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Preparation and Characterization of ZrO_2/ZnO Nanocomposite under Ultrasonic Irradiation via Sol-gel Route

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ABSTRACT

Nanocomposite of ZrO_2/ZnO was prepared under ultrasonic irradiation by sol gel process from directly mixing Zirconium and Zinc gels, and the mixture was placed under ultrasonic irradiation for 2 hours then aging time the filtrated composite gel was calcinated at 500°C for 3h in furnace. The precursor sol of zirconium was prepared from an aqueous solution of $ZrCl_4$ and zinc acetate dihydrated was dissolved in de-ionized water. The FT-IR analysis and the XRD study were exhibited that the crystal structure and purity of the ZrO_2/ZnO nanocomposite FESEM images was indicated the morphology and the average size of the NPs. The average size of the ZrO_2/ZnO nanocomposite was determined 37 nm.

Keyword: Zirconia ZnO; Nanocomposite; Particle size; Sol-gel; Ultrasonic irradiation.

1. INTRODUCTION

In recent years, there has been increasing interest in the application of nano size Zirconia and Zinc oxide for catalysts and supports, ceramics, inorganic membranes, gas sensing, water purification and solar energy conversion [1,2]. ZrO_2 has unique characteristics, such as weak acidity, basicity, redox and high thermal stability Since the beneficial physical-chemical properties strongly depend on the particle size, the controlled and reliable preparation of nano-ranged materials represents a particular challenge being reflected by numerous approaches, for instance flame synthesis [3], chemical vapor deposition [4], Sol-gel processes [5], hydrothermal synthesis [6], sonocation [7] and polyol synthesis [8]. Due to its unique properties ZrO_2 is widely used for gas sensors, ceramics, sorbents and catalysts; concerning the latter, ZrO_2 is particularly employed as catalyst carrier in the selective catalytic reduction of NOx by NH_3 (SCR) [9-11]. In most cases, the precursors are soluble zirconium salts like $ZrO(NO_3)_2.xH_2O$, $Zr(NO_3)_4$, $ZrOCl_2.xH_2O$ and $ZrCl_4$ [12-15], whereas organic zirconi-

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um compounds have been used as well [16,17].

Moreover, the sol-gel method allows for the homogeneous mixing of transition-metal cations at a molecular level, which enhances the formation of polycrystalline particles with special properties [18]. The crystalline phase of ZrO_2 strongly influences its catalytic activity and selectivity [19, 20].

More attention has been paid to ZnO nanostructures because ZnO is an important low cost basic II–VI wide band gap semiconductor material which is used considerably for its catalytic, electrical, photoelectrical and photodegradation properties [21]. Recently using of ultrasonic irradiation has been employed of synthesis and sono-catalyst properties of many nano materials [21, 22].

We have been synthesized the binary nanocomposite of ZrO_2/ZnO by using ultrasonic irradiation, the ultrasonic probe is very effective in preparation process.

2. EXPERIMENTAL

2.1. Preparation of Zinc gel

4.4 g (0.2 mol) $Zn(CH_3COO)_2.2H_2O$ was firstly dissolved in DI water (100 mL) and stirred to get a precursor solution. 15 mL (2M) NH_4OH solution was then dropped into the precursor solution until pH of mixture was adjusted 9 and the white suspension of $Zn(OH)_2$ was appeared. After that, the mixture was continuously stirred for 2 days then the tip of ultrasonic probe was introduced into the mixture and it was irradiation under ultrasonic irradiation for 30 min to achieve a ZnO homogenous gel.

2.2. Preparation of Zirconium gel

Firstly $ZrCl_4$ (4.7g, 0.2 mL) was dissolved in 2-propanol (100 mL) to get a precursor solution. A solution of H_2O_2 (6 mL, 30% v/v) was then dropped into the precursor solution under stirring. The pH of mixture was adjusted 9 by adding ammonium solution 2M until Zirconium gel ($Zr(OH)_4$) was prepared and the produced gel was aged and stirring for 2 days, Then the probe of ultrasonic was introduced in ZrO_2 gel and it was irradiated for 30 min.

