Temperature dependence of solar light assisted CO_2 reduction on Ni based photocatalyst

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Abstract.

Methanation of CO_2 by H_2 can be in the future an important reaction to store the surplus of renewable electricity during production peaks. The catalytic thermal CO_2 methanation (the *Sabatier* reaction) can be carried out at temperatures above 250 ^{o}C using Ni supported on silica-alumina (Ni/SiO_2-Al_2O_3). Recently it has been observed that this exothermic reaction can be promoted by solar light irradiation of Ni/SiO_2-Al_2O_3 at initial near ambient temperatures. In the present work we provide a study of the influence of the initial temperature on the photoassisted Ni/SiO_2-Al_2O_3 methanation of CO_2, under conditions in which the dark reaction is not observed. An increase of the photoassisted methanation rate with the initial temperature in the range from ambient to 150 ^{o}C has been observed. The reaction kinetics for lower initial temperatures exhibited an induction period not observed for reactions performed at higher temperatures. The results are discussed in terms of the operation of plasmon photochemistry in which the energy of photons is thermalised in a spatially confined space of the active nanoparticles leading to locally high temperatures and the simultaneous photogeneration of electrons and positive holes.

1. Introduction.

In the context of finding alternatives to conventional fossil fuels based on renewable primary energy resources, there is a large interest in the sustainable production of fuels that can act as energy vectors from primary renewable energy resources to the enduser.[1] One possibility that is gaining importance is the combination of renewable electricity based on wind and photovoltaics with the production of chemicals.[2] Development of efficient power-to-chemicals processes that could be fully integrated with electricity derived from renewables is a topic of much current interest. This can be one way to store the surplus of electricity from renewable during production peaks that can be consumed later on demand.[2] The global management of energy from renewable resources and the interconversion between electricity and the production of fuels for transportation has given rise to the concept of *Solar Refineries* in where all these transformations from power to chemicals and *viceversa* would take place.[3]

In this scenario, H_2 from water electrolysis would become widely available and reactions using H_2 as feedstock will be highly important. One of these reactions is the Sabatier methanation of CO_2 (eq. 1), a catalytic process that is carried out at temperatures from 250 to about 400 ^{o}C, depending on the catalyst activity and the specific application, although temperatures about 350 ^{o}C are common in order to have sufficiently fast reaction rates with high CO_2 conversions.[4] The use of CH_4 and other chemicals obtained from CO_2 would allow reduction of greenhouse gases emissions and would be attractive as a way to to store solar energy into chemical compounds.

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O \qquad \Delta H = -165 \text{ kJ mol}^{-1} \qquad \text{(eq. 1)}$$
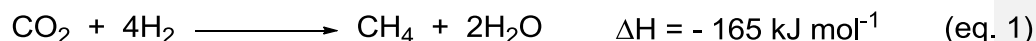
Recently, we and others have found that CO_2 methanation can be carried out under apparent low temperatures promoted by solar light using $Ni/SiO_2\text{-}Al_2O_3$ as catalyst.[5, 6] Similar low temperature photoassisted methanation has been reported on ruthenium nanoparticles supported on wide[7] or narrow[8] band gap semiconductors and attributed to thermosolar effects.[7]

In a related precedent to the present work, it has been found that indium oxide can also promote CO_2 methanation and that for a given reaction temperature there is a clear enhancement with light irradiation with respect to the analogous dark process at the same temperature.[9] In view of this related study, it is of interest to undertake also for the commercial $Ni/SiO_2\text{-}Al_2O_3$ catalyst a study to determine what is the influence of reactor temperature on the solar light promoted CO_2 methanation. This type of studies are crucial to gain information that should eventually lead to establish a likely mechanism clarifying the role of light on the process and, to develop new catalyst formulations specially suited for the photoassisted methanation.

