

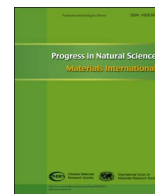
HOSTED BY



ELSEVIER

Contents lists available at ScienceDirect

## Progress in Natural Science: Materials International

journal homepage: [www.elsevier.com/locate/pnsmi](http://www.elsevier.com/locate/pnsmi)

Original Research

Role of support in photothermal carbon dioxide hydrogenation catalysed by Ni/Ce<sub>x</sub>Ti<sub>y</sub>O<sub>2</sub>

Salina Jantarang, Emma C. Lovell, Tze Hao Tan, Jason Scott\*, Rose Amal\*

Particles and Catalysis Research Group, School of Chemical Sciences and Engineering, The University of New South Wales, Sydney, NSW 2052, Australia

## ARTICLE INFO

## Keywords:

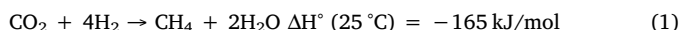
Photothermal  
CO<sub>2</sub> Methanation  
Ceria  
Titania  
Nickel  
Reducibility

## ABSTRACT

Nickel was supported on varied ratios of ceria-titania mixed oxides (Ni/Ce<sub>x</sub>Ti<sub>y</sub>O<sub>2</sub>) to evaluate the role the support plays in photothermal carbon dioxide hydrogenation to produce methane. In a batch photothermal reactor system, Ni/CeO<sub>2</sub> achieved the highest conversion rate, reaching a conversion of 93% in approximately 60–90 min. To decouple the influence of light and heat, the CO<sub>2</sub> hydrogenation was examined in an in-house designed photothermal reactor, whereby heat can be applied externally. Decoupling experiments revealed that heat from the thermalisation by light was the main driving force for the reaction. In addition, the conversion and temperature profile of the different catalysts revealed that the catalyst performance was governed by catalyst reducibility. H<sub>2</sub>-TPR analyses showed that the Ni became more readily reducible with increasing CeO<sub>2</sub> content, suggesting that the oxide plays a role in activating the Ni. The reduction temperature of the nickel catalyst (following a reduction and passivation process) was below 200 °C, which meant that the inherent heating temperature of the photothermal reactor was sufficient to initiate Ni/Ce<sub>x</sub>Ti<sub>y</sub>O<sub>2</sub> catalyst activity. The exothermic methanation reaction was then able to heat the system further, ultimately reaching a temperature of 285 °C. The ancillary rise in temperature promotes further nickel reduction and methane formation, leading to a “snow-ball” effect. The findings demonstrate that, to achieve a “snow-ball” effect in a photothermal system, designing a catalyst which is easy to reduce, active for CO<sub>2</sub> hydrogenation, and capable of converting light to heat for its initial activation is critical.

## 1. Introduction

Over time, an increase in carbon dioxide (CO<sub>2</sub>) emissions, particularly from the consumption of fuel, has contributed to global warming and climate change [1]. Therefore, the conversion of anthropogenic CO<sub>2</sub> to fuel has the potential to mitigate emissions to the atmosphere as well as produce renewable fuels. The conversion of CO<sub>2</sub> to methane allows direct utilisation in existing infrastructure or as carbon storage prior to subsequent reaction [2,3]. The methanation reaction, also known as the Sabatier reaction, is described as outlined in Eq. (1):



Photothermal technology essentially relies on the absorption of light by a material and converting the absorbed energy to heat [4–6]. The concept has been applied in cancer therapy to treat tumour cells by illuminating a suitable material, leading to localised heating [7–9]. Photothermal conversion allows the reaction to utilise solar energy to induce activity. The key advantage of this route is the localised

temperature increase of the catalyst, as opposed to the extensive heating required for thermal conversion, which provides an ultimately more sustainable process [10–16]. Although photocatalytic conversion is similarly dependent on solar energy availability, photocatalytic conversion rates are significantly lower (in the scale of μmol or μL) compared to thermal or photothermal catalysis [17–20].

The exothermic nature of CO<sub>2</sub> methanation is suitable for photothermal studies as illumination alone may induce heating to initiate activity, after which the exothermic nature can lead to an increase in temperature and accelerate the activity [13,14]. Despite photothermal methanation having been of interest to researchers, the influence of catalyst support has not been extensively studied. Supports assessed for photothermal systems include alumina [13] where metals such as ruthenium, rhodium, platinum, palladium, and nickel were deposited. The highest performing catalysts were found to be ruthenium and rhodium; however, the high price of noble metals limits their commercial viability. Impregnating ruthenium on Mg-Al layered double hydroxides nanosheets by Ren et al. [14] resulted in a highly stable catalyst and a fast temperature increase with both attributes suitable for

Peer review under responsibility of Chinese Materials Research Society.

