Synthesis and Characterization of Visible Light Active Cerium Zirconate

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Abstract

Due to the toxicity of organic compounds like dyes environmental pollution increases day by day. So it is essential to develop a technique which can decompose these toxic compounds effectively without creating any further toxicity. In this paper, we reported synthesis and characterization of visible light active cerium zirconate via solid state calcination method at 800^0C. In Solid state calcination reaction, highly photoactive powder of cerium zirconate was obtained by heating a 1:1 molar mixture of zirconyl oxychloride ($ZrOCl_2$. $8H_2O$) and ceric nitrate ($Ce(NO_3)_4$.$6H_2O$) at 800 ^{0}c for 24 hrs. The prepared photocatalysts were then characterized by XRD and UV-Vis diffuse reflectance analyses. The XRD spectra of as prepared sample can be indexed and matches with the Ce0.5Zr0.5O_2 (ICDD file 00-038-1436) having tetragonal structure with space group P42/nmc. The highest intensity of the (111) peak suggests that nano particles of CZ-SSR are growing along the (200) plane, providing active surface area for photocatalysis.

Keywords: Cerium zirconate, nano particles, photocatalysis

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1. Introduction

Titanium Dioxide (TiO_2) is most commonly used photocatalytic material for the degradation of organics and dyes present in water, because it has excellent physical or chemical properties and has ability to decompose organic species [1] but TiO_2 works under UV light due to its wide band gap and hence main part of solar spectrum cannot be used effectively. Several modifications of TiO_2 have been carried out to observe the changes in the photocatalytic

activity. Thus, TiO_2 needs to be modified by doping other element to reduce its wide band gap and extend the optical absorption range to long wavelength. By reducing the recombination rate of electrons-holes, decreasing TiO_2 grain size and increasing specific surface area of TiO_2, the photo-catalytic activity can be enhanced [2]. Recently, the modified composites of TiO2 with other oxides, particularly with ZrO_2 has been used , which have much better photocatalytic activities for decomposition of organic pollutants than TiO_2 under the same reaction conditions [3]. Yang and Ferreira (1998) also found that doping with a certain amount of Zr could improve the surface area of TiO_2 powder [4]. Meanwhile, they found that the augment of the surface area could increase the ability of surface to adsorb O_2 and –OH, and then increase the opportunity to accept electron. Over catalyst doped with Zr, some Zr^4+ are adsorbed on the particle surface, which boosts the surface potential to certain extent, and helps the free electrons diffuse from the interior to the surface, improving the photo-catalytic activity of catalyst.

Nowadays, CeO_2–ZrO_2 is one of the important catalytic supports due to its use in the three way catalysts [5]. It is applied in these systems due to its high oxygen storage capacity. The incorporation of zirconium into the ceria lattice creates a higher concentration of defects improving, the O^{2-} mobility, such mobility would explain the excellent ability to store and release oxygen [6]. CeO_2 is a fluorite type semiconductor crystal with bulk bandgap estimated to be 3.16 eV. That means a photo-irradiation with wavelength lower than 388 nm would be capable of exciting the photocatalytic activity in bulk ceria compounds. Actually, though not yet been intensively studied and used as photocatalysts, CeO_2 and CeO_2-based materials have already been exploited widely in various catalytic systems. The unique capability of exchanging lattice oxygen and environmental oxygen species due to their non-stoichiometric switch between Ce^3+ and Ce^4+ ionic states renders them effective catalysts as catalytic converters in automobiles, electrolytes in solid oxide fuel cells, gas sensors, etc [7-11].

The ion exchange reactivity and oxygen storage capacity is highly limited for pure ceria system due to the equilibrium ratio between Ce^{3+} and Ce^{4+} ions in room temperature. To improve their free radical scavenging activity and protective power on living systems, scientists have selected zirconium to substitute cerium to achieve the enhancement [12].