2. Results

The sample used in the present study is a commercial $Ni/SiO_2\text{-}Al_2O_3$ solid supplied by Aldrich having 65 % Ni supported on $SiO_2\text{-}Al_2O_3$ (Si/Al 0.23) with a specific surface area of 190 $m^2 \times g^{-1}$. XRD shows the diffraction peaks expected for Ni metal (ICDD 04-0850), while detectable amounts of NiO are not observed (Figure 1 A). The absence of peaks corresponding to SiO_2 and Al_2O_3 phases indicates that the support is amorphous $SiO_2\text{-}Al_2O_3$. The average particle size of Ni nanoparticles was determined to

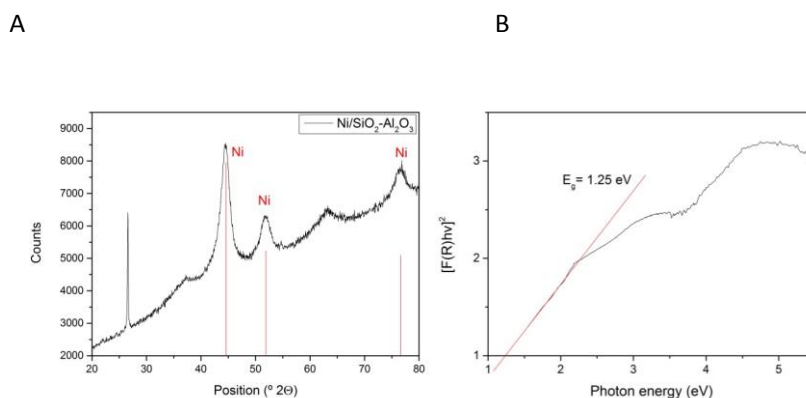be 5.5 nm from the width of the 111 peak at 2Θ 44.5 ° of the diffractogram by applying the Scherrer equation.

A   B

Figure 1. A: XRD of the commercial Ni/SiO$_2$Al$_2$O$_3$. In red typical pattern of the metal Ni. The sharp peak at about 26 ° corresponds to the sample holder. B: Tauc plot of Ni/SiO$_2$Al$_2$O$_3$ used to estimate the band gap of the catalyst.

Diffuse-reflectance UV-Vis spectrum of the commercial Ni/SiO$_2$-Al$_2$O$_3$ sample showed a continuous absorption in the UV and visible region with some relative maxima at about 260, 390 and 560 nm. This absorption spectrum indicates that commercial Ni/SiO$_2$-Al$_2$O$_3$ should absorb in a wide range of the solar spectrum. Tauc plot of the optical absorption is presented in Figure 1 B. This plot allows estimating by optical means that the band gap of this material is low (Eg 1.25 eV) , as it should be for a solid constituted by metal nanoparticles.

Photocatalytic reactions were carried out in a homemade quartz photoreactor of 300 ml of capacity with gas inlets that allow sampling of the gas phase (see experimental section for a photograph of the setup). The photoreactor was illuminated

with a 300 W Xe lamp with collimated light from the top at 10 cm distance (see experimental section).

The reaction temperature is measured and controlled with a calibrated thermocouple in contact with the $Ni/SiO_2-Al_2O_3$ catalyst. The catalyst was placed on a ceramic crucible as a thin bed of a few mm. To determine the influence of the initial reaction temperature the photoreactor was heated from the bottom with an electric plate, whose operation was controlled by the thermocouple. The system was allowed to equilibrate at the temperature set point before starting irradiation. Switching on the light corresponds to the initial reaction time. Reactants and products from the gas phase were sampled online with a microGC directly connected to the photoreactor, avoiding unnecessary errors that could be introduced by manual injection. The temporal profile of the methanation reaction was followed measuring H_2, CO_2, CO and CH_4 upon irradiation.

