LED-driven controlled deposition of Ni onto TiO$_2$ for visible-light expanded conversion of carbon dioxide into C$_1$–C$_2$ alkanes†

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Photocatalytic gas-phase hydrogenation of CO$_2$ into alkanes was achieved over TiO$_2$-supported Ni nanoparticles under LED irradiation at 365 nm, 460 nm and white light. The photocatalysts were prepared using photo-assisted deposition of Ni salts under LED irradiation at 365 nm onto TiO$_2$ P25 nanoparticles in methanol as a hole scavenger. This procedure yielded 2 nm Ni particles decorating the surface of TiO$_2$ with a nickel mass content of about 2%. Before the photocatalytic runs, Ni/TiO$_2$ was submitted to thermal reduction at 400 °C in a 10% H$_2$ atmosphere which induced O-defective TiO$_2$-x substrates. The formation of oxygen vacancies, Ti$^{3+}$ centers and metallic Ni sites upon photocatalytic CO$_2$ hydrogenation was confirmed by operando EPR analysis. In situ XPS under reaction conditions suggested a strong metal–support interaction and the co-existence of zero and divalent Ni states. These phototoxic species enhanced the photo-assisted reduction of CO$_2$ below 300 °C to yield CO, CH$_4$ and C$_2$H$_6$ as final products.

Introduction

The overall depletion of fossil fuels and the overwhelming evidence of the impact of greenhouse gas emissions on the global environment are among the major challenges of the humankind today and demand a swift transition to renewable and sustainable processes. Among the strategies advocated to overcome these issues are gas-phase capture and storage, and valorization by reduction to value-added products. In particular, the catalytic hydrogenation of CO$_2$ for synthetic fuel production is an appealing mid-term solution to reduce the concentration of greenhouse gases, mitigate the dependence on fossil fuels and promote an overall neutral CO$_2$ emission cycle.$^{1-7}$

Photocatalysis involves a greener vision of chemical processes, including the smart and selective transformation of chemicals into fuels and/or chemical intermediates of interest.$^8$–$^{10}$ The use of photocatalysts leads to an effective depletion of organic pollutants, either in the form of wastewater or as organic volatile compounds.$^{11,12}$ In fact, photocatalysis takes advantage of sunlight as an abundant and inexpensive energy source, providing a sustainable approach to solving the most pressing environmental issues. Alternatively, energy-efficient artificial light systems, such as light emitting diodes (hereafter LEDs) have revealed themselves as mighty allies for inducing photocatalytic processes with enhanced effectiveness (see for instance ref. 13). Current efforts are being devoted to developing novel photocatalysts that can exploit the full-solar spectrum.$^{14-16}$

Most of the current photoactive materials are based on semiconducting oxides and heterojunctions,$^{16,20}$ where light irradiation promotes the formation of an electron–hole pair, or an exciton (e$^-$–h$^+$), in the electronic band structure of the solid, followed by the redox reaction on the surface of the catalyst. Among them, titanium dioxide, TiO$_2$, is the most studied photocatalytic semiconductor, due to its high photoactivity, low cost, natural abundance and non-toxicity.$^{21}$ However, its wide band gap ($E_g$ = 3.2 eV for the anatase phase) limits its photocactivity to the UV region.$^{22,23}$ Some of the strategies to enhance the catalytic activity of TiO$_2$ involve the addition of...
nanostructured co-catalysts for improving the charge separation and the catalytic kinetics or the controlled generation of structural defects to enhance the solar absorption and the gas species adsorption on the surface. Since the seminal work on TiO$_2$ as a heterogeneous photocatalyst, there has been an outstanding development of semiconducting TiO$_2$-based nanostructured materials, particularly for environmental remediation applications under both liquid and gas phase conditions.

A wide variety of noble metal co-catalysts have been tested for the gas phase hydrogenation of CO$_2$ into alkanes mediated by the Sabatier’s reaction in the gas phase under diverse conditions. In addition, first-row elements have been deposited on the surface of nanosized TiO$_2$ under analogous conditions to develop efficient photocatalysts for numerous environmental applications. Particularly, nickel on TiO$_2$ exhibited a high activity for the methanation reaction with dependence on the morphology, crystalline state and metal-support interactions. The photo-assisted catalytic activity of Ni-containing TiO$_2$ catalysts has been tested, which showed that the work function of Ni lies in the appropriate range (5.3 eV) to enhance the charge separation of the TiO$_2$ electron bands. Furthermore, Meng et al. showed that even oxidized Ni species, such as Ni(OH)$_2$, on TiO$_2$ nanofibers were effective for the reduction of CO$_2$ to methane and carbon monoxide. Similarly, Ni nanoclusters on reduced TiO$_2$ supports have been reported to be effective for the photocatalytic conversion of CO$_2$ to alcohols via an aldehyde mechanism. To deposit metal crystallites on TiO$_2$, a variety of methods have been used, including hydrothermal, co-precipitation and thermal evaporation procedures, yielding metal nanoparticles with sizes down to 10 nm on the surface of TiO$_2$.

