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One-step synthesis and properties of MnO_x/TiO_2 nanocomposites prepared by chemical vapor condensation process

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ABSTRACT

MnO_x/TiO_2 nanocomposites were synthesized using metal-organic precursors in one-step by modified chemical vapor condensation. The flow rate of manganese precursor was supplied from 0.1 to 0.6 L min^{-1}. The titanium tetraisopropoxide precursor was supplied at a constant flow rate. The synthesized materials were characterized by TGA-DTG, BET, TEM, XRD, and XPS. The result of TGA showed the Mn precursor's main degradation to be above 100 °C. Characterization of the Mn/TiO_2 samples by BET and TEM showed that the flow rate of Mn precursor had little effect on surface area, pore volume, or particle size. XRD showed that amorphous Mn became crystalline with increasing Mn precursor vapor concentration.

1. Introduction

Nanoparticles of manganese oxide are applicable in some areas where submicron sized particles are not, such as in ion exchange, molecular adsorption, biosensors, energy storage, and particularly as electrodes for Li/MnO_2 batteries, due to novel properties induced by the smaller particles and their synthesis methods [1–4]. The increased surface area of the smaller crystals of nanosized MnO_x is expected to aid its applicability [5–7]. Various syntheses of manganese oxide have been reported, such as precipitation [8], redox precipitation under reflux [9], templating [10], and microwave heating [11]. Nanocomposites of Mn loaded onto support materials have also been used as catalysts. Nanocrystalline supports of TiO_2 [12,13], CeO_2 [14], Al_2O_3 [15], ZnS [16], and Cr_2O_3 [17] have been reported. Titania nanoparticles are notable for their chemical stability, large surface area, high pore volume, controllable pore size, morphology, and potential use as gas sensors and photocatalysts for degrading organic pollutants in water [18–20]. MnO_x/TiO_2 nanocomposites have been prepared by various processes, such as spray-pyrolysis [21], sol–gel synthesis [22], and impregnation [23] that generally involve complicated procedures and many chemicals. Chemical vapor condensation (CVC), developed originally for the synthesis of metallic and intermetallic nanoparticles, has broad applicability because of the wide range of available precursors and it allows the production of uniform and high-purity powders with small grain sizes [24–26].

TiO_2 and MnO_x nanoparticles have been synthesized by CVC. The resulting TiO_2 showed good photocatalysis of degrading organic dyes under UV light due to its large surface area and small crystallites. The MnO_x consisted of small particles (<30 nm) and showed a large surface area [27,28]. However, Mn/Ti nanocomposites simultaneously synthesized by CVC have not been fully explored [29,30].

This work reports the one-step CVC synthesis of TiO_2 and MnO_x nanomaterials from titanium tetraisopropoxide and manganese carbonyl precursors at 900 °C. The effects of manganese concentration on the structural characteristics of the MnO_x/TiO_2 nanocomposites were studied by adjusting the flow rate of the manganese precursor and the optimal synthesis conditions were determined. The resulting nanocomposite structure sizes, surface areas, and crystallinity were characterized.

2. Experiment

TiO_2 and MnO_x were prepared at 900 °C in an electric furnace modified-U-tube chemical vapor condensation (MUCVC, Fig. 1). The titanium tetraisopropoxide (TTIP) and manganese decacarbonyl ($Mn_2(CO)_{10}$) precursors were stored in a bubbler in oil baths at 95 and 105 °C, respectively. TTIP was introduced into the alumina U-tube reactor by bubbling argon (prepurified, 99.99%, 0.7 L min^{-1}), where it decomposed to form TiO_2 particles. After the flow rate of TTIP vapor stabilized, the Mn precursor vapor (prepurified, 98%) was transported to the center of the reactor at 0.1–0.6 L min^{-1} where it formed MnO_x/TiO_2 with the titania particles. The reactor contained an additional inlet for a 7 L min^{-1} air supply. The gas line was heated to avoid condensation of the precursor vapor. The nanocomposites were passed through columns quenched with cool water and ethanol to a minimum of 10 °C and collected by filtration, which was designed to collect

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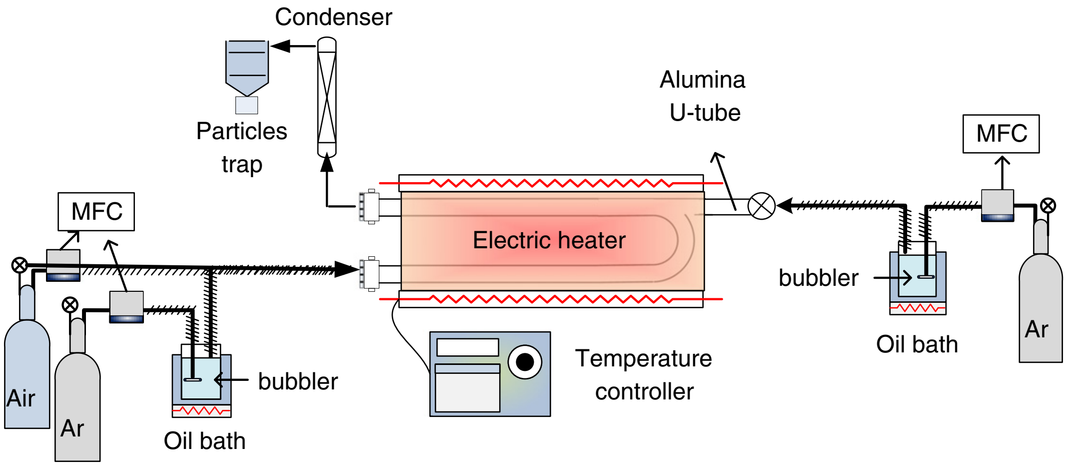