A clear influence of the apparent temperature in the range from 20 to 150 ^{o}C with methane conversion at 60 min was observed. Blank controls under the same conditions performed in the same system, but in the dark by wrapping the photoreactor with aluminum foil once the required temperature is reached and before to switch the lamp on, did not allow observation of any product. The failure of $Ni/SiO_2-Al_2O_3$ to promote CO_2 methanation at temperatures below 250 ^{o}C is in agreement with catalytic data reported in the literature.[10] These controls rule out the occurrence of a purely thermal reaction.

In contrast to dark controls, upon light irradiation, generation of CH_4 as the exclusive or major product (CO was also detected in much lesser amounts) was

observed for thermocouple temperatures above 100 ^{o}C. Figure 2 presents the influence of the temperature on CH_4 formation. It should be noted that 150 ^{o}C. is the maximum temperature to which the photoreactor can be heated in our experimental setup.
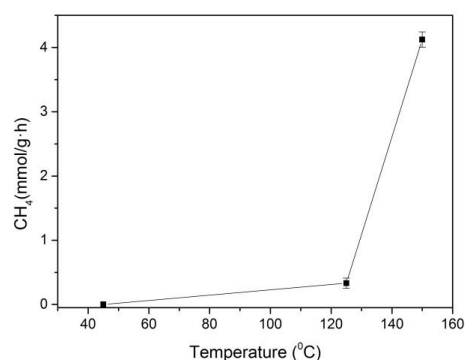

Figure 2. Methane production at 60 min as a function of the temperature measured at the catalyst by a thermocouple for the photoassisted reaction. Reaction conditions: H_2 (14.5 mmol, 80 v/v%), CO_2 (3.63 mmol, 20 v/v%), 250 mg catalyst, light intensity from a Xe lamp 1 KW/m^2, pressure ranging from 1.3 to 1.8 bar depending on the temperature.

The temporal profiles of the CO_2 methanation by Ni/SiO$_2$·Al$_2$O$_3$ catalyst at 125 and 150 ^{o}C are presented in Figure 3. As it can be seen there, the time-conversion plot for the reaction carried out at 125 ^{o}C increases the rate along the time, indicating the there is an induction period. Observation of induction period for photoassisted reactions at near ambient temperature has been previously observed.[6] In contrast, in the case of 150 ^{o}C, the presence of some CH_4 (73 μmol, 2 % yield) at initial reaction time was detected, although the temporal evolution of CH_4 generation follows a linear

relationship with the irradiation time and a final yield above 95 % methane was reached at 4 h. The presence of CH_4 at initial reaction time could be due to the manipulation of the photoreactor under laboratory light and the relatively long time (about 60 min) required setting the experimental conditions before switching on the solar simulator.
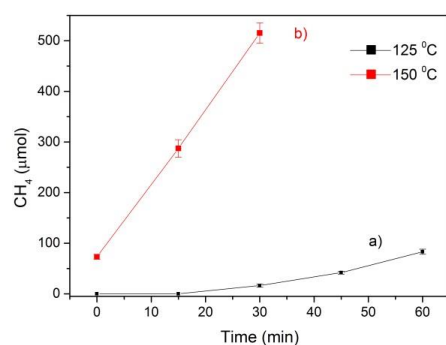

Figure 3. Temporal profiles of CH_4 generation in the photoassisted CO_2 reduction by light determined at two different temperatures, a) 125 ^{0}C and b) 150 ^{0}C . Reaction conditions: H_2 (14.5 mmol), CO_2 (3.63 mmol), 250 mg catalyst, light intensity from a Xe lamp 1 KW/m^2.

