Spray dried Cerium doped TiO_2: photocatalytic activity for NO_x and Ethanol abatement by visible light irradiation

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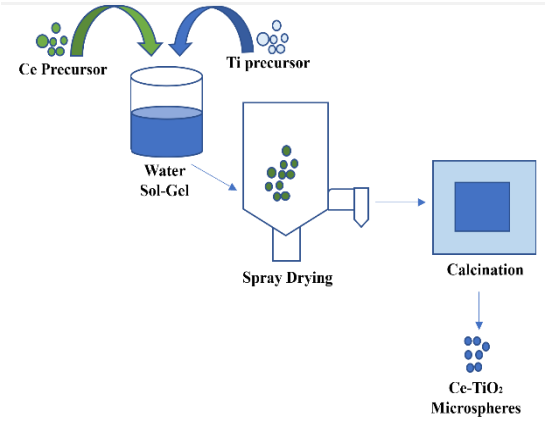

Nitrogen oxides (NO, NO_2) and volatile organic compounds (VOCs) are serious primary air pollutants responsible for acid rains and smog, respectively. TiO_2 is a well-known photocatalyst for their abatement due to its excellent photocatalytic performance in UV light range. By modifying TiO_2 lattice, it has been enabled a high visible light response. In this work, cerium was employed as a dopant in different weight ratios (0-1.0 wt.% Ce-TiO_2), and all the catalysts were synthesized by an aqueous-based sol-gel method followed by an unconventional drying procedure. The $Ce_{0.8}$-TiO_2 catalyst showed the highest degradation efficiency for both NOx (26±1.%) and ethanol degradation (23±1%) under visible light irradiation, 2.8 times and 1.5 times higher than TiO_2 activity.

Introduction

Air quality has received considerable attention in the last decades since many inorganic and organic pollutants impact human health [1]. Photocatalysis has been proposed as an alternative for their abatement, taking advantage of natural and artificial light. Titanium dioxide is one of the most outstanding photocatalyst for the degradation of NO_x and VOC_s. However, its wide energy bandgap (3.2 eV) makes it only effective under UV light [2]. Therefore, many strategies for extending the wavelength range to the visible part of the electromagnetic spectrum have emerged such as ion doping [3]. In this work, it was studied the incorporation of Ce, a rare earth metal, hosted in TiO_2 anatase structure in 0%, 0.2%, 0.4%, 0.6%, 0.8% and 1.0% (w/w). Bare TiO_2 and Ce-doped TiO_2 photocatalysts were synthesized through a water-based sol gel method followed by spray drying. The Ce-doped TiO_2 microspheres were tested towards the NO_x and ethanol degradation under LED light [4].

Methods

The photocatalytic degradation of NOx gases was carried out in a 20 L Pyrex glass cylindrical batch reactor. The initial concentration of NO_x was 500 ± 50 ppb. The photocatalytic tests were performed at room temperature for 3 hours under LED light (MW mean well, 350 mA, 16.8W, 400-700 nm) yielding an intensity of 1000 lx on the catalyst surface. The NO and NO_2 concentrations were measured after 30, 60, and 180 min of irradiation by a detector based on chemiluminescence technology (Ecotech Serinus 40NOx).

On the other hand, the photodegradation of ethanol was performed in a 5L Pyrex glass reactor connected to a GC-FID (Agilent 3000A Micro-GC) for monitoring the concentration of organic pollutant and its degradation products. A fixed amount of ethanol was introduced in the reactor and volatized to obtain a vapor concentration of 200 ppm. The surface catalyst was irradiated by a LED light (MW mean well, 350 mA, 16.8W, 400-700 nm) yielding an intensity of 5200 lx. The vapor analyses were carried out after 30, 60, and 180 min of light irradiation.

Results

Characterization

The XRD pattern (data not shown) evidenced the typical diffraction peaks of TiO_2 in anatase phase. Due to the low amount of Ce load, the Ce peaks could not be observed in the diffractogram.

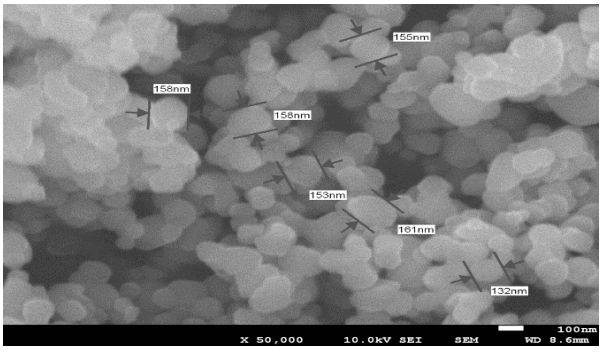

Fig 1. SEM image of $Ce_{0.8}$-TiO_2 microspheres.

Moreover, the energy band gaps (Table 1) were reduced from 3.2 to 2.8 eV as the load of dopant increased, demonstrating a broader absorption in the visible spectrum. On the other hand, SEM images (Figure 1) evidenced the spherical shape and agglomeration of $Ce_{0.8}TiO_2$ particles with an average particle dimension *ca.* 153 nm within micrometric system.

