

## Characterization and Decomposition of 2-Propanol By TiO<sub>2</sub> Doped with Organic Cerium Precursor

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**ABSTRACT:** Titanium oxide was synthesized by the sol-gel method, by first obtaining the TiO<sub>2</sub> xerogel precursor, on which, a dosage of Cerium 1 mol% was carried out using a Cerium non-nitrated precursor. Precursor was incorporated by both ultrasound and conventional stirring method. All three materials were characterized by Nitrogen physisorption, X-ray diffraction and SEM microscopy. Better results were reached with ultrasound assisted Cerium doping, obtaining materials with specific area from 59 to 96 m<sup>2</sup>/g; crystal size from 188 to 97 nm, and particles between 0.5-1 μm, which are smaller than those obtained with undoped TiO<sub>2</sub>. Through the conversion of 2-propanol at different temperatures, it was determined that, undoped TiO<sub>2</sub> has most acid sites and a small percentage of basic sites, because propylene production was higher compared to the acetone. The effect of Cerium was reflected in a slight increase in the production of acetone throughout the test presenting a maximum yield at 285 °C and then the acetone concentration was declining, leading to assume that at higher temperatures the basic character will disappear, and remaining acid sites.

**Keywords:** 2-Propanol Decomposition, Anatase, Titanium Oxide, Sol-Gel Method, Ultrasound Doping.

### I. INTRODUCTION

Titanium oxide had much attracted attention of researchers due to its acidity and basicity properties, which are adequate to carry out catalytic reactions that require these active sites types. As reported in literature, crystallographic anatase phase are more active than rutile phase mainly due to the surface acidity of this ceramic crystallographic phase, which tends to decrease when is synthesized at calcination temperatures above 500 °C. Actually, at 500 °C, titanium oxide has maximum amounts of weak, medium and strong acid sites, being medium and strong in higher proportions [1, 2].

Catalytic activity properties are strongly correlated to textural, structural and morphological properties. Ultrasound has widely been applied to enhance these physical properties, due to the physical phenomenon responsible for the sonochemical process, which is acoustic cavitation [3]. Acoustic cavitation produced by ultrasonic waves can strongly increase the surface area and mass transfer between two phases, both of which enhance better the diffusion coefficient on the interface mixing than conventional agitation [4]. During sonication, acoustic streaming leads to enhance the medium mixing and in addition the particle size of solids present in the medium reduces and the reactive surface area increases [5].

In some research works, is reported the influence of derived Cerium species doping on the catalytic activity of another ceramics materials tested in decomposition of alcohols, finding that activity was reduced [6], and can occurs an dehydrogenation pathway [7]. In particular, decomposition of 2-propanol is frequently used as a test to determine acid and basic properties of catalysts [8]. Propylene formation is attributed to the dehydration pathway by acid sites presence and acetone production is favored to the presence of basic sites from the dehydrogenation pathway [2].

In this contribution, titanium oxide was prepared by sol-gel method and doped with non-nitrated Cerium precursor using both ultrasound and a conventional dispersion method. Dopant and dispersion methods are proposed in order to determine the individual effect of Cerium ions over catalytic activity.

## II. EXPERIMENTAL

### 2.1. TiO<sub>2</sub> Synthesis

Titanium oxide was synthesized by sol-gel method using Titanium isopropoxide, isopropanol and distilled water under following molar ratios: (alcohol/alcoxide = 9) and (water/alcoxide = 6). In a tree neck glass reactor, placed into a humidity-free chamber, titanium isopropoxide and  $\frac{3}{4}$  of calculated total volume of isopropanol were weighed. The reactor with the mixture was kept with magnetic stirring by 1 hour at 65 °C. Then, hydrolysis step started adding to the former drop by drop a solution of water and the remaining  $\frac{1}{4}$  part of isopropanol to a rate of 1 mL/min. Hydrolysis time was 2 hours. White gel was obtained which was aged over 72 hours. After aging step, synthesis solvent was removed from aged gel obtaining a wet white powder. Obtained material was dried at 120 °C during 24 hours. Finally, the dried powder was calcined at 500 °C using a heating rate of 3 °C/min.

