

1 Low-cerium-content catalysts supported on silica and
2 alumina for the photocatalytic decomposition of
3 methyl red

4
5
6
7
8
9
10
11
12
13 *A.I. Mártir Bueno, A. Maroto-Valiente, and J. Alvarez-Rodríguez**

14 Dpto. Química Inorgánica y Química Técnica,
15 Facultad de Ciencias (UNED), 28232
16 Las Rozas de Madrid (Spain)
17

18 *corresponding author:

19 Email: jalvarez@ccia.uned.es

20 Tfn: +34 91 398 7241
21
22
23

ABSTRACT

The photocatalytic degradation of azo dyes in wastewater presents a critical environmental challenge, particularly given the persistence and toxicity of compounds such as methyl red (MR). In this study, CeO₂-based catalysts were synthesized by dispersing 5 wt% cerium nitrate onto silica gel and α -alumina supports via incipient wetness impregnation, followed by controlled calcination at 110, 200, and 400 °C. Comprehensive characterization by XRD, TGA, Raman spectroscopy, BET, UV–Vis diffuse reflectance, and XPS confirmed the formation of highly dispersed, non-stoichiometric cerium oxide species with variable Ce³⁺/Ce⁴⁺ ratios and surface oxygen vacancy densities, dependent on the support and thermal treatment. Photocatalytic performance was evaluated through the degradation of MR in aqueous solution under 365 nm LED irradiation. Alumina-supported catalysts exhibited the highest activity, with 5CeAl200 achieving up to 51% MR conversion in one hour, outperforming both pure CeO₂ at equivalent Ce loading and the silica-supported series. Optimal activity correlated not with surface area or Ce³⁺ content alone, but with the coexistence of Ce³⁺/Ce⁴⁺ species and the associated formation of oxygen vacancies, as evidenced by Raman and XPS analysis. These findings demonstrate that rational dispersion of cerium on inert oxide supports combined with mild thermal activation provides a sustainable and efficient alternative to more complex multicomponent or chemically assisted systems, enabling significant cerium savings without sacrificing catalytic performance.

KEYWORDS: CeO₂, Photocatalysis, Azo Dyes degradation, Ce³⁺/Ce⁴⁺ redox balance.

1.INTRODUCTION

The accumulation of pollutants in the environment because of dyes and organic pigments has emerged as a pressing concern, prompting investigators to focus on air purification, water disinfection and hazardous waste remediations in wastewater [1-5].

However, Cerium oxide (CeO_2) has been identified as an effective photocatalyst for the degradation of synthetic azo dyes [6], such as methyl red, despite cerium's relative abundance among rare earth elements, its classification as a critical material by the European Union and the United States highlights the need to reconsider its use, particularly in photocatalysis [7].

Water contamination by synthetic dyes in industrial effluents poses a serious environmental and public health challenge [8-11]. These dyes, often discharged without adequate treatment, are detrimental to both aquatic organisms and human health. Among them, azo dyes, including methyl red[12], are particularly hazardous due to their carcinogenic and mutagenic properties and their capacity to release toxic aromatic amines [13-15]. This study focuses on the degradation of persistent organic pollutants used in the textile industry and evaluates the viability of the photocatalyst under environmentally relevant conditions, with an emphasis on stability at controlled pH levels and in water matrices that simulate real industrial wastewater [16-18].

Recent developments in different visible light-responsive heterojunction systems are discussed for metal oxide–metal oxide and metal oxide–non-metal oxide heterojunctions [19-21]. The preparation of cerium oxide-based photocatalysts supported on silica and alumina is motivated by their potential to enhance photocatalytic efficiency through improved dispersion [22], increased surface area, and enhanced stability under reaction conditions.

In this work, cerium oxide-based photocatalysts were developed by dispersing CeO_2 onto alumina and silica supports, aiming to reduce the total cerium content while maintaining high

photocatalytic performance. The materials were thoroughly characterized using X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) surface area analysis, thermogravimetric analysis (TGA), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). Photocatalytic activity was evaluated through the degradation of methyl red in aqueous solution under conditions representative of industrial wastewater treatment. The interaction between CeO₂ and the oxide supports promotes enhanced charge separation and inhibits electron–hole recombination, while also modifying light absorption characteristics. Particular attention was given to the influence of the support nature and thermal treatment on the generation of oxygen vacancies and the Ce³⁺/Ce⁴⁺ redox ratio, which are known to be key factors in reactive oxygen species (ROS) formation. The results demonstrate that highly dispersed CeO₂ catalysts can achieve efficient degradation of persistent organic pollutants even at reduced cerium loadings, providing a more sustainable strategy for photocatalytic water treatment aligned with the goals of resource optimization and environmental protection.

2.EXPERIMENTAL

Initial samples were prepared following the same procedure of incipient wetness impregnation. Portions of 10 g of support, either silica gel or α -alumina, were gradually impregnated with 10 mL of an aqueous solution of Ce(NO₃)₃·6H₂O, supplied by Sigma-Aldrich, at a concentration necessary to achieve a final loading of 5% by weight of cerium in the sample. After impregnation, the samples were dried at 383 K for 12 hours to remove residual moisture. Once dried, the samples were labelled as 5CeSi (for silica gel) and 5CeAl (for alumina) and stored in sealed glass jars to prevent contamination.

Subsequently, the samples underwent thermal activation via calcination at three different temperatures: 110°C, 200°C, and 400°C. The thermal treatments were carried out in a tubular

furnace under a flow of synthetic air (100 mL/min) to ensure uniform heating and oxidation of the cerium precursor. Each sample was held at the designated temperature for 4 hours to allow for complete stabilization of the cerium oxide species. The samples were then cooled to room temperature under the same air flow.

For identification purposes, the samples were labelled according to the temperature at which they were treated: 5CeAl110, 5CeAl200, and 5CeAl400 for the alumina-supported catalysts, and similarly, 5CeSi110, 5CeSi200, and 5CeSi400 for the silica-supported catalysts. These labels reflect the specific thermal conditions used, which are expected to influence the structural properties and catalytic activity of the cerium oxide dispersed on the supports.

The crystalline structure of the samples was identified using X-ray diffractograms, measured with a PANalytical X'Pert MPD diffractometer equipped with Cu K α radiation (operating at 40 kV, 45 mA, wavelength $\lambda = 0.15418$ nm). The diffraction patterns were collected over a 2θ range of 5° to 50° , with a step size of 0.05° and a scan rate of 1° min^{-1} . This analysis provided insight into the crystalline phases present in the samples and any changes in crystallinity due to thermal treatment.

The thermal stability of the samples was assessed using thermogravimetric analysis (TGA) on a TA Instruments SDT Q600 thermobalance. The measurements were conducted under an air flow of 100 mL min^{-1} , heating the samples from 313 K to 1100 K at a heating rate of 10 K min^{-1} . This allowed for the determination of weight loss as a function of temperature, providing information on the decomposition of the cerium precursor, phase transitions, and thermal stability of the supports. Based on the mass loss transitions observed in the initial sample, specific temperatures were selected for the subsequent thermal treatments. These temperatures were chosen from the thermogram of the initial samples of 5CeSi and 5CeAl to isolate distinct surface cerium species at

different stages of the decomposition process, allowing for the controlled preparation of each catalyst with unique surface characteristics. This strategy aimed to explore the effect of thermal activation on the formation and distribution of cerium oxide species, potentially enhancing catalytic performance through the stabilization of different cerium phases in each catalyst.

The textural properties of the samples, including surface area and porosity, were determined from nitrogen adsorption isotherms using the BET (Brunauer-Emmett-Teller) method. Measurements were performed on a Micromeritics ASAP2020 unit, with 0.15 g of sample degassed under vacuum at 423 K for 10 hours to remove moisture and other adsorbed gases. This analysis provided data on the specific surface area and pore size distribution of the samples, critical factors influencing catalytic activity.

Diffuse reflectance UV–vis (DR UV–vis) spectra were recorded to investigate the optical absorption properties of the synthesized materials. Measurements were performed using a Varian Cary I spectrophotometer equipped with an integrating sphere, using BaSO₄ as a non-absorbing reflectance standard. Approximately 0.15 g of finely powdered sample was placed in the sample holder, and the diffuse reflectance was measured in the 250–800 nm range. The obtained reflectance data, R, were converted into the Kubelka–Munk function, F(R), using the equation:

$$F(R) = \frac{(1 - R)^2}{2R}$$

Assuming direct allowed transitions, the optical band gap was estimated by applying the Tauc formalism:

$$[F(R)h\nu]^2 = A[h\nu - E_g]$$

The linear portion of the Tauc plot was extrapolated to the abscissa to estimate the band gap energy.

Raman spectroscopy was carried out to identify surface and bulk chemical species present in the synthesized catalysts, such as cerium oxide (CeO_2) and residual nitrate groups. No mechanical or chemical pre-treatment was applied to the samples to avoid altering their surface chemistry. Spectra were recorded using a B&W Tek Raman spectrometer equipped with a 785 nm diode laser. The measurements were performed in the spectral range of 300–1800 cm^{-1} , with a laser power set to 50 mW to ensure adequate signal intensity while preventing sample damage.