Recently, the photocatalytic nature of some semiconducting metal oxides has been leveraged to reduce metal ions to nanosized metal particles upon light irradiation. This so-called photodeposition procedure is a liquid-phase reaction that uses light in the UV range to induce an exciton pair in the first trapped by surface oxygen atoms. The photogenerated holes at the Ti–OH sites act as active species for the oxidation of solvent molecules, e.g. methanol, through hydrogen evolution, and the electrons cause the reduction of metal cations present in the liquid, which precipitate as metallic particles on the surface of TiO$_2$. The hole scavenging process allows a longer life of the e$^-$–h$^+$ pair and therefore a more effective metal ion reduction and deposition is achieved. Usually, the photo-assisted deposition procedure leads to metal particles, with small sizes (e.g. 5 nm), on the semiconducting oxide.

In the present work, Ni-based nanosized particles have been deposited on the surface of TiO$_2$ nanoparticles by a photo-deposition method in methanol as a hole scavenger. These materials have been successfully tested in the gas-phase photocatalytic hydrogenation of CO$_2$ in a fixed-bed reactor under LED irradiation at different wavelengths, including the full visible spectrum. The generation of structural defects (i.e. oxygen vacancies and Ti$^{4+}$ defective centers) within the TiO$_2$ framework was investigated with operando EPR. In situ XPS studies under reaction conditions further elucidated the coexistence of metallic and divalent Ni domains partially buried or decorating the TiO$_2$ support, thereby suggesting a strong metal-support interaction (SMSI). We found that the ex situ thermal pre-activation of the Ni–TiO$_2$ strongly promoted the light-driven/light-assisted/LED-driven CO$_2$ hydrogenation towards carbon monoxide, methane and ethane.

### Experimental section

**Synthesis of Ni–TiO$_2$ by LED-assisted photodeposition**

A photodeposition method was used to attach Ni nanoparticles on the TiO$_2$ surface. Briefly, 25 mg of nanosized TiO$_2$ (Evonik P25, Dusseldorf, Germany) and 55 mg of nickel chloride hydrate (NiCl$_2$·6H$_2$O, Sigma-Aldrich) were added to 17 ml of DI water in a 20 ml Pyrex tube, which was then closed with a rubber septum. After 20 min of degasification under nitrogen gas flow, 1 ml of methanol (CH$_3$OH, Sigma-Aldrich) was added to the mixture. All reagents and precursors were used without purification. The suspension was subsequently irradiated with UV light using two LED lamps (OSRAM LED Engin, Wilmington MA) at 365 nm for 270 s and under continuous magnetic stirring to induce the photocatalytic reduction of Ni salts. The so-obtained suspension was further centrifuged at 7500 rpm for 5 minutes, washed several times with a mixture of double-deionized water and ethanol, and dried at 100 °C for 10 h. The final solid samples were stored in the dark for further use and characterization. Finally, some of the samples were submitted to a gas-phase ex situ reduction procedure before characterization and photocatalytic activity tests. Typically, 150 mg of the catalyst were loaded into a ceramic crucible and placed in a tube furnace (Carbolite, Hope Valley, UK) under a 10 : 90 H$_2$ : N$_2$ atmosphere at 50 sccm and heated up to 400 °C at a 10 °C min$^{-1}$ heating rate. The temperature was held for 2 h before cooling to room temperature under the same atmosphere. After thermal reduction, the TiO$_2$-based nanoparticles developed a greyish color. These nanomaterials were prepared at the Synthesis of Nanoparticles Unit 9 of the ICTS “NANBIO-SIS” at the Institute of Nanoscience of Aragon and the University of Zaragoza.

**Characterization**

The crystalline structures of the TiO$_2$ support and the photodeposited Ni nanoparticles were identified by the X-ray diffraction (XRD) technique using a Bruker D8 Advance Diffractometer (Bruker Corporation, Billerica MA) equipped with a (002) Ge monochromator using the CuK$_α$ line at 1.5405 Å. The UV-vis spectra were recorded in a JASCO V-670 UV-vis/NIR spectrophotometer (JASCO, Tokyo, Japan) using the solid-state diffuse reflectance technique in a 60 mm UV-vis/NIR integrating sphere from 200 nm to 900 nm, with a scanning step of 10 nm s$^{-1}$. Temperature-programmed reduction (TPR) tests were performed in a Quantachrome ChemBET Pulsar TPR/TPD analyzer (Quantachrome Instruments, Boynton Beach, FL) equipped with a Thermal Conductivity Detector (TCD). Usually, 50 mg powdered samples were loaded in one of the branches of
a U-tube quartz reactor suspended between quartz wool pieces. Before every TPR test, samples were heated up to 100 °C under Ar gas flow to remove adsorbed species on the material surface. After cooling to room temperature, samples were heated from room temperature to 900 °C at 10 °C min⁻¹ heating rate under 10 : 90 H₂/Ar gas flow at 20 sccm. The BET surface area and porosity of catalysts were determined by means of N₂ adsorption at 77 K using a Micromeritics TriStar 3000 analyzer (Micromeritics, Norcross, GA).

