Unraveling the Origin of Photocatalytic Deactivation in CeO₂/Nb₂O₅ Heterostructure Systems during Methanol Oxidation: Insight into the Role of Cerium Species

Łukasz Wolski,* Oleg I. Lebedev, Colin P. Harmer, Kirill Kovnir, Hanen Abdelli, Tomasz Grzyb, Marco Daturi, and Mohamad El-Roz*

Cite This: J. Phys. Chem. C 2021, 125, 12650−12662

ACCESS | Metrics & More

ABSTRACT: The study provides deep insight into the origin of photocatalytic deactivation of Nb₂O₅ after modification with ceria. Of particular interest was to fully understand the role of ceria species in diminishing the photocatalytic performance of CeO₂/Nb₂O₅ heterostructures. For this purpose, ceria was loaded on niobia surfaces by wet impregnation. The as-prepared materials were characterized by powder X-ray diffraction, nitrogen physisorption, UV−visible spectroscopy, X-ray photoelectron spectroscopy, high-resolution transmission electron microscopy, and photoluminescence measurements. Photocatalytic activity of parent metal oxides (i.e., Nb₂O₅ and CeO₂) and as-prepared CeO₂/Nb₂O₅ heterostructures with different ceria loadings were tested in methanol photooxidation, a model gas-phase reaction. Deep insight into the photocatalytic process provided by operando-IR techniques combined with results of photoluminescence studies revealed that deactivation of CeO₂/Nb₂O₅ heterostructures resulted from increased recombination of photo-excited electrons and holes. The main factor contributing to more efficient recombination of the charge carriers in the heterostructures was the ultrafine size of the ceria species. The presence of such highly dispersed ceria species on the niobia surface provided a strong interface between these two semiconductors, enabling efficient charge transfer from Nb₂O₅ to CeO₂. However, the ceria species supported on niobia exhibited a high defect site concentration, which acted as highly active recombination centers for the photo-induced charge carriers.

1. INTRODUCTION

Cerium dioxide is one of the most intensively studied model heterogeneous catalysts. Hitherto, it has been established that ceria can be successfully used not only as a support for various active phases but it can also be involved as a promising active component for various reactions. Recently, cerium dioxide has been thoroughly studied for applications in advanced oxidation processes, e.g., photocatalytic oxidation or Fenton-like reactions. Many authors have reported that loading of ceria on the surface of semiconducting metal oxides is an efficient method to improve the photocatalytic performance of parent oxides. For instance, Zhu et al. have documented that CeO₂/ZnO composites displayed highly enhanced photocatalytic activity in Rhodamine B (RhB) degradation compared to pristine ZnO and CeO₂. The increase in activity of the CeO₂/ZnO heterostructures was attributed by the authors to formation of Z-scheme heterojunction, which improved the separation of photo-generated charge carriers. Improved efficiency of charge carrier separation resulting from formation of heterojunctions has also been reported for CeO₂/TiO₂ systems in photooxidation of toluene and photodegradation of phenazopyridine drugs. However, the above-mentioned paradigm concerning the positive role ceria modifier plays in improving the photocatalytic activity of various semiconducting metal oxides has been recently rebutted by Morlando et al. The authors found that deposition of CeO₂ nanodots on the surface of TiO₂ led to a significant decrease in photocatalytic activity of the as-formed composite materials. The authors claimed that the decrease in activity of CeO₂/TiO₂ nanocomposites may have resulted from scavenging of reactive oxygen species by ceria species, increased recombination of photo-excited charge carriers caused by ceria doping and/or UV shielding effects from ceria loading on the surface of TiO₂. Deactivation of photocatalysts after loading of ceria was also observed for CeO₂/ZnO heterostructures. According to the authors, deactivation of this catalytic system arose from the presence of ultrafine CeO₂ nanoparticles with existing surface defects, which could impart some form of reactive oxygen species scavenging property. However, no evidence supporting the above-mentioned hypotheses, explaining...
deactivation of TiO₂ or ZnO photocatalysts after loading of ceria species, has been provided.

Besides ZnO and TiO₂, niobium pentoxide (Nb₂O₅) is another semiconductor, which has been successfully used in photocatalytic reactions.¹³ Niobia is known for its high Bronsted acidity, which can play an important role in controlling the selectivity of various processes.¹⁴,¹⁸,¹⁹ Previous reports show that the photocatalytic activity of Nb₂O₅ can also be improved by forming heterojunctions with other semiconductors (e.g., Nb₂O₅/TiO₂,²⁰ Nb₂O₅/ZnO,²² Nb₂O₅/B₃W₀₅,²³ NiO/Nb₂O₅,²⁴ and Nb₂O₅/g-C₃N₄).²⁵ However, studies concerning the influence of ceria modifier on the photocatalytic activity of niobium pentoxide are sparse. Ferraz et al.²⁶ have tested CeO₂/Nb₂O₅ heterostructures with low ceria loadings (up to 2 wt % of CeO₂ in the composite) in photocatalytic degradation of phenol and methylene blue under UV light (λ = 254 nm). The photocatalysts had a low surface area of ca. 15 m²/g and consisted of relatively large ceria particles (ca. 14 nm in diameter) supported on Nb₂O₅. The authors have established that a loading of 0.3 wt % of CeO₂ on the surface of niobia improved photocatalytic performance of the as-formed heterostructure, but at a higher ceria loading in the composite, the activity was slightly lower than that observed for parent Nb₂O₅. Thus, no remarkable deactivation effect was reported by the authors after modification of niobia with ceria. It is worth noting that the experiments were performed under monochromatic UV light (λ = 254 nm), which can activate both methylene blue and phenol. It means that both photocatalytic degradation and photochemical degradation processes could occur. Thus, the above-mentioned photocatalytic processes in the liquid phase are very complex and do not allow to gain clear information about the role of ceria modifier in controlling the photocatalytic performance of niobia-based heterostructures. In view of the recent results, reporting the ambiguous negative/positive role of ceria species in CeO₂/ZnO and CeO₂/TiO₂ heterostructures, a fundamental evaluation of the ceria species’ role in controlling the activity of niobia-based photocatalysts, is crucial for rational development of ceria-containing photocatalysts.

The present study establishes the influence of ceria modifier on the structure, texture, and photocatalytic performance of niobium pentoxide. Ceria species were loaded on the niobia surface by wet impregnation. Photocatalytic activity of parent metal oxides (i.e., Nb₂O₅ and CeO₂) and as-prepared CeO₂/Nb₂O₅ heterostructures with different ceria loadings was tested in methanol oxidation, a well-known model gas-phase reaction that allows us to determine the relationship between properties of materials and their catalytic performance. Opera
do-IR techniques provided insight into the mechanism of the photocatalytic process across CeO₂/Nb₂O₅ heterostructures while elucidating the role individual components of each heterostructure play in methanol photooxidation.²⁷⁻²⁹

2. EXPERIMENTAL SECTION

2.1. Synthesis of Nb₂O₅. Niobium pentoxide was synthesized using the hydrothermal procedure described by Murayama et al.³⁰ In a typical synthesis route, ammonium niobate(V) oxalate hydrate (Sigma-Aldrich, C₂H₄NNbO₅·H₂O, 99.999%) (9.0894 g, 30 mmol) was dissolved in 200 mL of deionized water. Following 1 h of vigorous stirring, the pellucid solution was sealed in a Teflon-lined stainless steel autoclave and heated for 24 h at 175 °C. The solid formed during hydrothermal treatment was then separated by filtration, washed with deionized water, dried at room temperature, and calcined for 2 h at 400 °C (temperature ramp: 1.6 °C/min). The as-prepared material was denoted as Nb₂O₅.

