

Photodegradation of Thiophene by TiO₂/Zrnanocomposite from Petrochemical Units Waste Water

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ABSTRACT: TiO₂/Zrnanocomposite with different molar ratios of Zr via calcination (>580°C) of Titanium tetra Isopropoxy (TTIP) was prepared by the sol-gel method. The particle sizes observe in the scanning electron microscopy (SEM) and X-ray diffraction (XRD) methods. The XRD study exhibited that the crystallization behaviour of the nanocomposites was associated with the molar ratios of Zr. The SEM images indicated that with increasing the molar ratio of Zr until 0.4 mmol, regular morphology can be seen. It should be of interest for catalytic purposes since it expectantly improves the surface area. Furthermore, the photocatalytic activity of the synthesized nanocomposites was investigated for degradation of Thiophene (C₄H₄S) under UV irradiation in a batch reactor. The results revealed that the photocatalytic activity of nanocomposite with 0.4 mmol of Zr was the best.

KEYWORDS: "TiO₂/Zrnanocomposite" "Degradation" "Sol-Gel" "UV irradiation" "Thiophene".

I. INTRODUCTION

Titanium dioxide (TiO₂) is one of the most widely used photocatalysts because of its suitable band gap (ca. 3.2 eV), chemical stability and nontoxicity [1].

The positions of the energy levels of dopants determine their contributions to the photocatalytic activity. Dopants that have energy levels between the conduction and valence bands act as charge recombination centers and are detrimental to the photocatalytic performance of TiO₂. Zirconium ions with unoccupied 4d states above the conduction-band minimum of TiO₂ have been demonstrated to improve the photocatalytic activity [2]. The sol-gel method is a simple and feasible method for the fabrication of nanocomposite with tailored sizes. Conventionally, the sol-gel method uses a hydrolytic route that involves initial hydrolysis of the precursors and subsequent continuous condensation between the hydrolyzed precursors to form oxide gels. The sol-gel (SG) method to metal oxides proceeds very efficiently for high purity, good uniformity of the microstructure of powder, synthesis at low temperature and easily controlled reaction conditions. Therefore this method has been used to prepare of TiO₂/Zrnanocomposite[4]. In this work, TiO₂/Zrnanocomposite was prepared by sol gel method and characterized by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), and The photocatalytic activity of the synthesized nanocomposite was investigated for degradation of Thiophene under UV irradiation in a batch reactor. The effect of Zr molar ratio on the photocatalytic behavior of nanocomposite was studied in detail.

II. MATERIALS AND METHOD

chemicals used were Titanium tetra Isopropoxy (TTIP) (Panreac Co; Spain), zirconium tetrachloride (ZrCl₄), Hydroxy propyl cellulose (HPC), Thiophene (Merck Chemical Company) and ethanol (BidestanCo;Iran).

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In this study, TiO_2/Zr nanocomposite with different molar ratios of Zr was prepared by the sol–gel methods. The TiO_2 sol was made at room temperature, and TTIP was used as a precursor as follows: In the first stage, TTIP was dissolved in ethanol and then was stirred for 15 min, to obtain a precursor solution. After that added 0.1 gr HPC, a mixture was continuously stirred for 15 min to achieve a yellow transparent sol. Zr sol was prepared as follows: Firstly zirconium tetrachloride was dissolved in absolute ethanol with four different molar ratios, 0.1/0.2/0.3/0.4 After that, stirred for 5 min, then a mixture of absolute ethanol and Nitric acid was added slowly into the precursor by a fast stirring and it was continuously stirred for 15 min to achieve a transparent sol. This sol aged for 24-48 h. After that, the prepared sol was dried in the air, then heat treated at 80-100 °C for 10 min and then at 580 °C for 5 h. The samples were naturally cooled after the heat treatment.

Phase identification of the nanocomposites was done by XRD from SCIFERT-3003 PTS with CuK α radiation from 0 to 100 (2 θ) at room temperature. The morphology and microanalysis of the nanocomposites were studied by SEM (HITACHI S-4160). Varian UV–Vis spectrophotometer (Cary UV-Vis 100) was used to determine the degradation concentration. Photocatalytic degradation experiments were carried out in a cubic wooden reactor with 2 L capacity. 6 (4 W) UVc (Osram) was applied as a light source and they were installed inside the reactor. Initially, 0.01 g of catalyst was added into a 25ml solution of Thiophene with an initial concentration of 5 ppm.

III. RESULTS AND DISCUSSION

Surface morphology of the synthesized nanocomposite has been studied and their SEM is shown in Fig 1.