The TiO₂ P25 and Ni/TiO₂ were investigated by in situ and operando Electron Paramagnetic Resonance spectroscopy (EPR) on a Bruker EMX EPR instrument fitted with a ST4102 cavity and a Bruker variable temperature unit and quartz insert. The materials were pressed into pellets, then crushed and fractioned (150–300 μm). ~25 mg of sample were immobilized with quartz wool in a 4 mm inner diameter quartz tube and placed in the cavity. The EPR spectra (9.45 GHz, 20 mW, 5 Gauss modulation amplitude at 100 kHz) were continuously obtained while introducing a total gas flow of 50 Nml min⁻¹ during the sample analysis. To study the influence of light irradiation, UV light pulses in 100 s intervals (Dymax Blue Wave 75) were directed via a glass fiber to shine on the sample tube through a grid on the side of the EPR cavity. The same experimental protocol (see the ESIf) was performed on P25 and on Ni/TiO₂ while monitoring with EPR to compare the responses of the photocatalysts under UV light exposure and different reaction atmospheres (see Table S1 in the ESIf). Samples were first activated in 30% H₂ at 250 °C. Then the influence of UV light and of the H₂/CO₂ gas (separately and together) was investigated at room temperature. Then the sample was reactivated and the procedure was repeated at 250 °C. In general, the spectra exhibited lower resolution at higher temperatures and the changes were more difficult to discern. Overall, the same evolution was observed, but it was less clear and thus only room temperature spectra are shown in the text. The spectrum assigned to Ni species (type 1, see the main text) changed with temperature.

The Ni metal loading was evaluated using a microwave plasma-atomic emission spectrometer (4100 MP-AES, Agilent) and X-ray photoelectron spectroscopy (XPS) spectra were obtained before and after activation using a Kratos AXIS Ultra DLD surface analysis spectrometer (Kratos Analytical Ltd., Durham, UK). In situ XPS studies were performed using a customized system incorporating a hemispherical analyzer (SPECS Phoibos 100), a non-monochromatized X-ray source (Al Kz; 1486.6 eV, Mg Kz, 1253.6 eV) and a high temperature–high pressure cell (SPECS-HPC-20) that allows sample heating and gas flow. The analyzer was operated at a fixed transmission and 50 eV pass energy with an energy step of 0.1 eV. Binding energies were calibrated using C 1s or Ti 2p (284.6 eV or 458.8 eV) as an internal reference. The high temperature–high pressure cell design allowed sample heating up to 800 °C, under flow or static conditions, at pressures up to 20 bar or dynamic flows in the range 20–500 Nml min⁻¹. This arrangement enabled a transfer of post-reaction samples from the reaction chamber to the spectrometer under UHV conditions, avoiding exposure to the laboratory atmosphere. Prior to each analysis, the samples were evacuated to 10⁻⁹ mbar at room temperature. In a typical experiment, the sample was initially placed in the sample holder (in the form of a pelletized disc) and transferred to the spectrometer chamber where XPS spectra were acquired. The sample was then transferred under vacuum to the high-pressure cell where it was exposed to the reactive gases and heated to the appropriate temperature. The flow and concentration of gases were similar to those used for catalytic testing (vide infra). After the treatment the sample was cooled to room temperature under the reaction atmosphere, evacuated down to 10⁻⁷ mbar in less than two minutes and then transferred back to the spectrometer chamber for analysis, avoiding ambient exposure. Aberration corrected scanning transmission electron microscopy (Cs-corrected STEM) images were acquired using a high angle annular dark field detector in an FEI XFE TITAN electron microscope operated at 300 kV equipped with a CETCOR Cs-probe corrector from CEOS Company allowing the formation of an electron probe of 0.08 nm. The geometric aberrations of the probe-forming system were controlled to allow a beam convergence of 24.7 mrad half-angle to be selected. Elemental analysis was carried out with an EDX detector for EDS experiments in scanning mode. EDX mapping was performed with an Oxford Instruments Detector and analysed with AZtec software provided by the detector manufacturer.