### 2.2. Ultrasound dispersion method (UDM)

Cerium acetylacetonate was used as source of Cerium ions. Needed amount of Cerium precursor was weighed to introduce theoretical 1 mol % of Cerium ions according to (Ce/(Ti+Ce)) molar ratio and was ultrasonically dispersed in methanol over 60 minutes. Dried xerogel was added to the former and mixed with ultrasound stirring to ensure the homogeneous dispersion of Cerium ions. Later, synthesis solvent was evaporated by drying treatment at 120°C during 24 hours and finally, dried powder was calcined at 500 °C over 6 hours using a heating rate of 3 °C/min.

### 2.3. Magnetic dispersion method (MDM)

This method is similar to the above explained. Cerium precursor was dispersed, at the same molar ratio, in isopropanol using ultrasonic stirring. Unlike the above dispersion method, magnetic stirring was employed to blend dried xerogel and Cerium precursor and isopropanol solution. Synthesis solvent was evaporated by the same drying treatment at 120 °C along 24 hours. By last, dried Cerium doped material was calcined at 500 °C during 24 hours using a heating rate of 3 °C/min.

### 2.4. Characterization of synthesized materials

The textural properties were analyzed by nitrogen physisorption (BET and BJH models) using a Quantachrome Instruments Autosorb-iQ device. X-ray diffraction patterns (XRD) were performed in a Brucker AXS D8 Advance diffractometer. Scanning Electron Microscopy was performed on a JEOL JSM-7600F microscope for study the morphology and elemental analysis with energy dispersive spectroscopy (EDS) attached to microscope. The decomposition of 2-propanol was carried out using a handmade microplant coupled a Varian 3400 gas chromatograph. Flow of nitrogen of 20 mL/min as was employed carrier gas and saturated of 2-propanol at 10 °C. In a U-like tubular glass reactor was deposited 50 mg of each synthesized material and operation temperatures range was from 150-310 °C.

## III. RESULTS AND DISCUSSION

### 3.1. Structural properties

According to the Fig. 1, anatase phase was detected in all prepared materials, which is identified with (101) crystallographic peak at 25.3 on the 2 theta scale [9, 10]. Regarding to Cerium doped samples, intensity of anatase peaks was decreased. It means that, incorporation of Cerium ions inhibit TiO<sub>2</sub> nanoparticles sintering and crystallinity was minimized. Comparing both UDM and MDM doping methods, it can be notice the inhibited crystal growth but, with ultrasound assisted method, crystallinity is decreased more than with conventional stirring method (MDM), obtaining smaller particles compared to undoped TiO<sub>2</sub>. In table 1 are presented the crystal size of each synthesized material, calculated by Scherrer equation [11] from width main peak (101), whose values, confirm the existence of nanoparticles obtained by ultrasound assisted doping method.

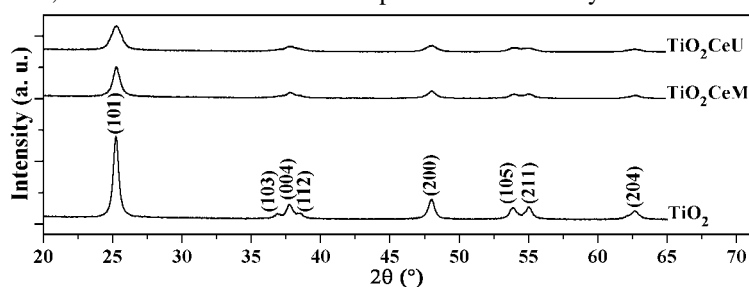


Figure 1. X-ray diffraction patterns of un-doped and Cerium doped TiO<sub>2</sub> materials.

### 3.2. Textural Properties

As shown in Table 1, Cerium doping methods modified specific surface area, pore size distribution and pore total volume of titanium oxide. It can be observe that the use of ultrasound doping method incremented the specific area more than magnetic stirring doping method as well as the total pore volume. Besides, pore size distribution obtained with magnetic doping method was bimodal arrangement while with ultrasound method was unimodal arrangement as shown in Fig. 2. These results are in agreement with XRD analyses, which indicate that Cerium doping inhibits the sintering of TiO<sub>2</sub> nanoparticles after calcination treatment obtaining good textural properties. This means that, using UDM doping method, textural properties can be improve more than using the other conventional doping method (MDM), because applying ultrasound radiation, acoustic cavitation produced by ultrasonic waves can greatly increase the surface area, as well as mass transfer between dopant agent and TiO<sub>2</sub> nanoparticles [4], resulting in rapid formation of nanoparticles with narrow size distributions.