However, to our knowledge, Zhong et al, has been studied effect of metal doping into $Ce_{0.5}Zr_{0.5}O_2$ on photocatalytic activity of $TiO_2/Ce_0.45Zr_{0.45}M_{0\cdot 1Ox}$ (M =Y, La, Mn) [13]. The catalytic activities of binary composite photo-catalysts CeO_2/TiO_2, ZrO_2/TiO_2 and the ternary composite photo-catalysts $H_3PW_{12}O40$-CeO_2/TiO_2, $H_3PW_{12}O_{40}$-ZrO_2/TiO_2 were significantly higher than un-doped TiO_2 [14]. Fe-substituted $CeVO_4$ synthesized by solution combustion method has higher photocatalytic activity for degradation of dyes as compared to commercial Degussa P-25 TiO_2 and $CeVO_4$ [15]. Monophasic $Ce_{0.5}Zr_{0.5}O_2$ Solid solution synthesized by microwave induced combustion method has been used for various application [16]. Omata et al, has been studied photocatalytic degradation of methylene blue aqueous solution over a pyrochlore-related *k*-$CeZrO_4$ phase under irradiation with Xe discharge light within 8hrs. [17]. Hence the objective of this work is to Synthesize $Ce_{0.5}Zr_{0.5}O_2$ by Solid state method used under visible light for free radical scavenging application .

2. Experimental Section Setup

2.1 Synthesis of Photocatalyst

All reagents used during experiment are of A R grade. Deionized water was used throughout the experiments. In solid state calcination Reaction, highly photoactive powder of cerium zirconate was obtained by heating a 1:1 molar mixture of zirconyl oxychloride ($ZrOCl_2$. $8H_2O$) and ceric nitrate ($Ce(NO_3)_4.6H_2O$) at 8000C for 24 hrs. Both the fine powder reagent were mixed in mortar and grinded finely and then heated in oven at 100^{0}C for 24 hrs. During heating at 800^{0}C in muffle furnace, repeated grinding of the powder is carried out for the high agglomeration and compositional in homogeneity of the powders.

These samples synthesized by solid state calcination reaction was labeled as CZ-SSR.

The crystalline phase structure was determined by Bruker D8 Advance X-ray diffractometer (XRD) using Cu K- radiation. Optical Properties of synthesized material were studied by using UV- VIS diffuse reflectance spectroscopy (UV-1800, Shimandzu).

3. Result and Discussion

3.1 XRD Analysis

The crystalline nature of the synthesized CZ-SSR photocatalysts was studied by powder X-ray diffraction (XRD) as shown in Figure 1. The XRD spectra of as prepared sample can be indexed and matches with the $Ce_{0.5}Zr_{0.5}O_2$ (ICDD file 00-038-1436) having tetragonal structure with space group P42/nmc. The highest intensity of the (111) peak suggests that nano particles of CZ-SSR are growing along the (200) plane, providing active surface area for photocatalysis. The XRD patterns of the mesoporous CZ-SSR nano particles show that the (111), (200) and (220) peaks and the broadening of XRD peaks clearly indicates the nanocrystalline nature of CZ-SSR.

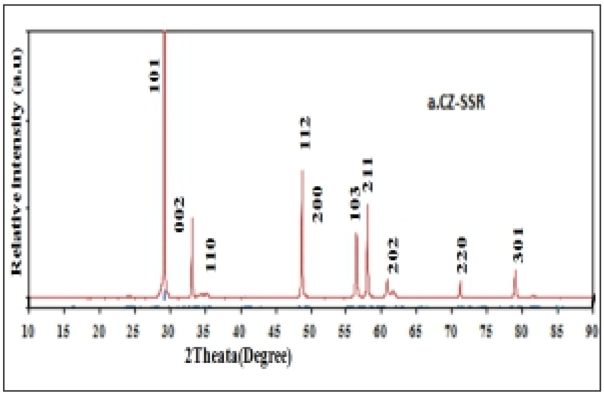

Figure 1: The XRD patterns of cerium zirconate - CZ-SSR .