2.2. Loading of Ceria Species on the Niobia Support. Ceria species were loaded on the surface of Nb₂O₅ via a facile wet impregnation method. In a typical synthesis, 6 g of as-prepared Nb₂O₅ was dispersed in 10 mL of deionized water. Meanwhile, cerium(III) nitrate hexahydrate (Sigma-Aldrich, 99.99%) was dissolved in 35 mL of deionized water (the amount of cerium source was adjusted to obtain 1.0, 5.0, or 10.0 wt % of Ce on the niobia support). Next, the solution of cerium(III) nitrate hexahydrate was stirred into the mixture containing niobium pentoxide dispersed in water. Following 1 h of agitation at room temperature, the mixture was transferred to a round-bottom flask and sonicated for 10 min. In the next step, water was evaporated from the mixture using a rotary evaporator and the as-obtained powder was dried in a furnace at 80 °C for 12 h. Finally, the dry powder was calcined at 400 °C for 2 h (temperature ramp: 1.6 °C/min). The as-prepared ceria-modified catalysts containing 1.0, 5.0, or 10.0 wt % of Ce were labeled as Ce1/Nb₂O₅, Ce5/Nb₂O₅, and Ce10/Nb₂O₅, respectively.

Mechanical CeO₂/Nb₂O₅ mixtures were prepared using Nb₂O₅ and commercial CeO₂. For this purpose, appropriate amounts of metal oxides were mixed with a small amount of deionized water and then crushed in an agate mortar to get a homogeneous mixture. Next, the as-obtained mechanical mixtures of metal oxides were dried overnight at 70 °C to obtain dry powders. The as-prepared materials were used as reference samples.

2.3. Characterization of Catalysts. The catalysts were characterized with the use of inductively coupled plasma-optical emission spectrometry (ICP-OES), nitrogen phys
desorption, powder X-ray diffraction (PXRD), high-resolution transmission electron microscopy (HRTEM), UV–visible spectroscopy (UV–vis), X-ray photoelectron spectroscopy (XPS), and photoluminescence measurements (PL).

Powder X-ray diffraction patterns were collected on a benchtop Rigaku Miniflex 600 with Cu Kα radiation (λ = 1.5406 Å) and Ni-Kα filter. Peak locations of each sample were refined against a Si internal standard (Si 640d, Fd3m, a = 5.43123 Å) via Rietveld refinement in GSAS-II.³¹ Rietveld refinement was initiated by determining sample displacement from the Si internal standard. Then, size and preferred orientation were refined to best fit each sample before refining unit cell parameters.

Transmission electron microscopy (TEM) was performed using a JEM ARM200F cold field emission microscope, operated at 200 kV and equipped with a large angle CENTURIO EDX detector, Orius Gatan CCD camera, and Quantum GIF. The TEM samples were prepared in conventional way—depositing a solution of the material in ethanol on a carbon holey Cu grid.

Diffuse reflectance UV–vis spectra (DR UV–vis) were recorded on a Varian Cary 300 Scan spectrophotometer equipped with a diffuse reflectance accessory. Spectra were recorded at room temperature from 200 to 800 nm using Spectralon as a reference material.

Photoluminescence properties were studied at room temperature using a PIXIS:256E Digital CCD camera equipped with an SP-2156 Imaging Spectrograph (Princeton Instrument).
Instruments) and Opolette 355LD UVDM tunable laser as the excitation source (with a repetition rate of 20 Hz; 0.5 mJ pulse energy at 250 nm). All spectra were corrected for spectral response of the equipment. The beam size and laser powers were determined by a 10A-PPS power meter (Ophir Photonics).

The N₂ adsorption—desorption isotherms were obtained at −196 °C using a Micromeritics ASAP 2020 Physisorption Analyzer. Before the measurements, samples were degassed at 120 °C for 10 h. The surface area of the materials obtained was estimated by the Brunauer—Emmett—Teller (BET) method.

X-ray photoelectron spectroscopy (XPS) was performed using an ultra-high vacuum photoelectron spectrometer based on a Phoibos150 NAP analyzer (Seps, Germany). The analysis chamber was operated under vacuum with a pressure close to 5 × 10⁻⁹ mbar, and the sample was irradiated with a monochromatic Al Kα (1486.6 eV) radiation. Any charging that occurred during the measurements (due to incomplete neutralization of ejected surface electrons) was accounted for by rigidly shifting the entire spectrum by a distance needed to set the binding energy of the C1s assigned to adventitious carbon to the assumed value of 284.8 eV.

2.4. Photocatalytic Tests. The photocatalysts were pressed into self-supported wafers of similar density (Ø = 16 mm, m ≈ 11.7 mg/cm²) and about 65 ± 2 μm in thickness. Thus, FTIR spectra of different samples recorded in transmission mode could be directly and quantitatively compared without any additional normalization. The outlet gas phase evolution was followed by both IR spectroscopy and mass spectrometry. FTIR spectra of the gas phase were collected using a Nicolet 5700 FTIR spectrometer. FTIR spectra of di-

Figure 1. (a) Activity of catalysts in methanol photooxidation at the steady state for 2 h of reaction. (b) Graph presenting differences between activity of ceria-modified catalysts prepared by wet impregnation, mechanical mixtures of metal oxides, and theoretical methanol conversion expected at the given concentration of Nb₂O₅ and CeO₂ in the composite materials (theoretical conversion of methanol was estimated by summing up activity of given amounts of commercial CeO₂ and parent Nb₂O₅ in the heterostructures). A mechanical mixture of metal oxides was prepared using parent Nb₂O₅ and commercial CeO₂ (see Section 2).

The surface area of the materials obtained was estimated by the Brunauer—Emmett—Teller (BET) method.

X-ray photoelectron spectroscopy (XPS) was performed using an ultra-high vacuum photoelectron spectrometer based on a Phoibos150 NAP analyzer (Seps, Germany). The analysis chamber was operated under vacuum with a pressure close to 5 × 10⁻⁹ mbar, and the sample was irradiated with a monochromatic Al Kα (1486.6 eV) radiation. Any charging that occurred during the measurements (due to incomplete neutralization of ejected surface electrons) was accounted for by rigidly shifting the entire spectrum by a distance needed to set the binding energy of the C1s assigned to adventitious carbon to the assumed value of 284.8 eV.

2.4. Photocatalytic Tests. The photocatalysts were pressed into self-supported wafers of similar density (Ø = 16 mm, m ≈ 11.7 mg/cm²) and about 65 ± 2 μm in thickness. Thus, FTIR spectra of different samples recorded in transmission mode could be directly and quantitatively compared without any additional normalization. The outlet gas phase evolution was followed by both IR spectroscopy and mass spectrometry. FTIR spectra of the gas phase were collected using a Nicolet 5700 FTIR spectrometer (64 scans/spectrum) equipped with an MCT detector. The operando-IR system was connected to a flow setup.32 Gases were introduced into the lines by mass flow controllers. The system allows the two gas mixtures, the so-called “activation” and “reaction” flows, to be prepared and sent independently to the reactor cell. The “sandwich” type reactor cell used in this study is described in ref 33. It was made of a stainless steel cylinder that carries a toroidal sample holder in its center, where the catalyst self-supporting wafer was placed. Tightness was obtained by O-rings, and the dead volume (typically defined as the residual space between each sample face and the windows) was reduced to about 0.4 mL by filling the empty space with KBr windows placed on each side of the sample holder. The sample analysis was made possible without the superposition of the gas phase signal and fluid dynamics. Gases were introduced to the sample and evacuated by two 1/8 inch OD pipes connected to the opposite sides of the sample holder. In this study, UV irradiation was carried using a UV light guide (A10014-50-0110) mounted at the entrance to the IR cell and connected to a polychromatic light of Xe-Hg lamp (LC8 spot light Hamamatsu, Li0852, 200 W) equipped with a filter to enable monochromatic UV irradiation (λ = 365 nm). More details on the operando-IR system for photocatalysis can be found in refs 33 and 34. The employed configuration allowed a low partial pressure of methanol to be achieved using a saturator at a controlled temperature. The gas mixture composition was fixed then at 0.12 vol. % methanol and 20 vol. % O₂ in Ar, and the total flow was adjusted to 20 cm³/min.

Outlet gases were characterized by a Pfeiffer Omnistar mass spectrometer. FTIR spectra of the gas phase were collected using a gas microcell. The conversions were calculated at the steady state.