Fig 1(e) reveals TiO_2 nanoparticles which, synthesized from TTIP hydrolysis without adding any Zr. It is seen that pure TiO_2 does not show a regular surface. They were irregularly shaped as aggregates due to the high viscosity of the sol, which reduced the dispersion of particles. Fig. 1(a)-1(d) exhibits the TiO_2/Zr nanocomposite at different molar ratios of Zr. The lowest particle size of each samples in the X axis [(a){27.34 nm}(b){27.34 nm}(c){35.16 nm}(d)) {27.34 nm} (e)) {23.44 nm}] were reported Through SEM, it was observed that the particle morphology of the TiO_2 was affected by the addition of Zr and the size distribution of TiO_2/Zr nanocomposite was improved with increasing Zr molar ratio. The Fig 1(d) reveals well ordered and good size (27.34 nm) distribution of particles and it should be of interest for photocatalytic purposes since it expectantly improves the surface area and showed no aggregation in comparison with other samples.

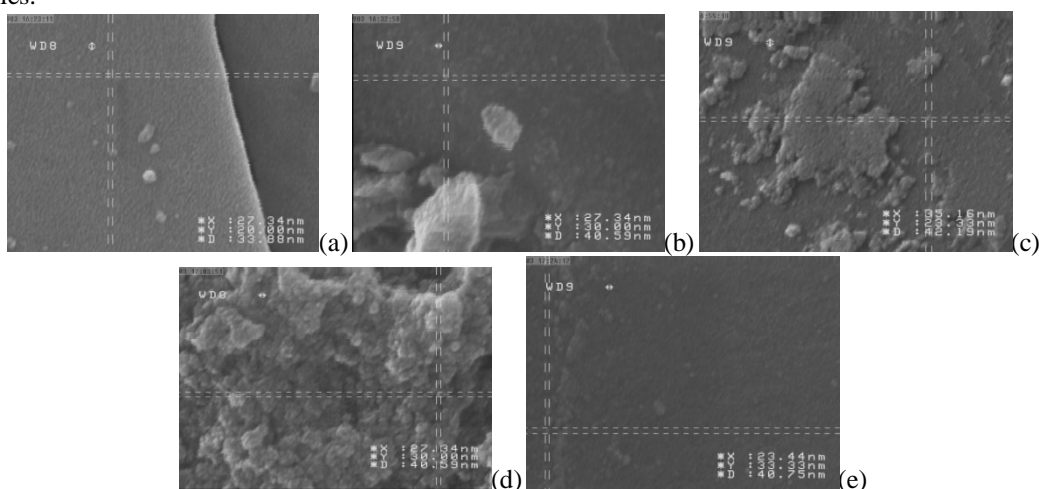


Fig.1.SEM images analysis of catalyst samples. (a) TiO_2/Zr 0.1 mmol,(b) TiO_2/Zr 0.2 mmol, (c) TiO_2/Zr 0.3 mmol. (d) TiO_2/Zr 0.4 mmol, (e) TiO_2

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The XRD patterns of catalysts that were crystallized by using different molar ratios of TiO_2/Zr shown in Fig. 2. Five remarkable peaks were observed which related to Anatase (25.2/37.8/48/55), rutile (27.5/39/45.2/51.1), Zirconium Titanium Oxide (30.3/36.5/53.7/62.8/77.9), titanium oxide (16/31.2/36.3/38/45/78) and zirconium oxide (36.2/50.2/69) phases.

It can be seen anatase phase as the dominant phase is observed in all samples and it will be revealed that with increasing the molar ratio of Zr until 0.4mmol sharpness of anatase peaks increased.

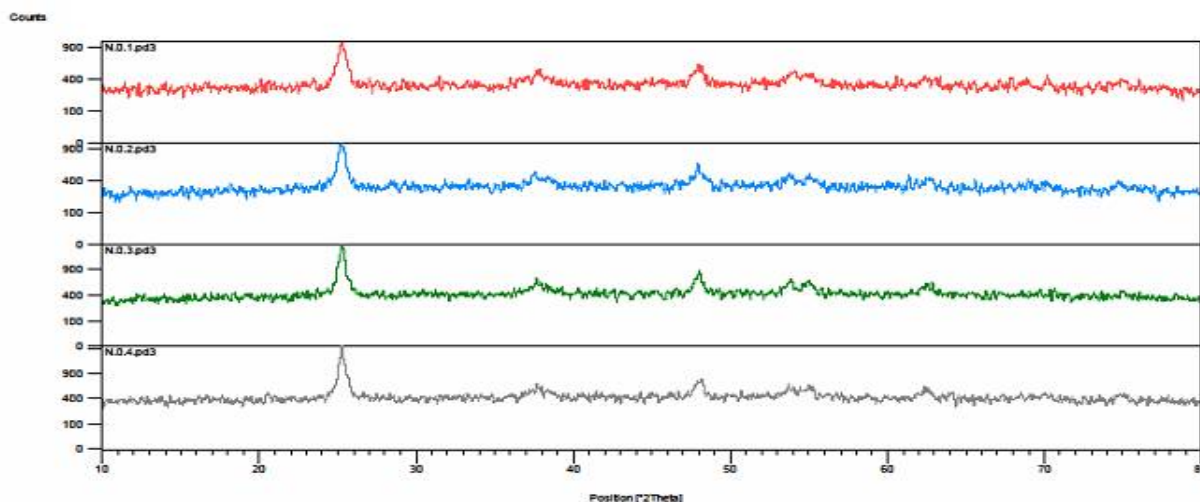


Fig.2XRD patterns of Catalyst samples.