3.2 UV–Vis diffuse reflectance characterization

The UV-Vis diffuse reflective properties of synthesized material strongly influence photocatalytic activity. Diffuse reflectance spectra of CZ-SSR that materials absorb in 400nm – 600nm range. DRS spectra of synthesizes material CZ-SSR in Figure 2. This result is in good consentient with the result of photocatalytic activity. Cerium zirconate, CZ-SSR absorb at 443nm which shows that catalyst is visible light active. The band gap of the samples was determined by the equation $Eg=1239.8/\lambda$, where Eg the band gap (eV) is and λ (nm) is the wavelength of the absorption edges in the spectrum34. The band gap energies of CZ-SST was estimated using UV-visible absorption spectra at λ onset 443 nm found to be about 2.79. This CZ-SSR can absorb in visible light .

Figure 2: DRS of cerium zirconate CZ-SSR.

4. Conclusions

Cerium zirconate, CZ-SSR was successfully synthesised via solid state calcination method and its crystalline nature was studied by XRD and their optical absorption spectra were recorded. The low band gap of CZ-SSR (2.79 eV) make it visible light active. The band gap energies of CZ-SST was estimated using UV-visible absorption spectra at λ onset 443nm found to be about 2.79. Thus CZ-SSR can absorb in visible light and can work in presence of solar spectrum.

References

1. C. G. Wu, C. C. Chao, F. T. Kuo, Catalysis Today, 97, (2004), 103.

2. M. E. Manrıquez, T. Lopez and R. Gomez, J. Navarrete, J.Mol. Catal. A., 220, (2004), 229.

3. J. Yang, J. M. F. Ferreira, Materials Research Bulletin, 33, (1998), 389.

4. P. Fornasiero, R. D. Monte, G. Rao, J. Kaspar, S. Meriani, A. Trovarelli and J. Graziani, J. Catal., 151, (1995), 168.

5. Y. Nagai, T. Yamamoto, T. Tanaka, S. Yoshida, T. Nonaka, T. Okamoto, A. Suda and M. Sugiura, Catal. Today, 74, (2002), 225.

6. J. J. Miao, H. Wang, Y. R. Li, J. M. Zhu, J. Zhu, J. Journal of Crystal Growth , 281, (2005), 525.

7. A. Fujishima and K. Honda, Nature, 238, (1972), 37.

8. A. Fujishima, K. Kohayakawa and K. Honda, 122, (1975), 1487.

9. W. Jaegermann, New York: Plenum Press, (1996), 1–185.

10. M. A. Fox and M. T. Dulay, , J. Photochemistry & Photobiology a-Chemistry, 98, (1996), 91.

11. A. Mills, S. LeHunte, J. Photochemistry & Photobiology a-Chemistry, 108, (1997), 1.

12. A. Troverelli, Catalysis by Ceria and Related Materials. London: World Scientific Publishing Company, (2002).

13. J. B. Zhong, G. Lintao Maochu, W. L. Jian, Z. M. Liu, M. Zhao and Yaoqiang C., J. Hazardous Materials, 143, (2007), 516.

14. C. Tiejun, L. Yuchao, P. Zhenshan, L. Yunfei, W. Zongyuan and D. Qian, J Environmental Sciences, 21, (2009), 997.

15. P. A. Deshpande, G. Madras, Chemical Engineering Journal, 158, (2010), 571.

16. B. M. Reddy, G. K. Reddy, A. Khan and I. Ganesh, J. Material Sci., 42(10), (2007), 3557.

17. T. Omata, K. Ono and S. Otsuka Yao Matsuo, Materials Transactions, 44 (8), (2003), 1620.

18. A. R. Gandhe and J. B. Fernandes, J. Solid State Chem., 178, (2005), 2953.

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