3. RESULTS AND DISCUSSION

3.1. Photocatalytic Tests. Photocatalytic activity of materials was tested via methanol oxidation in the gas phase. The results are shown in Figure 1a. The highest methanol conversion of 24.6% was observed for parent Nb₂O₅. Commercial CeO₂ was significantly less active than pristine niobium pentoxide and its activity at 5.3%. As can be seen from Figure 1a, all ceria-modified samples exhibited significantly lower activity than parent Nb₂O₅. In the case of Ce1/Nb₂O₅, activity was reduced by more than 50% compared to pristine niobia (24.6% vs 11.9% of methanol conversion for Nb₂O₅ and Ce1/Nb₂O₅, respectively). A more pronounced decrease in the activity of the composite catalysts was observed for Ce5/Nb₂O₅, Ce10/Nb₂O₅, and Nb₂O₅. Interestingly, for Ce10/Nb₂O₅, photocatalytic activity of the heterostructure was totally quenched. There were no products formed during the methanol photooxidation over this catalyst.

To gain deeper insight into the quenching of catalysts’ activity after loading of ceria on niobia, we performed additional measurements with mechanical mixtures of metal oxides as reference samples. We found that activity of these
mechanical mixtures of metal oxides containing 1 wt % and 10 wt % of Ce was only slightly lower than that observed for unmodified Nb$_2$O$_5$ (see Figure 1b). Interestingly, the activity of mechanical mixtures of CeO$_2$ and Nb$_2$O$_5$ oxides was not quenched even at a very high concentration of CeO$_2$ in the composite material (Nb$_3$O$_5$:CeO$_2$ weight ratio of 1:1). As can be seen from Figure 1, such a mixture of metal oxides was still slightly more active than commercial CeO$_2$. To shed light on the role of ceria species in deactivation of ceria-modified samples, prepared by wet impregnation, we compared the activity of these materials with the activity of mechanical mixtures of metal oxides and theoretical activity of the composite materials expected at a given concentration of CeO$_2$ and Nb$_2$O$_5$ in the heterostructures (theoretical methanol conversion was estimated by summing up the activity of a given amount of Nb$_2$O$_5$ and commercial CeO$_2$ in the composite). According to our results, the activity of mechanical mixtures of metal oxides was always lower than the expected theoretical values but was still significantly higher than the activity of samples prepared by wet impregnation (see Figure 1b). This observation led us to conclude that deactivation of the composite catalysts prepared by wet impregnation should be somehow related to the unique properties of these materials and their interaction.

To further probe the role of the ceria modifier in the photocatalytic process, operando-IR studies have been performed. According to the literature, the first step of methanol photooxidation is the adsorption of methyl alcohol on the catalyst surface and consequently the formation of surface methoxy species. Operando-IR studies show that exposure of all catalysts to the gas feed led to immediate disappearance of IR bands typical of surface hydroxyl groups of niobia and ceria (e.g., IR bands at ca. 3662 cm$^{-1}$ characteristic of bridged OH groups in the fluorite structure of ceria$^{36,37}$) and appearance of several new IR bands typical of adsorbed methanol molecules (e.g., IR bands in the range from 2750 to 3000 cm$^{-1}$). Detailed analysis of the adsorbed methoxy species, in the range of wavelengths shown in Figure S1, is problematic since characteristic vibrations of adsorbed methanol molecules are not overlapped with other vibrational bands (i.e., at 1200–1000 cm$^{-1}$). Figure 2 shows surface FTIR spectra of catalysts at the equilibrium state during methanol adsorption under dark conditions. In the case of ceria, it is easy to identify the bands due to linearly (1112 cm$^{-1}$) and two-fold (1057 cm$^{-1}$) coordinated methoxy species on Ce$^{4+}$. The components at 1039 cm$^{-1}$ is assigned to bridged species on Ce$^{4+}$ cations in the proximity of an oxygen vacancy. The other observed bands at higher wavenumbers are due to carbonate impurities belonging to ceria exposure to air and to residual oxalates on the surface of niobia. Analysis of IR spectra recorded for niobia-based samples allowed discrimination of three components at ca. 1158, 1125, and 1105 cm$^{-1}$. The first component at ca. 1158 cm$^{-1}$ is characteristic of $\rho$(CH$_3$) rocking mode of methoxy species, while the latter two IR bands are typical of $v$(OC) vibration modes of linearly (1125 cm$^{-1}$) and may be two-fold (or another linear species coordinated on different exposed crystal planes, at 1105 cm$^{-1}$) coordinated methoxy species on niobia. We found no significant differences in the forms and concentration of methoxy species on the surface of unmodified Nb$_2$O$_5$ and ceria-modified samples prepared by wet impregnation. Even at a relatively high loading of ceria in Ce10/Nb$_2$O$_5$ catalyst, no noticeable IR bands typical of aforementioned methoxy species bonded to the ceria surface were found. In view of these observations, we concluded that quenching of niobia activity through loading of ceria by wet impregnation cannot be attributed to covering of the niobia surface by ceria species and/or hindering of niobia ability to adsorb methanol molecules.

The second step in photocatalytic oxidation of methanol is oxidation of adsorbed methoxy species to formaldehyde. The as-formed formaldehyde can then be desorbed from the catalyst surface or further transformed into other products such as methyl formate, formic acid, or carbon dioxide. According to the literature, oxidation of formaldehyde to other products leads to appearance of some reaction intermediates, such as adsorbed formate species, characterized by the vibrational bands at ca. 1565, 1371, and 1356 cm$^{-1}$ for commercial CeO$_2$ and ca. 1577, 1385, and 1365 cm$^{-1}$ for niobia-based photocatalysts. As can be seen from sample FTIR spectra of pristine Nb$_2$O$_5$ and commercial CeO$_2$ shown in Figure 3a, typical IR bands for these reaction intermediates showed up immediately after irradiation of the catalysts with UV light and continued to increase the intensity upon irradiation. The increase in intensity of typical IR bands of adsorbed formate species was associated with a decrease in intensity of characteristic IR bands of adsorbed methanol molecules (IR bands in the range of 1200–1000 cm$^{-1}$). This observation led us to conclude that methanol is efficiently oxidized on the surface of these two unmodified metal oxides. Interestingly, it was revealed that methanol oxidation on ceria proceeds until formation of CO$_2$, as witnessed by the formation of bidentate carbonate on the surface of the samples (bands at 1594 and 1304 cm$^{-1}$). However, a different trend was observed for ceria-modified samples prepared by wet impregnation. As can be seen from Figure 3b, the changes in intensity of IR bands characteristic of adsorbed formate species was significantly suppressed for the Ce1/Nb$_2$O$_5$ and Ce5/Nb$_2$O$_5$ catalysts. In the case of a reaction with the use of Ce10/Nb$_2$O$_5$, almost no changes in intensity of IR bands typical of adsorbed formate species were found. Also, no changes were observed for this catalyst in the range of wavenumbers characteristic of adsorbed methoxy species (see Figure 3a). It is worth noting that for all niobia-based samples methanol conversion was found to be
proportional to the intensity of IR bands characteristic of adsorbed formate species (see Figure 3c). Thus, IR experimental data indicated that a decrease in activity of heterostructures prepared by wet impregnation resulted from their reduced ability to oxidize methanol molecules adsorbed on the niobia surface.

3.2. Characterization of Catalysts. To understand the origin of photocatalytic deactivation of ceria-modified samples prepared by wet impregnation, the as-prepared catalysts were precisely characterized by a variety of complementary methods, providing information about their composition, structure, texture, optical, and electronic properties.

To confirm the presence of ceria species on the niobia surface, the chemical composition of catalysts was analyzed with the use of ICP-OES. As can be seen from Table 1, for all ceria-containing catalysts, the real loading of Ce was only slightly lower than the assumed values and was found to be 0.7, 3.7, and 7.9 wt % of Ce for Ce1/Nb2O5, Ce5/Nb2O5, and Ce10/Nb2O5, respectively.

Structure of materials was characterized by powder X-ray diffraction (\(\lambda = 1.5406 \text{ Å}\)). As can be seen from Figure 4, PXRD patterns of all samples exhibited two distinct diffraction peaks at 22.7 and 46.3° 2\(\theta\), which are similar to the reported PXRD pattern of the deformed orthorhombic Nb2O5 phase. It should be noted that no crystalline CeO2 or other cerium species was identified for all ceria-modified materials.