X-ray photoelectron spectra were recorded with a multi-technique ultra-high vacuum system equipped with a PHOIBOS 150 MCD-7 energy analyzer (SPECES GmbH), with unmonochromated $\text{MgK}\alpha$ radiation (200 W) as the excitation source. Prior to the measurements, the samples were degassed for 24 hours at a residual pressure below 10^{-10} mbar. The binding energies (BEs) were calibrated using the Si2p peak at 103.3 eV for silica-supported samples or the Al2p peak at 74.0 eV for alumina-supported samples. The instrument's error in energy determinations was less than 0.01 eV. XPS provided detailed information on the oxidation states of cerium and other surface elements, as well as their relative atomic concentrations.

The photocatalytic activity of the synthesized catalysts in the decomposition of methyl red (MR) was evaluated in a batch-type photocatalytic reactor. The reactor was irradiated with UV light ($\lambda = 365$ nm) using an Asynt-LightSyn Illumin8 photoreactor equipped with a 10W LED light source. The reaction was carried out in an aqueous solution of MR dye (1.8 mg/L) at pH 11, thermostated at 303 K, and continuously stirred at 500 rpm. A 10 mg portion of the photocatalyst was suspended in 10 mL of the MR solution. Before illumination, the mixture was stirred under dark conditions for 10 minutes to establish adsorption/desorption equilibrium between the catalyst and the MR molecules.

After an initial step program of 30 min for adsorption and equilibration period, the catalyst suspension was exposed to light ($\lambda = 365$ nm), and the decomposition of the dye was monitored. After the reaction, the photo-reacted suspension was centrifuged at 4000 rpm for 30 minutes to separate the photocatalyst from the solution. The absorbance of the solution was measured using a UV-visible spectrophotometer (Jasco V-530) in the wavelength range of 200–800 nm, with the absorbance at $\lambda = 417$ nm used to monitor the concentration of MR during the photocatalytic degradation.

The conversion of the compound during the photodegradation reaction was calculated using the standard formula: $X(\%) = ((C_0 - C_t)/C_0) \cdot 100$; where C_0 is the initial concentration of the compound in solution (measured before irradiation), and C_t is the concentration measured after a specific reaction time (t). The concentrations (C_0 and C_t) were determined using UV-Vis spectroscopy with a standard calibration curve based on absorption data.

3. RESULTS AND DISCUSSION

The incorporation of cerium nitrate (III) into α -alumina and silica gel supports was studied using thermogravimetric analysis (TGA), revealing distinct differences in the interaction of the cerium precursor with each support material. The thermograms of the α -alumina-supported samples and the silica gel-supported samples showed weight loss profiles that diverged notably from the pure cerium nitrate decomposition thermogram (Figure 1), suggesting that the nature of the support also influences the thermal decomposition of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$.

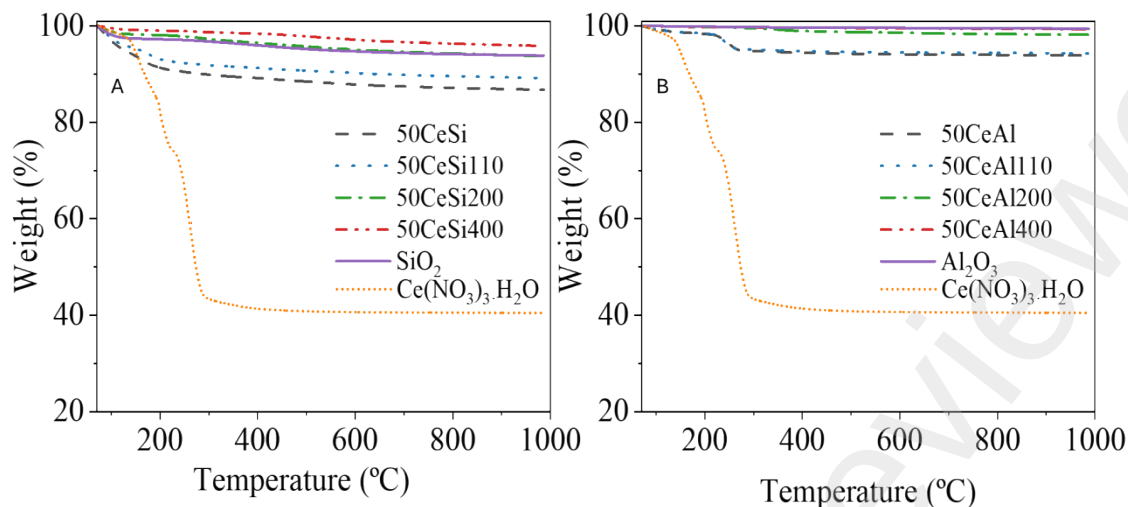


Figure 1. Thermogravimetric analysis (TGA) profiles in air of the synthesized catalysts: (A) Silica-supported samples: SiO₂, 5CeSi110, 5CeSi200, Cerium precursor and 5CeSi400; (B) Alumina-supported samples: α-Al₂O₃, 5CeAl110, 5CeAl200, Cerium precursor and 5CeAl400

The full decomposition of Ce(NO₃)₃·6H₂O in air, with a molar mass of approximately 434 g/mol, proceeds according to the following reaction:



In some thermal treatments (or under less extreme decomposition conditions), it is possible that the precursor does not decompose completely, so that the final product retains some of the nitrate groups and/or a certain amount of hydroxide groups is formed (due to partial hydrolysis) [23]. This would lead to a material whose formula can generally be expressed as: Ce(NO₃)_δ(OH)_α(H₂O)_βO_γ, where the parameters δ, α, γ and β are small fractions that indicate the non-stoichiometry.

The weight loss measurements indicate the mass lost during heat treatment, which could result from further decomposition of residual nitrate/hydroxide groups on the support. The theoretical weight loss from full decomposition of cerium nitrate (9.3%) compares to observed weight losses, suggesting a percentage for the fraction of decomposition and residue. The final molecular mass

by subtracting cerium's mass from the intermediate compound's weight, then identifying the extra mass as ligands by balanced calculation of the retained fraction of each species per cerium, considering condensation effects like hydroxide formation.

Now, if we observe instead a weight loss of 6.2% (as in the 5CeAl sample), the fraction of the “volatile” groups that have been removed is 67%. Thus, for each Ce atom the final nonstoichiometric species would consist of the “fully decomposed” CeO_2 moiety plus the residual groups equivalent to one nitrate and two hydroxide units. In other words, one may write an approximate formula as $\text{CeO}_{(2-x)}(\text{OH})_y(\text{NO}_3)_z$.

The textural characteristics of 5CeAl and 5CeSi were assessed by XRD, as depicted in Figure 2. The diffraction pattern of the 5CeAl sample reveals sharp, well-defined peaks at 2θ values of 25.66° , 35.24° , 43.45° , 52.65° , 57.59° , 66.62° , and 68.3° , corresponding to the (012), (104), (110), (113), (024), (116), (214), and (300) planes, respectively (JPDS-00-005-0712). These peaks confirm the presence of the $\alpha\text{-Al}_2\text{O}_3$ phase, indicative of a hexagonal close-packed crystalline structure, and demonstrate the high purity of the alumina support. Notably, no diffraction peaks corresponding to cerium oxide are observed, suggesting that cerium may either be highly dispersed on the alumina surface or present in quantities too low to be detected by XRD, given the dominant crystalline structure of $\alpha\text{-Al}_2\text{O}_3$.

Conversely, the 5CeSi sample exhibits a diffraction pattern characterized by a broad, low-intensity peak around $2\theta = 22^\circ$, which is characteristic of amorphous silica. This broad peak suggests that the silica support is largely non-crystalline, with significant structural porosity. As in the case of 5CeAl, no distinct cerium oxide peaks are detected in the 5CeSi sample. The absence of cerium-related diffraction peaks in both samples can be attributed to the low cerium content (5 wt%), which may not be sufficient to form detectable crystalline domains within the predominant

SiO₂ or α -Al₂O₃ matrices. Additionally, if cerium is uniformly dispersed at a nanoscale level within the supports, it could remain undetectable by XRD, as small, well-dispersed cerium particles or clusters may lack the crystallinity needed to generate discernible peaks. Another possibility is that cerium exists in an amorphous state, leading to a lack of long-range order, which further prevents the formation of clear diffraction signals.

