Photocatalytic CO₂ methanation over NiO/In₂O₃ promoted TiO₂ nanocatalysts using H₂O and/or H₂ reductants

Muhammad Tahir a, *, Beenish Tahir a, Nor Aishah Saidina Amin a, Ayyaz Muhammad b, 1
a Chemical Reaction Engineering Group (CREG), Department of Chemical Engineering, Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia
b Chemical and Materials Engineering Department, Faculty of Engineering, King Abdulaziz University, P.O. Box 80204, Jeddah 21589, Saudi Arabia

A R T I C L E   I N F O

Article info:
Received 2 February 2016
Received in revised form 14 April 2016
Accepted 15 April 2016
Available online 26 April 2016

Keywords:
Photocatalysis
CO₂ methanation
H₂O/H₂ reductants
TiO₂, NPs
Ni/In metals

A B S T R A C T

Photocatalytic CO₂ methanation using H₂O vapors and/or H₂ reductants over nickel (Ni) and indium (In) promoted TiO₂ nanocatalysts has been investigated. The physical-chemical characteristics of the catalysts, prepared through a sol–gel method with different Ni and In doping levels, were characterized by XRD, FESEM, TEM, FTIR, XPS, N₂ adsorption–desorption, UV–vis diffuse reflectance, Raman and photoluminescence spectroscopy. The controlled crystalline growth with increased specific surface area and reduced pore diameter were observed by NiO and In₂O₃ loading into TiO₂. In and Ni metals present in TiO₂, oxidized as In₂O₃ and NiO, promoted efficient separation of photo-generated charges (e⁻/h⁺). Using H₂O as a reductant, CO₂ was efficiently converted to CH₄ over co-loaded TiO₂ catalysts and the optimal loading amount was determined to be 1 wt.% NiO and 3 wt.% In₂O₃, giving a CH₄ production rate of 240 μmole g⁻¹ h⁻¹ at selectivity 80%. This photoactivity of NiO and In₂O₃ loaded TiO₂ catalyst for CO₂ methanation was 2 fold more than the yield rate over In₂O₃/TiO₂ and 6.5 times more the amount produced over the pure TiO₂. The enhancement was attributed to charge transfer property and efficient separated recombination rate by Ni and In metals. In the presence of H₂ reductant, both CO and CH₄ were produced in significant amount and the maximum yield rates detected were 243 and 208 μmole g⁻¹ h⁻¹, respectively. Therefore, H₂O reductant found to be more efficient for CH₄ production, yet the CO₂ reduction process was more favorable with H₂, where the total amounts of products were considerably enhanced. In addition, a photocatalytic reaction mechanism is proposed to understand experimental results over the NiO and In₂O₃ loaded TiO₂ catalysts.

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1. Introduction

Carbon dioxide (CO₂) methanation has been considered as an ideal path for the future, a potential low-carbon based energy source that can replace fossil fuels, and attractive process for the fixation of CO₂ [1]. The conventional route of CH₄ production involves two steps; conversion of carbon feedstock into synthesis gas and its subsequent conversion to CH₄ via CO-methanation reaction. However, renewable methane production is still a challenge due to the high cost of conventional production [2]. Photocatalytic CO₂ methanation, a single step method of CO₂ conversion to CH₄ at normal temperature, has sparked a new sustainable development path. This offers a promising way to generate clean, low cost and environment friendly production of methane using solar energy [3–5]. Among the semiconductor materials that promoted the development, photocatalytic CO₂ reduction to CH₄ onto TiO₂ has been the most popular photocatalyst due to its high activity, low-cost, low toxicity and high stability [6]. However, CH₄ generation over the pure TiO₂ was very low due to the fast recombination of photo-generated charges and inability to utilize visible light.