\* Corresponding authors.

E-mail addresses: [jason.scott@unsw.edu.au](mailto:jason.scott@unsw.edu.au) (J. Scott), [r.amal@unsw.edu.au](mailto:r.amal@unsw.edu.au) (R. Amal).<https://doi.org/10.1016/j.pnsc.2018.02.004>

Received 23 November 2017; Accepted 5 February 2018

1002-0071/ © 2018 Chinese Materials Research Society. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

photothermal methanation. Other photothermal carbon dioxide studies include its conversion to carbon monoxide by encapsulated iron in carbon [15] and volatile organic compound oxidation [21].

Nickel is widely used for methanation as it is commercially friendly and has high CO<sub>2</sub> conversion and methane selectivity [11,12,22–24]. Several studies have examined supported nickel catalysts for methanation. These include the work of Tada et al. [12] which explored nickel supported on ceria, alumina, and titania for thermal carbon dioxide methanation and related the catalyst reducibility and intermediate formation to activity. For the photocatalytic reduction of carbon dioxide, Sastre et al. [25] studied nickel supported on silica-alumina which showed 95% methane selectivity and 90% carbon dioxide conversion with the performance attributed to metal dispersion and stability. In the work of Zhou et al. [26], Ni/CeO<sub>2</sub> was examined for the thermal methanation of carbon dioxide. After reduction, metallic nickel and surface oxygen vacancies were concluded to be the active sites for carbon dioxide conversion. As nickel is easily oxidised, the ease of its reduction to the metallic phase is important for methanation. Given photothermal methanation is solely dependent on light absorption and conversion to heat, it is pivotal that the nickel is reducible at a low temperature.

Ceria is a semiconductor and active for photocatalytic reactions [27]. The interaction of ceria and nickel has been demonstrated to aid with the nickel reducibility making it a suitable candidate as support [28]. Titania has been well-studied for photocatalytic work [17]. Under light, Lin et al. [29] reported that the band-gap excitation of TiO<sub>2</sub> can transfer electrons to Ru sites for CO<sub>2</sub> methanation. Ni supported on TiO<sub>2</sub> is also active for CO<sub>2</sub> methanation [30]. The combination of ceria and titania has been reported to increase photocatalytic activity, as compared to titania (for methyl orange degradation) [31] and decrease bandgap compared to either titania or ceria [32,33].

Here, nickel supported on varied ratios of mixed ceria and titania, Ni/Ce<sub>x</sub>Ti<sub>y</sub>O<sub>2</sub>, was studied for the photothermal methanation of CO<sub>2</sub> to explore the roles of light and support in this system. The research considers in-depth the Ni/Ce<sub>x</sub>Ti<sub>y</sub>O<sub>2</sub> system for the purpose of understanding the role of light and heat. The effects of light and heat were decoupled to examine the dominant effects in the photothermal system. Characterisation techniques such as hydrogen temperature programme reduction (H<sub>2</sub> – TPR), ultraviolet-visible-near infrared (UV-Vis-NIR) absorption, and X-ray photoelectron spectroscopy (XPS) were used to examine catalyst reducibility, light absorbance, interaction between the nickel and support, and the impact of support on the oxidation state of the nickel.

## 2. Experimental

### 2.1. Materials

Cerium(III) nitrate hexahydrate ( $\geq 99\%$ ), titanium(IV) butoxide (reagent grade, 97%), and nickel(II) nitrate hexahydrate (99.999% trace metals basis) were purchased from Sigma-Aldrich. Ethanol (undenatured 100%) was acquired from Chem-Supply. Nitric acid (70 vol %) was obtained from RCI Labscan. All chemicals were used as purchased. Milli-Q water (Millipore, 18.2 M $\Omega$  cm) was used throughout the experiments. Dry compressed air, 10.05% H<sub>2</sub>/Ar gas, 0.97% O<sub>2</sub>/He gas, Ar (> 99.997%), CO<sub>2</sub> (> 99.5%), H<sub>2</sub> (> 99.99%), He (> 99.996%), and O<sub>2</sub> (> 99.5%) were purchased from Coregas.