Fig. 1. The MUCVC system.

particles bigger than 0.2 nm for improved productivity. Samples were labeled by the flow rate of manganese precursor vapor. For example, the sample produced using a 0.4 L min^{-1} precursor flow was labeled $0.4Mn/TiO_2$.

The manganese precursor was characterized simultaneously by thermogravimetric analysis (TGA) in a Pyris 1 instrument. X-ray diffraction (XRD) patterns were recorded on a high-resolution X-ray diffractometer (focal spot size: 5 mm^2, Cu rotating anode). High-resolution transmission electron microscopy (HR-TEM) was performed using an F-20 microscope (Philips; operated at 200 kV, image resolution <0.25 nm). Samples' powder specific surface areas (SSA, $m^2\ g^{-1}$) were determined by nitrogen adsorption (>99.999%) at 77 K on Micromeritics Tristar 3000 apparatus using the Brunauer Emmett Teller (BET) method. Pore volume distributions were determined from the desorption isotherms (Micromeritics ASAP 2010 Multigas system) using the Barrett Joyner Halenda (BJH) method. Assuming monodispersed, spherical primary particles, particle size (d_{XRD}) was estimated using the Scherrer equation. X-ray photoelectron spectra (XPS) were measured on a VG scientific ESCA Lab II spectrometer (resolution 0.1 eV) with Mg Kα (1253.6 eV) radiation as the excitation source.

3. Results and discussion

TG analysis of individual sample has been analyzed separately to record the different peak temperatures and corresponding temperature ranges of mass losses. To find out the optimal range of the vaporizing temperature, we carried out TG analysis experiments with the manganese decacarbonyl precursor at different heating rates. Fig. 2 shows the results of the experiments. The fractional conversion is as follows: $x = (m_o - m)/(m_o - m_\infty)$, in which m_o is the initial sample weight, m_∞ is the residual weight at infinite time, and m is the residual sample weight at time t. As the heating rate increased, the temperature range at which weight loss took place moved to a higher-temperature region.

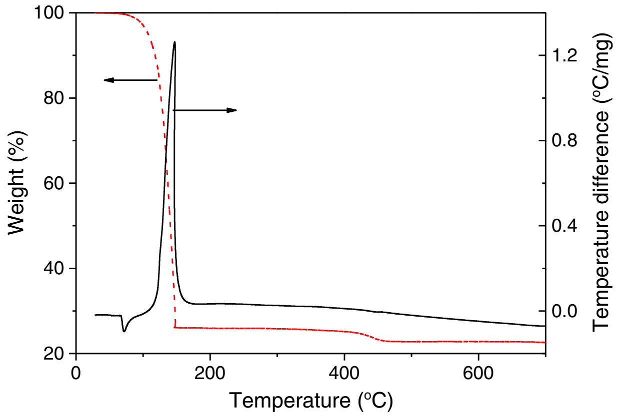

Fig. 2. TG-DTG curves of the $Mn_2(CO)_{10}$ precursor.

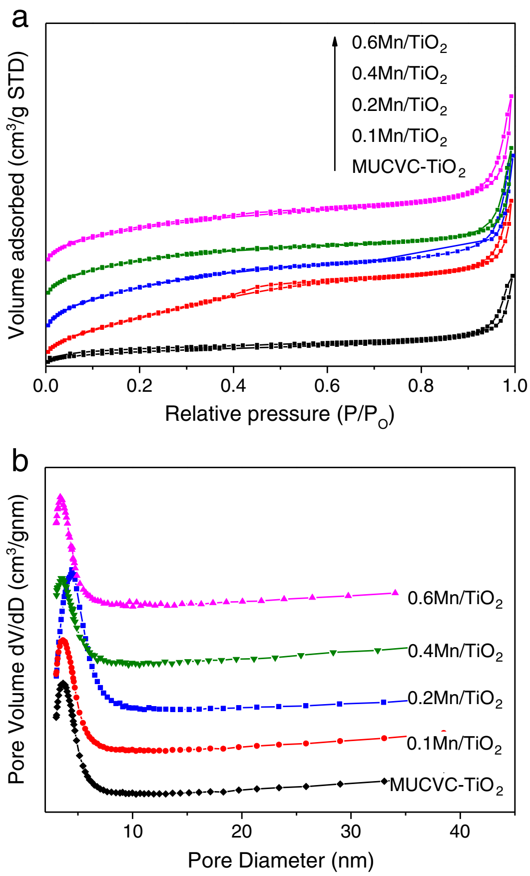

Fig. 3. Mn/TiO_2 nanocomposites (a) nitrogen adsorption/desorption isotherms and (b) BJH pore size distributions.