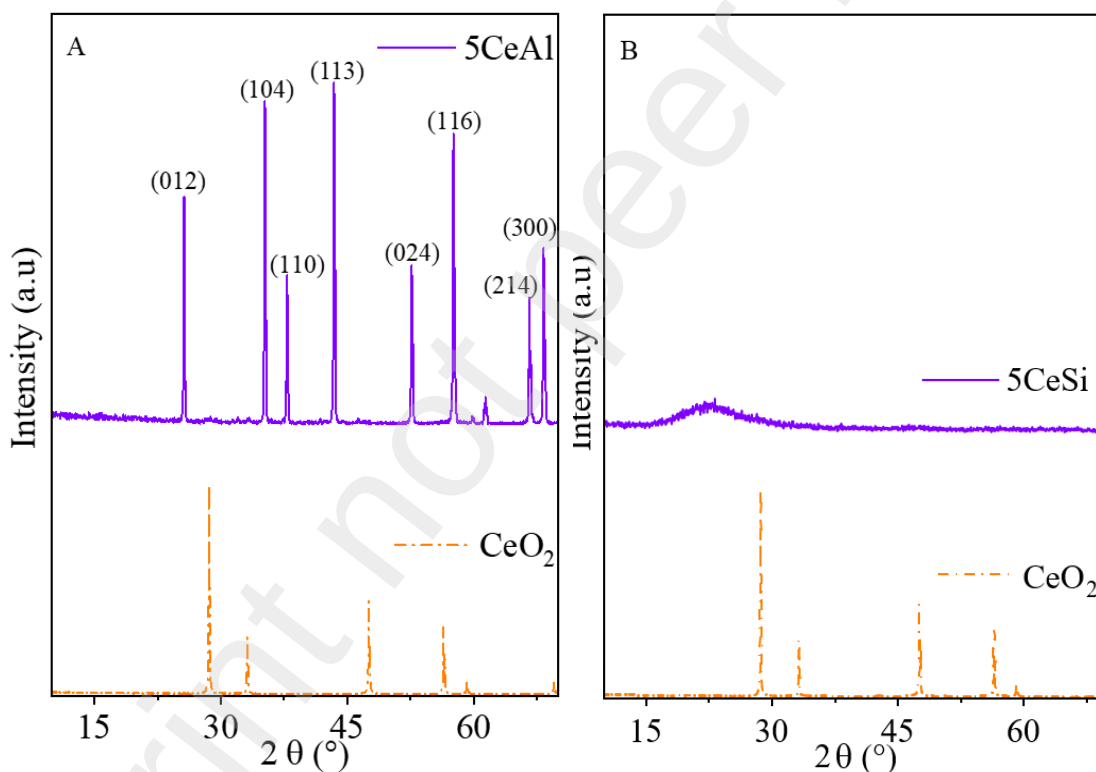


Figure 2. Powder X-ray diffraction (XRD) patterns of the synthesized catalysts: (A) Alumina-supported sample: 5CeSi and CeO₂; and, (B) Silica-supported sample: 5CeAl and CeO₂.

The elemental distribution of cerium (Ce) in all the catalysts was examined using Energy Dispersive X-ray Spectroscopy (EDS) coupled with Scanning Electron Microscopy (SEM), Figure 3. The EDS analysis revealed a homogeneous distribution of Ce throughout the surface of both α -alumina and silica gel supports.

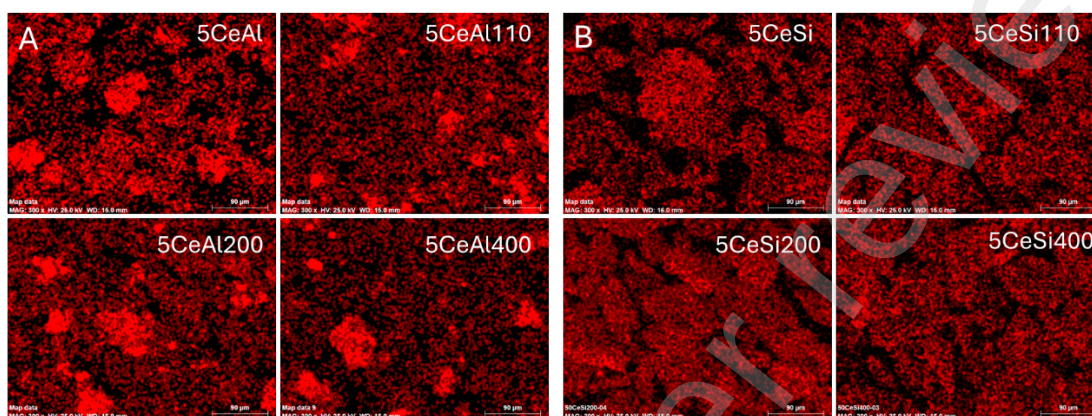


Figure 3. EDX mapping analysis of cerium within A) 5CeAl and B) 5CeSi catalyst.

For the 5CeAl samples, the cerium appeared evenly distributed across the alumina surface, confirming the successful impregnation and absence of large cerium oxide clusters. This homogeneous dispersion is particularly advantageous for catalytic applications, as it maximizes the number of accessible active sites and enhances the interaction between the catalytic material and reactants.

Similarly, the 5CeSi samples showed excellent cerium dispersion on the highly porous silica gel surface. The uniformity in cerium distribution across the silica support, as observed in the EDS mapping, indicates that the porous structure of silica allowed for effective incorporation of the cerium precursor, ensuring that the catalytic sites are evenly spread throughout the material.

Overall, the EDS results confirm the effectiveness of the preparation method in achieving a well-distributed loading of Ce in both types of supports, which is crucial for optimizing catalytic activity and ensuring consistent performance across all catalysts.

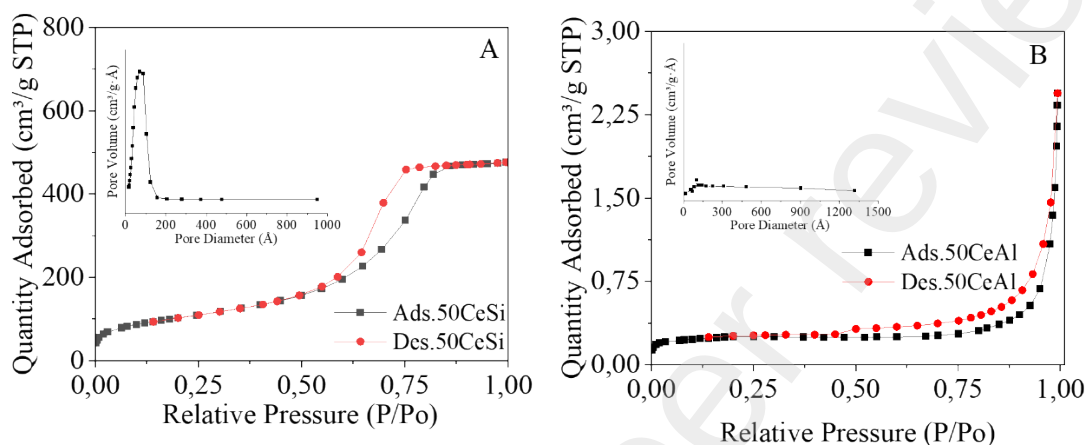


Figure 4. EDX mapping analysis of cerium within A) 5CeSi and B) 5CeAl catalyst.

The textural properties of α -alumina and silica gel were characterized through nitrogen adsorption and analyzed using the Brunauer-Emmett-Teller (BET) method (Figure 4). This analysis provided valuable insights into their porosity and specific surface areas. For α -alumina, specific surface areas of 1, 5, 10, and 6 m²/g were observed for the 5CeAl, 5CeAl110, 5CeAl200, and 5CeAl400 samples, respectively. These values indicate a poorly developed porous structure, which is characteristic of α -alumina. However, even with its limited porosity, α -alumina is suitable for applications that require high dispersion of active catalytic sites, as the low surface area can still facilitate good distribution of cerium species, especially when uniformly dispersed on the support.

In contrast, the silica gel exhibited significantly higher specific surface areas, with values of 365, 363, 403, and 414 m²/g for the 5CeSi, 5CeSi110, 5CeSi200, and 5CeSi400 samples, respectively. These values highlight the highly porous nature of silica gel, making it an excellent catalytic support. The large surface area provides a vast environment for the adsorption of reactants and the dispersion of active sites, enabling more efficient catalytic reactions.

In both cases, the decomposition of Ce(NO₃)₃·6H₂O during the calcination process contributed to changes in surface area, especially in the case of silica gel, where the specific surface area increased after thermal treatment. This evolution toward larger surface areas further underscores the potential of silica as a catalytic support, offering more active sites for adsorption and reaction of chemical species.

On the other hand, for α -alumina, which initially exhibits extremely low surface area and porosity, thermal activation at moderate temperatures (up to 200°C) led to a significant increase in surface area. However, at 400°C, the specific surface area decreased slightly, likely due to sintering effects that partially reduced the surface area by closing some of the pores. Despite this, the activated α -alumina still demonstrated improved textural properties compared to the untreated sample, enhancing its capacity for catalytic applications where a higher dispersion of cerium species is required.

The analysis of the Raman spectra of the samples (Figure 5) allowed the detection of characteristic vibrational modes associated with the F_{2g} symmetric stretching of Ce–O in CeO₂ (typically observed near 465 cm⁻¹)[24], as well as possible bands attributable to surface nitrate species (e.g., symmetric and asymmetric N–O stretching modes in the 1040–1380 cm⁻¹ range) [25], which may be retained from the precursor or formed during incomplete thermal

decomposition. The presence and evolution of these bands are key to understanding the structural and compositional properties of the materials as a function of synthesis conditions.

Raman spectroscopy provided key insights into the structural evolution of the cerium species in the synthesized catalysts, Figure 5. In silica-supported samples (5CeSi, 5CeSi110, 5CeSi200, and 5CeSi400), a broad band in the 1040–1380 cm^{-1} range was clearly observed, with an intensity trend of 5CeSi > 5CeSi110 > 5CeSi200, and complete disappearance in 5CeSi400 (Figure 5B). This band is attributed to symmetric and asymmetric N–O stretching modes of residual nitrate species, suggesting incomplete thermal decomposition of the cerium nitrate precursor in the lower temperature samples. Notably, no vibrational mode corresponding to the F_{2g} symmetric stretching of Ce–O in fluorite-type CeO_2 (typically near 465 cm^{-1}) was detected in these samples, indicating the absence of well-crystallized CeO_2 domains. A weak band near 608 cm^{-1} [26] was observed across the silica-supported series, which may be associated with defect-related modes linked to oxygen vacancies or non-stoichiometric cerium environments ($\text{Ce}^{3+}/\text{Ce}^{4+}$).