Loading metals onto a TiO₂ surface via the introduction of defects in the lattice can alter the physicochemical properties and overcomes the problem of its low efficiency. Metals such as Pt, Au, and Ag have been evidenced to be very efficient for the improvement of TiO₂ photoactivity. Ag-deposited TiO₂ nanorods were tested for photocatalytic CO₂ reduction with H₂O and found more favorable for the selective CH₄ evolution [7]. Similarly, CO₂ was efficiently converted to CH₄ over Pt-doped TiO₂ [8] and Cu/TiO₂ catalysts [9]. Instead, indium (In) is well-established as an efficient metal to enhance photocatalysis and product selectivity...
Our previous work indicated that In can improve the photocatalytic activity of TiO₂ catalyst for selective photocatalytic CH₄ production during CO₂ reduction with H₂O vapors. This behavior was observed due to charge transfer property and hindered charges recombination rate by In–metal [11].

On the other hand, Ni promoted TiO₂ catalysts are, probably, the most used due to low cost, high stability, good selectivity and acceptable photocatalytic activity [12,13]. In recent years, Ni-promoted TiO₂ has been tested for the photocatalytic CO₂ reduction by H₂O to CH₄ with enhanced photocatalytic activity and selectivity [14]. The activity of NiO/TiO₂ photocatalyst prevailed for CO₂ reduction with H₂O to CH₄ in the presence of NiO [15]. Many other investigations also reported NiO as an efficient promoter for the enhancement of TiO₂ photocatalytic activity for CO₂ reduction [16–18]. However, recently, much interest has been focused on the modification of TiO₂ with two types of metals to develop co-catalysts.

Simultaneous doping two kinds of metals into TiO₂, an additional viable method, has attracted considerable interest, since it can result into higher photocatalytic activity. The co-doped TiO₂ catalysts can provide reduction or oxidation active sites to catalyze the surface reactions, effectively trap charge carriers and inhibited their recombination rate [19]. The enhanced photocatalytic activity of In and Ni co-doped TiO₂–Pd nanocomposites has been reported for hydrogen generation [20]. Lately, we reported Au–In co-doped TiO₂ photocatalyst for enhanced photocatalytic CO₂ reduction with H₂ to CO [21]. Therefore, it is anticipated that the photocatalytic CO₂ reduction to CH₄ over nickel and indium co-modified TiO₂ catalyst would be appreciable to promote photocatalytic CO₂ methanation reaction with improved selectivity.

In addition to photocatalysts, the choice of a reductant is of utmost importance since the overall efficiency of the CO₂ reduction process predominately determined by the role of reductant and photocatalyst. Water has been the most commonly used reducing agent in CO₂ photoreduction applications. Recently, H₂ is reported as a potentially viable reductant for CO₂ reduction [22]. According to thermodynamics, the reduction potential to generate H₂ from water is lower (0 V) than CO₂ standard reduction potential (−1.9 V) to reduce it. A reduction competition between CO₂ and H₂O can be developed and photo-reactions probably be more favorable for H₂O reduction instead of CO₂ [23]. However, enhancement mechanisms remained unclear and more demonstrations are needed to fully understand the role of H₂ and H₂O reductants on the catalyst activity and product selectivity. Therefore, it is appropriate to study combine effects of H₂O and H₂ reductants for a photocatalytic CO₂ methanation reaction over co-catalysts.

The objective of this study is to investigate photocatalytic CO₂ methanation over Ni and In promoted TiO₂ catalysts using H₂O and/or H₂ reductant. A series of different nickel and indium co-catalysts were prepared and their photocatalytic activity was examined for CH₄ production. The role of H₂O and H₂ reductant for the transformation of CO₂ to CH₄ were critically discussed. The probable mechanism of the photocatalytic CO₂ reduction over NiO and In₂O₃ loaded TiO₂ catalysts were postulated.