Photo-assisted carbon dioxide hydrogenation tests

The CO₂ hydrogenation was conducted in a fixed-bed reactor as shown in Scheme 1. Typically, 120 mg of powdered catalyst was packed in a 30 × 10 × 2 mm prismatic quartz reactor that was positioned between two LED sources of different wavelengths, namely 365 nm, 460 nm and white light. Before irradiation, a gas mixture of CO₂ and H₂ with a 1 : 4 molar ratio was fed into the reactor for 30 min to ensure air removal from inside the reactor. After that, the reactor was closed and filled with the gas.
mixture until an absolute pressure of 1.7 bar was reached. A recirculating OEM pump (Verderflex M1500, Groeningen, NL) caused a 7.5 ml min⁻¹ gas flow through the reactor circuit that included a 500 ml chamber to buffer pressure oscillations and provide enough total volume for gas sampling in prolonged experiments. The reaction was started by turning on the LEDs, which also caused a sharp increase in the solid temperature to reach a stable value around 250 °C. A sample of the gases was periodically analyzed using an on-line 490 micro-GC analyzer (Agilent Technologies, Santa Clara, CA, equipped with three columns: a 10 m molecular sieve column with a 5 m PPQ pre-column, a 10 m PBQ column and a 10 m CP-wax). DC current was set at 0.9 A and 12 V during LED irradiation for all tested materials.

Results and discussion
Photodeposition of Ni nanoparticles on TiO₂ P25
The photo-assisted deposition method involves the photonic excitation of a semiconductor immersed in a solution that

![Fig. 1](image)

**Fig. 1** Characterization of the Ni–TiO₂ photocatalyst: (a) scheme of the photo-assisted deposition process; (b) HAADF-STEM representative image of the Ni–TiO₂ photocatalyst. Dots displaying lighter contrast correspond to the small Ni domains homogeneously dispersed on the TiO₂ support; (c) EDX images corresponding to the selected areas shown in the inset STEM image accounting for the presence of Ti and Ni domains altogether in the catalyst nanoparticles; (d) XRD patterns of TiO₂ nanoparticles after photodeposition of Ni from NiCl₂ as the precursor and CH₃OH as the hole-scavenging solvent. Crystalline Ni species remained undetected and only the reflections of anatase and rutile could be found. The activation procedure at 400 °C in a 10% H₂ atmosphere reduced the relative height of the (100) reflection of anatase together with a slight increase in the peak width; (e) XPS spectra corresponding to the Ni 2p₃/2 region before and after activation in a reducing environment. A strong increase of reduced Ni species is observed after activation.
contains the ionic precursor of the material to be deposited and at least one liquid component that can act as a hole scavenger. When the incident photon energy is larger than the $E_g$, the valence band electrons can be excited to the conduction band.

The pumped electrons are therefore used for the reduction of the metallic cations in the electrolyte, Ni$^{2+}$ in this case, to deposit nanosized metallic particles on the surface of the semiconducting oxide. To avoid fast electron–hole pair recombination or the oxidation of the photodeposited metallic particles, methanol, an easy to oxidize substrate, is used, which acts as a sacrificial agent and hole scavenger when added to the electrolyte (Fig. 1a). The photo-deposition process provided white solids with a Ni mass concentration of $1.10 \pm 0.11\%$ calculated by MP-AES spectrometry (see the Experimental section). The subsequent thermal activation at 400 °C in a 10%-H$_2$ atmosphere produced light grey-colored solids with a Ni mass concentration of $1.18 \pm 0.05\%$, i.e., thermal activation in the hydrogen atmosphere did not alter the Ni loading of the prepared catalysts. The Ni/TiO$_2$ catalyst particles exhibited similar size before and after thermal activation, between 20 and 25 nm. High-resolution HAADF-STEM images of individual Ni/TiO$_2$ nanostructures showed 2 nm Ni/NiO crystallites homogeneously dispersed on the TiO$_2$ nanoparticles (Fig. 1b). EDX analysis of individual nanoparticles confirmed the presence of Ni domains (see Fig. 1c). XRD analysis (Fig. 1d) showed the blend of anatase and rutile diffraction peaks expected for TiO$_2$ P25 nanoparticles, without any diffraction pattern attributable to Ni or nickel oxides. This might be attributed to the concentration of deposited Ni (<2 wt%), particularly to its extraordinary dispersion and small particle size. These 2 nm sized Ni particles could be assigned to either Ni or NiO nanoparticles. Two different chemical processes could explain the presence of NiO after photodeposition: oxidation of the deposited Ni$^0$ nanoparticles can take place upon environmental exposure, or the direct photodeposition of NiO particles may take place in a methanol-deficient medium.\textsuperscript{48,49}