Table 1. Characteristics of Niobia-Based Catalysts

| catalyst      | BET surface area [m²/g] | average pore size [nm] | Ce loading [wt %] |
|---------------|-------------------------|------------------------|-------------------|
| Nb2O5         | 157                     | 8.8                    | -                 |
| Ce1/Nb2O5     | 153                     | 9.0                    | 0.7               |
| Ce5/Nb2O5     | 156                     | 8.3                    | 3.7               |
| Ce10/Nb2O5    | 143                     | 8.1                    | 7.9               |
| CeO2c         |                         |                        |                   |

"Estimated with the use of the BJH method from the adsorption branch. "Determined with the use of ICP-OES. "Commercial CeO2.

Figure 3. (a) FTIR spectra of catalyst surfaces recorded at the beginning of photocatalytic oxidation of methanol under UV light (\(\lambda = 365 \text{ nm}\)). (b) Graph presenting changes in intensity of the most intense IR band typical for adsorbed formate species (i.e., band at 1577 cm\(^{-1}\) for Nb2O5 and Ce1/Nb2O5; band at 1584 cm\(^{-1}\) for Ce5/Nb2O5 and Ce10/Nb2O5; and band at 1565 cm\(^{-1}\) for commercial CeO2) at the beginning of photocatalytic process. (c) Relationship between the activity of catalysts and increase in intensity of the most intense IR band typical of adsorbed formate species. The variations of the IR band’s intensities (in panels (b) and (c)) were measured by the dedicated tool in OMNIC software, after having subtracted the IR spectrum of the catalyst at the equilibrium steady state during methanol adsorption under dark conditions, from the IR spectrum after about 25 min of photocatalytic reaction.

Figure 4. PXRD patterns of catalysts normalized to the intensity of the (001) peak.
orthorhombic structure of Nb$_2$O$_5$

Detailed analysis of electron diffraction (ED) patterns and high-resolution TEM images of niobium pentoxide led us to observe discrepancy between the previously reported deformed orthorhombic structure of Nb$_2$O$_5$\(^{30}\) and the structure obtained in this study. For this reason, identification of a niobia structural model was determined by first attempting to fit the PXRD data to known structures. Although we did not find any matches to known structurally characterized Nb–O binaries, a search among tantalum oxides (note the similar size of Ta and Nb) revealed orthorhombic Ta$_2$O$_5$ crystallizing in the Cmmm space group as a reasonable fit.\(^{42}\) Ta$_2$O$_5$ is composed of Ta–O octahedra with Ta on the $ab$ plane bridged by equatorial O atoms and stacked along the $c$ axis by axially bridging O atoms. In this model, the equatorial O atoms are fully occupied with half occupancy for the axial O site. This is an average structure, which was shown to be incommensurately modulated. The equivalent atomic size and bonding characteristics between Nb and Ta allowed us to build an isostructural Nb$_2$O$_5$ model (Figure S2, Supporting Information). A further database search verified no previously reported Nb–O binaries in the orthorhombic Cmmm space group.

Analysis of PXRD data collected with the Si internal standard demonstrates that loading of ceria on niobia by wet impregnation resulted in a slight shift of the diffraction peaks at 22.7 and 46.3\(^{\circ}\) $2\theta$ toward higher angles (see Figure S3, Supporting Information). Rietveld refinement of our Nb$_2$O$_5$ model against PXRD data from each sample collected with a Si internal standard revealed a slight compression of the $c$ parameter of the niobia structure with increasing Ce loading (see Table 2). The highest decrease in the $c$ parameter value was typical of the sample with the highest concentration of ceria modifier, i.e., Ce10/Nb$_2$O$_5$. In view of these observations, we claim that ceria species loaded on Nb$_2$O$_5$ by wet impregnation strongly interacted with the niobia support.

To confirm the novel orthorhombic Cmmm structure of Nb$_2$O$_5$ proposed by PXRD, electron diffraction (ED), high-angle annular dark field scanning TEM (HAADF-STEM) imaging, and annular bright-field STEM (ABF-STEM) analyses were performed. The chemical composition and Ce distribution over the samples was confirmed by STEM-EDX elemental mapping. It was found that, irrespective of Ce amount, ceria-modified samples showed similar features as parent Nb$_2$O$_5$ (see Figure 5 and Figure S4, respectively). All samples consisted of needle-type nanostructures with typical dimensions: length of around 20–40 nm and diameter of 7–10 nm. They were stuck together in a random array, creating nanopores in the volume of the sample. The corresponding ED pattern of ceria-modified niobium pentoxide (Figure 5d, inset) can be fully indexed based on the proposed orthorhombic Cmmm structure. No extra rings belonging to Ce or Ce–O structures are present, in agreement with PXRD data. EDX elemental mapping in STEM mode evidenced homogeneous distribution of ceria species over the Nb$_2$O$_5$ sample (Figure 5b). STEM–EDX and ED studies support the conclusion drawn based on PXRD studies regarding the amorphous character or very high dispersion of ceria species on the niobia surface.

High-resolution HAADF-STEM and simultaneously acquired ABF-STEM images along the main crystallographic zones, [010] and [110], agree with the structural model determined by PXRD (see inset in Figure 6). Using two complementary techniques, such as high-resolution HAADF-STEM and ABF-STEM, provides information about position of heavy (Nb, Ce) and light (O) elements. Regardless of the imperfect orientation of nanostructures due to their small size exactly along the zone axis, the overlaid structural model shows good correspondence to the experimental images. Due to the

![Figure 5](https://doi.org/10.1021/acs.jpcc.1c02812)

**Figure 5.** (a) Bright-field low magnification TEM image of the representative ceria-modified sample prepared by wet impregnation. (b) Low magnification HAADF-STEM image and simultaneously acquired EDX elemental mapping of Nb L, Ce L, and O K. (c) HRTEM and (d) high-resolution HAADF-STEM images of the representative Ce/Nb$_2$O$_5$ sample and corresponding ring ED pattern indexed based on the orthorhombic Cmmm Nb$_2$O$_5$ structure ($a = 3.62$ Å; $b = 3.56$ Å; $c = 3.91$ Å) obtained from PXRD.

![Figure 6](https://doi.org/10.1021/acs.jpcc.1c02812)

**Figure 6.** HAADF-STEM (left panel) and simultaneously acquired ABF-STEM (right panel) high-resolution images along the two main crystallographic zone axes, (a) [010] and (b) [110], of the orthorhombic Cmmm Nb$_2$O$_5$ structure ($a = 3.62$ Å; $b = 3.56$ Å; $c = 3.91$ Å). The magnified [010] HAADF-STEM and ABF-STEM images together with the overlaid structural model are given as an inset in (a) (Nb atoms, orange spheres; O atoms, blue spheres).

| catalyst | $c$ parameter [Å] | Rwp$^{46}$ [%] | GoF$^{46}$ |
|----------|-------------------|----------------|----------|
| Nb$_2$O$_5$ | 3.9147(4) | 2.84 | 1.22 |
| Ce1/Nb$_2$O$_5$ | 3.9146(3) | 2.88 | 1.24 |
| Ce5/Nb$_2$O$_5$ | 3.9076(3) | 3.2 | 1.39 |
| Ce10/Nb$_2$O$_5$ | 3.9009(4) | 3.56 | 1.66 |

$^{46}$Weighted residual of the least-squares refinement. $^{46}$Goodness of fit.

was typical of the sample with the highest concentration of ceria modifier, i.e., Ce10/Nb$_2$O$_5$. In view of these observations, we claim that ceria species loaded on Nb$_2$O$_5$ by wet impregnation strongly interacted with the niobia support.
relatively large difference in atomic numbers between Nb(41) and Ce(58), it should be possible to distinguish positions of these two atoms in high-resolution HAADF-STEM images. However, no difference in atomic columns contrast in HAADF-STEM images was detected, suggesting very high dispersion of ceria species on the niobia surface.

