Synthesis and characterisation of zinc oxide catalyst and its composite with polymer additives

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Abstract. Nano-sized zinc oxide (ZnO) particles and its composite were synthesised with xanthan gum (XG) and carboxymethyl cellulose (CMC) polymers. This work studied different concentrations of the surface adsorption of these polymers onto the Zinc oxide (ZnO) nanoparticles.

The concentrations used as mass ratio were (1:1, 1:0.5 and 1:0.25w/w) for ZnO/polymer. The nanoparticles are then analysed using scanning electron microscopy (SEM), X-ray diffraction (XRD), atomic force microscopy (AFM), particle size and BET surface area.

Composition of the samples was recognised with X-ray diffraction. The shape of particles changes with addition polymeric additives. It has been indicated that the low concentration polymers display a weaker effect on the surface of particles in comparison to the polymers with high concentration and CMC polymer better than XG polymer since it facilitated to produce finest nanoparticles with higher surface area.

1. Introduction

Nanoparticles have identified individual characteristics in materials, which have been variant from bulk materials by an increase in the specific surface area and a reduction in volume. Properties, such as enhancement of reactivity as a result of increasing particular surface area and bandgap of nanoparticles by quantum confinement, have been studied by researchers in varied fields. These materials could be used for light-emitting systems, catalysts, fluorescent materials and paint [1].

Zinc oxide is classically used as a catalyst [2], gas sensor material [3], UV absorber [4], pigment in cosmetics [5] and paints [6]. It can be made by different synthetic processes in various particle sizes and shapes [7, 8]. Advanced applications use nanoparticles with defined particle shape and narrow particle size distribution. Therefore, the research studies on the synthesis and characterisation of nanoscale ZnO have increased considerably in the last few years. Different synthetic approaches have been denoted in the literature, including sol-gel method [9], solvothermal methods [10, 11], microemulsion [12], hydrothermal [13] and thermal decomposition of precursors [14, 15]. These chemical processes are effective for producing nanoparticles and may be scaled up to produce large amounts of material [16, 17]. Though, the general problem is aggregation which takes place through the formation of these particles.

Efforts have been employed to evolve modern techniques for production and modifying preparation methods of the nanoparticle. The desired control of the precipitate can be often obtained with consideration to its shape, size, and chemical composition, with the use of polymeric additives [5]. The modification of the crystal outgrowth can be created by adsorbing onto individual crystal planes, or by altering the charge at the surface of the particles, [18]. The synthesis of polymer-supported ZnO has succeeded in adjusting morphology and particle size, resulting in different shapes such as flower-like particles [19], hexagonal Plates [20], or nanorods [21].
Taking into consideration that the fine size of zinc oxide nanoparticles is one of the main parameters of the characteristic, so, the synthesis method should be done in a manner that the particles do not accumulate with each other since the agglomeration leads to an unfavourable creation of zinc oxide nanoparticles [22]. Accumulation of nanosized ZnO may happen as a result of the following reasons: 1) Zinc oxide nanoparticles possess a capability to attract with other nanoparticles that having high surface energy; therefore aggregation may take place when they are dissipated in an organic solvent and matrices. 2) The consistency of the Zn-O-Zn bonds among nanoparticles by mean of the presence molecules of water giving rise to dense aggregations, which interrupt the implementations of zinc oxide nanoparticles [23]. Hence, elimination of water moiety in precursors is a significant method for decreasing complex aggregation. Different processes were applied to exclude the water in precursors, e.g. washing via organic solvent, and this has then been selected by one research group [24]. Composite of polymer is an efficient method for modifying the surface of particles, and so it prohibits the aggregation of ZnO nanoparticles. A large number of researches have been induced to consider the influences of polymers on the rheological and stability manners of several suspensions of metal oxide; such as suspension of zirconium oxide [25], suspension of aluminium oxide [26], and suspension of aluminosilicates [27]. The affinity of polymeric additives on the metal oxide surface is related to the incorporation of chemical and electrostatic interactions, hydrogen bonding and van der Waals force. For nonionic polymers, hydrogen bonding is the essential attraction technique [28].

