

Synthesis of ZnO Nanoparticles by Spray Pyrolysis Method

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ABSTRACT: Zinc oxide (ZnO) nanoparticles were synthesized by spray pyrolysis method using an aqueous solution of zinc acetate at various concentrations from 5 to 25 wt%. The decomposition of precursor solutions was carried out at 800, 1000 and 1200°C under different atomizing pressures. The crystal structure and morphology of synthesized nanoparticles were characterized by X-Ray Diffraction (XRD) spectrometry and Transmission Electron Microscopy (TEM), which indicated that ZnO nanoparticles were of hexagonal wurtzite structure. The XRD, TEM and BET analyses of prepared ZnO powders with concentrations of 5-20 wt% showed that the crystallite size diameter and specific surface area of particles were in the range of 10-25 nm and 44-56 m²/g, respectively. It was found that impurity and unreacted zinc acetate appeared in the product with increase of precursor solution concentration beyond 20wt%.

KEY WORDS: ZnO, Spray pyrolysis, Nanoparticles, Specific surface area.

INTRODUCTION

In recent years, nano zinc oxide has found wide ranging applications in various areas due to its unique and superior physical and chemical properties compared with bulk ZnO. The large specific surface area, high pore volume, nanostructured properties, low cost and low toxicity of nano ZnO [1] make it a promising candidate particularly in catalysts [2], chemical absorbents [3], polymer filler and additives [4], antiwear additives in oil lubricants [5] and advanced ceramics [6]. Zinc oxide nanoparticles have optical, electrical and photochemical activity [7], which can be used in photocatalysts [8], solar energy conversion cells [9,10], Ultra Violet (UV) detectors and UV emitting devices [11], chemical sensors sensitive to chemicals such as alcohol and benzene [12], and gas

sensing materials for many sorts of gases such as ammonia, hydrogen and ozone [13-15]. Some researches have shown the performance of ZnO nanoparticles in degradation of some organic compounds [16], antibacterial effect [17] and killing human cancer cells [18].

Various chemical synthesis methods such as sol-gel [19], solvothermal [20], and microemulsion [21], and physical methods including chemical vapor deposition [22], thermal decomposition of organometallic precursors [23], arc plasma [24], laser ablation [25], and levitation gas condensation [26], have been used in preparation of ZnO nanoparticles. Physical methods are often advantageous compared to chemical ones, since such methods do not require some steps of wet chemistry such

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1021-9986/11/1/

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as washing, drying and calcination and they can produce higher purity particles [27].

Spray pyrolysis is a physical method, which is relatively simple, reproducible, size controllable, low cost and continuous for synthesis of some nano metal oxides, mixed metal oxides and metals on metal oxides [28]. Powders prepared by this method, compared with those from wet chemical ones, are more crystalline, less agglomerated with higher purity and also have large specific surface areas [29]. Metal acetate, chloride and nitrate precursor solutions are used to synthesize metal oxides nanoparticles by spray pyrolysis methods [28]. Since the latter two compounds produce acid gases, which are environmental pollutants and corrosive, metal acetate is preferred. Furthermore, metal acetate precursors produce fine-grained, high specific surface area and aggregate-free powders due to their exothermic decomposition in the reaction whereas nitrate precursors produce strongly aggregated powders [30]. Many workers have applied zinc acetate for synthesis of ZnO nanoparticles [8,12,19,31,32]. In this research, spray pyrolysis method using zinc acetate and a tubular reactor were applied to synthesize ZnO nanoparticles and the effects of different parameters, concentration of starting material, temperature and atomizing pressure on the particle size diameter were investigated.

EXPERIMENTAL SECTION

Starting materials

Zinc acetate dehydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) with purity of 99.5% was purchased from Aldrich Chemical Company. The precursor solutions were prepared from above zinc acetate and distilled water. A few drops of glacial acetic acid were then added to stabilize the solution. To obtain the optimal concentration of starting material, the concentration of zinc acetate in precursor solution was chosen to be 5, 15, 20 and 25 wt%. Dry air was used as the carrier gas for carrying precursor solutions into the nebulizer and also supplying the required pressure for atomizing the solutions. Bulk zinc oxide with a purity of 99.5% was purchased from Pars Company (Iran).

Apparatus

Fig.1 shows a convenient system, which was assembled in our investigation for preparation of size controlled ZnO nanoparticles by spray pyrolysis method.