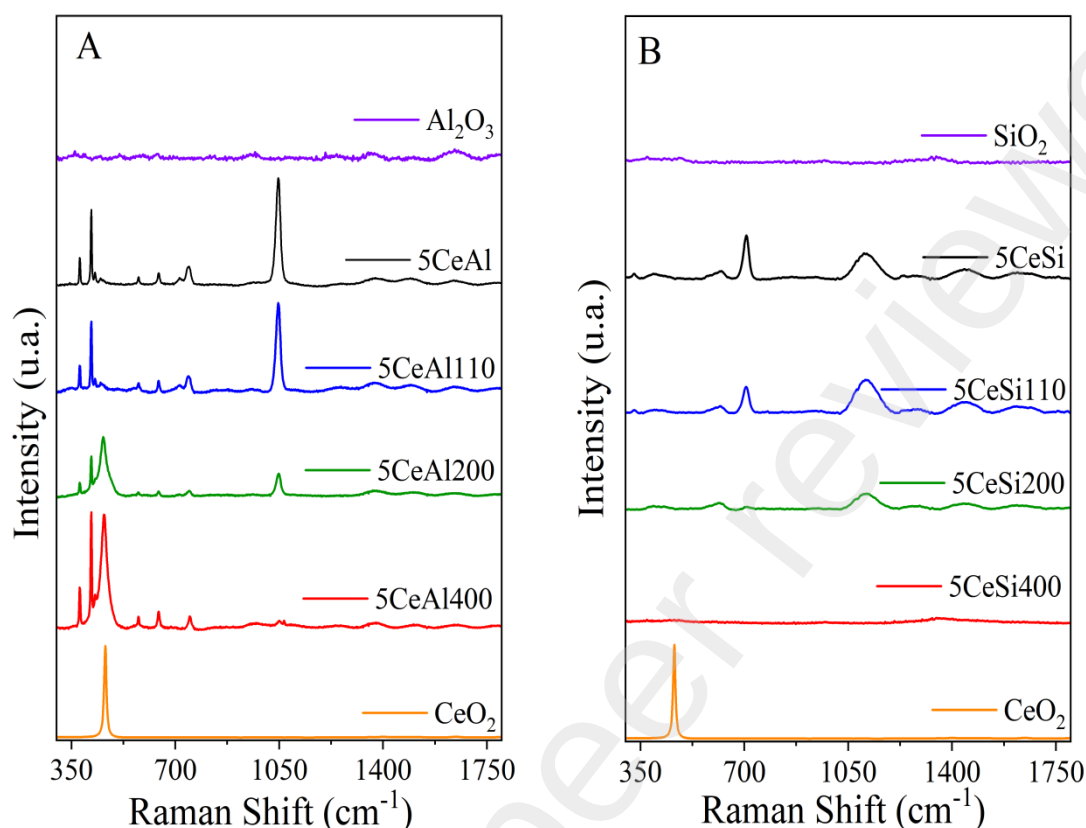


Figure 5. Raman spectra of the synthesized catalysts: (A) Alumina-supported samples: Al_2O_3 , 5CeAl110, 5CeAl200, and 5CeAl400; (B) Silica-supported samples: SiO_2 , 5CeSi110, 5CeSi200, and 5CeSi400.

In contrast, alumina-supported samples (5CeAl, 5CeAl110, and 5CeAl200) displayed a narrow band centered at 1065 cm^{-1} , also ascribed to surface nitrate groups, with a markedly decreasing intensity as the thermal treatment temperature increased (Figure 5A). Concurrently, a band at $\sim 465\text{ cm}^{-1}$ emerged and intensified progressively ($5\text{CeAl} < 5\text{CeAl110} < 5\text{CeAl200}$), consistent with the formation and growth of CeO_2 crystallites with fluorite structure. Additionally, a band of moderate intensity near 585 cm^{-1} [27] was detected in the alumina-supported catalysts and tentatively assigned to defect-induced modes associated with lattice distortions or oxygen vacancies. The comparative presence of bands in the $580\text{--}610\text{ cm}^{-1}$ region in both catalyst series suggests the

coexistence of Ce^{3+} and Ce^{4+} species and highlights the role of the support and calcination temperature in modulating the local structure and redox state of cerium oxide.

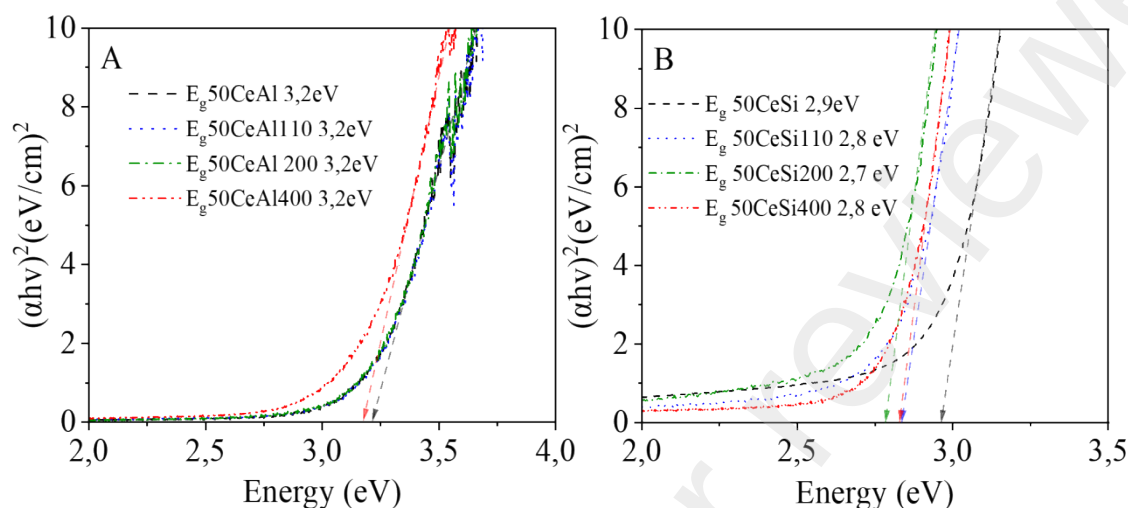


Figure 6. Tauc plots derived from UV-vis diffuse reflectance spectra of the synthesized catalysts: (A) Silica-supported samples: 5CeSi110, 5CeSi200, and 5CeSi400; (B) Alumina-supported samples: 5CeAl110, 5CeAl200, and 5CeAl400.

The relationship between the chemical processes involved in the thermal decomposition of cerium (III) nitrate on α -alumina and the band gap values obtained from diffuse reflectance UV-Vis (DRS) analyses, using the Tauc method, reveals notable trends. The DRS analysis of the 5CeAl samples shows an absorption band centred around 380 nm in the UV region, with slight broadening towards higher-energy wavelengths. As seen in Figure 6, after applying the Tauc method, the calculated band gap is approximately 3.2 eV.

This value is consistent with previous studies on cerium oxide (ceria) [28-30], suggesting that the thermal treatment did not significantly alter the absorption properties of the ceria supported on α -alumina. This band gap corresponds to the typical values of cerium dioxide (CeO_2), which is known for its activity under UV light, making it suitable for photocatalytic applications that rely on high-energy UV irradiation.

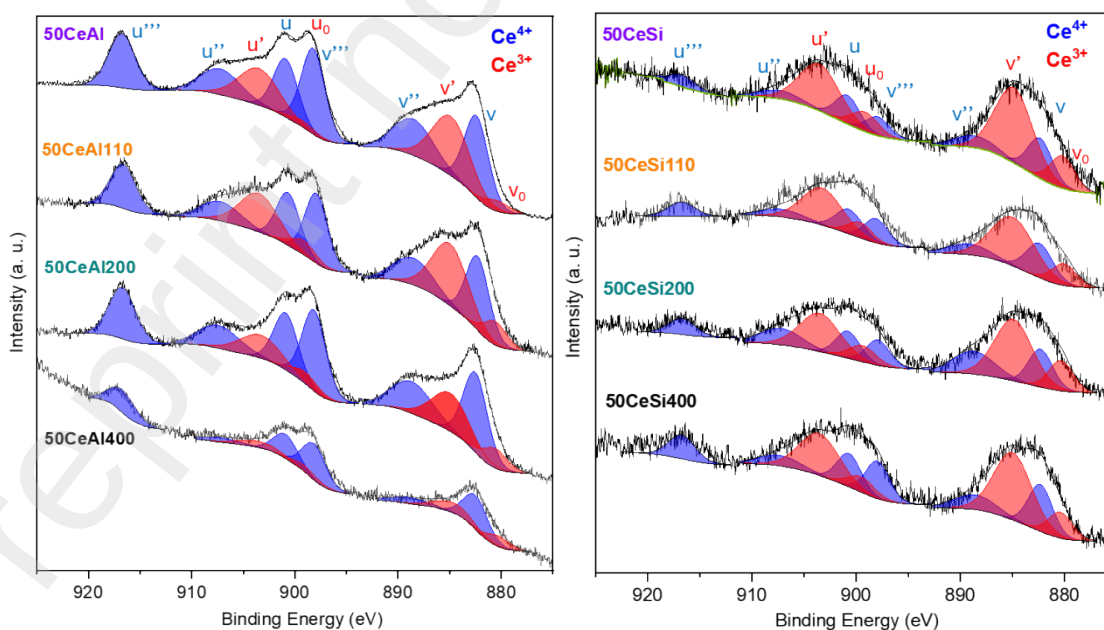
However, the behavior of the silica gel-supported samples exhibits a more significant transformation in their optical properties. After the application of the Tauc method to the DRS data, it is evident that the 5CeSi sample, before thermal treatment, has a band gap of 2.96 eV, which is lower than the typical 3.2 eV observed for cerium oxide. This indicates that the cerium precursor interacts differently with the amorphous silica matrix, potentially due to the formation of cerium species with altered electronic structures. After thermal treatment at 200°C, the band gap further decreases to 2.79 eV in the 5CeSi200 sample. Although this variation appears modest, the decrease in band gap has important implications for photocatalytic applications.