Texture of the catalysts was characterized with the use of low-temperature nitrogen adsorption−desorption measurements. As can be seen from Figure 7a, all isotherms were of type IV(a), indicating the mesoporous structure of the catalysts.43 Textural parameters of materials estimated from nitrogen physisorption are summarized in Table 1. The highest BET surface area of 157 m²/g was observed for parent niobium pentoxide. Deposition of ceria species on niobia by wet impregnation led to a decrease in the catalyst surface area, but differences between samples were insufficient to justify the drastic difference in catalytic activities. Deposition of ceria species on niobia by wet impregnation led to a decrease in the catalyst surface area, but differences between samples were insufficient to justify the drastic difference in catalytic activities. The lowest surface area of 143 m²/g was characteristic of the catalyst containing the highest amount of ceria modifier, i.e., Ce10/Nb2O5. Figure 7b shows that loading of ceria on the niobia support also had a negligible influence on textural properties of the Nb2O5-based samples. All the catalysts exhibited a broad pore size distribution ranging from ca. 2 nm to more than 50 nm. The average pore size estimated for all the catalysts from adsorption branch using Barrett−Joyner−Halenda (BJH) method ranged from 8 to 9 nm (see Table 1). The negligible influence of ceria modifier on the BET surface area and pore size distribution estimated for the catalysts is further evidence of the high dispersion of ceria species on the niobia surface, which is also coherent with the presence of ceria hydroxyls in the IR spectra reported above.

The optical property of each catalyst was studied by diffuse reflectance UV−vis spectroscopy. As can be seen from Figure 8a, parent niobia exhibited a broad absorption band with maximum absorbance at ca. 272 nm. According to the literature,44 this absorption band is typical of charge transfer transitions from O2− to Nb5+, which are associated to the energy gap between the O 2p valence band and the Nb 4d conduction band of Nb2O5 bulk. Commercial CeO2 exhibited two absorption bands with maximum intensities centered at ca. 352 and 268 nm. According to the literature,45,46 these absorption bands are attributed to O2− → Ce4+ charge transfer transitions and inter-band transitions, respectively. As can be seen from Figure 8a, deposition of ceria species on niobia increased the ability of the composite materials to absorb light in the range of wavelengths typical of O2− → Ce4+ charge.
transfer transitions. It is worth noting that the increase in light absorption observed for ceria-modified samples was proportional to the amount of Ce. The higher concentration of ceria species in the composite material, the higher the materials ability to absorb light in the range of wavelengths typical of O$^{2−}\rightarrow$Ce$^{4+}$ charge transfer transitions.

Band gap values estimated for parent Nb$_2$O$_5$ and commercial CeO$_2$ using Tauc’s plot method were 3.22 and 2.96 eV, respectively, and are in agreement with previous literature data concerning optical properties of Nb$_2$O$_5$ and CeO$_2$. Interestingly, the composite material prepared by a loading of 10 wt% of Ce on niobia by wet impregnation exhibited a significantly lower band gap value than that observed for both pristine metal oxides (see Figure 9). Such a decrease in band gap value of the composite material may result from the formation of a large quantity of defect sites in the structure of CeO$_2$ (e.g., Ce$^{4+}$ ions with neighboring oxygen defects or Ce$^{3+}$ ions), which shifted the absorption edge of ceria toward higher wavelengths (i.e., lower energy values).

To get a deeper insight into the oxidation state of metals in the composite materials, the catalysts were characterized by X-ray photoelectron spectroscopy (Figure 9). The Nb 3d region of unmodified Nb$_2$O$_5$ was characterized by two components, namely, Nb 3d$_{5/2}$ and Nb 3d$_{3/2}$, with a binding energy of 207.3 and 210.0 eV, respectively. According to the literature, these components are assigned to Nb$^{5+}$ species in bulk Nb$_2$O$_5$. In the case of ceria-modified samples prepared by wet impregnation, Nb 3d peaks overlapped with the peak typical of Ce 4p$_{3/2}$. Precise deconvolution of experimental data led us to distinguish these components (see Figure 9). The only form of niobium species in all heterostructures was Nb$^{5+}$. Deconvolution of Ce 3d spectra of commercial CeO$_2$ allowed distinguishing 10 components, namely, v$_0$, v, v′, v″, v‴, u$_0$, u, u′, u″, and u‴ (see Figure 9). According to the literature, v, v′, v″ and u, u′, u″ are assigned to Ce$^{3+}$ species, while v$_0$, v′, and u$_0$, u′ are attributed to Ce$^{4+}$ species. Analysis of Ce 3d XP spectra of ceria-modified samples prepared by wet impregnation was more complex due to the low intensity of peaks at low ceria loadings. To avoid misinterpretation of experimental data, we have omitted deconvolution of Ce 3d spectra collected for Ce1/Nb$_2$O$_5$ and Ce5/Nb$_2$O$_5$. Nevertheless, it is important to stress that Ce 3d spectra recorded for these two samples had a different shape than that observed for commercial CeO$_2$. The most important difference can be considered in terms of a very low relative contribution of components characteristic of Ce$^{4+}$ species, in particular u‴, which is not overlapped with other peaks (see Figure 9).

More information about the oxidation state of cerium species in ceria-modified samples was provided by detailed analysis of Ce 3d spectra of Ce10/Nb$_2$O$_5$, for which the signal was the most intense. As shown in Figure 9, relative contribution of XP peaks characteristic of Ce$^{3+}$ species was significantly more pronounced for Ce10/Nb$_2$O$_5$ than that observed for commercial CeO$_2$. Since FTIR measurements for both samples did not reveal any noticeable IR band typical of methanol molecules adsorbed on Ce$^{3+}$ cations, we claimed that a higher relative contribution of XP peaks characteristic of Ce$^{3+}$ species established for Ce10/Nb$_2$O$_5$ resulted most probably from a higher concentration of defect sites in the structure of this catalyst (i.e., Ce$^{4+}$ ions surrounded by oxygen vacancies in which electrons are trapped). However, the presence of some Ce$^{3+}$ species in all ceria-modified Nb$_2$O$_5$ catalysts cannot be totally excluded. As it was documented by Baldim et al., the concentration of defect sites on the surface of CeO$_2$ nanoparticles often increases with decreasing particle size. Since ceria species in all catalysts prepared by wet impregnation were highly dispersed on the niobia surface, we claim that a high concentration of the above-mentioned defect sites in the structure of these materials is very likely. It is worth noting that our hypothesis is in agreement with results of UV–vis studies, in which a significant shift of the absorption edge of Ce10/Nb$_2$O$_5$ toward lower energy values was observed (see Figure 8b).