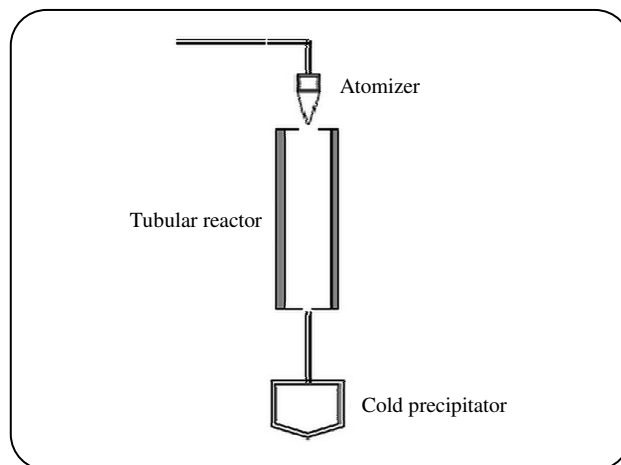


Fig. 1: Schematic illustration of spray pyrolysis apparatus used for synthesis of zinc oxide nanoparticles.

This system consists of three main parts: (1) a twin fluid nebulizer, which atomizes the precursor solutions and converts them to droplets, (2) a vertical tubular reactor (length: 130 cm, diameter: 5 cm) with controllable temperature zones from 200°C to 1200°C, and (3) a precipitator to collect prepared nanoparticles.

A Phillips PW 1840 x-ray diffractometer with Cu-K α radiation source in the range of 20° to 80° was used to determine the crystal phase and crystallite size analysis of prepared particles. A Bruker AT-210 transmission electron microscope was applied to investigate morphology of synthesized nano size samples. A Bruker IFS 88 Fourier Transform Infrared spectrophotometer (FT-IR) was employed for identification of unreacted compounds in the ZnO nanoparticles. The Specific Surface Area (SSA) of nano samples were measured by N₂ adsorption method using Brunauer-Emmet-Teller (BET) technique.

Synthesis

To synthesize ZnO nanoparticles, at first the precursor solution was atomized by nebulizer under the pressure of air (7 bar). The droplets decomposed inside the reactor, where the temperature was 1200°C. The obtained nanoparticle product was collected into the cold precipitator and dried in an oven at 100°C. Unreacted zinc acetate present in the product can be removed by washing the nanoparticles with water.

Four samples with concentrations of 5, 15, 20 and 25 wt% zinc acetate were synthesized at 1200°C and designated ZnO-5, ZnO-15, ZnO-20 and ZnO-25, respectively.

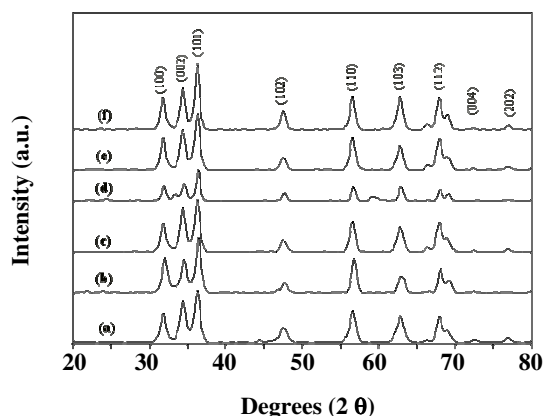


Fig. 2: XRD patterns of synthesized samples: (a) ZnO-5, (b) ZnO-15, (c) ZnO-20, (d) ZnO-25, (e) ZnO-20a, (f) ZnO-20b.

Two samples were also synthesized with 20 wt% concentration of zinc acetate at 1000°C under atomizing pressure of 7 and 4 bar and designated ZnO-20a and ZnO-20b, respectively.

RESULTS AND DISCUSSION

Figs. 2(a)-(d) show the XRD patterns of ZnO nanoparticles, synthesized using different concentrations of starting materials at 1200°C. Figure 2(e) and 2(f) represent the XRD patterns for samples ZnO-20a and ZnO-20b prepared using 20wt% zinc acetate as a precursor solution at 1000°C under the atomizing pressure of 7 and 4 bar, respectively.