The UV-vis spectra showed very significant changes with respect to the absorption bands of TiO$_2$ P25 (Fig. 2a), which displayed a strong absorption below 400 nm corresponding to the ground excitonic state of TiO$_2$. The absorption bands of Ni/TiO$_2$ were expanded towards the visible–near infrared region resulting from the formation of either metallic Ni or NiO nanoparticles.\textsuperscript{42,50,51} After thermal activation, the absorption in the visible region is greatly enhanced, which is due to the reducing conditions that led to the formation of oxygen vacancies and the incorporation of H-containing species or even Ti$^{3+}$ cations on the surface of TiO$_2$.\textsuperscript{52,53} Such structural modifications induced the formation of intermediate energy levels in the band gap, leading to broader light absorption.\textsuperscript{54} Furthermore, the optical band gap estimated using the Tauc plots (Fig. 2b) returned a value of $E_g = 3.2$ eV for TiO$_2$, in good agreement with values reported elsewhere.\textsuperscript{23,25} For Ni/TiO$_2$, a red-shift in the optical band gap could be observed which can be ascribed to an interfacial charge transfer process, consisting in the migration of electrons from the semiconducting substrate to the metallic nanoparticles directly from the valence band after excitation.\textsuperscript{24,55}

The TPR tests (Fig. 3) showed that Ni$^{2+}$, presumably as NiO, and Ni$^0$ were both likely present on Ni/TiO$_2$ and Ni/TiO$_2$-A. This was concluded after the detection of reduction peaks at $T_{II} \sim 330$ °C and $T_{III} \sim 370$ °C which were attributed to the reduction of NiO species with low and high interaction with the support.
A noticeable decrease in the signal intensities was observed for the Ni/TiO2 catalysts before and after LED-assisted gas-phase photocatalytic CO2 hydrogenation.

In the present study, three different types of EPR signals were observed when performing the in situ and operando protocol. Fig. 4 shows a selection of EPR spectra and the most relevant changes observed under reaction conditions. Type 1 is observed for Ni/TiO2, but not for P25 TiO2. It is a huge broad peak centered at g ~ 2.1 (Fig. 4a), constantly present for Ni/TiO2 but changes during activation, and is unaltered upon exposure to UV light. In order to follow the subtle change during activation, the spectra of the fresh sample were subtracted from the spectrum of the activated sample (Fig. 4a).

The spectral change corresponded to a broad EPR spectrum with a g-value of ~2.34 and a tiny sharp peak at 2.0035. The g-value of the broad signal in the difference spectrum was significantly shifted compared to the g-value of the overall spectrum (~2.1). Type 1 was assigned to paramagnetic Ni centers or defects in the Ni nanoparticles, which suggests the contribution from several types of Ni species, which could be either Ni^{2+} or Ni^{3+}. The EPR spectrum is largely featureless for a precise assignment, but it is noted that the g-value of 2.34 for the evolved species is similar to the value observed for defect sites in pure NiO nanoparticles. The type 2 signal was a small sharp isotropic signal centered at 2.0035, which was absent for the fresh materials but showed up after a few minutes and in comparable intensities for both TiO2 and Ni/TiO2 after activation (heating to 250 °C in 30% H2). The signal of Ni/TiO2-A increased during exposure to UV light (still under H2), but returned back to the initial state after the light was turned off (Fig. 4b). No clear development in the signal was observed for TiO2 during interaction with UV light (data not shown). The signal is not influenced by either of the materials being exposed to the H2/CO2 gas mixture. The type 2 signal was assigned to sites in the bulk of the nanoparticles: either an F-center, an electron caught in an oxygen vacancy, or a V-center, an oxygen ion caught at a cation vacancy.

Finally, type 3 was a small anisotropic signal centered at 2.011 which is visible only for Ni/TiO2-A. It overlapped with the type 1 signal and was barely influenced by exposure to UV light; however, it disappeared completely after exposure to the H2/CO2 mixture (notice the negative change in the spectrum in Fig. 4b). It was tentatively assigned to oxygen-centered surface hole trapping sites in the anatase polymorph of TiO2 P25. The anisotropy of the signal is due to the direction dependence of surface sites. This type of site is observed in the literature on pure TiO2 at low temperatures (<100 K) where the signal to noise ratio of EPR is much better. In our catalyst such evidence suggests that the introduction of very small Ni particles by photodeposition has promoted the number of these sites to the extent that they are now observable by EPR at room temperature and above. The fact that they are sensitive to the H2/CO2 mixture confirms the assignment as surface sites and is an indication that they are involved directly in the reaction of CO2 on the surface of the material.

The state of Ni species on the TiO2 substrates was further explored using XPS analysis (Fig. 4c and Table 1). It is interesting to note that the XPS signals corresponding to the Ni 2p levels were rather complex, being deconvoluted up to three Gaussian/Lorentzian peaks (see the ESI, Table S2 and Fig. S1†). This situation is typically found in the presence of multiplet contributions and satellite structures, whose formation could be found in recent papers. For Ni^{2+}, the satellite at about +6.0 eV might be assigned to a final state effect associated with a (core) 3d^{4}L configuration (where L stands for ligands). However, the intensity and position of this satellite depended on many factors such as bonding with ligands, symmetry, particle size and crystallinity.