To verify whether loading of ceria on niobia has any impact on recombination of charge carriers in the composite materials, we have performed photoluminescence measurements. According to the literature, photoluminescence emission mainly originated from radiative recombination of photo-generated electrons and holes trapped in the band tails of semiconductors. The higher the emission intensity, the higher the efficiency of charge carrier recombination. Parent niobium pentoxide exhibited three broad emission peaks.
CeO$_2$. Therefore, we hypothesize that the more pronounced Ce$_{10}$/Nb$_2$O$_5$, the intensity of the emission at 425 nm increases due to a more efficient recombination of charge carriers in CeO$_2$ (recombination of emission peak can be attributed to the direct band to band recombination of Nb$_2$O$_5$ can be identified). For Nb$_2$O$_5$ and/or from promoted recombination of photoexcited electrons in the Nb 4d conduction band and holes in the O 2p valence band of CeO$_2$). The emission energy of the peaks at ca. 380 nm, 500 nm, and 545 nm (Figure 10) is similar to the optical band gap of CeO$_2$ nanoparticles to the O 2p valence band of CeO$_2$. The emission energy of the peaks at ca. 380 and 425 nm exhibit energy close to the optical band gap of Nb$_2$O$_5$ (3.22 eV; see Figure 8b) and may be attributed to near-band gap emission from Nb$_2$O$_5$ (recombination of photoexcited-electrons in the Nb 4d conduction band and holes in the O 2p valence band of Nb$_2$O$_5$) and the second one at ca. 500 nm). The energy of the former emission peak (~2.92 eV) is close to the optical band gap of commercial CeO$_2$ (2.96 eV; see Figure 8b). Thus, this emission peak can be attributed to the direct band to band recombination of charge carriers in CeO$_2$ (recombination of photoexcited electrons in the Ce 4f conduction band and holes in the O 2p valence band of CeO$_2$). According to the literature, the latter broad emission peak can be attributed to the transitions from electronic energy levels of defects (mainly oxygen vacancies) localized below the Ce 4f band of the CeO$_2$ nanoparticles to the O 2p valence band of CeO$_2$. In the Nb$_2$O$_5$-based samples, loading of ceria species on niobia results in a significant increase in emission intensity of composite materials at ca. 425 nm, 500 nm, and 545 nm (Figure 10). Increased emission at ca. 425 nm may result from the promotion recombination of photoexcited electrons in the Nb 4d conduction band and holes in the O 2p valence band of Nb$_2$O$_5$ and/or from promoted recombination of photoexcited carriers in CeO$_2$. For Ce$_5$/Nb$_2$O$_5$, Ce$_{10}$/Nb$_2$O$_5$, and Ce$_{15}$/Nb$_2$O$_5$, the intensity of the emission at 425 nm increases with the increase in the ceria loading. However, the Ce$_{1}$/Nb$_2$O$_5$ catalyst, characterized by the lowest ceria loading, exhibited almost the same intensity as unmodified Nb$_2$O$_5$ and CeO$_2$. Therefore, we hypothesize that the more pronounced emission at 425 nm observed for ceria-modified niobia catalysts results from a direct band to band recombination of charge carriers in CeO$_2$ (recombination of photoexcited electrons in the Ce 4f conduction band and holes in the O 2p valence band of CeO$_2$). The emission energy of the peaks at ca. 500 nm (2.48 eV) and 545 nm (2.28 eV) is similar to the optical band gap of Ce$_{10}$/Nb$_2$O$_5$ (optical band gap resulted from the presence of CeO$_2$ species with a high concentration of defect sites; $E_g \approx 2.52$ eV; Figure 8b). Thus, the increase in intensity of these emission peaks observed for ceria-modified samples may be attributed to improved charge recombination related to transitions from electronic energy levels of defects (mainly oxygen vacancies) localized below the Ce 4f band of the CeO$_2$ nanoparticles to the O 2p valence band of CeO$_2$. As shown in Figure 10, the Ce$_{1}$/Nb$_2$O$_5$ catalyst exhibited a significantly higher emission intensity at 500 and 545 nm than unmodified CeO$_2$ and other niobia-based samples. We hypothesize that this phenomenon may result from differences in ceria loading. As documented by Baldim et al., the concentration of defect sites on the surface of CeO$_2$ nanoparticles often increases with decreasing particle size. One can expect that, for the Ce$_{1}$/Nb$_2$O$_5$ sample, characterized by the lowest ceria loading, dispersion of ceria species and concentration of surface defects should be the highest from among all niobia-based catalysts. Thus, it is very likely that these two features of the Ce$_{1}$/Nb$_2$O$_5$ catalyst may facilitate efficient recombination of the charge carriers resulting from presence of ceria (charge recombination related to transitions from electronic energy levels of defects localized below the Ce 4f band of the CeO$_2$ nanoparticles to the O 2p valence band of CeO$_2$). This hypothesis is in agreement with results shown in Figure 10, in which emission related to the presence of defect sites was the most pronounced for the sample with the lowest ceria loading (i.e., Ce$_{1}$/Nb$_2$O$_5$), while emission related to direct band to band recombination of the charge carriers was the most intense for the samples with the highest concentration of ceria modifier loaded on the niobia surface (i.e., Ce$_{10}$/Nb$_2$O$_5$). As far as differences in recombination of charge carriers are concerned, it is worth noting that improved emission of the Ce$_{1}$/Nb$_2$O$_5$ catalyst at 545 nm may result not only from the presence of oxygen vacancies but also Ce$^{3+}$ ions where the broad emission can be expected from 400 to 650 nm, depending on the host compound. Similar emission spectra were recorded for Y$_3$Al$_2$Ga$_3$O$_{12}$:Ce$^{3+}$ ceramics and Sr$_5$AlO$_4$F:Ce$^{3+}$ phosphors, where the maximum of Ce$^{3+}$ emission occurred at around 500–550 nm due to the $5d^{1-2}F_{5/2}$ and $5d^{1-2}F_{7/2}$ transitions. As described in the XPS section, relative contribution of Ce 3d peaks typical of ceria defect sites (e.g., Ce$^{3+}$ ions and/or Ce$^{4+}$ ions surrounded by oxygen vacancies in which electrons are trapped) peaks labeled as $u_0$,$u_1$ and $v_0$,$v_1$ in Figure 9) was significantly higher for all ceria-modified Nb$_2$O$_5$ catalysts than that observed for commercial CeO$_2$. Thus, the presence of some Ce$^{3+}$ ions in niobia-based samples is very probable. The reason why the emission peak was less pronounced for materials containing a higher amount of ceria modifier (i.e., Ce$_5$/Nb$_2$O$_5$ and Ce$_{10}$/Nb$_2$O$_5$) can be related to concentration quenching between Ce$^{3+}$ ions, which are highly sensitive for this phenomenon. Költe et al. observed almost the total emission quenching of Sr$_3$Al$_2$Si$_2$O$_7$:Ce$^{3+}$ phosphors when the concentration of Ce$^{3+}$ ion exceeded 2%. Therefore, it would be difficult to expect the emission of Ce$^{3+}$ ions in Ce$_5$/Nb$_2$O$_5$ and Ce$_{10}$/Nb$_2$O$_5$ samples.

3.3. Discussion on the Role of Ceria in Deactivation of CeO$_2$/$\text{Nb}_2\text{O}_5$ Heterostructures. Detailed characterization of as-prepared catalysts led us to observe that ceria species loaded on the niobia surface by wet impregnation were not only highly dispersed but also strongly interacted with the niobia support. As implied by UV–vis and XPS studies, such highly dispersed ceria species are substantially different from

![Figure 10. Photoluminescence spectra of catalysts.](image-url)
bulk CeO₂. The heterostructures prepared by wet impregnation exhibited a much higher relative concentration of ceria lattice defects, which were responsible for changes in electronic and optical properties of ceria species. As revealed by photoluminescence studies, defect sites in the ceria lattice not only modified electronic and optical properties of ceria but they acted also as recombination centers for photo-excited electrons and holes. To shed more light on recombination of the photo-induced charge carries in CeO₂/Nb₂O₅ heterostructures, we have predicted theoretically the conduction (Eₜ) and valence (Eₐ) band edges of pristine Nb₂O₅ and commercial CeO₂ using the following empirical equations:

\[ Eₜ = X - E^e - 0.5 \times E_g \]  
\[ Eₐ = E_g - Eₜ \]  

where X is the absolute electronegativity of the semiconductor, obtained from the geometric mean of the electronegativity of its constituent atoms (X values for Nb₂O₅ and commercial CeO₂ are 5.55²⁰ and 5.57 eV⁴⁹ respectively); Eₜ is the band gap of the semiconductor (3.22 and 2.96 eV for Nb₂O₅ and commercial CeO₂ respectively); E^e is the energy of free electrons vs the hydrogen scale (4.5 eV). The calculated conduction band edge potential of Nb₂O₅ was found to be −0.56 eV and is more negative than that of commercial CeO₂ (−0.41 eV). The corresponding valence band edge potential estimated for Nb₂O₅ was 2.66 eV and more positive than that of commercial CeO₂ (2.55 eV). We propose that irradiation of mechanical mixtures of the metal oxides with UV light resulted in the formation of photo-excited electrons (e⁻) and positively charged holes (h⁺) both in CeO₂ and Nb₂O₅. According to the band edge positions, the as-formed h⁺ were transferred from the valence band of Nb₂O₅ to the valence band of commercial CeO₂. At the same time, photo-excited electrons from the conduction band of Nb₂O₅ were transferred to conduction band of CeO₂. Thus, the band edge alignments in CeO₂/Nb₂O₅ heterostructures resulted in accumulation of both positively charged holes and photo-excited electrons in ceria species according to type I heterojunction.⁶⁶ We hypothesize that such accumulation of the charge carriers in ceria promotes their efficient recombination and diminishes the photocatalytic performance of mechanical mixtures of the metal oxides. More pronounced deactivation of the heterostructures prepared by wet impregnation resulted from two unique features of these materials. First, ceria species in these materials were highly dispersed on the niobia surface, providing great interface between the modifier and the support and improving the photo-excited charge carriers transfer from one semiconductor to another. Second, such highly dispersed ceria species exhibited a high concentration of defect sites, which played the role of recombination centers for photo-generated electrons and holes, promoting their efficient recombination (see Figure 11).