2. Experimental

2.1. Synthesis of nanocatalysts

Modified TiO₂ nanocatalysts were prepared through a sol–gel method according to our previous work [24]. All chemicals were of analytical grade and were used as received without further purification. In a typical synthesis, titanium sol was prepared by hydrolyzing aqueous solution of 10 mL tetra-isopropyl ortho-titanate and 30 mL isopropanol with acetic acid (I M) under vigorous stirring, kept stirring for 12 h at room temperature to get a clear titanium sol. Nickel and indium metals were loaded into the titanium sol using a specified amount of In(NO₃)₃·H₂O and Ni(NO₃)₂·3H₂O and aged for another 6 h to get a thick titanium sol. Finally, samples in the oven at 80 °C were dried and then calcined in a furnace at a rate of 5 °C min⁻¹ up to 500 °C for 5 h. TiO₂ with different In and Ni loading levels were prepared by varying the quantity of In(NO₃)₃·H₂O and Ni(NO₃)₂·3H₂O. Pure TiO₂ nanoparticles were prepared using the same procedure without metal loading.

2.2. Characterization

The crystal structure of the powder samples was investigated by X-ray powder diffraction (XRD) (Bruker D8 advance diffractometer) using Cu Kα radiation (λ = 0.154178 nm) operated at 40 kV and 40 mA. The XRD patterns were obtained with a scan rate of 1.2° min⁻¹ and scanning range of 10–70° of 2θ. The morphology of the samples was examined by field emission scanning electron microscopy (FESEM, Hitachi SU8020). The particle size and lattice structure of the individual crystals were visualized by high-resolution transmission electron microscopy (HR-TEM) with FEI-Tecnai G2 TEM. The chemical composition was analyzed using X-ray photoelectron spectroscopy (XPS, Axis Ultra DLD Shimadzu). The XPS spectrum was calibrated with respect to the binding energy of the Cls signal at 284.60 eV as the internal standard. The specific surface area of the samples was measured by N₂ adsorption–desorption at 77 K using a surface area and porosity analyzer (Micrometrics ASAP 2020). The infrared spectra were measured at room temperature with a resolution of 4 cm⁻¹ in the IR range 4000–400 cm⁻¹ with Spectrum 2000 Explorer Fourier Transformed Infrared Spectrometer. Ultraviolet–visible (UV–vis) diffuse reflectance absorbance spectra were measured using UV–vis spectrophotometer (Agilent, Cary 100) equipped with an integrated sphere in the wavelength range of 200–800 nm. Raman and photoluminescence measurements of the powder samples were acquired at room temperature using Raman Spectrometer (LabRAM HR Evolution, HORIBA) with a 532 nm emitting laser as an excitation source.

2.3. Photocatalytic activity test

The photocatalytic CO₂ reduction was H₂O and H₂ reductant in the gas phase was investigated in a batch photoreactor system of total volume 108 cm³ as shown in Fig. 1. The light source used to activate photocatalyst was a 500 W Hg lamp located inside the quartz cold trap, having maximum irradiation intensity at 365 nm with light intensity 25 mW/cm². Quartz glass window of 10 mm thickness was fixed at the top of the reactor, enabling efficient transfer of the irradiation form lamp to the catalyst surface. The lamp was ignited using high voltage power supply connected to a lamp through an igniter and a stabilizer. The reactor was covered with aluminum foil to ensure all the lights participated in the reaction came through the quartz window only. 0.25 g of powder photocatalyst was uniformly dispersed at the bottom of the reactor to ensure light is powerfully distributed over the entire catalyst surface.

The reactor, checked for leakage at 2 bar pressure for several hours, was purged with helium (He) gas. The compressed CO₂ (99.99%) regulated by a mass flow controller (MFC) was flowing through the water bubbler at 20 mL/min to carry moisture. The CO₂ saturated with H₂O was mixed with a He flowing at a rate of 80 mL/min in a gas mixture to dilute CO₂ concentration. The mixture of gases (CO₂, He, H₂O) was passed through reactor for 30 min to purge and saturate the catalyst. Thereafter, outlet valve was closed and pressure inside the photoreactor was increased to 0.20 bars above atmospheric pressure, then the inlet valve was
closed and batch experiment was started by turning on the lamp. In the case of CO₂ reduction with H₂, flow rates of gasses were regulated at a rate of 20, 20 and 60 mL/min for CO₂, H₂ and He, respectively. Similarly, during CO₂ reduction with H₂O/H₂ reductant, CO₂ saturated with H₂O was mixed with H₂ in a gas mixture before feeding to the reactor.