### 2.2. Catalyst preparation

A series of ceria-titania mixed oxides were synthesised via a modified sol-gel method [16]. Cerium(III) nitrate hexahydrate was dissolved in 20 mL ethanol, 1.5 mL Milli-Q water and 0.36 mL nitric acid. The solution was then added dropwise to titanium(IV) butoxide in 60 mL ethanol whilst stirring. After aging for 48 h, the gel was calcined at 550 °C in air for 3 h (ramp rate of 1 °C/min). The synthesised material

was then ground with a mortar and pestle. A determined amount of cerium(III) nitrate hexahydrate and titanium(IV) butoxide was added to obtain ceria:titania nominal molar ratios of 0, 20:80, 50:50, 80:20, and 100. The sol-gel synthesised supports are denoted as Ce<sub>x</sub>Ti<sub>y</sub>O<sub>2</sub>, where x and y are the molar fraction of ceria and titania, respectively.

Synthesised sol-gel supports were then impregnated with nickel. Typically, nickel(II) nitrate hexahydrate was dissolved in 5 mL Milli-Q water then added to 1 g of support to obtain a 10 wt% nominal metal loading. The mixture was stirred at 120 °C to form a paste then further dried in an oven at 110 °C overnight. After drying and grinding, the powder was transferred to a glass flow-through reactor and calcined in dry air at 50 mL/min at 400 °C at a ramp rate of 5 °C/min, and held for 3 h. Nickel impregnated supports are denoted as Ni/Ce<sub>x</sub>Ti<sub>y</sub>O<sub>2</sub>.

### 2.3. Activity tests

Prior to activity tests and characterisation, approximately 300 mg catalyst was reduced and passivated in a Micromeritics Autochem 2910. The sample was first reduced in 10.05% H<sub>2</sub>/Ar gas at 20 mL/min, temperature was ramped at a rate of 5 °C/min to 400 °C and held for 1 h. After being cooled to ambient temperature in Ar, the catalyst was passivated using 0.97% O<sub>2</sub>/He for 12 h at 10 mL/min for uniform formation of an oxide layer on the Ni deposits, in order to prevent the uncontrollable oxidation of the reduced catalysts when exposed to the atmosphere.

#### 2.3.1. Photothermal activity

Activity tests in the batch photothermal rig involved irradiating the catalyst with a Xenon lamp to simulate solar energy. The experimental procedure was adapted from Kho et al. [16]. In this system, the rig was configured such that the gases flow in a downward direction through the catalyst bed. Heat losses from the reactor system were reduced by insulating the reactor with glass wool and using a water jacket to keep the inlet and outlet reactor gas lines at 25 °C.

The catalyst was supported within the reactor using a glass fibre filter matrix. Pretreated catalyst (100 mg) was dispersed in Milli-Q with the aid of an ultrasonic bath then drop-cast onto 7 cm<sup>2</sup> of a glass fibre filter (Merck Millipore Ltd.). After drying at 70 °C for 2 h, the loaded glass fibre was pressed flat, then allowed to dry for 1 h at 70 °C to remove any moisture prior to placing into the reactor (Supplementary Information, Fig. S1). The system (Fig. S2), was first evacuated with the aid of a vacuum pump, followed by CO<sub>2</sub> and H<sub>2</sub> injection at a ratio of 1:4, respectively (approximately 15 kPa CO<sub>2</sub> and 60 kPa H<sub>2</sub>). Samples were taken at defined time intervals (0.5 h) and analysed by a Shimadzu GC-2010 Plus gas chromatograph (GC) fitted with a Supelco Carboxen 1010 column. The GC was equipped with a methaniser and flame ionisation detector (FID) as well as a thermal conductivity detector (TCD). The reactor was illuminated with 300 W Xenon lamp (Pecell CX-04E) with an Eagle R300-3J lamp housing at 20 A.

#### 2.3.2. Photo and thermal activity

To understand the role of light and heat, the energy sources were decoupled using a flow-over photo and thermal rig [34]. Thermal activity tests were conducted by supplying heat to the catalyst from a furnace located below the reactor. For the photo and thermal reaction, light from Xenon lamp was used to illuminate the catalyst in addition to the heat supplied from below.

In preparation for the decoupled reaction, 100 mg of the pretreated catalyst was spread onto an aluminium plate (1.5 cm x 1.5 cm), and then placed into the reactor chamber which contained an annealed Kodial glass window (alkali borosilicate 7046), as shown in Fig. S3. The temperature of the chamber base was controlled by a furnace and measured with a temperature probe underneath the catalyst holder. The temperature controller (Shimaden FP21) was programmed such that the chamber was ramped from 50 °C to 400 °C in 50 °C intervals, and held at each step for 1 h. A continuous flow of gases was provided at a

Download English Version:

<https://daneshyari.com/en/article/7934696>

Download Persian Version:

<https://daneshyari.com/article/7934696>

[Daneshyari.com](https://daneshyari.com)