3. Discussion.

Available experimental data confirms that CO_2 methanation can be promoted by light irradiation at temperatures well below 250 ^{o}C using Ni/SiO$_2$·Al$_2$O$_3$ as catalyst. The mechanism of how light assists the exothermic process is, however, unclear. According to a proposal in the literature, [11] the energy of the light is thermalised at the metal nanoparticles and converted into heat. This process should, in principle, cause an increase of the catalyst bed temperature. However, all the measurements indicate that the temperature of the bed measured by thermocouple does not

increase substantially upon irradiation. Importantly, the temperature reading of the thermocouple was always lower than the temperature threshold required observing operation of the conventional thermal catalytic reaction. Thus, blank controls by placing the photoreactor exactly at the same position, but avoiding illumination by careful wrapping of the system with aluminum foil did not lead to the detection of CH_4. Even manual measurements of the temperature by infrared, pointing at different points of the bed (estimated spatial resolution of the infrared camera 0.5 cm^2) did not detect temperature values much different from the thermocoupling. Nevertheless local hot spots on the catalyst cannot be ruled out.

The results of the photoassisted CO_2 methanation can be interpreted based on the current knowledge of the simultaneous phenomena occurring upon plasmon irradiation of metal nanoparticles.[11] Thus, plasmon irradiation can result in a thermal effect or in the photogeneration of electrons and positive holes.[11]

Accordingly, it could be that photon absorption produces a local (nanometric scale) and temporal (during a few microseconds) burst of temperature just at the catalytic center that could be very efficient in promoting thermally the reaction following the same mechanism of the catalytic process. Scaiano and coworkers have estimated that the equivalent macroscopic temperature reached at Au nanoparticles as consequence of thermalization of photons absorbed at the metal plasmon band can be 500 ^{o}C.[12] According to this rationalization, light would be a very unique way to *heat* the nanometric particles acting as active sites, being the local temperature undetectable by conventional temperature measurements of the bulk system and even by infrared measurements lacking nanometric resolution. In a certain way, the efficient action of light in this proposal may have certain similarities to the effect that

is observed comparing conventional and microwave heating for some reactions involving polar molecules.[13] The induction period observed at lower initial temperatures can derive from the temperature increase caused by the exothermicity of the reaction as the conversion increases.

In addition to thermal effects, other possible operating mechanism could derive from the absorption of photons of energy larger than the band gap of the Ni nanoparticles, resulting probably in the photoejection of electrons from the nanoparticles to the surroundings. In this way, particularly high energy photons could produce a photochemical effects derived from the generation of charge separation and the presence of photogenerated electrons and holes. Electrons will effect reductions and can result in the photocatalytic formation of Ni-H. Holes will oxidize H_2 to H^+ that will become attached to the basic centers of the support. It is known that metal hydrides can reduce CO_2 successively to formate, formaldehyde in the way towards CH_4. Scheme 1 summarizes the proposal.
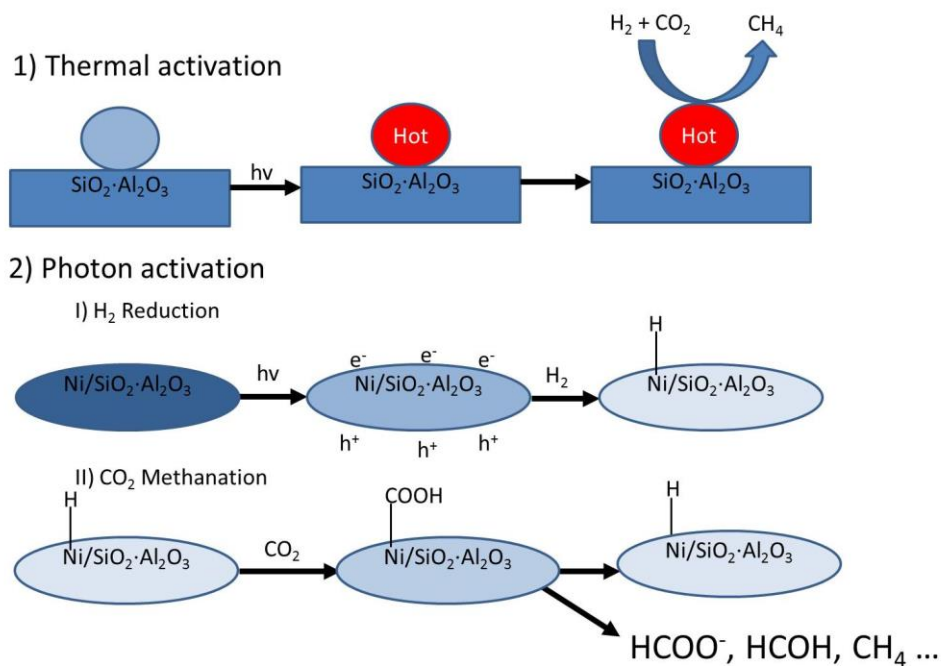
Scheme 1. Proposed mechanisms of the CO_2 methanation with the NiO/$SiO_2\cdot Al_2O_3$ catalyst.