Furthermore, a noticeable decrease of the atomic concentration of Ni was observed after thermal activation under a H2 atmosphere at 400 °C (Table 1). This might be attributed to the process of Ni nanoparticle growth by sintering or, alternatively, to an incomplete immersion of the Ni particles into the support.

Table 1: Binding energies (BE, eV) and surface concentration (at%) obtained by XPS analysis for the as-prepared and activated Ni/TiO2 catalysts before and after LED-assisted gas-phase photocatalytic CO2 hydrogenation.

| BE (eV), surface concentration (at%) | O 1s | Ti 2p | Ni 2p | C 1s |
|-------------------------------------|------|-------|-------|------|
| Ni/TiO2                             | 530.0| 458.8 | 856.0 | 285.0|
|                                      | 48.99%| 21.69%| 3.06% | 26.26%|
| Ni/TiO2 (post-reaction)             | 530.3| 458.3 | 856.3 | 285.3|
|                                      | 51.69%| 20.33%| 1.03% | 26.94%|
| Ni/TiO2-A                           | 529.8| 458.6 | 855.6 | 285.0|
|                                      | 48.50%| 23.92%| 0.66% | 26.92%|
| Ni/TiO2-A (post-reaction)           | 529.4| 458.4 | 855.4 | 284.4|
|                                      | 51.45%| 21.63%| 0.14% | 26.78%|

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due to the “decoration” effect of the TiO2 over the Ni particles. This has been previously reported for a variety of metal catalysts on different supports, within the context of the strong metal–support interaction (SMSI) effect. Both events would be enhanced in the case of nanosized particles and under treatment with hydrogen. In addition, the absence of complete reduction of Ni particles (only 57% of Ni0 after the reduction treatment) would also support this hypothesis.

In situ XPS observations were carried out to evaluate the evolution of the oxidation states of Ni and Ti under activation or CO2 hydrogenation conditions at 225 °C giving interesting and complementary insights into the operando EPR results. Although the change of the oxidation state of Ti was unclear (Fig. 4c), after the initial CO2/H2 treatment, an incomplete recovery of Ni signal intensity and a notable oxidation of the particles were noticed (Ni2+ concentration about 84%). These facts would be in agreement with the expected behavior in a SMSI scenario, with the CO2 serving as a mild re-oxidation agent. After the second reduction treatment at 450 °C, the situation was similar to that described before, and a decrease in intensity and a partial reduction of the Ni particles were noticed (Fig. 4c and Table S3†).

Nevertheless, after the second treatment with the CO2/H2 mixture, neither the Ni signal intensity nor the Ni2+/Ni0 ratios were remarkably altered. This could reflect a more permanent coverage of the Ni particles caused by the reduction at a higher temperature.
temperature under hydrogen and would reinforce the close interaction between Ni and TiO₂ as suggested by EPR. Actually, the HAADF-STEM images of the catalysts after reaction revealed that while a fraction of Ni domains have coarsened, the majority of the catalyst maintained similar particle size distributions (see Fig. S2†).

**Light-assisted gas-phase photocatalytic CO₂ hydrogenation**

The photocatalytic conversion of CO₂ into CO, CH₄ and C₂H₆ alkanes was observed under LED irradiation at different wavelengths (Fig. 5). The photocatalytic performance of TiO₂ P25 under UV light was evaluated before Ni photodeposition (see Fig. S4a†). Also, a control experiment was carried using Ni/TiO₂ under 365 nm LED irradiation in 4/1 Ar/H₂ stream. No CO, CH₄ or C₂H₆ signals were detected after reaction for 6 h (Fig. S4b†).

Results showed CO productivity around 100 μmol g⁻¹ h⁻¹ during the 6 h of reaction time. The signals attributed to both CH₄ and C₂H₆ were also detected, at concentrations below the quantification limit. In contrast, when Ni/TiO₂ catalysts were illuminated at 365 nm (Fig. 5a), the main product obtained was CH₄ with a maximum initial productivity of 450 μmol g⁻¹ h⁻¹ and an increased CO productivity of 250 μmol g⁻¹ h⁻¹. Also, the production of C₂H₆ remained almost constant during the reaction, reaching about 2 μmol g⁻¹ h⁻¹. Catalyst activation by the high temperature hydrogen treatment produced two main effects: first, the photocatalytic activity increased significantly under UV light (Fig. 5b), and second, the catalytic response is expanded to the visible region of the solar spectrum (Fig. 5c and d). This increase in the CO and C₂H₆ (~4 μmol g⁻¹ h⁻¹) productivity under UV light for the Ni/TiO₂-A could be attributed to the formation of both bulk and surface oxygen vacancies (Vₐ) on the TiO₂ phase upon hydrogenation and the enhancement of the SMSI effect as suggested by the in situ XPS data. These Vₐ induced donor intermediate energy levels in the bandgap, which might act as electron traps, facilitating charge-carrier separation and charge transfer to the adsorbed species. The irradiation under UV LEDs was more effective for the generation of CO. A similar trend with lower productivity was also found for the Ni/TiO₂-A under LED illumination at blue light (460 nm, Fig. 5c) and white light (Fig. 5d). Interestingly, similar catalytic activity tests under blue or white LED irradiation using the as-synthesized Ni/TiO₂ catalysts before thermal activation showed CO productivity lower than 25 μmol g⁻¹ h⁻¹ up to 4 h of reaction (data not shown).