Table 1 BET surface area and energy band gap of synthesized photocatalysts.

Sample	BET surface area (m^2/g)	Band gap (eV)
TiO_2	12.2	3.2
$Ce_{0.2}$- TiO_2	13.7	3.18
$Ce_{0.4}$- TiO_2	13.5	3.1
$Ce_{0.6}$- TiO_2	15.2	3.0
$Ce_{0.8}$- TiO_2	16.1	2.8
$Ce_{1.0}$- TiO_2	14.5	3.0

Photocatalytic performance

Figure 2 shows the photocatalytic degradation of NO_x by the synthesized materials prepared under visible light irradiation. Comparing to pristine TiO_2, all Ce-doped catalysts showed enhanced photocatalytic activity. The highest value was obtained by $Ce_{0.8}TiO_2$ and $Ce_{1.0}TiO_2$ (26±1%), which was 2.8 times greater than bare TiO_2 after 3 hours of irradiation.

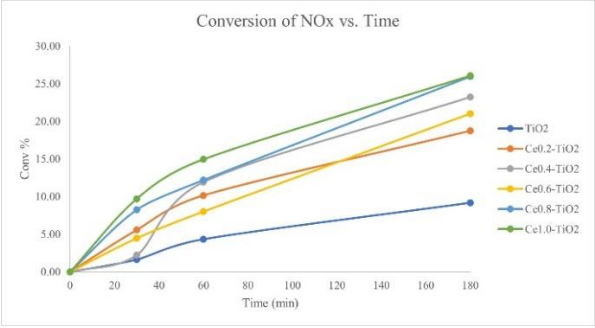

Fig. 2 Evaluation of photocatalytic efficiency of Ce-doped TiO_2 catalysts for NOx degradation under visible light.

Furthermore, Figure 3 illustrates the photocatalytic degradation of ethanol under LED light by Ce_x-TiO_2 samples. The bare TiO_2 achieved 15 (± 1) % of photodegradation, whereas, as observed for NO_x abatement, all the Ce-doped TiO_2 samples exhibited greater performance, specially $Ce_{0.8}$-TiO_2 (23 ± 1%).

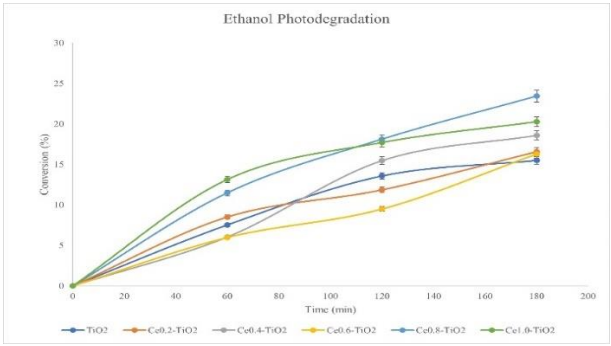

Fig. 3 Visible photocatalytic activity of the synthesized Ce-doped TiO_2 catalysts for Ethanol degradation in gas phase under LED light.

These behaviors were attributed to the narrow bandgap due to the introduction of Ce ions into the lattice of TiO_2 confirmed by UV-DRS (Table 1) and XPS (data not shown). Moreover, Ce ions can act as electron trap center decreasing the recombination rate of e^-/h^+ charges [5].

Conclusions

In summary, rare earth doped TiO_2 photocatalysts with different weight ratios (Cerium percentage from 0 wt.% to 1.0 wt.%) were effective synthesized by an environmentally friendly sol-gel technique followed by spray drying. The photocatalytic activity of these materials were assessed towards the degradation of NO_x gases and ethanol under visible light, resulting in an enhancement in the activity after the introduction of Ce into the TiO_2 lattice. The $Ce_{0.8}$-TiO_2 photocatalyst demonstrated the best photocatalytic efficiencies in both scenarios, improving 2.8 times the activity for NO_x degradation and 1.5 times for ethanol abatement compared to bare TiO_2. The present work suggests a new method of synthesis for doping semiconductors with an unconventional, simple and cost-effective operation procedure that could be in consideration for industrial applications.

Keywords: Cerium-doped TiO_2, nitrogen oxides, ethanol, photocatalysis, spray drying.

References

[1] Ren. Hangjuan, Koshy. Pramod, Chen. Wen-fan, Qi. Journal of Hazardous Materials 325 (2016), 340-366.
[2] Angelo. Joana, Andrade. Luisa, Madeira. Luis, Journal of Environmental Management, 129 (2013), 522-539.
[3] Mohtar, Safia S., Farhana Aziz, Ahmad F. Ismail, Catalyst, 11 (2021), 1160.
[4] Boffitto. Daria Camilla, Khan. Hayat, Gar Alalm. Mohamed, Journal of Environmental Chemical Engineering , 9 (2021), 106813.
[5] Jimin. Xie, Deli. Jiang, Min. Chen, Colloids and Surfaces A: Physicochemical and Engineering Aspects, (2010), 372 (1-3).