4. Conclusions.

Experimental data conclusively show that light irradiation of Ni/$SiO_2\cdot Al_2O_3$ catalyst can promote CO_2 methanation under conditions in which the dark reaction fails to form CH_4. In the photoassisted CO_2 methanation, the initial *apparent* temperature of the system plays a key role increasing the reaction rate and influencing the reaction kinetics, presenting or not an induction period. These results can be interpreted based on the current knowledge of plasmon photochemistry that can result in spatially and temporally localized temperature peaks and the photogeneration of electrons and holes.

5. Experimental Section.

Commercial $Ni/SiO_2 \cdot Al_2O_3$ (Aldrich, 208779) photocatalyst was used without further pretreatment. The photocatalyst contains approximately a 65 % of Ni loading and the surface area is 190 m^2/g. A photoreactor with a quartz window was load with 250 mg of the $Ni/SiO_2 \cdot Al_2O_3$ photocatalyst placed on a ceramic crucible was in contact with a nickel alloy thermocouple. H_2 and CO_2 were introduced in proper amounts up to achieve a final pressure of 1.5 bar. The photoreactor was heated at different temperatures prior irradiation by means of a heating plate, and when the desired temperature was stabilized the photocatalyst was irradiated with a UV-Vis light from a 300 W Xe lamp. Note that the time required before temperature equilibration can be about 60 min. At that moment the lamp is switched on and this is the initial time of the experiment. Except for the minor generation of methane (2 % yield) in the experiment carried out at 150 ^{o}C, no change in the gas phase composition was observed at initial reaction time. Figure 4 shows a typical photoreaction setup. The CH_4 formation was followed by direct measurement of the reactor gases with an Agilent 490 MicroGC having two channels both with TC detectors and Ar as carrier gas. One channel has MolSieve 5A column and analyses H_2. The second channel has a Pore Plot Q column and analyses CO_2, CO and up to C_4 hydrocarbons. Quantification of the percentage of each gas was based on prior calibration of the system injecting mixtures with known percentage of gases.
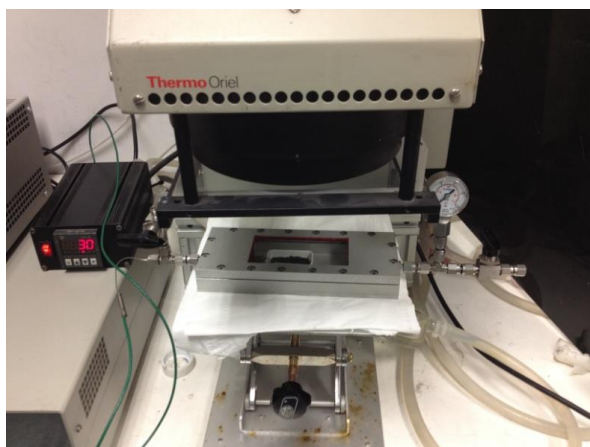
Figure 4. Photograph of the system used in the present study showing the light source place on top of the flat photoreactor with quartz windows (10×5 cm^2) placed 10 cm below the light beam.

6. Acknowledgements

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