Investigation of Effect of Ceria on Phase Behavior and Photocatalytic Properties of Colloidal and Polymeric Nano-Titania

H. Sarpoolaki[1] V. Tajer-Kajinebaf[2] H. Heydari Boroujeni[3]

1- Introduction

Nano-titania, as a photocatalyst, has problems such as agglomeration of nanoparticles, phase transformation, reduction of surface area at high temperatures, recombination of electron-hole, lack of activity in the visible light range, problem of nanocatalyst recycling of aqueous suspension and so on. Studies have recently been carried out on the addition of rare earth elements such as Ln, Nd, Eu and Ce to titania, which reported activity in the visible light range. Rare earth elements mixed with titania show a red shift due to doping leading to the formation of inter band states. Moreover, addition of rare earth element is found to reduce recombination of the electrons and holes effectively by trapping them as well as by facilitating their faster movement along the surface of titania. Among the various rare earths, Ce has been reported to consistently show activity in visible region when mixed with titania. Among the lanthanide oxides, the catalytic properties of ceria have received much attention due to two features of (1) the redox couple Ce^{3+}/Ce^{4+} with the ability of ceria to shift between CeO_2 and Ce_2O_3 under oxidizing and reducing conditions; and (2) the easy formation of labile oxygen vacancies with the relatively high mobility of bulk oxygen species. The band-gap energy of titania and doped titania with ceria with concentrations of doping (1-10%) has been studied. As expected, the replacement of Ce decontamination in the TiO_2 structure will change the edge of the initial absorption to a higher wavelength, called the "red shift", and reduce the band-gap energy to a concentration of 9% of the dopant. Cerium is a particular lanthanide element and it has two stable oxidation states: Ce^{4+} and Ce^{3+}. As a result of an apparent difference in the ionic radius between Ce and Ti ions, CeO_2 and TiO_2 phases can coexist in the mixed oxides.

2- Experimental

Isopropoxide titanium, isopropanol, nitric acid 65%, chloridric acid 37%, cerium nitrate and deionized water were used as raw materials in this research. The preparation processes of the colloidal and polymeric titania-ceria composites are shown in Fig. 1 and Fig. 2, respectively. The molar ratio of Ce/Ti in the synthesis of titania-ceria sol was 0.05, 0.1 and 0.15.

3- Results and Discussion

SEM. Fig. 3 shows SEM images of the colloidal and polymeric samples. As shown, the particle size is below 100 nm for Ce-doped titania samples with different mole ratio. The small size of the crystallites leads to improved surface properties, increased surface area and photocatalytic properties.

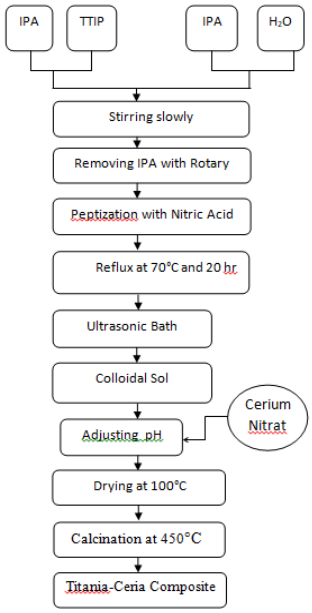

Fig. 1 Preparation process of colloidal titania-ceria composite

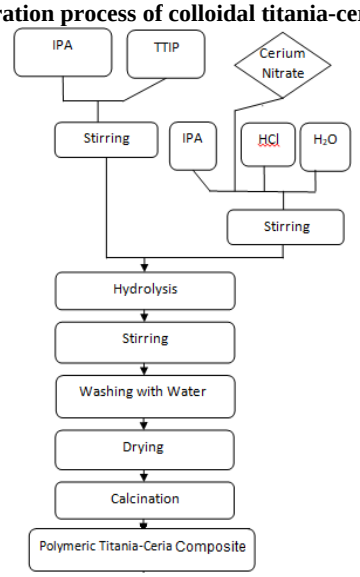

Fig. 2 Preparation process of polymeric titania-ceria composite

The XRD peaks at 2θ=25.241 and 47.981 belong to anatase TiO_2. The intensity of anatase TiO_2 peak decreased when ceria content increased.

Photocatalytic Properties. Fig. 6 shows photocatalytic activity of the colloidal samples with different Ce/Ti molar ratios. According to the results, the titania-ceria composites synthesized by the polymeric method showed better photocatalytic activity than the pure titania. Photocatalytic efficiency increased from 67.39% for pure polymeric titania to 81.39% for cerium-doped polymeric titania with a molar ratio of Ce/Ti equal to 0.05. The photocatalytic efficiency of samples with Ce/Ti molar ratio of 0.1 and 0.15 was calculated to be 80.25 and 79.34, respectively. Also, the

[1] Corresponding Author: Professor, School of Metallurgy and Materials Engineering, Iran University of Science and Technology, Tehran, Iran. Email: hsarpoolaky@iust.ac.ir

[2] Department of Materials Engineering, Takestan Branch, Islamic Azad University, Takestan, Iran.

[3] School of Metallurgy and Materials Engineering, Iran University of Science and Technology, Tehran, Iran.

colloidal titania-ceria composites exhibited more photocatalytic activity than pure titania in the early times of radiation. Fig. 7 compares photocatalytic efficiency of the colloidal samples.