Diffraction peaks of all samples except ZnO-25 can be well indexed to the hexagonal wurtzite structure of ZnO reported in international center diffraction data (JCPDS 36-1451) and no peaks from other phase of zinc oxide and impurities were detected, which indicated that pure products were formed. Peaks at 2θ: 33.2 and 59.6 in XRD patterns of sample ZnO-25 in Figure 2(d) correspond to impurity. In addition, FT-IR analysis of ZnO-25 indicated the presence of unreacted zinc acetate in the sample. Therefore, extraction of zinc acetate was carried out with distilled water. The solvent was evaporated and the sample was then dried in an oven at 100°C. Fig.3 shows the FT-IR spectrum of obtained sample from ZnO-25. The absorption broad bands at 1580 and 1401 cm^{-1} in the spectrum are due to asymmetric and symmetric stretching vibrations of carbonyl group (COO-Zn) in the zinc acetate, respectively. In spray pyrolysis method, the reaction temperature, concentration and residence time of

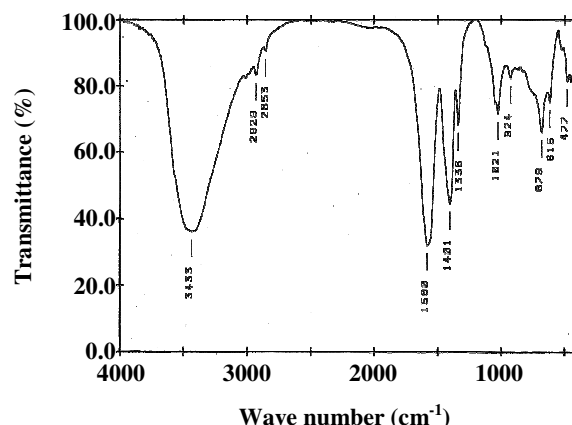


Fig. 3: FT-IR spectrum of extracted zinc acetate from ZnO-25.

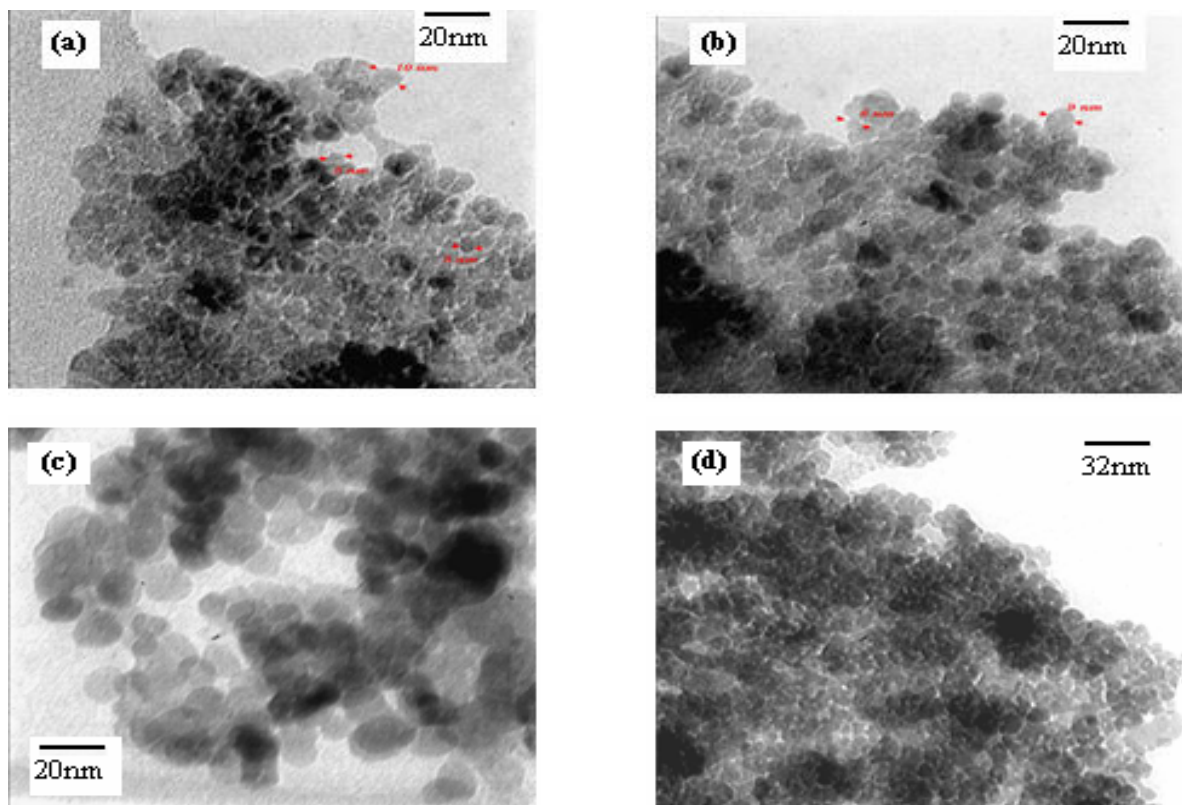
precursor solutions inside the reactor are the most important parameters, which can affect size and morphology of nanoparticles as well as the purity of product. It seems that the atomized droplets of sample ZnO-25 do not decompose in the core of reactor because of their high concentrations, which do not allow heat from hot walls of the reactor to reach the droplets. Therefore, the zinc acetate of these droplets remains in the product as the impurity.

