic compounds (VOCs) [1,2]. The use of activated carbon (AC) as a support material in these applications offers the advantage of a porous carbon structure that can be tailored to obtain high-surface area and pore-size distribution needed for specific reactions. The AC structure is also resistant to temperature as well as to acidic or basic conditions [3], and any metal oxide catalyst impregnated in the structure can be easily recovered by burning away the support [4]. It has also been shown that carbon support materials exhibit lower coking propensity than metal oxide supports such as alumina or silica [5]. In addition, unlike alumina and silica, activated carbon does not generally adsorb water vapor, and will not therefore be deactivated by water generated during VOC oxidation [6]. On the contrary, adsorption of (volatile) organic compounds should be favored in any metal oxide/AC nanocomposites, thus facilitating VOC oxidation.

Conventional techniques (such as impregnation) for dispersing catalyst particles on support materials generally permit limited control over particle size, and size distribution [7]. Combining activated carbon as a catalyst support and metal oxide nanoparticles as an active catalyst phase, however, makes it possible to take advantage of both the enhanced retention of organic pollutants in the porous carbon [8], as well as the control of particle size made possible by confining the metal oxide particles in the pores of the support [9].

The use of supercritical water as a solvent/medium for synthesizing metal oxide nanoparticles via hydrolysis and dehydration of metal salts has been extensively explored in the literature [10–13]. In addition, a few studies have also explored the reactive and transport properties of supercritical water to deposit particles on pre-shaped catalyst supports [9,13]. The recent work of Otsu and Oshima [13] was the first to describe the deposition of metal oxides in the pores of alumina supports using compressed water. However, XRD patterns of their manganese oxide/alumina nanocomposites indicated that several manganese oxides (MnO_2, Mn_3O_4, Mn_5O_8 and $MnAl_2O_4$) were present in the product. Similarly, they also reported the presence of several lead oxides (PbO and $Pb_2Al_2O_5$) in their lead oxide/alumina nanocomposites. In addition, intense peaks of AlOOH were detected in nanocomposites prepared at high-water densities, where hydrothermal reactions are promoted. Finally, the prolonged reaction times used in their experiments also resulted in cracking of the ball-type alumina support. It is clear from these results that water at temperatures between 373 and 673 K is capable of causing a loss of physical integrity in conventional oxide supports such as alumina and silica, and is therefore too aggressive for processing such supports [14]. On the other hand [9], we have shown that supercritical water can be used for the in situ synthesis and deposition of α-Fe_2O_3 nanoparticles in AC supports. We were able to disperse α-Fe_2O_3

---

* Corresponding author. Tel.: +1 404 894 3098; fax: +1 404 894 2866.
E-mail address: amyn.teja@chbe.gatech.edu (A.S. Teja).

0926-860X/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcata.2008.07.002

particles and control their size and size distribution by manipulating process variables such as temperature, pressure, and precursor concentration. In a separate study, we also demonstrated that metal oxide/AC nanocomposite catalysts prepared in supercritical water were more effective than conventional catalysts for the ozonation of propanal, a regulated VOC [15]. In the present work, we report on the effect of process variables on the loading and morphological characteristics of iron oxide/AC nanocomposites prepared using subcritical and supercritical water.

2. Experimental

We prepared iron oxide/AC nanocomposites by the in situ synthesis and deposition of α-Fe_2O_3 nanoparticles in the pores of AC pellets. The synthesis of α-Fe_2O_3 was achieved via the hydrolysis and dehydration of ferric nitrate in supercritical water. Details of the apparatus and experimental procedure are given elsewhere [9].

Two sizes of cylindrical pellets of fresh activated carbon (Norit RX 3 Extra and Norit ROX 0.8) were obtained from NORIT Americas Inc. and used as-received in our experiments. Technical data provided by the manufacturer are given in Table 1. Precursor solutions were prepared by dissolving known masses of $Fe(NO_3)_3 \cdot 9H_2O$ (ACS reagent, minimum purity 98 wt.%, Sigma–Aldrich) in 150 ml of deionized water, and each solution was transferred in turn to a 250 ml stainless steel autoclave (Parr Instrument Co., IL, USA, model 4576). A known mass of AC pellets was added to the autoclave and allowed to soak in the precursor solution at ambient temperature T_a and pressure P_a for time τ_1 to allow the solution to penetrate the porous pellet structure. The solution was then heated at a rate of 5 K min^{-1} to a temperature T_h and pressure P_h with constant stirring (the time interval τ_2 for this heating step was approximately 75 min in most experiments). The autoclave was maintained at this temperature (T_h) and pressure (P_h) for time τ_3 (90 min). The temperature profile to which the solution was subjected is shown in Fig. 1 and resulted in the precipitation of α-Fe_2O_3 nanoparticles in the pores of the AC pellets (as well as in the bulk solution in contact with the AC) during the heating and digestion stages of the profile. Reaction conditions in each experiment are summarized in Table 2. Most experiments were repeated to confirm the reproducibility of the results.