The reduction in the band gap from 2.96 eV to 2.79 eV corresponds to a shift in the absorption wavelength from approximately 419 nm to 444 nm, which allows the material to absorb light with lower energy, extending its activity into the visible spectrum. This shift is particularly advantageous for pollutant degradation under solar or visible light conditions, as the catalyst can now utilize a broader range of the light spectrum. Lower energy requirements for activation make these materials more suitable for photocatalytic processes driven by natural sunlight, enhancing their potential for practical environmental remediation applications, such as the degradation of organic pollutants in wastewater.

The observed shift in the band gap for the silica-supported samples suggests that the thermal treatments led to changes in the cerium species, possibly due to variations in cerium oxide particle size, changes in the oxidation state of cerium ($\text{Ce}^{3+}/\text{Ce}^{4+}$), or the formation of mixed cerium oxide-silica phases that influence the electronic structure. These modifications in the optical properties could enhance the photocatalytic efficiency of the 5CeSi200 sample, particularly in reactions that benefit from visible light activation, making these materials promising candidates for more energy-efficient environmental applications.

The general spectrum of the samples supported on α -alumina and silica gel provided a comprehensive overview of the elemental composition of the material's surface, covering a wide range of binding energies and allowing for the identification of key elements. Peaks corresponding to cerium (Ce), oxygen (O), aluminium (Al), and nitrogen (N) were identified in both cases. The atomic composition of these elements was quantified by integrating the peak areas, with the Al2p peak at 74.2 eV and the Si2s peak at 103.3 eV [31] serving as references. This approach allowed for a precise, quantitative measure of the relative abundance of each element on the surface of the materials, revealing differences in elemental distribution between the two supports.

Following the overall elemental analysis, specific attention was given to the cerium spectra to better understand its surface distribution and oxidation states. The characteristic peaks observed at $881.5 \text{ eV} \pm 2.1 \text{ eV}$ and $901 \text{ eV} \pm 1.6 \text{ eV}$ correspond to Ce 3d 5/2 and Ce 3d 3/2, respectively, while the peak at $917 \text{ eV} \pm 0.7 \text{ eV}$ is attributed to CeO₂, indicating the presence of cerium in the Ce⁴⁺ oxidation state [32]. These binding energy values align with previous studies of cerium oxides, confirming the formation of both Ce³⁺ and Ce⁴⁺ species on the surface.



361

Figure 7. High-resolution Ce 3d XPS, deconvoluted spectra to highlight the components associated with Ce³⁺ (red) and Ce⁴⁺ (blue) oxidation states, of the synthesized catalysts: (A) Silica-supported samples: 5CeSi110, 5CeSi200, and 5CeSi400; (B) Alumina-supported samples: 5CeAl110, 5CeAl200, and 5CeAl400.

The deconvolution of the Ce 3d region revealed 10 contributions, Figure 7, assigned as follows: the peaks labelled as v_0 , v' , u_0 , and u' are associated with Ce³⁺ species, while the peaks labelled v , v'' , v''' , u , u'' , and u''' correspond to Ce⁴⁺ species [30, 33-35]. These contributions were carefully quantified, and the relative areas of each peak were determined to calculate the proportion of Ce³⁺ and Ce⁴⁺ species on the surface. The areas of these peaks were used to compute the contribution of each oxidation state using the method proposed by Pfau [36], with the following equations:

$$Ce^{3+} = v_0 + v' + u_0 + u'$$

$$Ce^{4+} = v + v'' + v''' + u + u'' + u'''$$

$$\%Ce^{3+} = \frac{Ce^{3+}}{Ce^{3+} + Ce^{4+}}$$

The calculated Ce³⁺/Ce⁴⁺ ratios for the samples supported on α -alumina and silica gel are presented in Table 1, highlighting the differences in cerium oxidation states depending on the support and thermal treatment.

Table 1. Surface Ce³⁺/Ce⁴⁺ Atomic Ratios of the Synthesized Catalysts Estimated from Ce 3d XPS Peak Deconvolution

	u'''	u''	u'	u	u_0	v'''	v''	v'	v	v_0	Ce^{3+}/Ce^{4+}
50CeAl	8.6	6.0	8.7	8.3	1.0	17.2	12.3	19.0	16.8	2.2	31/69
50CeAl110	7.4	5.0	9.7	8.0	2.4	14.9	10.1	21.1	16.2	5.2	38/62
50CeAl200	9.1	6.2	6.3	9.0	2.1	18.2	12.5	13.7	18.4	4.5	27/73
50CeAl400	11.2	3.2	4.6	10.6	3.1	22.5	6.4	10.1	21.5	6.7	25/75
50CeSi	2.7	2.9	16.0	5.9	4.5	5.5	6.0	34.8	12.0	9.7	65/35
50CeSi110	3.9	3.2	15.2	6.7	3.8	8.5	6.5	30.8	13.6	7.8	58/42

50CeSi200	3.7	5.8	13.1	5.6	3.7	7.4	11.7	28.6	11.3	9.1	55/45
50CeSi400	5.2	3.5	13.6	6.5	3.4	10.4	7.1	29.6	13.3	7.3	54/46

The key distinction between the α -alumina and silica gel supports lies in the interaction of cerium with each material, which affects both the distribution and the oxidation state of cerium after thermal treatment. In the case of the α -alumina-supported samples, there is a clear tendency for cerium to oxidize to the Ce^{4+} state, as evidenced by the larger contribution of Ce^{4+} species in the XPS analysis. This suggests that α -alumina promotes the formation of a more defined and possibly more catalytically active ceria layer, likely due to stronger interactions between cerium and the alumina surface, which facilitate the oxidation of Ce^{3+} to Ce^{4+} .

On the other hand, the silica gel-supported samples exhibited a higher proportion of Ce^{3+} species, indicating that the silica gel has a lower propensity to fully oxidize cerium. This could be attributed to the amorphous nature of silica, which allows for more uniform dispersion but potentially less intense interaction with cerium, leading to a higher stabilization of Ce^{3+} species. The presence of both oxidation states (Ce^{3+} and Ce^{4+}) in varying ratios suggests that the silica support allows for a more flexible and dispersed distribution of cerium, which could have different catalytic implications, particularly in reactions where the redox cycling between Ce^{3+} and Ce^{4+} plays a critical role or in oxygen vacance, as results of these.

The chemical composition of the non-stoichiometric ceria-based materials was determined by integrating quantitative data from X-ray Photoelectron Spectroscopy (XPS), Raman spectroscopy, and Thermogravimetric Analysis (TGA). XPS established the Ce(III)/Ce(IV) ratios, defining the average cerium oxidation state (Z_{avg}) for each sample. Residual nitrate content (δ , as average NO_3^- groups) was quantified via Raman spectroscopy. TGA-derived weight loss data facilitated

the estimation of total retained volatile species originating from the precursor, allowing the average number of hydroxide groups (α) per Ce to be inferred. Stoichiometric formulas, in the general form $\text{Ce}(\text{NO}_3)_\delta(\text{OH})_\alpha(\text{H}_2\text{O})_\gamma\text{O}_\gamma$, were subsequently derived by ensuring charge neutrality against established the Ce(III)/Ce(IV) ratios. This methodology revealed a spectrum of compositions as $\text{Ce}(\text{NO}_3)_3\text{O}_{0.4}$, $\text{Ce}(\text{NO}_3)_3(\text{OH})_{0.04}\text{O}_{0.33}$, $\text{Ce}(\text{NO}_3)_{0.52}(\text{OH})_{3.21}(\text{H}_2\text{O})_{3.44}$, $\text{Ce}(\text{NO}_3)_{0.03}(\text{OH})_{3.72}(\text{H}_2\text{O})_{4.58}$ for cerium aggregates in alumina samples and $\text{Ce}(\text{NO}_3)_3\text{O}_{0.35}$, $\text{Ce}(\text{NO}_3)_3(\text{OH})_{0.42}(\text{H}_2\text{O})_{0.29}$, $\text{Ce}(\text{NO}_3)_{0.42}(\text{OH})_{3.03}(\text{H}_2\text{O})_{2.57}$, $\text{Ce}(\text{OH})_{3.46}(\text{H}_2\text{O})_{2.54}$ for cerium aggregates in silica samples. These results indicate that with increasing retention of volatile components (i.e., less thermal decomposition), the average positive charge of cerium becomes increasingly balanced by nitrate and hydroxide ligands, thereby reducing or, in samples with minimal decomposition, eliminating the structural oxide component. For alumina-supported materials calcined at a moderate temperature of 400°C, these findings suggest the formation of a highly dispersed ceria phase. The significant presence of Ce(III) along with residual nitrate and hydroxide ligands is expected to promote strong interactions with the alumina surface, likely through interfacial Ce-O-Al type bonding. Crystalline cerium aluminate phases, such as CeAlO_3 , are not anticipated at this calcination temperature, as their formation typically requires significantly higher thermal input. Detailed characterization of the ceria-alumina interface, for instance SEM or advanced XPS analysis, could further elucidate the nature of these interactions.