The products were analyzed using an on-line gas chromatograph (GC-Agilent Technologies 6890 N, USA) equipped with thermal conductivity detector (TCD) and a flame ionized detector (FID). Furthermore, FID detector was connected with a HP-PLOT Q capillary column (Agilent, length 30 m, ID 0.53 mm, film 40 μm) for separation of C₁–C₆ paraffin and olefins hydrocarbons, alcohols and oxygenated compounds. The TCD detector was connected to UCW982, DC-200, Porapak Q and Mol Sieve 13X columns. C₁–C₂, C₃–C₅ compounds and light gasses (H₂, O₂, N₂, CO) were separated using Porapak Q, DC-200 and MS-13X column, respectively. The quantification of the products was based on the external standard and the use of a calibration curve.

3. Results and discussion

3.1. Morphology of nanocatalysts

Fig. 2(a) presents XRD patterns of the pure TiO₂ and doped TiO₂ samples with different metal loading levels. The contents of rutile were not detected, suggesting that pure anatase and crystalline phase TiO₂ was produced at 500 °C. The XRD patterns of the Ni and In modified TiO₂ samples are similar to those of pure TiO₂. However, the signals corresponding to Ni and In in metal or oxides states were not observed even in the samples with 2% Ni and 5% In contents. This was possibly due to the lower metals amounts, which were below the detection limit of XRD or the species were highly dispersed inside TiO₂ structure. However, the existence of Ni and In was confirmed by FESEM and XPS analysis. Compared to TiO₂, the peaks of InₓOᵧ/TiO₂ and NiO–InₓOᵧ/TiO₂ became broader suggesting smaller TiO₂ crystal size. The average crystalline sizes of the samples were gradually reduced in Ni and In loaded TiO₂ samples as listed in Table 1.

Raman spectroscopy was employed to investigate the structural properties of TiO₂ and shifts of Raman bands associated with the particle size. Fig. 2(b) shows the Raman spectra of TiO₂, InₓOᵧ/TiO₂, NiO/TiO₂ and NiO–InₓOᵧ/TiO₂ samples. In the case of pure TiO₂, several characteristics bands at 142, 197, 394, 513, and 634 cm⁻¹ correspond to the E₁g, E₂g, B₁g, A₁g, and E₃g modes are attributed to anatase phase of TiO₂ [25]. From the Raman spectra, it is evident that both pure and metal-loaded TiO₂ are in the anatase phase. There appeared no impurity related modes in the Raman spectra of doped samples, in good agreement with
XRD results. With the NiO and In$_2$O$_3$-loading the position of the Raman bands, in particular the E$_{g}$(1) mode near 142, shifted toward higher wavenumber, attributed to the reduction of particle size of the loaded TiO$_2$ samples [26].

Fig. 3 shows the FESEM and mapping images of pure TiO$_2$, 3% In$_2$O$_3$-TiO$_2$ and 1% NiO–3% In$_2$O$_3$/TiO$_2$ samples. The uniform and spherical nanoparticles of TiO$_2$ with mesoporous structure are obvious in Fig. 3 (a). The EDX mapping analysis in Fig. 3 (b) shows the presence of Ti and O elements in TiO$_2$. In/TiO$_2$ nanoparticles have a smaller particle size, compared with TiO$_2$ as shown in Fig. 3(c). The uniform In-distribution over the TiO$_2$ could be seen in Fig. 3(d). Fig. 3(e) and (f) revealed Ni–In loaded onto TiO$_2$ surface with their particle size distribution and mesoporous structure. Noticeably, Ni and In metals, evenly distributed over the TiO$_2$ surface, can provide more active sites for the reactants.

