Research Article

Synthesis and Characterization of ZrO₂ and TiO₂ Nanoparticles

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Abstract: The objective of this project is to synthesis ZrO₂ and TiO₂ nanoparticles by chemical methods. 4.2 g of ZrCl₄ was dissolved in 300 mL distilled water, the source solution. 0.03 M/mL as a molar concentration of sorbitol and ammonia was made as a solution, called a “target” and stirred for 5 min. The source and target were mixed and stirred slowly. The final solution was heated to 70°C with stirring. Finally The solution was filtered and washed to obtain the nanoparticles; 5 mL of titanium isopropanol was added to 15 mL of isopropanol. A solution of water, HNO₃ and NH₄OH was added to the first solution in order to tune pH to be 4. Then the mixture was stirred at 60-70°C for 20 h. Thereafter the precipitate was filtered and washed with ethanol and then dried at 100°C for 4 h under vacuum. Finally the powder was annealed at 600°C for 2 h to obtain TiO₂ nanoparticles. UV-VIS, XRD and SEM analyses were made to these powders, compared with other ones and then found that these particles obtained are in Nano range.

Keywords: Chemical method, nanoparticles, titanium dioxide, zirconium dioxide

INTRODUCTION

ZrO₂ nanoparticles have many special properties like low thermal conductivity and high thermal stability and its thermal expansion coefficient is very high. So ZrO₂ nanoparticles (ZrO₂NPs) could be used in thermal barrier cutting, medical uses and as fillers in human bones and tooth (Shukla and Seal, 2005; Liang et al., 2003; Chandra et al., 2010).

The researchers used several methods in the past to producing ZrO₂NPs like sol-gel (Ehrhart et al., 2006), hydrothermal (Torres-Huerta et al., 2009) and Chemical Vapor Deposition (CVD) (Rozo et al., 2008) method. In this study, there is a novel method to produce ZrO₂NPs called "co-precipitation" which was discovered by Alaei et al. (2014).

As for TiO₂ nanoparticles (TiO₂NPs), since the beginning of the researches about nanoparticles, scientists attended in formation and applications of TiO₂NPs specially in medicine because they are biocompatible with the human body and used indelivery drugs to its tissues (Wu et al., 2014; Liu et al., 2009; Hang et al., 2011; Miao et al., 2012).

TiO₂ has good properties in optics, dielectrics and as catalytic. For these interesting properties, TiO₂ is used, as a bulk or nanoparticles, as a filler, catalytic and photocatalytic material (Barbè et al., 1997; Ahmed and Attia, 1995; Ferroni et al., 1996).

So, the formation of TiO₂NPs became very important in industrial and medical applications.

The aim of this study: The aim of this study is to producing ZrO₂ and TiO₂.

EXPERIMENTAL PROCEDURES

Preparation of ZrO₂ nanoparticles:
Chemical used: ZrCl₄ as a precursor, sorbitol and ammonia.

The procedure: 4.2 gm of ZrCl₄ was dissolved, according to the procedure mentioned in Alaei et al. (2014), in 300 mL distilled water, this is called "the source solution".

Thereafter, 0.03 M/mL, as a molar concentration, of sorbitol and ammonia solution were made, called a target and stirred for 5 min. Thereupon, the source and the target were mixed and stirred slowly at room temperature. The final solution were heated to 70°C for few minutes with stirring. The solution was filtered by paper funnel and washed with distilled water many times to obtaining the nanoparticles, then the solution was vaporized with existing of N₂ gas. Thereafter the powder was dried in an oven for six hours and calcined at 550°C for two hours. During all the operation, Ph was tuned to be 4.

Preparation of TiO₂ nanoparticles:
Chemical used: Titaniumisopropoxide, isopropanol and distilled water.
The procedure: According to the procedure discovered by Mahshad et al. (2006), 5 mL of titanium isopropoxide was added to 15 mL of isopropanol. A solution of water, HNO₃ and NH₄OH was added to the first solution in order to pH becomes two. Then the mixture was stirred at 60-70°C for 20 h. Finally we obtained a white blue gel suspension. Therefrom the precipitate was filtered and washed with ethanol to get the nanomaterial and then dried at 100°C for 4 h under vacuum, thereon the powder was annealed for 2 h at 600°C to obtain TiO₂ nanoparticles.