The temperature at the center of the fixed bed during the reaction was about 250 °C when 460 nm and white LED units were used, but increased to 270 °C and 300 °C for the Ni-TiO₂ and Ni/TiO₂-A under UV illumination, respectively, which could simply be a result of a higher absorbance of the catalyst at 365 nm, but may also reflect the contribution of plasmonic effects in the Ni/NiO nanoparticles located at the surface of the TiO₂, as recent studies have shown that plasmonic nanoparticles deposited on TiO₂ could act as nanoheaters on the surface of the semiconductor.

The photothermal CO₂ hydrogenation is expected to proceed through the exothermic Sabatier reaction (CO₂ + 4H₂ → CH₄ + 2H₂O, ΔH° = −165 kJ mol⁻¹). Alternatively, for TiO₂-based materials the reverse water gas shift (RWGS) reaction has also been proposed, yielding CO and water vapor (CO₂ + H₂ → CO + H₂O, ΔH° = +41 kJ mol⁻¹). It has been suggested that these reactions could occur through the dissociation of physisorbed CO₂ into CO intermediates that either evolve to formate or to...
carbide to finally form CH₄ molecules upon further hydrogenation. In our case the CO₂ hydrogenation progressed to the formation of CH₄ on active centers, namely Ni/NiO nanoclusters, followed to a certain extent by a C–C coupling up to the formation of C₂H₆. At this point, it should be noted that the direct formation of ethane from CO₂ over Ni was reported to be very minimal. On the other hand, the C–C coupling in the gas phase to generate higher hydrocarbons, such as ethane, over Ni-based catalysts was recently reported to be independent of the structure and only controlled by the hydrogenation rate. The photo-assisted deposition of Ni was critical for the CO hydrogenation to alkanes (Fig. 6). For Ni-containing catalysts, the initial selectivity to CH₄ is close to 70%, decreasing down to 60% after 6 h of catalytic test. After activation (Ni/TiO₂-A), the selectivity slightly evolved towards CH₄, which can be attributed to an increase in the SMSI after the reduction treatment.

Finally, the thermally activated catalysts (Ni/TiO₂-A) also exhibited a higher production of both C₂ and C₁ alkanes. In this case, the formed VO in the TiO₂ could act as centers for the enhanced adsorption of CO₂, thus improving the hydrogenation rate. The oxygen-defective TiO₂ also induced the formation of Ti³⁺ species (see TPR data in Fig. 3), which have been reported to have a photonic response upon illumination with UV photons. These combined effects resulted in enhanced conversion of CO₂ even under illumination in the visible range.

Conclusions

Ni/NiO nanosized particles were effectively deposited on the surface of TiO₂ nanoparticles by a photodeposition procedure that used Ni²⁺ salts as precursors and CH₃OH as a hole scavenger. The synthesis of very small Ni crystals on TiO₂ was achieved under the irradiation of LEDs at 365 nm. A thermal activation under a reducing atmosphere allowed the stabilization of Ni⁰ on the catalyst surface, as well as the formation of oxygen vacancies that could enhance the CO₂ adsorption.

Under LED illumination at different wavelengths, the Ni/TiO₂ catalysts induced the photocatalytic hydrogenation of CO₂ at 300 °C to produce CO, CH₄ and C₂H₆ with a productivity of about 450 μmol g⁻¹cat⁻¹ h⁻¹. The thermally reduced catalysts (Ni/TiO₂-A) showed enhanced photocatalytic response in the UV region and higher CO productivities in all the studied wavelengths. As the thermal reduction induces the formation of active sites in the TiO₂ support, the RWGS reaction is favored, increasing the CO selectivity. Further EPR and XPS analyses suggested that the close interaction of the metal and support plays an important role in the enhancement of photoactivity.

Conflicts of interest

There are no conflicts to declare.