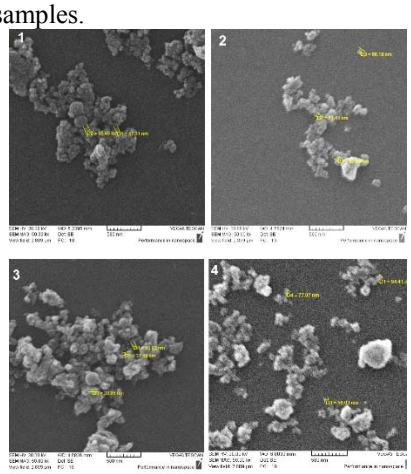

Fig. 3 SEM images of titania-ceria composites with molar ratio of Ce/Ti: 1) 0.05 (colloidal), 2) 0.1 (colloidal), 3) 0.05 (polymeric), 4) 0.1 (polymeric)

XRD. Fig. 4 shows the XRD patterns of colloidal samples.

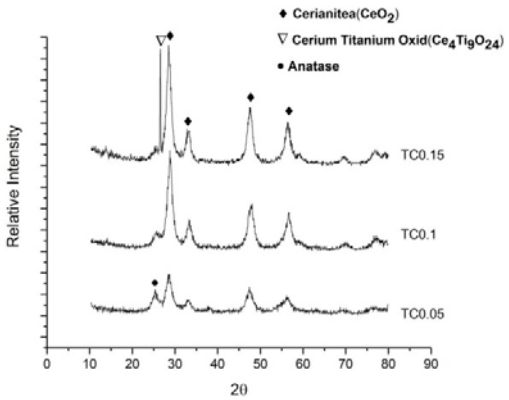

Fig. 4 XRD patterns of the colloidal samples calcined at 450°C

Fig. 5 compares the XRD patterns of the polymeric samples.

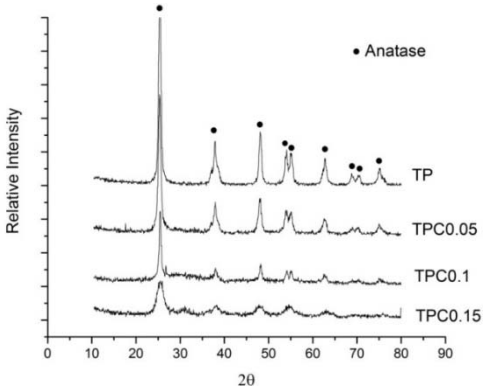

Fig. 5 XRD patterns of the polymeric samples calcined at 450°C

4- Conclusions

In this study, titania sol was separately synthesized by colloidal and polymeric methods. Titanium tetra-isopropoxide, isopropanol, cerium nitrate, deionized water; nitric acid and chloride acid were used as raw materials for the preparation of titania sols. Cerium-doped titania sols were prepared by different ratios of 0.05, 0.1 and 0.15 in colloidal and polymeric methods. According to the results, the titania-ceria composites produced by the polymeric method showed better photocatalytic activity than the pure titania. Photocatalytic efficiency increased from 67.39% for pure polymeric titania to 81.39% for cerium-doped polymeric titania with a molar ratio of Ce/Ti equal to 0.05. The photocatalytic efficiency of samples with Ce/Ti molar ratio of 0.1 and 0.15 was calculated to be 80.25 and 79.34, respectively. Also, the colloidal titania-ceria composites exhibited more photocatalytic activity than pure titania in the early times of radiation.

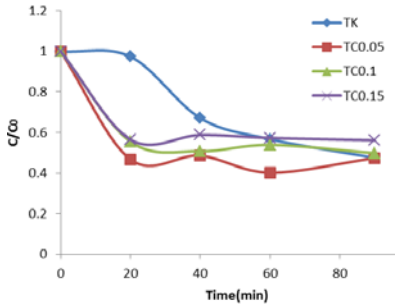

Fig. 6 Photocatalytic activity of the colloidal samples

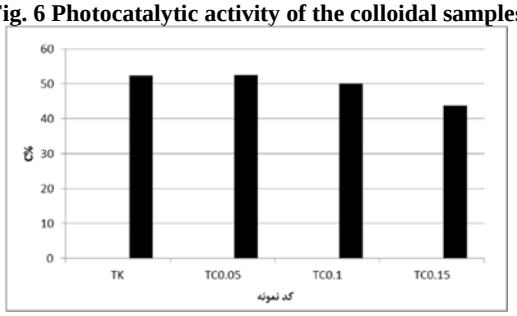

Fig. 7 Photocatalytic efficiency of the colloidal samples

Fig. 8 and Fig. 9 compare photocatalytic activity and efficiency of polymeric samples.

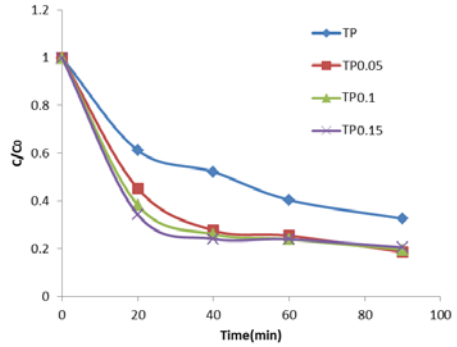

Fig. 8 Photocatalytic activity of the polymeric samples

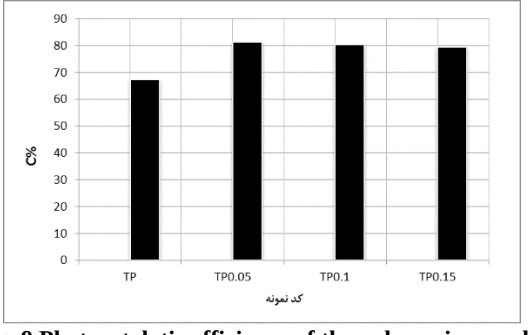

Fig. 9 Photocatalytic efficiency of the polymeric samples