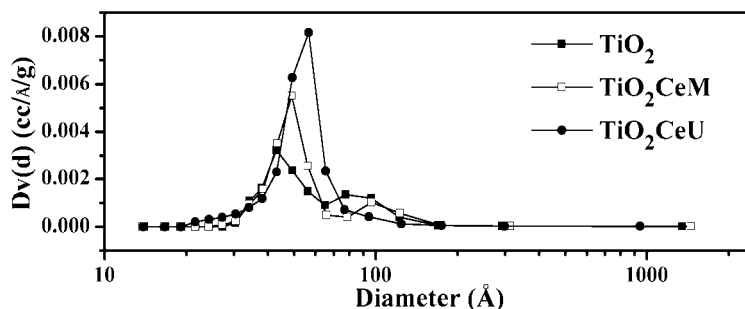


Figure 2. Pore size distribution of all synthesized materials.

Table 1. Textural properties of all TiO<sub>2</sub> based materials.

Material	Specific Surface Area (m <sup>2</sup> /g)	Pore Diameter (Å)		Total Adsorbed Volume (cc/g)	Ce EDS weight (mol %)	Crystal size (nm)
		43	77			
Pure TiO <sub>2</sub>	59	43	77	91	---	188
TiO <sub>2</sub> Ce1.0 M	65	49	96	95	0.89	138
TiO <sub>2</sub> Ce1.0 U	93	57		121	0.72	97

### 3.3. Morphology properties

In Fig. 3, SEM micrographs of all prepared materials are depicted, as well as the EDS analysis of Cerium doped material prepared by ultrasound method. In pure TiO<sub>2</sub> and TiO<sub>2</sub>CeUM micrographs, clusters from 2 to 3 μm were formed drawing semispherical shapes and it can be observe heterogeneous particle diameters. In TiO<sub>2</sub>CeU, clusters with semispherical shapes were also observed but clustered particles diameter is about 0.2 μm. These results are in good agreement with XRD and BET techniques which suggested that, sintering process is delayed with Cerium doping and here is very clear to observe this behavior. In table 1, EDS analysis is presented, evidencing the presence of Cerium ions. The percentage determined by this technique is not very representative, because the technique makes the analysis in a very specific area.

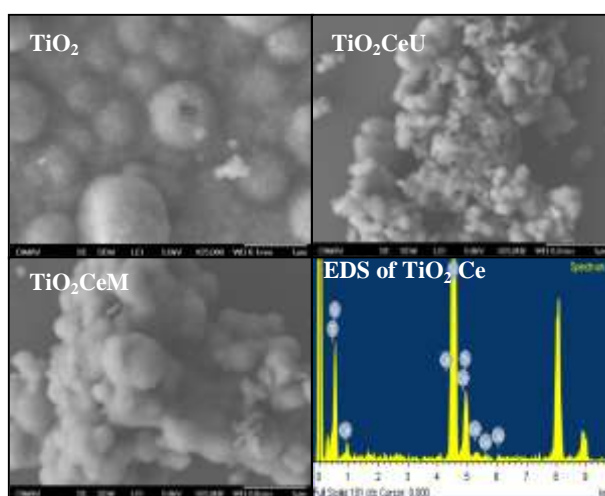


Figure 3. SEM micrographs of TiO<sub>2</sub> based materials and EDS analysis of Cerium-doped material.

### 3.4. Decomposition of 2-propanol

In Fig. 4, conversion of 2-propanol versus reaction temperature using each synthesized material are plotted. All prepared materials performed similar behaviors between 150 and 230 °C, but, from 230-280 °C is appreciated a little effect of Cerium doping dispersion method over 2-propanol conversion. At temperatures above 285 °C, conversion values are greater than 99%. Undoped TiO<sub>2</sub> and TiO<sub>2</sub>CeU conversion profiles are very similar, which means, it could be assumed that active sites density was not modified with the UDM method. Conversion profile corresponding to TiO<sub>2</sub>CeM is shifted towards higher temperatures, indicating that active sites are decreased employing MDM method to dope Cerium ions in TiO<sub>2</sub>. These behaviors are correlated to morphology results showed above in SEM images, due to, when Cerium ions are incorporated using ultrasound assisted method, particles with less tendency to agglomerate are obtained, favoring the textural properties.