2.3.Preparation of ZrO_2/ZnO nanocomposite

The Zirconium and Zinc gels were mixed together then the mixture gels were irradiated by the probe of ultrasonic instrument for 2 h. The mixture was stirred for 48 h, then it was filtrated and washed several times. After drying at room temperature, the white precipitated was calcinated at 500ºC for 3 h in furnace.

$$Zn(CH_3COO)_2 + 2NH_4OH \rightarrow Zn(OH)_2 + 2NH_4CH_3COO$$

$$ZrCl_4 + 2H_2O_2 \xrightarrow{\Delta} Zr(OH)_4 + 2Cl_2$$

$$Zr(OH)_4 + Zn(OH)_2 \rightarrow ZrO_2 / ZnO + 3H_2O$$

3. RESULTS AND DISCUSSION

3.1. FESEM image

Surface and morphology of the synthesized nanocomposite have been studied and the FESEM images are

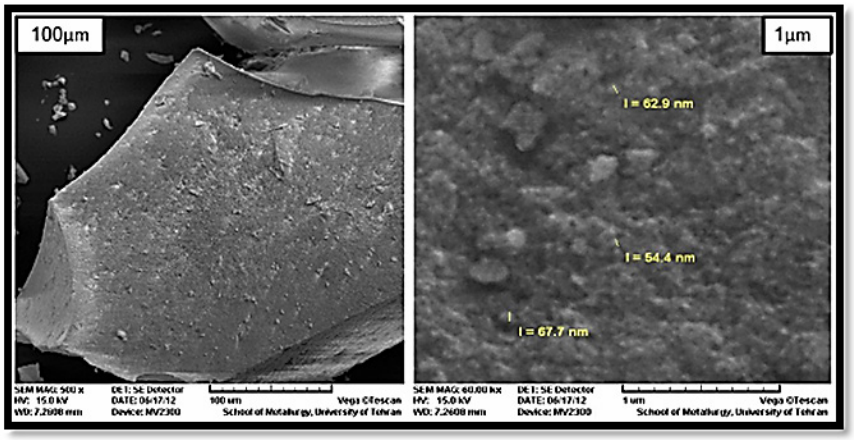

Figure 1: *FESEM images of ZrO_2/ZnOnanocomposite.*

shown in Figure 1. The ZrO_2/ZnO nanoparticles are seen uniform. The size of particles is 50-60 nm

3.2. XRD diffraction

The XRD pattern of the ZrO_2/ZnO nanocomposite is shown in Figure 2. The distinct peaks corresponding to ZnO and ZrO_2 are observed. It is concluded that both the materials exist in perfect crystalline phases and retain their physical structure and hence confirmed to form a ZrO_2/ZnO nanocomposite (according to card no. 37-1484 for ZrO_2 and card no. 36-1451, for ZnO Joint Committee on Powder Diffraction Standards (JCPDS)). The ZrO_2/ZnO nanoparticles are seen pure The average particle size Dv of crystallites in the composite was also roughly calculated based upon the XRD spectra for quantitative purpose using the Scherrer equation:

$$Dv = \frac{K\lambda}{\beta \cos\theta}$$

where: Dv is the "volume weighted" crystallite size = ¾ d (crystallite diameter) K is the "Scherer constant" (around 0.9) , λ is the wavelength of the X-Rays here is λ , CuKα = 1.541 Å, θ is the Bragg angle for the peak at 2 θ, β is the "integral breadth" of the peak at 2θ. The β = (π/2) FWHM (full width at half maximum) for a Gaussian shaped peak. The crystallite size of ZrO_2/ZnO nanocomposite according to XRD Pattern is estimated to be 37 nm.