After time $\tau = \tau_1 + \tau_2 + \tau_3$ (Fig. 1) had elapsed, the contents of the autoclave were cooled to ambient conditions by circulating cold water through the reactor jacket. The iron oxide/AC nanocomposites produced were then separated from the bulk solution by filtration, washed several times with deionized water, and dried overnight in an oven at 323 K prior to analysis. Iron oxide nanoparticles in the bulk solution were also separated from the solution by filtration, washed with deionized water, and dried overnight in an oven at 323 K prior to analysis (different sizes of filters were used to separate the dispersed submicron particles and the mm-sized pellets from the bulk solution).

The metal oxide content of the nanocomposite samples and the ash content of fresh AC were determined by burning a known mass of the material in air at 1273 K for 150 min, and weighing the residue left after burning away all the carbon.

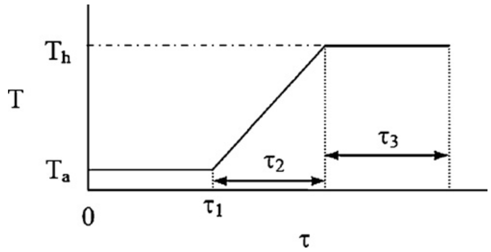


Fig. 1. Temperature–time profile during one experiment.

Nitrogen physisorption isotherms were measured for selected samples at 77 K using a Micromeritics ASAP 2010 system (Micromeritics, Norcross, GA). The samples were dried at 343 K for 1 h and then overnight in a vacuum oven at 323 K before analysis. The apparent surface areas were obtained by the Brunauer–Emmett–Teller (BET) method, and the average pore size was determined using the Barrett–Joyner–Halenda (BJH) method based on a desorption model. The total pore volume was estimated from the volume of liquid nitrogen adsorbed at a relative pressure $P/P^* \sim 0.97$–0.98. The micropore volume was calculated using the *t*-plot method.

The nanocomposites were characterized by powder X-ray diffraction using a PANalytical X-ray diffractometer (Model PW 1800, Phillips, MA, USA) with a Cu Kα radiation source. The X-ray analyses were performed on samples obtained by scraping off deposited particles from the surface of the pellets, and also on samples obtained by grinding the pellets to a powder (after the surface particles had been scraped off).

α-Fe_2O_3 particles obtained from the interior of the impregnated pellets and from the bulk solution were analyzed by SEM (LEO 1530 FEG field-emission instrument, Leo Electron Microscopy Ltd., UK) by energy-dispersive X-ray spectroscopy (EDS), and by TEM (JEOL 100C TEM, Japan Electron Optics Laboratory Co. Ltd., Tokyo, Japan). Images of lateral cross-sections of several cylindrical pellets were analyzed by SEM at the centre of each cross-section ($r = 0$) at approximately half the distance between the centre and the surface ($r = 0.5$R), and near the edge of each cross-section ($r = $ R) of the pellet (see Fig. 2). Average particle sizes were estimated from images of at least 500 particles. Ground pellets were also analyzed by TEM after scraping off particles deposited on their surfaces. The ground powder was dispersed in deionized water and a drop of the dispersion was placed on a carbon-coated copper grid for analysis by TEM. In addition, particles in the bulk liquid were analyzed by TEM after placing a drop of the bulk liquid on a carbon-coated copper grid for analysis. Average particle sizes in this case were estimated from measurements on at least 100 particles.

3. Results

Representative SEM micrographs of lateral sections of pellets of fresh and impregnated AC are shown in Fig. 3(a) and (b). The images show that a large number of nanoparticles were synthesized and deposited in the pores of the pellets. EDS analysis and XRD patterns confirmed that the particles consisted mostly of α-Fe_2O_3 (hematite).

Table 1
Technical data for as-received AC pellets

AC	Raw materials	Surface area, BET (m^2/g)	Iron content	Ash, mass (%)	AC pellet diameter (mm)
Norit RX 3 Extra	Peat	1370	<0.02 mass %	3	3
Norit ROX 0.8	Peat	1100	<300 mg/kg	3	0.8