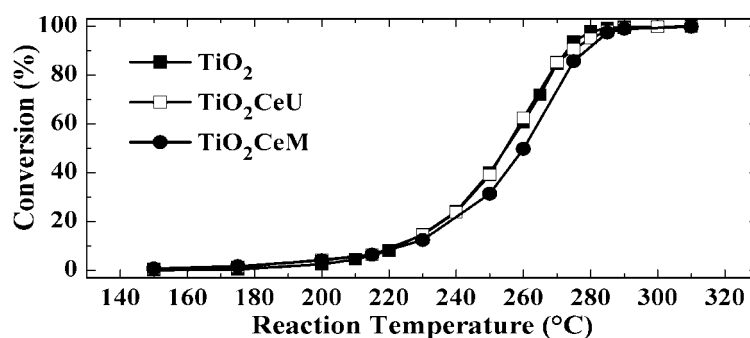


Figure 4. 2-propanol conversion profiles as temperature function using undoped and Cerium doped TiO<sub>2</sub> materials.

Catalytic decomposition of 2-propanol is a routine test very applied to determine acidity grade of prepared catalysts according to the formation products. Propylene formation is due to the acid sites presence and acetone from basic sites [2]. In Fig. 5, concentration profiles of acetone and propylene are presented using all prepared materials as catalysts. In Fig. 5A is notice that with both UDM and MDM methods, Cerium presence increases the acetone formation rate along entire test, indicating that there is an increment of TiO<sub>2</sub> basicity using both Cerium doping methods. There is a maximum value of acetone concentration around 285 °C in all cases and then, basic nature begins to decrease until the end of the test at 310 °C. According to these results, at higher temperatures of 310°C, basicity properties could be completely disappears. Acetone formation is due to the dehydrogenation of 2-propanol, and it assumed by researchers that, dehydrogenation pathway is carried out by concerted mechanism in which, involving both acid and basic sites in materials with metallic properties [12-14]. Regarding to the propylene conversion profiles showed in Fig. 5B, concentration values are greater than those obtained of acetone using all prepared materials. It means that, acid properties are predominant over TiO<sub>2</sub> active surface remaining at temperatures higher than 310 °C. With these tests, it could assume that with higher loads of Cerium ions the basic nature can be increase. Similar experiments are reported by Bedia et al [15] using different materials based-on activated carbon, finding similar behaviors in 2-propanol decomposition tests. In this sense, it could be assume that, propylene is formed by dehydration route of 2-propanol, which is due to two Langmuir–Hinshelwood elimination mechanisms, E1 and E2 type [15]. E1 mechanism type involves the initial protonation of the OH group in the molecule of 2-propanol, followed by CO bond cleavage, producing a carbocation and a water molecule as leaving group. The formation of the propylene molecule is supposed to occur in two sequential elementary steps. In E2 mechanism type, the formation of the propylene molecule is supposed to occur in a single concerted step [13-15].

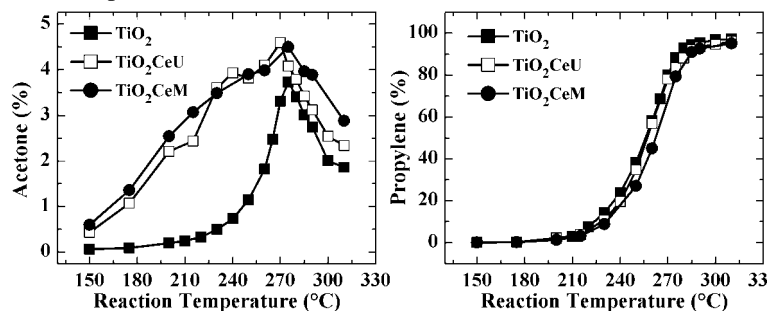


Figure 5. Acetone and Propylene formation derived from 2-propanol decomposition at different reaction temperatures.