Photocatalytic experiments confirmed that the degradation of methyl red (RM) in aqueous solution is predominantly driven by light irradiation, as no measurable conversion was observed in the absence of light. Under 365 nm LED irradiation, the photocatalytic activity observed for the α -alumina and silica gel supports resulted in a limited RM conversion of ~10%, comparable to that

423 achieved by photolysis alone, thus establishing a baseline for comparison with the supported
424 catalysts.

425 Ceria-based catalysts supported on α -alumina and silica gel exhibited significantly enhanced
426 photocatalytic performance relative to both dark and photolysis controls (Figure 8). For the
427 alumina-supported series, the untreated 5CeAl sample reached 33% RM conversion, while thermal
428 treatment improved the activity up to a maximum of 51% for the 5CeAl200 sample. Samples
429 treated at 110°C and 400°C achieved conversions of 44% and 42%, respectively. This trend
430 suggests that moderate thermal treatment enhances surface reactivity of dispersed cerium species,
431 likely by favoring partial nitrate decomposition and improving the $\text{Ce}^{3+}/\text{Ce}^{4+}$ redox balance, which
432 may facilitate ROS generation. The UV-visible absorption spectra obtained after the
433 photocatalytic reaction experiments reveal an appreciable increase in the absorption bands
434 corresponding to those characteristic products of RM degradation, *N*¹,*N*¹-dimethylbenzene-1,4-
435 diamine and 2-aminobenzoic acid. Specifically, the emergence of a primary band at 246 nm and a
436 minor signal at 292 nm indicates the formation or accumulation of MR degradation species. In
437 parallel, the appearance of a main absorption band at 218 nm and secondary features at 246 and
438 334 nm is consistent with the spectral profile of 2-aminobenzoic acid. These changes in the spectral
439 envelope confirm the generation of intermediate or final photoproducts absorbing in these regions
440 and therefore provide evidence of chemical transformations occurring throughout the reaction
441 course.

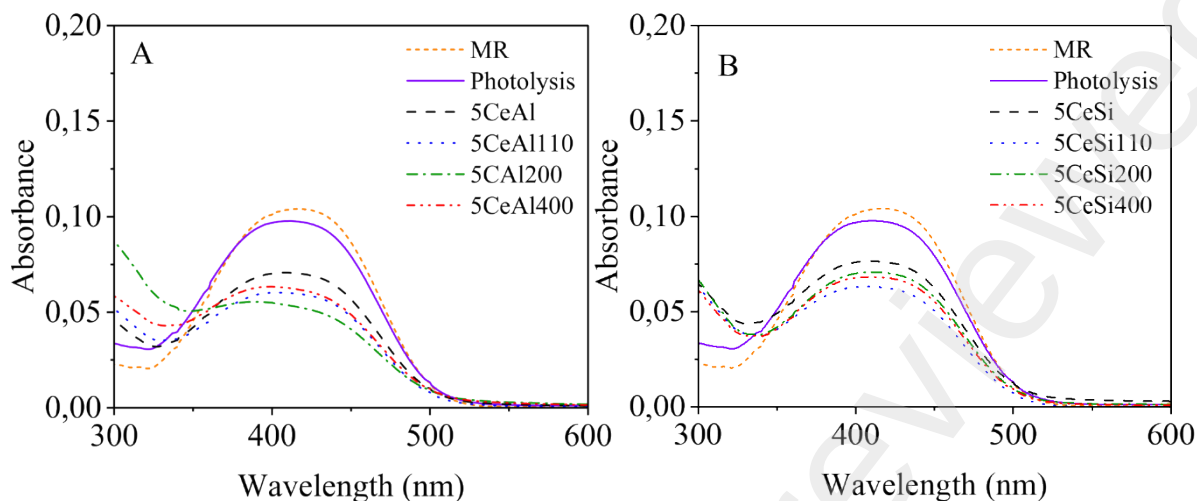


Figure 8 Photocatalytic degradation of methyl red on cerium-content catalysts supported on silica and alumina.

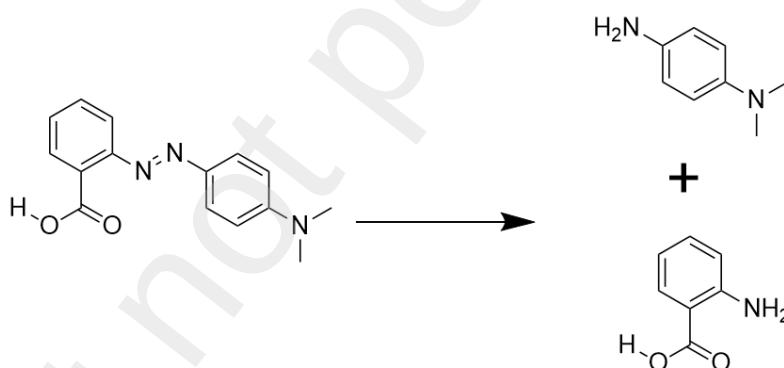


Figure 9. Degradation pathway of methyl red in N,N-dimethyl-p-benzenediamine and 2-amino-benzoic acid.

A similar trend, though with lower overall efficiencies, was observed for silica-supported samples. The untreated 5CeSi catalyst achieved a conversion of 27%, which increased to 41%

upon treatment at 110°C. However, activity declined at higher treatment temperatures (33% at 200°C and 36% at 400°C).

To contextualize these results, control tests with unsupported CeO₂ were conducted using increasing catalyst loadings. A CeO₂ dose of 0.5 mg—corresponding approximately to the cerium content present in the supported samples—resulted in 28% RM conversion. This value is notably lower than those obtained for all thermally treated alumina-supported samples and comparable to the performance of the best-performing silica-supported catalyst (5CeSi110). These findings highlight the beneficial role of high-surface-area supports not only in improving cerium dispersion but also in promoting interfacial charge transfer processes that enhance photocatalytic efficiency at reduced CeO₂ loadings.

Taken together, the results demonstrate that supporting CeO₂ on oxide carriers such as α -Al₂O₃ and SiO₂ enables a substantial reduction in the total cerium content without sacrificing photocatalytic performance. In particular, α -Al₂O₃ emerges as a more effective support than silica under the conditions tested, with optimal performance achieved after mild thermal activation at 200°C.

The photocatalytic performance of the ceria-based catalysts was found to correlate only partially with the surface area of the support. For the α -alumina-supported materials, the surface area increased with mild thermal treatment, reaching a maximum of 9.6 m²/g for 5CeAl200 before declining to 5.7 m²/g at 400°C. This trend is reflected in the photocatalytic activity, which also peaked at 5CeAl200, suggesting that enhanced dispersion and moderate textural development contribute positively to the reaction. However, the magnitude of the surface area increase is modest, and the relatively low values across the series indicate that other factors—such as cerium speciation and interfacial effects—play a dominant role. In contrast, silica-supported catalysts

exhibited high specific surface areas in all cases (365–414 m²/g), yet their photocatalytic performance remained lower than that of their alumina-supported counterparts. This discrepancy indicates that surface area alone is not sufficient predictor of catalytic efficiency in these systems, and that the chemical environment of cerium and its interaction with the support are critical determinants of activity.

Given that all catalysts contain equivalent amounts of cerium, the oxidation state of Ce becomes a critical factor in determining photocatalytic performance. The comparison between supports reveals that α -alumina-based catalysts—despite presenting lower overall Ce³⁺ content—consistently outperformed their silica counterparts, in which Ce³⁺ was dominant. This observation suggests that the mere prevalence of Ce³⁺ does not guarantee higher activity, and that Ce⁴⁺-rich environments may be more effective for promoting oxidative pathways involving reactive oxygen species (ROS). However, when considering the Ce³⁺/Ce⁴⁺ ratio as a whole, a clearer trend emerges for alumina-supported catalysts, the highest activity was obtained for 5CeAl200 (Ce³⁺/Ce⁴⁺ = 27/73), while for silica-supported samples, the best performance was observed in 5CeSi110 (Ce³⁺/Ce⁴⁺ = 58/42). These results point toward an optimal balance between Ce³⁺ and Ce⁴⁺, where the coexistence of both oxidation states facilitates charge separation and supports redox cycling critical to photocatalytic efficiency.