The ZnO crystallite diameter size D was calculated using the Debye-Scherrer formula $D = K\lambda / \beta \cos\theta$, where K is Sherrer constant, λ is the x-ray wavelength (1.54 Å), β is full width at half-maximum of the peak, and θ is the Bragg diffraction angle. The particles size and Specific Surface Area (SSA) of nano ZnO samples and bulk ZnO are shown in Table 1.

As shown in Table 1, the prepared ZnO nanoparticles with concentrations in the range of 5-20 wt% at 1200°C have 14.3-17.1 nm diameter size and 50-56 m^2/g specific surface area range. Comparing the obtained results for samples ZnO-5, ZnO-15 and ZnO-20 in Table 1 exhibited that the 20wt% is the optimal zinc acetate concentration for synthesis of nano ZnO at 1200°C in spray pyrolysis method. To lower energy consumption, the experiment with this concentration was also carried out at 800 and 1000°C under the atomizing pressure of 7 and 4 bar. It was observed that when the reaction temperature decreased from 1200°C to 1000°C at atomizing pressure of 7 bar, the diameters of obtained nanoparticles decreased from 17.1 to 10.0 nm and when the atomizing pressure of solution decreased from 7 to 4 bar,

Table 1: Diameter size and BET specific surface area of different ZnO nano particles.

| Sample | Zinc acetate concentration wt% | Reactor T(°C) | Atomizing pressure (bar) | Crystal size (nm) | BET-SSA(m ² /g) |
|----------|--------------------------------|---------------|--------------------------|-------------------|----------------------------|
| ZnO-5 | 5 | 1200 | 7 | 14.3 | 56 |
| ZnO-15 | 15 | 1200 | 7 | 15.3 | 51 |
| ZnO-20 | 20 | 1200 | 7 | 17.1 | 50 |
| ZnO-20a | 20 | 1000 | 7 | 10.0 | 54 |
| ZnO-20b | 20 | 1000 | 4 | 25.1 | 44 |
| Bulk ZnO | - | - | - | 243.0 | 5 |

**Fig. 4: TEM images of synthesized samples: (a) ZnO-5, (b) ZnO-15, (c) ZnO-20, (d) ZnO-20a.**

the diameters of particles increased from 10.0 to 25.1 nm (Table 1). Increasing the heating temperature increases the diameters of particles because of the higher growth of ZnO crystals at higher temperature. Decreasing the atomizing pressure increases the droplet diameter, which results in increasing particles diameter. FT-IR analysis of powder synthesized at 800°C showed the presence of too much unreacted zinc acetate in the sample, which indicated that the heat from hot walls of reactor is not sufficient to decompose zinc acetate inside the droplets.

Figs. 4(a)-(d) show typical TEM images of samples ZnO-5, ZnO-15, ZnO-20 and ZnO-20a, respectively. As shown in Fig. 4, the ZnO nanoparticles size of all samples is less than 20nm, which is in agreement with those of ZnO diameter size calculated from the XRD diffraction peaks (Table 1).

To investigate the performance of prepared nanoparticles, they were used for removal of hydrogen sulfide (H₂S) in water based drilling mud and their performances were compared with those of bulk ZnO.

Zinc oxide nanoparticles were completely capable of removing H₂S from mud in just 15 minutes, whereas bulk zinc oxide could remove 2.5% of H₂S in as long as 90 minutes under the same conditions. Details have been fully described elsewhere [3].

CONCLUSIONS

Spray pyrolysis, which is a simple, size controllable and continuous method, was used to synthesize ZnO nanoparticles. Obtained results from XRD data show that all nano powders prepared with concentrations of 5-20 wt% zinc acetate at 1000 and 1200°C have wurtzite hexagonal phase without any impurity. FT-IR analysis of obtained powder from precursor solution containing 25wt% zinc acetate reveals that increasing precursor solution concentration beyond 20wt%, results in an impurity and unreacted zinc acetate in the products. It was observed that the decrease in reaction temperature from 1200 to 1000°C decreased the crystallite diameter size from 17.1 to 10.0 nm and with decreasing the atomizing pressure of precursor solution, increased crystallite size. The higher particle size at lower atomizing pressure can be explained by increasing the droplet size produced in atomizer, which results in increasing particles diameter.

Received : Jan. 13, 2009 ; Accepted : Jun. 29, 2010

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