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References

1 IEA, World Energy Outlook 2018, IEA, Paris, 2018, https://doi.org/10.1787/weo-2018-en.
2 BP p.l.c., BP Energy Outlook, 2019.
3 K. Li, X. An, K. H. Park, M. Khraisheh and J. Tang, Catal. Today, 2014, 224, 3–12.
4 P. R. Yaashikaa, P. Senthil Kumar, S. J. Varjani and A. Saravanan, J. CO₂ Util., 2019, 33, 131–147.
5 L. Wang, M. Ghousoub, H. Wang, Y. Shao, W. Sun, A. A. Tountas, T. E. Wood, H. Li, J. Y. Y. Loh, Y. Dong, M. Xia, Y. Li, S. Wang, J. Jia, C. Qiu, C. Qian, N. P. Kherani, L. He, X. Zhang and G. A. Ozin, Joule, 2018, 2, 1369–1381.
6 Y. Wang, J. Zhao, Y. Li and C. Wang, Appl. Catal., B, 2018, 226, 544–553.
7 F. Zhang, Y. H. Li, M. Y. Qi, Z. R. Tang and Y. J. Xu, Appl. Catal., B, 2020, 268, 118380.
8 X. Liu, X. Duan, W. Wei, S. Wang and B. J. Ni, Green Chem., 2019, 21, 4266–4289.
9 Q. Mu, W. Zhu, X. Li, C. Zhang, Y. Su, Y. Lian, P. Qi, Z. Deng, D. Zhang, S. Wang, X. Zhu and Y. Peng, Appl. Catal., B, 2020, 262, 118144.
10 F. Xu, J. Zhang, B. Zhu, J. Yu and J. Xu, Appl. Catal., B, 2018, 230, 194–202.
11 O. Tursunov, L. Kustov and A. Kustov, Oil Gas Sci. Technol., 2017, 72, 30.
65 M. C. Biesinger, B. P. Payne, A. P. Grosvenor, L. W. M. Lau, A. R. Gerson and R. C. Smart, Appl. Surf. Sci., 2011, 257, 2717–2730.
66 V. Biju and M. Abdul Khadar, J. Nanopart. Res., 2002, 4, 247–253.
67 N. S. McIntyre, D. D. Johnston, L. L. Coatsworth, R. D. Davidson and J. R. Brown, Surf. Interface Anal., 1990, 15, 265–272.
68 L. E. Oi, M. Y. Choo, H. V. Lee, H. C. Ong, S. A. Hamid and J. C. Juan, RSC Adv., 2016, 6, 108741–108754.
69 Z. Xu, Y. Li, J. Zhang, L. Chang, R. Zhou and Z. Duan, Appl. Catal., A, 2001, 210, 45–53.
70 A. Caballero, J. P. Holgado, V. M. Gonzalez-De la Cruz, S. E. Habas, T. Herranz and M. Salmeron, Chem. Commun., 2010, 46, 1097–1099.
71 V. M. Gonzalez-De la Cruz, J. P. Holgado, R. Pereníguez and A. Caballero, J. Catal., 2008, 257, 307–314.
72 R. Wang, Y. Li, R. Shi and M. Yang, J. Mol. Catal. A: Chem., 2011, 344, 122–127.
73 J. Zhao, B. Liu, L. Meng, S. He, R. Yuan, Y. Hou, Z. Ding, H. Lin, Z. Zhang, X. Wang and J. Long, Appl. Catal., B, 2019, 256, 117823.
74 L. B. Hoch, P. G. O’Brien, A. Jelle, A. Sandhel, D. D. Perovic, C. A. Mims and G. A. Ozin, ACS Nano, 2016, 10, 9017–9025.
75 K. Stangeland, D. Kalai, H. Li and Z. Yu, Energy Procedia, 2017, 2022–2027.
76 C. Heine, B. A. J. Lechner, H. Bluhm and M. Salmeron, J. Am. Chem. Soc., 2016, 138, 13246–13252.
77 C. Vogt, E. Groeneveld, G. Kamsma, M. Nachtegaal, L. Lu, C. J. Kiely, P. H. Berben, F. Meirer and B. M. Weckhuysen, Nat. Catal., 2018, 1, 127–134.
78 S. Abelló, C. Berrueco and D. Montané, Fuel, 2013, 113, 598–609.
79 C. Vogt, M. Monai, E. B. Sterk, J. Palle, A. E. M. Melcherts, B. Zijlstra, E. Groeneveld, P. H. Berben, J. M. Boereboom, E. J. M. Hensen, F. Meirer, I. A. W. Filot and B. M. Weckhuysen, Nat. Commun., 2019, 10, 1–10.
80 E. Lira, S. Wendt, P. Huo, J. Ø. Hansen, R. Streber, S. Porsgaard, Y. Wei, R. Bechstein, E. Lægsgaard and F. Besenbacher, J. Am. Chem. Soc., 2011, 133, 6529–6532.
81 J. Ye, J. He, S. Wang, X. Zhou, Y. Zhang, G. Liu and Y. Yang, Sep. Purif. Technol., 2019, 220, 8–15.