More importantly, the observed photocatalytic trends correlate more consistently with the generation of oxygen vacancies associated with non-stoichiometric CeO_{2- δ} domains. Such defects are structurally linked to the coexistence of Ce³⁺ and Ce⁴⁺, and their presence was indirectly confirmed through the appearance of broad Raman bands in the 580–610 cm⁻¹ region. These bands, more pronounced in 5CeAl200 and 5CeSi110, are commonly associated with lattice distortions and oxygen-deficient surface structures. The improved activity of these two samples suggests that

oxygen vacancies, rather than absolute Ce^{3+} content, play a central role by enhancing the adsorption of molecular oxygen, stabilizing superoxide intermediates, and promoting interfacial charge transfer. Thus, tuning the redox distribution of cerium toward defect-rich but structurally coherent environments appears to be a more effective strategy than maximizing either oxidation state individually.

The photocatalytic performance of the CeO_2 -based catalysts developed in this work, though moderate in absolute conversion compared to multicomponent or chemically activated systems, offers a compelling balance between efficiency, sustainability, and material simplicity. For instance, the best-performing sample, 5CeAl200, achieved a 51% conversion of methyl red under UV-A irradiation without the need for dopants, carbonaceous additives, or sacrificial agents. This contrasts with the 95% degradation reported for an N,F-TiO₂/SiO₂/rGO nanocomposite under visible light, where performance is enhanced by heteroatom doping and graphene-mediated charge transfer [37]. Similarly, the sulfite-assisted degradation over defect-engineered CeO_2 reported by Li et al. [38] approaches near-complete mineralization but requires chemical activation with SO_3^{2-} ions and controlled pH. In contrast, the catalysts reported here rely solely on thermally tuned surface defects and $\text{Ce}^{3+}/\text{Ce}^{4+}$ redox heterogeneity to generate reactive oxygen species. Compared with the slower biodegradation of MR by [39], which requires incubation times over 100 hours, the photodegradation pathway herein offers faster kinetics and robustness under synthetic wastewater conditions. These comparisons emphasize that rational control of Ce speciation and oxygen vacancy concentration via mild thermal treatment and dispersion over inert oxide supports can provide a viable, resource-efficient alternative for dye degradation in real-world applications.

Overall, the data demonstrate that dispersing small amounts of CeO_2 on high-surface-area supports markedly enhances photocatalytic activity compared to conventional applications where

CeO₂ is used solely as a catalyst support in a similar way of Farooq et al. [40]. This approach leverages the synergistic effects of optimized thermal treatment, improved textural properties, and a favourable oxidation state balance to achieve superior degradation of persistent organic pollutants.

4.CONCLUSIONS

This study demonstrates that dispersing low amounts of CeO₂ onto oxide supports, such as silica gel and α -alumina, significantly enhances the photocatalytic degradation of synthetic azo dyes in aqueous media. Using incipient wetness impregnation followed by mild thermal treatments (110°C, 200°C, and 400°C), highly dispersed cerium species were successfully obtained, as evidenced by complementary characterization techniques.

Thermogravimetric analysis (TGA) revealed support-dependent decomposition behavior of the cerium precursor: silica-supported samples exhibited broader and more gradual weight losses, while alumina-supported samples showed sharper transitions and lower overall weight loss, indicative of stronger precursor–support interactions. X-ray diffraction (XRD) confirmed the crystallinity of α -alumina and the amorphous nature of silica gel, and the absence of distinct CeO₂ reflections suggests the formation of amorphous or highly dispersed ceria domains in both cases. BET analysis highlighted the markedly higher surface area of silica-based systems (365–414 m²/g) compared to their alumina counterparts, which nonetheless experienced modest improvements in textural properties upon thermal activation. X-ray photoelectron spectroscopy (XPS) revealed that the Ce³⁺/Ce⁴⁺ redox balance is finely modulated by the support and calcination temperature, with an optimal ratio at 200°C. The coexistence of Ce³⁺ and Ce⁴⁺ correlates with the formation of surface oxygen vacancies—defect sites that are essential for reactive oxygen species (ROS) generation and efficient photocatalytic activity. The presence of Raman bands in the 580–610 cm⁻¹ range

further supports the existence of such oxygen-deficient $\text{CeO}_{2-\delta}$ structures. Subtle pH shifts during reaction also point to the role of support–catalyst interactions in modulating the local reaction environment.

Photocatalytic degradation of methyl red (MR) under near-UV (365 nm) irradiation confirmed that thermal treatment at 200°C resulted in the highest activity. Notably, α -alumina-supported catalysts achieved up to 42% conversion (5CeAl200), while silica-supported systems reached up to 27% conversion under the same conditions, both outperforming pure CeO_2 with equivalent Ce loading. These results underscore the capacity of oxide supports to promote CeO_2 dispersion and defect stabilization, enabling efficient catalysis at reduced rare-earth usage.

In conclusion, the strategy of minimizing cerium content by dispersing CeO_2 on inert oxide supports offers an effective and sustainable route to photocatalytic water treatment. This approach reduces dependence on critical raw materials while maintaining high catalytic performance, thus aligning with the principles of green chemistry and advancing the objectives of SDG 6 (Clean Water and Sanitation) and SDG 13 (Climate Action).

ACKNOWLEDGEMENT

The authors acknowledge financial support from the Spanish Ministry of Science and Innovation (project TED 2021-131914B-I00), funded by the European Union—NextGenerationEU/PRTR.

REFERENCES

- [1] Han, Y.; Chen, X.; Jiang, L. Enhanced Photocatalysis by Defect-Engineered CeO₂ with Sulfite Activation under Visible Light Irradiation. *Appl. Surf. Sci.* 2024, 637, 161072. <https://doi.org/10.1016/j.apsusc.2024.161072>
- [2] Zahra Shokri Aghbolagh, Mohammad Saim Rahmatyan, Mohammad Reza Khanmohammadi Khorrami Catalytic degradation of methyl red using PZnW₁₁/m-GO as a high-performance photocatalyst. *Environ. Prog. Sustain. Energy* 2021, 40, e13657. <https://doi.org/10.1002/ep.13657>
- [3] Susan Samadi, Elahe Khalili, Mohammad Reza Allahgholi Ghasri Degradation of methyl red under visible light using N,F-TiO₂/SiO₂/rGO nanocomposite. *J. Electron. Mater.* 2019, 48, 7836–7845. <https://doi.org/10.1007/s11664-019-07585-w>
- [4] Chen, Z.-X.; Jin, X.-Y.; Chen, Z.-L.; Megharaj, M.; Naidu, R. Removal of methyl orange from aqueous solution using bentonite-supported nanoscale zero-valent iron. *J. Colloid Interface Sci.* 2011, 363 (2), 601–607. <https://doi.org/10.1016/j.jcis.2011.07.003>
- [5] Ambigadevi, J., Kumar, P. S., Vo, D. V. N., Haran, S. H., & Raghavan, T. S. (2021). Recent developments in photocatalytic remediation of textile effluent using semiconductor based nanostructured catalyst: A review. *Journal of Environmental Chemical Engineering*, 9(1), 104881. <https://doi.org/10.1016/j.jece.2020.104881>
- [6] Herzog, Austin E., Michael, Tara J., Dunkelberger, Adam D., Johannes, Michelle D., Rolison, Debra R., DeSario, Paul A., Novak, Travis G. Nanostructured CeO₂ photocatalysts: optimizing surface chemistry, morphology, and visible-light absorption, *Nanoscale*, 2024, 16, 9659-9679

- [7] Chang Liu, Longhua X, Jiushuai Deng, Jia Tian, Donghui Wang, Kai Xue, Xi Zhang, Yan Wang, Jinmei Fang, Jiongtian Liu, A review of flotation reagents for bastnäsite-(Ce) rare-earth ore. *Adv. Colloid Interface Sci.* 2023, 321, 103029. <https://doi.org/10.1016/j.cis.2023.103029>
- [8] P.Venkata Laxma Reddy, Beluri Kavitha, Police Anil Kumar Reddy, Ki-Hyun Kim, TiO₂-based photocatalytic disinfection of microbes in aqueous media: A review. *Environ. Res.* 2017, 154, 296–303. <https://doi.org/10.1016/j.envres.2017.01.018>
- [9] Şerife Parlayıcı, Erol Pehlivan, Fast decolorization of cationic dyes by nanoscale zero-valent iron immobilized in sycamore tree seed-pod fibers: Kinetics and modelling study. *Int. J. Phytoremediation* 2019, 21 (11), 1130–1144. <https://doi.org/10.1080/15226514.2019.1606786>
- [10] Bibek Saha, Animesh Debnath, Biswajit Saha, Fabrication of PANI@Fe–Mn–Zr hybrid material and assessments in sono-assisted adsorption of methyl red dye: Uptake performance and response-surface optimization. *J. Indian Chem. Soc.* 2022, 99 (9), 100635. <https://doi.org/10.1016/j.jics.2022.100635>
- [11] Vo Thi Thu Nhu, Do QuangMinh, Nguyen Ngoc Duy, Nguyen QuocHien, Photocatalytic degradation of azo dye (methyl red) in water under visible light using Ag-Ni/TiO₂ synthesized by irradiation method. *Int. J. Environ. Agric. Biotechnol.* 2017, 2, 529–538. <https://doi.org/10.22161/ijeab/2.1.66>
- [12] Bouzid, T.; Abdelali Grich, Aicha Naboulsi , Abdelmajid Regti, A. Alaoui Tahiri, Mamoune El Himri, Mohammadine El Haddad. Adsorption of methyl red on porous activated carbon from agricultural waste: Characterization and response-surface-methodology optimization. *Inorg. Chem. Commun.* 2023, 158, 111544. <https://doi.org/10.1016/j.inoche.2023.111544>