The morphology and structure of 1% NiO–3% In$_2$O$_3$/TiO$_2$ catalyst was further analyzed using transmission electron microscope (TEM). Fig. 4(a) revealed that this material consists of spherical

<table>
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<tr>
<th>Catalysts</th>
<th>Crystallite size $^a$ (nm)</th>
<th>Surface area $^a$ (m$^2$ g$^{-1}$)</th>
<th>BJH pore volume (cm$^3$ g$^{-1}$)</th>
<th>BJH pore width (nm)</th>
<th>Band gap energy $^b$ (eV)</th>
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<td>0.217</td>
<td>10</td>
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<td>107</td>
<td>0.187</td>
<td>9</td>
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<tr>
<td>2% NiO–3% In$_2$O$_3$–TiO$_2$</td>
<td>8</td>
<td>93</td>
<td>149</td>
<td>0.217</td>
<td>8</td>
</tr>
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$^a$ Crystal size calculated using Scherrer equation based on 101 peak of TiO$_2$.

$^b$ Band gap energy calculated using Tauc equation, from a plot of $(ahv)^2$ versus photon energy ($h\nu$).
nanoparticles of mesoporous structure with size 6–16 nm, which fits well with the crystal size calculated by Scherrer equation. Some amount of agglomeration persists in the sample, resulting in the larger particle size. The planar distance of the crystalline particles measured from HRTEM images corresponded well with the distance of anatase planes (0.35 nm) as depicted in Fig. 4(b). No segregated nickel/indium particles or species were detected which confirmed uniform dispersion of these metals over the TiO$_2$ surface.

Fig. 5 explains FTIR spectra of TiO$_2$, 3% In$_2$O$_3$/TiO$_2$, and 1% NiO–3% In$_2$O$_3$/TiO$_2$ samples. Apparently, no changes in the characteristics FTIR spectra of TiO$_2$ detected due to Ni and In co-metal incorporation. The absorption broad band at about 3400 and 1624 cm$^{-1}$ correspond to stretching vibration of –OH group that are linked with titanium atoms (Ti–OH) and to the bending vibration of H–O–H, respectively [27]. The absorption bands corresponding to metals not detected, probably, because of lower loading contents of metals.

X-ray photoelectron spectroscopy (XPS) was used to determine the oxidation state of Ti, In, Ni and chemical states of the component elements in 3% In$_2$O$_3$/TiO$_2$ and 1% Ni–3% In$_2$O$_3$/TiO$_2$ samples as presented in Fig. 6. The Ti 2P$_{3/2}$ and Ti 2P$_{1/2}$ binding energies (BE) in Fig. 6(a) attributed to the presence of titanium as Ti$^{4+}$ oxidation state in both In$_2$O$_3$/TiO$_2$ and NiO–In$_2$O$_3$/TiO$_2$ samples. Fig. 6(b) shows spectra of O1s for the In$_2$O$_3$/TiO$_2$ and NiO–In$_2$O$_3$/TiO$_2$ samples. The XPS spectrum of O1s in In$_2$O$_3$/TiO$_2$ reveals a peak with two main components, one at 529.54 eV, characteristics of lattice oxygen (O$^{2-}$) and a high binding energy component at 532.48 eV related to metal–OH bond or free hydroxyl group (OH) on the surface. The same kind of analysis fitting can be determined for NiO-promoted In$_2$O$_3$/TiO$_2$ sample with O 1s peak components centered at 530.76 and 532.72 eV. The main difference is related to the peak concentrations. The relative concentration of lattice oxygen peak increases, but metal–OH peak decreases significantly in NiO–In$_2$O$_3$/TiO$_2$ compared to In$_2$O$_3$/TiO$_2$ sample. Metal–OH peak also slightly shifted in the NiO–In$_2$O$_3$/TiO$_2$ sample, indicating Ni–OH bonds have more contribution to the spectra. The C1 s peaks for In$_2$O$_3$/TiO$_2$ and NiO–In$_2$O$_3$/TiO$_2$ samples are presented in Fig. 6(c). The main peak at 284.60 eV is assigned to C–C and C–H hydrocarbon bonds. The peak at 286.63 eV is due to C–OH and C–O bonds while other peak at 288.33 eV can be attributed to carbon atoms bound to oxygen with double bond C=O. The relative concentration of peak at 284.60 eV was much more than the other peaks. The presence of this carbon may be recognized as the carbon from carbon tap used for sample analysis.