#### IV. CONCLUSION

Titanium oxide was successfully synthesized by the sol-gel method and doped with 1 mol% of Cerium ions. It was noticed an individual effect of Cerium ions on the textural, structural and morphological properties, as well as in the catalytic activity of titanium oxide. The best method to disperse the dopant agent was the Ultrasound assisted method, obtaining high specific area, lower crystallinity and smaller particle size. The catalytic activity of 2-propanol showed that acetone production was higher using Cerium doped materials, however propylene production was not affected by the introduction of cerium by ultrasound method, probably because the density of sites acids was not affected significantly.

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#### REFERENCES

- [1]. K. Tanabe, "Chapter 4 - Acid and Base Centres: Their Structure and Acid-Base Properties," Solid Acids and Bases, pp. 45–101, 1970.
- [2]. J. E. Rekoske and M. A. Barteau, Kinetics and Selectivity of 2-Propanol Conversion on Oxidized Anatase TiO<sub>2</sub>, Journal of Catalysis, 165(1), 1997, 57–72.
- [3]. A. Gedanken, Using sonochemistry for the fabrication of nanomaterials, Ultrasonics Sonochemistry, 11(2), 2004, 47–55.
- [4]. N. Ghows and M. H. Entezari, Ultrasound with low intensity assisted the synthesis of nanocrystalline TiO<sub>2</sub> without calcination, Ultrasonics Sonochemistry, 17(5), 2010, 878–883.
- [5]. M. H. Entezari, N. Ghows, and M. Chamsaz, Ultrasound facilitates and improves removal of Cd(II) from aqueous solution by the discarded tire rubber, Journal of Hazardous. Materials, 131(1–3), 2006, 84–89.
- [6]. R. S. Rodrigo, J. M. H. Enríquez, A. C. Mares, J. A. M. Banda, R. G. Alamilla, M. Picquart, and T. L. Goerne, Effect of CeO<sub>2</sub> on the textural and acid properties of ZrO<sub>2</sub>-SO<sub>4</sub>-, Catalysis Today, 107-108, 2005, 838–843.
- [7]. M. I. Zaki and N. Sheppard, An infrared spectroscopic study of the adsorption and mechanism of surface reactions of 2-propanol on ceria, Journal of Catalysis, 80(1), 1983, 114–122.
- [8]. A. Hanprasopwattana, S. Srinivasan, A. G. Sault, and A. K. Datye, Titania coatings on monodisperse silica spheres (characterization using 2-propanol dehydration and TEM), Langmuir, 12(13), 1996, 3173–3179.
- [9]. J. Matos, K. Quintana, and A. García, Influence of H-Type and L-Type Activated Carbon in the Photodegradation of Methylene Blue and Phenol under UV and Visible Light Irradiated TiO<sub>2</sub>, Modern Research in Catalysis, 2012(1), 2012, 1–9.
- [10]. N. A. Quiroz, J. D. Ramos Gutierrez, S. Silva Martínez, and C. Lizama Bahena, Degradation of Gesaprim Herbicide by Heterogeneous Photocatalysis Using Fe-Doped TiO<sub>2</sub>, International Journal of Geoscience, 2(4), 2011, 669–675.
- [11]. Charanpahari, S. S. Umare, and R. Sasikala, "Effect of Ce, N and S multi-doping on the photocatalytic activity of TiO<sub>2</sub>," Applied Surface Science, 282, 2013, 408–414.
- [12]. C. Martín, I. Martín, V. Rives, B. Grzybowska, and I. Gressel, A FTIR spectroscopy study of isopropanol reactivity on alkali-metal-doped MoO<sub>3</sub>/TiO<sub>2</sub> catalysts, Spectrochimica Acta Part A, 52(7), 1996, 733–740.
- [13]. A. Gervasini and A. Auroux, Acidity and Basicity of Metal Oxide Surfaces II. Determination by Catalytic Decomposition of Isopropanol, Journal of Catalysis, 198, 1991, 190–198.
- [14]. S. Al-Kandari, H. Al-Kandari, A. M. Mohamed, F. Al-Kharafi, and A. Katrib, Catalytic Active Sites in Molybdenum Based Catalysts, Modern Research in Catalysis, 2013(2), 2013, 1–7.
- [15]. J. Bedia, R. Ruiz-Rosas, J. Rodríguez-Mirasol, and T. Cordero, A kinetic study of 2-propanol dehydration on carbon acid catalysts, Journal of Catalysis, 271(1), 2010, 33–42.