- [13] Akash Deb, Animesh Debnath, Biswajit Saha. Sono-assisted enhanced adsorption of Eriochrome Black T dye onto a novel polymeric nanocomposite: Kinetic, isotherm, and response-surface-methodology optimization. *J. Dispersion Sci. Technol.* 2021, 42 (11), 1579–1592. <https://doi.org/10.1080/01932691.2020.1775093>
- [14] J. oyasree Bhattacharjee, Sunanda Mishra, Alok Prasad Das Recent advances in sensor-based detection of toxic dyes for bioremediation application: A review. *Appl. Biochem. Biotechnol.* 2022, 194 (10), 4745–4764. <https://doi.org/10.1007/s12010-021-03767-7>
- [15] V. Selvaraj, T. Swarna Karthika, C. Mansiya, M. Alagar, An over-review on recently developed techniques, mechanisms and intermediates involved in advanced azo-dye degradation for industrial applications. *J. Mol. Struct.* 2021, 1224, 129195. <https://doi.org/10.1016/j.molstruc.2020.129195>
- [16] Nidhi Puri, Anjali Gupta, Water remediation using titanium- and zinc-oxide nanomaterials through disinfection and photocatalysis: A review. *Environ. Res.* 2023, 227, 115786. <https://doi.org/10.1016/j.envres.2023.115786>
- [17] Xiaobo Gong, Jinling Xie, Xiaofang Pan, Xuan Luo, S,N co-doped carbon-material-functionalized catalytic membrane for efficient peroxymonosulfate activation and continuous refractory-pollutant flow treatment. *Chem. Eng. Sci.* 2023, 282, 119353. <https://doi.org/10.1016/j.ces.2023.119353>
- [18] Saurabh K. Patel, Sunil G. Patel & Geeta V. Patel ,Degradation of reactive dye in aqueous solution by Fenton, photo-Fenton process and combination process with activated charcoal and TiO₂. *Proc. Natl. Acad. Sci. India A* 2020, 90, 579–591. <https://doi.org/10.1007/s40010-019-00618-3>

- [19] Khurshida Afroz, Md Moniruddin, Nurlan Bakranov, Sarkyt Kudaibergenov and Nurxat Nuraje A heterojunction strategy to improve the visible-light-sensitive water-splitting performance of photocatalytic materials. *J. Mater. Chem. A* 2018, 6, 21696–21718. <https://doi.org/10.1039/c8ta04165b>
- [20] Sugang Meng, Jinfeng Zhang, Shifu Chen, Sujuan Zhang, Weixin Huang, Perspective on construction of heterojunction photocatalysts and complete utilization of photogenerated charge carriers. *Appl. Surf. Sci.* 2019, 476, 982–992. <https://doi.org/10.1016/j.apsusc.2019.01.246>
- [21] Stefanos Giannakis, Siting Liu, Anna Carratalà, Sami Rtimi, Masoud Talebi Amiri, Michaël Bensimon, César Pulgarin, Iron-oxide-mediated semiconductor photocatalysis vs heterogeneous photo-Fenton treatment of viruses in wastewater: Impact of the oxide particle size. *J. Hazard. Mater.* 2017, 339, 223–231.
- [22] Wierzbicka, E.; Syrek, K.; Mączka, K.; Sulka, G.D. Photocatalytic decolorization of methyl red on nanoporous anodic ZrO_2 of different crystal structures. *Crystals* 2021, 11 (2), 215. <https://doi.org/10.3390/cryst11020215>
- [23] J. Lee, P. Christopher, *Angew. Chem. Int. Ed.* 2024, e202414388. <https://doi.org/10.1002/anie.202414388>
- [24] Jose Manuel López, Alexander L. Gilbank, Tomás García, Benjamín Solsona, Said Agouram, Laura Torrente-Murciano, The prevalence of surface oxygen vacancies over the mobility of bulk oxygen in nanostructured ceria for the total toluene oxidation, *Applied Catalysis B: Environmental* 174–175 (2015) 403–412

- [25] H. E. Hallam, M.Sc., Ph.D., F.R.I.C. Infrared and Raman spectra of inorganic compounds. Royal Institute of Chemistry, Reviews 1968, 1, 49
- [26] Hamed Shooshtari Gugtapeh, Abdolreza Simchi. Enhancing selective nitrate reduction to ammonia by oxygen vacancies in cerium-modified copper and iron oxides derived from metal organic frameworks, Journal of Colloid and Interface Science 699 (2025) 138175
- [27] Zili Wu, Meijun Li, Jane Howell, Harry M. Meyer, Steven H. Overbury, Probing Defect Sites on CeO₂ Nanocrystals with Well-Defined Surface Planes by Raman Spectroscopy and O₂ Adsorption. Langmuir 2010, 26(21), 16595–16606
- [28] Vatanparast, M.; Saedi, L. Sonochemical-assisted synthesis and characterization of CeO₂ nanoparticles and their photocatalytic properties. J. Mater. Sci.: Mater. Electron. 2018, 29 (9), 7107–7113. <https://doi.org/10.1007/s10854-018-8698-8>
- [29] Ayesha Mushtaq, Nelofer Jamil, Sabeena Rizwan, Fazeela Mandokhel, Musarrat Riaz, G L Hornyak, M Najam Malghani and M Naeem Shahwani Engineered silica nanoparticles and silica-based controlled-release fertilizer for drought and saline areas. IOP Conf. Ser. Mater. Sci. Eng. 2018, 414 (1), 012029. <https://doi.org/10.1088/1757-899X/414/1/012029>
- [30] Latha, P.; Prakash, K.; Karuthapandian, S. Enhanced visible-light photocatalytic activity of CeO₂/alumina nanocomposite synthesized via facile mixing-calcination method for dye degradation. Adv. Powder Technol. 2017, 28 (11), 2903–2913. <https://doi.org/10.1016/j.appt.2017.08.017>

- [31] Wang, L.; Ren, G.; Xie, W. Jingwei Zhang, Deng Pan, Shudong Wang. Simple and facile synthesis of single-crystal CeO₂ abrasives and their highly efficient removal mechanism on SiO₂ film. *Appl. Surf. Sci.* 2024, 654, 159510. <https://doi.org/10.1016/j.apsusc.2024.159510>
- [32] Damyanova, S.; Pérez, C. A.; Schmal, M.; Bueno, J. M. C. Characterization of ceria-coated alumina carrier. *Appl. Catal. A* 2002, 234 (1–2), 271–282. [https://doi.org/10.1016/S0926-860X\(02\)00233-8](https://doi.org/10.1016/S0926-860X(02)00233-8)
- [33] Luo, X. , Rong Wang, Jun Ni, Jianxin Lin, Bingyu Lin, Xianming Xu & Kemei Wei. Effect of La₂O₃ on Ru/CeO₂–La₂O₃ catalyst for ammonia synthesis. *Catal. Lett.* 2009, 133 (3–4), 382–387. <https://doi.org/10.1007/s10562-009-0177-7>
- [34] Romeo, M.; Bak, K.; El Fallah, J.; Le Normand, F.; Hilaire, L. XPS study of the reduction of cerium dioxide. *Surf. Interface Anal.* 1993, 20 (6), 508–512. <https://doi.org/10.1002/sia.740200607>
- [35] Zohari-Moafi, M.; Habibi-Yangjeh, A.; Habibi, M.; Akinay, Y. Binary CeO_{2-x}/Ag₄V₂O₇ photocatalysts: Impressive performances in detoxification of organic and inorganic pollutants. *Mol. Catal.* 2024, 556, 113920. <https://doi.org/10.1016/j.mcat.2024.113920>
- [36] A. Pfau, K.D. Schierbaum. The electronic structure of stoichiometric and reduced CeO₂ surfaces. *Surface Science* 321 (1994) 71-80
- [37] Samadi, S., Khalili, E. & Allahgholi Ghasri, M.R. Degradation of Methyl Red under Visible Light Using N,F-TiO₂/SiO₂/rGO Nanocomposite. *J. Electron. Mater.* 48, 7836–7845 (2019). <https://doi.org/10.1007/s11664-019-07585-w>

[38] Yaning Han, Xiaowei Chen, Miguel Tinoco, Susana Fernández-Garcia, Ana B. Hungría, Youxun Li, Jiyan Nai, Ren'an Wu, Almudena Aguinaco, Eduardo Blanco, José J. Calvino, Lei Jiang,. Enhanced photocatalysis by defect-engineered CeO₂ with sulfite activation under visible light irradiation: Applied Surface Science 2024, 678, 30 161072

[39] Simran Takkar, Bhawna Tyagi, Naveen Kumar, Taruna Kumari, Khushboo Iqbal, Ajit Varma, Indu Shekhar Thakur, Arti Mishra, Biodegradation of Methyl Red dye by *Zhihengliuella* sp. ISTPL4: Kinetic studies, isotherm and biodegradation pathway, Environmental Technology & Innovation, 2022, 26, 102348

[40] Farooq, N.; Khan, M. I.; Rehman, Z. U. et al. Barium-doped ceria–fabricated graphitic carbon nitride (BDC/g-C₃N₄) nanomaterial as improved photocatalyst for efficient vitiation of organic dyes from industrial effluents. Inorg. Chem. Commun. 2024, 159, 111830. <https://doi.org/10.1016/j.inoche.2023.111830>