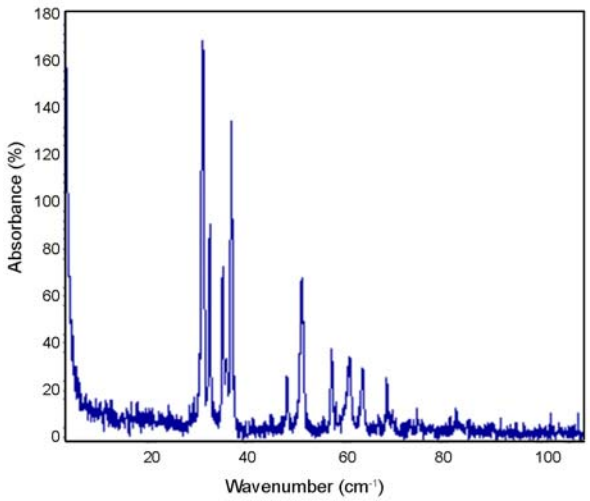

Figure 2: *XRD patterns of the ZrO_2/ZnO nanocomposite powder.*

3.3. FT-IR analysis

FT-IR spectrum of the ZrO_2/ZnO nanocomposite is shown in Figure 3, in the wave number range from 4000 to 400 cm^{-1}. The peaks at 567, 671 and 762 cm^{-1} can be attributed to symmetric and asymmetry stretching vibration of the Zr–O–Zr bond and O–Zr–O flexion, .The peaks at 869 cm^{-1} were attributed to the vibration mode of Zn–O–Zr. The peaks at 420 and 497 cm^{-1} can be assigned to stretching vibration of the Zn-O-Zn bond and O-Zn-O bond respectively. The peak at 1630 cm^{-1} resulted from bending vibration of the adsorbed H_2O molecules, which were not removed completely after Sol-gel synthesis. The wide peak at

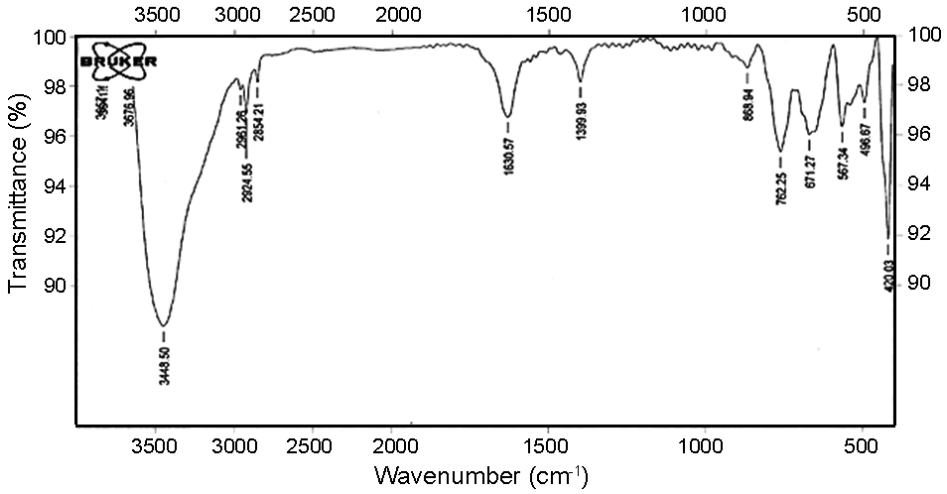

Figure 3: *FT-IR spectra of the ZrO_2/ZnO nanocomposite powder.*

3448 cm^{-1} has been assigned to the OH symmetry and asymmetry stretching vibration of surface hydroxyl group.

4. CONCLUSIONS

ZrO_2/ZnO nanocomposite has been synthesized by a facile Sol-gel method using ultrasonic irradiation. $Zn(CH_3COO)_2.2H_2O$ and $ZrCl_4$ have been used as starting materials. The nanocomposite of ZrO_2/ZnO molar ratio 1:1 was calcinated at 500ºC, Comparison of the FT-IR spectra of ZrO_2/ZnO nanocomposite with the pure ZrO_2 and ZnO nanoparticles have been showed formation of ZrO_2/ZnO nanocomposite. Crystal phase and particle size of NPs can be detected by XRD. According to XRD Patterns, the calculated value as crystallite size of ZrO_2/ZnO nanocomposite was obtained around 37 nm.

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