As far as mechanism of the charge carrier separation is concerned, it is important to stress that formation of type II heterojunction is impossible in our case because of alignments of valence and conduction band edges in Nb₂O₅ and CeO₂,⁶⁶ even when we consider band edges estimated for highly deficient CeO₂−ₓ species loaded on the niobia surface (see Figure 11). As far as other alternative mechanisms of charge carrier separation are concerned, one can expect that this process could proceed according to the Z-scheme mechanism.⁶⁶ However, it is important to stress that this mechanism should lead to improved separation of the photo-excited charge carriers, and thus it should not result in total deactivation of the heterostructures. We can consider two possibilities. In the first scenario, photo-excited electrons from the conduction band of CeO₂ could recombine with photo-generated holes localized in the valence band of Nb₂O₅. This process would lead to accumulation of photo-generated electrons in the conduction band of Nb₂O₅ and photo-generated holes in the valence band of CeO₂. Since ceria itself is active in methanol photooxidation and Z-scheme mechanism would improve separation of the charge carriers, methanol molecules adsorbed on the surface of the composite catalysts should be efficiently oxidized by photo-generated holes localized in the valence band of CeO₂. Thus, total deactivation of CeO₂/Nb₂O₅ heterostructures cannot be explained by this mechanism of the charge separation. In the second scenario, photo-excited electrons from the conduction band of Nb₂O₅ could recombine with photo-generated holes localized in the valence band of CeO₂. This process would lead to accumulation of photo-generated electrons in the conduction band of CeO₂ and photo-generated holes in the valence band of Nb₂O₅. Since niobia is highly active in methanol photooxidation and Z-scheme mechanism would improve separation of the charge carriers, this mechanism should enhance the activity of CeO₂/Nb₂O₅ heterostructures (it was not observed in our case). Thus, in a view of the above discussion, one can conclude that the formation of type I heterojunction is the most probable phenomenon that can fully explain more efficient recombination of the charge carriers in CeO₂/Nb₂O₅ heterostructures and total deactivation of ceria-modified samples during methanol photooxidation.

![Figure 11. Schematic representation of charge transfer process resulting in deactivation of ceria-modified Nb₂O₅ samples prepared by wet impregnation; CB: conduction band, VB: valence band, V₀: energy level of defects (mainly oxygen vacancies, Oₓ) localized below the Ce 4f band of highly deficient ceria species (CeO₂−ₓ) loaded on Nb₂O₅.](https://doi.org/10.1021/acs.jpcc.1c02812)
4. CONCLUSIONS

We demonstrated that addition of ceria modifier to niobium pentoxide led to a significant decrease in the photocatalytic activity of CeO$_2$/Nb$_2$O$_5$ nanostructures in methanol oxidation. We have established that, at any given concentration of ceria species on the niobia surface, the photocatalytic activity of both CeO$_2$ and Nb$_2$O$_5$ in the composite material was totally quenched. Operando-IR studies demonstrated that deactivation of ceria-loaded Nb$_2$O$_5$ samples resulted from quenching the catalyst ability to oxidize adsorbed methanol molecules. Deeper insight into the mechanism of the photocatalytic process provided by photoluminescence measurements showed that deactivation of heterostructures and ineffective oxidation originated from promoting the recombination of photo-generated charge carriers. The main factors responsible for efficient recombination of photo-excited electrons and holes in the composite catalysts were high dispersion of ceria species on the niobia surface, which provided excessive interface between these two semiconductors, and high concentration of defect sites in the structure of such ultrathin ceria species (also shown by IR spectra of chemisorbed methanol), which acted as recombination centers for photo-excited charge carriers.

The results obtained in this study provide deep insight into the role of ceria modifier in controlling the photocatalytic activity of semiconductor-based photocatalysts. It is expected that new fundamental knowledge about quenching of niobia activity by deposition of ceria species may play an important role in the development of new composite nanomaterials as UV filters. Furthermore, the knowledge about the origin of poisoning effect of Nb$_2$O$_5$ by ceria species is important for developing future heterogeneous ceria-modified photocatalysts too. In the case of the Nb$_2$O$_5$ modification with ceria will require a linker promoting a Z-scheme charge transfer (electron or hole) from niobia to ceria and minimizing the ceria/niobia interfaces.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/10.1021/acs.jpcc.1c02812.

FTIR spectra of catalyst surfaces at the beginning of methanol adsorption under dark conditions (Figure S1); crystal structure of the derived Nb$_2$O$_5$ model (Cmmm) (Figure S2); PXRD patterns for Ce/Nb$_2$O$_5$ samples collected with the Si (NIST Si 640d) internal standard (Figure S3); and bright-field and HAADF-STEM low magnification images of the Nb$_2$O$_5$ sample and overview bright-field HRTEM image and the corresponding ED pattern indexed based on the orthorhombic Cmmm structure (Figure S4) (PDF)

AUTHOR INFORMATION

Corresponding Authors

Łukasz Wolski — Faculty of Chemistry, Adam Mickiewicz University, Poznań 61-614, Poland; Normandie Univ, ENSICAEN, UNICAEN, CNRS, Laboratoire Catalyse et Spectrochimie, Caen 14050, France; orcid.org/0000-0002-1207-0546; Email: wolski.lukasz@amu.edu.pl

Mohamad El-Roz — Normandie Univ, ENSICAEN, UNICAEN, CNRS, Laboratoire Catalyse et Spectrochimie, Caen 14050, France; orcid.org/0000-0003-4450-211X; Email: mohamad.elroz@ensicaen.fr

Authors

Oleg I. Lebedev — Normandie Univ, ENSICAEN, UNICAEN, CNRS, Laboratoire CRISMAT, Caen 14050, France

Colin P. Harmer — Department of Chemistry, Iowa State University, Ames, Iowa 50011, United States; U.S. Department of Energy, Ames Laboratory, Ames, Iowa 50011, United States; orcid.org/0000-0003-0902-8731

Kirill Kovnir — Department of Chemistry, Iowa State University, Ames, Iowa 50011, United States; U.S. Department of Energy, Ames Laboratory, Ames, Iowa 50011, United States; orcid.org/0000-0003-1152-1912

Hanen Abdelli — Normandie Univ, ENSICAEN, UNICAEN, CNRS, Laboratoire Catalyse et Spectrochimie, Caen 14050, France

Tomasz Gryzb — Department of Rare Earths, Faculty of Chemistry, Adam Mickiewicz University, 61-614 Poznań, Poland; orcid.org/0000-0002-2947-6366

Marco Daturi — Normandie Univ, ENSICAEN, UNICAEN, CNRS, Laboratoire Catalyse et Spectrochimie, Caen 14050, France; orcid.org/0000-0001-5147-3260

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jpcc.1c02812

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The National Science Centre, Poland (grant no. 2018/28/C/ST5/00255) is acknowledged for the financial support of this work. PXRD studies performed by C.P.H. and K.K. were supported by the National Science Foundation DMR-2003783 grant. L.W. wishes to thank Prof. Marcin Ziolek and Maria Ziolek (Adam Mickiewicz University, Poznań, Poland) for very helpful discussions and Adrian Walkowiak (Adam Mickiewicz University, Poznań, Poland) for nitrogen physisorption measurements.