Fig.3 shows the effect of Zr molar ratio on photodegradation of Thiophene (5 ppm) under UV irradiation in a batch reactor at different time intervals. Then Sample including Zr 0.4 mmol has the best photocatalytic activity in comparison to other samples and the absorbance of Thiophene solution has been reached to 0 after 75 min of irradiation. According to Fig. 3, the photocatalytic activity enhances when Zr molar ratio increases until 0.4. In samples 0.1–0.2–0.3, absorbance of Thiophene would be reached to 0 after 115 min/90min/90min of irradiation. Sample TiO_2 without Zr, showed the lowest photocatalytic activity and the Thiophene degradation time increased to 145min.

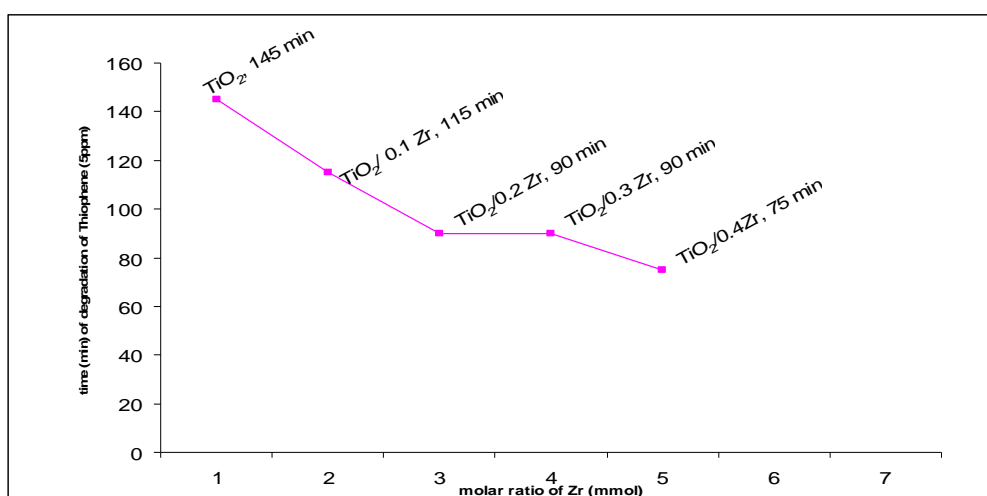


Fig.3Degradation of Thiophene solution under UV radiation for catalyst samples.

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IV. CONCLUSION

The TiO₂/Zrnanocomposite was prepared with different molar ratios of TiO₂/Zr using the sol–gel method. The SEM images indicated that sample of Zr 0.4 mmol reveals well ordered and good size distribution of particles and it was used for photocatalytic dye degradation. In addition, this sample showed no aggregation in comparison with other samples. It is important for photocatalytic activity that the particle size of the photocatalyst should be homogeneous. The XRD study exhibited that in sample of Zr 0.4 with increasing the molar ratio of Zr until 0.4mmol, the particle size decreased from 40 to 27 nm. The photocatalytic activity of the synthesized nanocomposite was investigated for degradation of Thiophene. The results showed that after increasing the molar ratio of Zr until 0.4mmol, the photocatalytic activity is enhanced gradually from sample 0.1–0.4. Addition of a high dose of Zr to TiO₂ decreases the light penetration and reduces the degradation rate. So sample of Zr 0.4 mmol has the best photocatalytic activity in comparison to other samples and the absorbance of Thiophene solution has been reached to 0 after 75 min of irradiation.

REFERENCES

- [1] S.Chang, R.Doong, and A. Irajizad, "Characterization of Zr-Doped TiO₂Nanocrystals Prepared by a NonhydrolyticSol-Gel Method at High Temperatures", *J. Phys. Chem. B*, 110, pp.20808-20814,2006.
- [2] S.M.Chang, Hou,Y. P.H.Ch.and Lo. Chang,T. Ch"Preparation of phosphatedZr-doped TiO₂ exhibiting high photocatalyticactivity through calcination of ligand-capped nanocrystals", *Applied Catalysis B: Environmental* 90 pp.233–241,. 2009
- [3] A. Udomporn, S.Ananta, "Effect of calcination condition on phase formation and particle size of lead titanate powders synthesized by the solid-state reaction", *Materials Letters* 58/ 7–8, pp.1154–1159. 2004
- [4] Sh. Moradi, P . Aberomand-Azar ,S.Raeis-Farshid,; S.Abedini-Khorrami, and M.H. Givianrad, " The effect of different molar ratios of ZnO on characterization and photocatalytic activity of TiO₂/ZnOnanocomposite, *Journal of Saudi Chemical Society*.2012