Characterization: Figure 1 represents the UV-VIS chart, Fig. 2 is for XRD and Fig. 3 is for SEM.
Fig. 3: SEM for ZrO$_2$-NPs prepared

Fig. 4: UV-VIS spectrophotometry for TiO$_2$ nanoparticles prepared
Fig. 5: XRD flow chart of TiO$_2$-NPs prepared

Fig. 6: SEM image of TiO$_2$-NPs that was prepared
As for TiO₂, UV-VIS spectrophotometry is in Fig. 4, XRD is in Fig 5 and SEM is represented by Fig. 6.

**RESULTS AND DISCUSSION**

UV-VIS spectrophotometry of ZrO₂ NPs prepared, shown in (Fig. 1), tells us that this powder of ZrO₂ is in nano range since it has a peak at 271 nm as mentioned by Mahmoud et al. (2013) (Fig. 7). This peak results from the transition of the electron from valance band to conduction band across the band gap which equals to 3.8 to 6.1 e.v.

XRD pattern of the ZrO₂ powder prepared (Fig. 2), was compared with the standard one available in the study of Zakeri et al. (2013) (Fig. 8) and found that these nanoparticles are for monoclinic ZrO₂.

From Fig. 3, the average particle size of ZrO₂ NPs prepared was measured by debye-sherrer equation:

\[
D = \frac{0.89 \lambda}{B \cos \omega}
\]

where,
- \(D\) = The grain size
- \(\lambda\) = The wavelength at \(k\alpha\), which is intrinsic value for Cu, \(\lambda = 0.154\) nm
- \(B\) = The full wave half maximum of every peak
- \(\omega\) = The diffraction angle

It was found to be 14.14 nm.

SEM in Fig. 3 reveals that ZrO₂ powder prepared is in nano size, but the particles are aggregated.

The agglomeration is attributed to the high surface activity of the nanoparticles so that the nanoparticles react with the other materials easily or agglomerate about themselves especially if the preparation method was sol-powder (Scholz et al., 1998; Jiang et al., 2009; Maynard and Pui, 2007; Faure et al., 2013; Simard, 2007).

Sauter et al. (2008) found a solution for this phenomenon by projecting an ultrasonic waves on these nanoparticles agglomerated in the last step of preparation and succeeded in collapsing the agglomeration.

As to TiO₂ NPs, from UV-VIS spectrometry (Fig. 4), it could be concluded that these particles are in nano size because it has two peaks at nearly 244 and 285 nm as mentioned in research of Li et al. (2009) (Fig. 9).

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Fig. 7: UV spectrum of ZrO₂ NPs (Mahmoud et al., 2013)

Fig. 8: Standard XRD graph of ZrO₂ nanoparticles
filling diatomite and nanosized silica

<Fig. 10: The standard XRD pattern of TiO$_2$.>

The standard XRD pattern of TiO$_2$ (Fig. 10) was compared with the standard XRD of TiO$_2$ nanoparticles. Iran J. Chem. Chem. Eng., 33(2): 47-53.

<Fig. 9: The UV-VIS spectrophotometry of TiO$_2$ nanoparticles done by Li et al. (2009).>

The first peak is attributed to the electron transition, in a nanoparticle, from the valance band of oxygen O$_{2p}$ to the conduction band of titanium Ti$_{3d}$ when absorbing UV photon. The second peak is attributed to the absorbing a UV photon by an electron and transformation to a vibrational wave and then the vibration wave comes back to UV photon in less energy and in another direction or what is called scattering (Li et al., 2009).

The XRD pattern of TiO$_2$-NPs prepared, (Fig. 5), was compared with the standard XRD of TiO$_2$ (Fig. 10) and found that they are correspondent.

The grain size was calculated and found to be of nearly 10.29 nm.

As concerns SEM, we see from its image (Fig. 6), that the grain size is of about 67 nm and the nanoparticles are aggregated because of the reasons mentioned already.

CONCLUSION

ZrO$_2$ and TiO$_2$ nanoparticles have been obtained by chemical (sol-powder) method with the presence of the agglomeration.

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