In this study, both of xanthan gum (XG) and carboxyl methylcellulose (CMC) are used to determine the effects of their concentration on particle size and morphology of zinc oxide. The bonds formed between XG and CMC molecules are due to the presence of hydrogen bonds and the ionic affinity between them.

2. Experimental Work

2.1 Materials

Zinc sulfate heptahydrate \([\text{ZnSO}_4 \cdot 7\text{H}_2 \text{O}]\) was purchased from Fluka chemika with an assay 99.5%. Sodium hydroxide with purity 99.9% was supplied by Panreac. Xanthan gum‘ polymer that produced in a pure culture fermentation process by the microorganism is an anionic polysaccharide. Xanthomones campestus with molecular weight \(5 \times 10^6 \text{g/mole}\) and Carboxyl methylcellulose as an anionic polymer with molecular weight \(400000 \text{g/mole}\) were supplied from local market in Baghdad. Distilled water used as a solvent.

2.2 Preparation of nano zinc oxide

First of all, dissolving 10g of zinc sulfate in 100 ml distilled water under constant stirring then 100ml of NaOH aqueous solution with concentration 1M was added dropwise to zinc sulfate solution and continue stirring for 1h. The precipitate was washed until pH reached seven and filtrated. Finally, leaving the sample to dry overnight at 120°C and then calcined at 400°C for 3h.

2.3 Preparation of XG/ZnO composite

For prepare composite xanthan gum/zinc oxide with ratio 1:1 w/w, prepare a solution of (A) xanthan gum by dissolving 2g polymer in 100ml distilled water under vigorous stirring at temperature 40°C for two days until polymer was dissolved entirely and become homogeneous, (B) Zinc sulfate with amount of 2g was dissolved in 100ml distilled water to prepare another solution. Solution (A) and (B) were mixed for 30min to be one phase and then NaOH solution (1M) was added dropwise to reduce zinc sulfate to zinc oxide nanoparticles, which finally got immobilised within the polymeric xanthan mesh. The mixture was stirred for another 1h and left overnight. It was put in dryer 24 h to vapourise water to obtain a dry powder of XG/ZnO composite. For preparing other ratios of composite
xanthan gum/zinc oxide (0.5:1)w/w and (0.25:1)w/w repeat the same procedure but with different amount of xanthan gum that satisfy the required ratio.
The above method was applied for prepare CMC/ZnO composite with ratio (1:1), (0.5:1) and (0.25:1)w/w.

3. Results and discussion

3.1 X-Ray Diffraction

The XRD pattern of synthesised zinc oxide and zinc oxide composites are shown in Figures 1, 2 and 3. The XRD for zinc oxide powders synthesised shows characteristic diffraction peaks of crystalline with hexagonal structure with sharp peaks at 2θ=31.8°; 34.5°; 36.2°; 47.6°; 56.6°; 62.9°; 66.4°; 67.9°; 69.1°; 72.6°; 76.9°. For zinc composites of xanthan gum and carboxyl methylcellulose, the peaks for zinc oxide also appear very narrow diffraction which indicates relatively large crystallite sizes. The polymeric additives were reacted with remaining raw material and forming sodium carbonate sulfate component which appears by peaks at 2θ=20°, 23°, 25.5°, 29°, 42°, 52° (Natl. Bur. Stand. (U. S.) Monger. 25, 11, 52, 1972) as shown in figs.2 and 3 for all concentrations of two composites.

Figure 1. XRD for zinc oxide

(A)  (B)
Figure 2. Zinc oxide composite for
(a) ZnO/ XG (1:1), (B) ZnO/XG (1:0.5), (C) ZnO/XG (1:0.25),

Figure 3. Zinc oxide composite for
(A) ZnO/CMC (1:1), (B) ZnO/CMC (1:0.5), (C) ZnO/CMC (1:0.25)
3.2 Scanning electron microscopy

The SEM images of the pure and composite ZnO particles are shown in Figures 4, 5 and 6. The images show that ZnO nanoparticles have flakes shape of small sizes (Figure 4). For Composite nanoparticles, the shape of particles differs and have a better homogeneity in size and morphology with irregular shape such as granular particles and whiskers as illustrated in (Figures. 5 and 6).