REFERENCES

(1) Montini, T.; Melchionna, M.; Monai, M.; Fornasiero, P. Fundamentals and Catalytic Applications of CeO$_2$-Based Materials. Chem. Rev. 2016, 116, 5987–6041.
(2) Bakkiyaraj, R.; Bharath, G.; Hasini Ramsait, K.; Abdel-Wahab, A.; Alsharaeh, E. H.; Chen, S. M.; Balakrishnan, M. Solution Combustion Synthesis and Physico-Chemical Properties of Ultrathin CeO$_2$ Nanoparticles and Their Photocatalytic Activity. RSC Adv. 2016, 6, 51238–51245.
(3) Cui, Z.; Zhou, H.; Wang, G.; Zhang, X.; Zhang, H.; Zhao, H. Enhancement of the Visible-Light Photocatalytic Activity of CeO$_2$ by Chemisorbed Oxygen in the Selective Oxidation of Benzyl Alcohol. New J. Chem. 2019, 43, 7355–7362.
(4) Majumder, D.; Chakraborty, I.; Mandal, K.; Roy, S. Facet-Dependent Photodegradation of Methylene Blue Using Pristine CeO$_2$ Nanostructures. ACS Omega 2019, 4, 4243–4251.
(5) Hamoud, I. H.; Finnqueneisel, G.; Azambre, B. Removal of Binary Dyes Mixtures with Opposite and Similar Charges by Adsorption, Coagulation/Floculation and Catalytic Oxidation in the Presence of CeO$_2$/H$_2$O$_2$ Fenton-like System. J. Environ. Manage. 2017, 195, 195–207.
(6) Cai, W.; Chen, F.; Shen, X.; Chen, L.; Zhang, J. Enhanced Catalytic Degradation of AO7 in the CeO$_2$-H$_2$O$_2$ system with Fe$^{3+}$ doping. Appl. Catal., B 2010, 101, 160–168.
Nanorod Composites and the Mechanism Study of the Degradation of Acid Orange 7. Appl. Catal., B 2012, 121-122, 223–229.

Zhu, L.; Li, H.; Xia, P.; Liu, Z.; Xiong, D. Hierarchical ZnO Decorated with CeO2 Nanoparticles as the Direct Z-Scheme Heterojunction for Enhanced Photocatalytic Activity. ACS Appl. Mater. Interfaces 2018, 10, 39679–39687.

Muñoz-Batista, M. J.; Gómez-Cerezo, M. N.; Kubacka, A.; Tudela, D.; Fernández-García, M. Role of Interface Contact in CeO2-Nb2O5 Nanoparticles with Reduced Photocatalytic Activity and Increased Biocompatibility towards a Human Keratinocyte Cell Line. J. Mater. Chem. B 2020, 8, 4016–4028.

Morlando, A.; Chaki Borrás, M.; Rehman, Y.; Bakand, S.; Barker, P.; Sluyter, R.; Konstantinov, K. Development of CeO2 Nanodot Encrusted TiO2 Nanoparticles with Reduced Photocatalytic Activity and Improved Biocompatibility towards a Human Keratinocyte Cell Line. J. Mater. Chem. B 2020, 8, 4016–4028.

Mueen, R.; Morlando, A.; Qtaish, H.; Lerch, M.; Cheng, Z.; Konstantinov, K. ZnO/CeO2 Nanocomposite with Low Photocatalytic Activity as Efficient UV Filters. J. Mater. Sci. 2020, 55, 6834–6847.

Su, K.; Liu, H.; Gao, Z.; Fornasiero, P.; Wang, F. Nb2O5-Based Photocatalysts. Adv. Sci. 2021, 8, 2003156.

Riente, P.; Noël, T. Application of Metal Oxide Semiconductors in Light-Driven Organic Transformations. Catal. Sci. Technol. 2019, 9, 5186–5232.

Tamai, K.; Hosokawa, S.; Teramura, K.; Shishido, T.; Tanaka, T. Synthesis of Niobium Oxide Nanoparticles with Plate Morphology Utilizing Solvothermal Reaction and Their Performances for Selective Photooxidation. Appl. Catal. B Environ. 2016, 182, 469–475.

Kulkarni, A. K.; Praveen, C. S.; Sethy, A. Y.; Panman, R. P.; Arubj, S. S.; Naik, S. D.; Ghule, A. V.; Kale, B. Nanostructured N-Doped Orthorhombic Nb2O5 as an Efficient Stable Photocatalyst for Hydrogen Generation under Visible Light. Dalton Trans. 2017, 46, 14859–14868.

Zhao, Y.; Eley, C.; Hu, J.; Foord, J. S.; Ye, L.; He, H.; Tsang, S. C. E. Shape-Dependent Acidity and Photocatalytic Activity of Nb2O5 Nanocrystals with an Active TT (001) Surface. Angew. Chem. Int. Ed. Engl. 2012, 51, 3846–3849.

Nowak, I.; Ziolek, M. Niobium Compounds: Preparation, Characterization, and Application in Heterogeneous Catalysis. Chem. Rev. 1999, 99, 3603–3624.

Ftouni, K.; Lakiss, L.; Thomas, S.; Daturi, M.; Fernandez, C.; Bazin, P.; El Fallah, J.; El-Roz, M. TiO2/Zeolite Bifunctional (Photo)Catalysts for a Selective Conversion of Methanol to Dimethoxymethylene: On the Role of Bronsted Acidity. J. Phys. Chem. C 2018, 122, 29359–29367.

Yan, J.; Wu, G.; Guan, N.; Li, L. Nb2O5/TiO2 Heterojunctions: Synthesis Strategy and Photocatalytic Activity. Appl. Catal., B 2014, 152–153, 280–288.

De Andrade, F. V.; De Lima, G. M.; Augusti, R.; Coelho, M. G.; Assis, Y. P. Q.; Machado, I. R. M. A New Material Consisting of TiO2 Supported on Nb2O5 as Photocatalyst for the Degradation of Organic Contaminants in Aqueous Medium. J. Environ. Chem. Eng. 2014, 2, 2352–2358.

Lam, S. M.; Sin, J. C.; Satoshi, I.; Abdullah, A. Z.; Mohamed, A. R. Enhanced Sunlight Photocatalytic Performance over Nb2O5/ZnO Nanorod Composites and the Mechanism Study. Appl. Catal. A Gen. 2014, 471, 125–135.

Hashemzadeh, F.; Gaffarinejad, A.; Rahimi, R. Porous p-NiO/n-Nb2O5 Nanocomposites Prepared by an EISA Route with Enhanced Photocatalytic Activity in Simultaneous Cr(VI) Reduction and Methyl Orange Decolorization under Visible Light Irradiation. J. Hazard. Mater. 2015, 286, 64–74.

Hong, Y.; Li, C.; Zhang, G.; Meng, Y.; Yin, B.; Zhao, Y.; Shi, W. Efficient and Stable Nb2O5 Modified g-C3N4 Photocatalyst for Removal of Antibiotic Pollutant. Chem. Eng. J. 2016, 299, 74–84.

Ferraz, N. P.; Nogueira, A. E.; Marcos, F. C. F.; Machado, V. A.; Rocca, R. R.; Assaf, E. M.; Assencio, J. Y. O. CeO2–Nb2O5 Photocatalysts for Degradation of Organic Pollutants in Water. Rare Mat. 2020, 39, 230–240.

Tatibouet, J. M. Methanol Oxidation as a Catalytic Surface Probe. Appl. Catal., A 1997, 148, 213–252.

Kähler, K.; Holz, M. C.; Rohe, M.; Van Veen, A. C.; Muhler, M. Methanol Oxidation as Probe Reaction for Active Sites in Au/ZnO and Au/TiO2 Catalysts. J. Catal. 2013, 299, 160–170.

Crampton, A. S.; Cai, L.; Janvelyan, N.; Zheng, X.; Friend, C. M. Methanol Photo-Oxidation on Rutile TiO2 Nanowires: Probing Reaction Pathways on Complex Materials. J. Phys. Chem. C 2017, 121, 9910–9919.

Murayama, T.; Chen, J.; Hirata, J.; Matsumoto, K.; Ueda, W. Hydrothermal Synthesis of Octahedral-Based Layered Niobium Oxide and Its Catalytic Activity as a Solid Acid. Catal. Sci. Technol. 2014, 4, 4250–4257.

Toby, B. H.; Von Dreele, R. B. GSAS-II: The Genesis of a Modern Open-Source All Purpose Crystallography Software Package. J. Appl. Crystallogr. 2013, 46, 544–549.