![Figure 4. SEM for nano zinc oxide](image)

(a)  (b)
Figure 5. SEM for ZnO composites
(a) ZnO/XG (1:0.25), (b) ZnO/XG (1:0.5), (c) ZnO/XG (1:1)

Figure 6. SEM for ZnO composites
(a) ZnO/CMC (1:0.25), (b) ZnO/CMC (1:0.5), (c) ZnO/CMC (1:1)
3.3 Effect of polymer on the diameter of nano zinc oxide

The size of zinc oxide nanoparticles was measured by atomic force microscopy (AFM). Comparison of diameters of ZnO synthesised in polymeric solutions and without the addition polymer was shown in figure (7). Two types of polymer were tested xanthan gum and carboxymethylcellulose at a weight ratio of polymer to zinc oxide (1, 0.5, and 0.25) to one. This figure indicated that carboxymethylcellulose polymer produced smaller nanoparticles and higher concentration produced also smaller nanoparticles than the one with lower concentration.

For ratio (1:1) the diameter was 45nm when using xanthan gum compared with 30nm if using carboxymethyl cellulose at the same ratio. Also when the concentration of CMC increased the particle size become more nano, this reduces from 45nm to reach 35 and 30nm as CMC ratio 0.25, 0.5 and 1 respectively while for nano zinc oxide without polymeric additive the diameter was 69nm. The differences in sizes of nanoparticles may be associated with differences in the chemical compositions, structure and numerous properties of the nanoparticles and so multiple interactions produce between nanoparticles and polymer.

Furthermore, these results agree with Liu and Rattan [29] who studied the effect of two types of carboxymethyl cellulose with different molecular weight (120000 (CMC 500) and 240000 Dalton (CMC 1050)) and concentration (0.05%-0.5% w/w) on the synthesis of Nanosized apatite particles (nAP). Results illustrated that 0.05% CMC500 solution conferred particle size of 148.7-134.9nm, compared with 0.05% CMC1050 solution which produced nanoparticles of 6.8-3.2 nm. While for concentration effect, 0.25% CMC-1050 gave least nAP of 4.3-3.2 nm, and the smallest size nanoparticles, with diameter of 3.0-2.1 nm 0.5% CMC-1050 was produced.

![Figure 7. Polymer effect on the size of nano zinc oxide](image)

AFM for three-dimensional surface profiles which displayed the detailed observation of events on the crystal surface, and the layer growth of crystal and the height of the terraces was shown in figures 8, 9 and 10 for pure nano zinc oxide and its composite respectively.
Figure 8. AFM for nano zinc oxide

Figure 9. AFM for ZnO composites
(a) ZnO/XG (1:0.25), (b) ZnO/XG (1:0.5), (c) ZnO/XG (1:1)
3.4 Specific surface area

BET measurements used for the analysis of the surface area. This parameter is controlled actively by the process maintained for the dispersion of nanoparticles, the structure of the original material (macroporous or gel-type resin), or by the kind of polymer (biopolymers or synthetic) [30].

The surface area for zinc oxide nanoparticles and two composites at different ratio is presented in Figure 11. The material obtained without an additive presented a surface of 16.36 m²g⁻¹. The additives had different effects on the $S_{BET}$, xanthan gum (XG) and carboxymethylcellulose (CMC) led to a higher $S_{BET}$, whereas ratio 0.25:1 (XG/ZnO) indicated nearly no change. The addition of XG with weight ratio 0.5 and 1 led to a significant increase of $S_{BET}$ to 23.61 and 29.17 m²g⁻¹. For CMC addition this induced increase of the surface area of nano ZnO. The samples obtained had high $S_{BET}$ of 29.43, 41.53 and 48.61 m²g⁻¹ for (CMC/ZnO) ratio of 0.25, 0.5 and 1 respectively.
4. Conclusions

To conclude, this study firstly indicates that the size of zinc oxide nanoparticles in the composite can be affected by varying the type of polymers and their concentrations. Therefore, higher polymer concentrations generally produce smaller particle size than solutions with lower concentration at the nanometer scale. However, Carboxymethyl cellulose was better than xanthan gum since it reduces particle diameter of zinc oxide more than that with Xanthan gum and gave higher surface area. Finally, XRD analysis shows that the crystalline structure of all composite is the same. The morphology varies without additives than that for polymeric additive.

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