Fig. 6(d) shows the spectra of In 3d peaks for In-doped TiO$_2$ with BE regions centered at ~444.21 eV (3d$_{5/2}$) and 451.73 eV (3d$_{3/2}$), respectively, indicating indium as In$^{3+}$ or indium oxide (In$_2$O$_3$).

The corresponding In 3d spectra for Ni–In/TiO$_2$ sample revealed the same kind of analysis with indium as In$^{3+}$. The main difference is related to shift in peaks, indicating Ni is contributing to the spectra. The XPS spectra for Ni 2P$_{3/2}$ and Ni 2P$_{1/2}$ core levels appeared at 856.56 and 874.74 eV, respectively, and corresponding satellite peak is observed at 861.63 eV as shown in Fig. 6(e). The difference between both Ni 2p spectra is the characteristics of nickel as Ni$^{2+}$ or nickel oxide (NiO). The satellite peak also confirmed NiO state of the nickel [28]. The peaks of In$_2$O$_3$ and NiO observed in XPS analysis were not detected by XRD, perhaps due to lower amount of these metals in the TiO$_2$ samples.

The N$_2$ adsorption–desorption tests were performed to determine surface area, pore volume and pore width of the catalysts. The isotherms of TiO$_2$, In$_2$O$_3$/TiO$_2$ and NiO–In$_2$O$_3$/TiO$_2$ samples are illustrated in Fig. 7(a). Obviously, all the samples exhibited typical type IV isotherms with an increase in the volume of gas uptake within the relative pressure (P/Po) range of approximately 0.55–1.0. The hysteresis loops observed in TiO$_2$ and doped TiO$_2$ samples, indicating mesoporous pore structure of TiO$_2$. Suggestively, capillary and condensation reflections were observed in the TiO$_2$ sample, while the similar trends appeared in the NiO and In$_2$O$_3$ modified TiO$_2$ samples. Fig. 7(b) reveals pore size distribution in which mean pore diameter of TiO$_2$ was gradually decreased in In$_2$O$_3$ and NiO modified TiO$_2$ samples.

The surface area ($S_{BET}$), total pore volume and pore size of the catalysts are listed in Table 1. The loading NiO and In$_2$O$_3$ into TiO$_2$ have increased the BET surface area and pore volume. The
increased in the surface area was, perhaps, due to a reduction in the crystal size. The BJH adsorption surface areas of NiO and In$_2$O$_3$ modified TiO$_2$ samples were much larger compared to the pure TiO$_2$, which has confirmed that mesoporous structure of TiO$_2$ can be enhanced by loading Ni and In metals. Similar trends were observed for the pore volume of TiO$_2$ in different samples. Mesoporous structures and total pore volume play an important role in the photocatalytic activity. Therefore, well-developed mesoporous structures with larger pore volume and smaller pore diameter could minimize mass transfer limitations to increase catalyst activity.

Fig. 8(a) shows UV–vis diffuse reflectance absorbance spectra of pure TiO$_2$, In$_2$O$_3$/TiO$_2$ and NiO–In$_2$O$_3$/TiO$_2$ catalysts. The addition of NiO into In$_2$O$_3$/TiO$_2$ sample can obviously enhance the absorbance of TiO$_2$ under visible light irradiations. The energy band gaps ($E_{bg}$) of all the samples were obtained from the extrapolation of Tauc plot to the abscissa of photon energy and results are presented in Table 1. The energy band gap of pure TiO$_2$ (3.12 eV) shifted toward longer wavelength with In$_2$O$_3$ loading TiO$_2$ samples. This increase in the energy band gap was attributed to the higher In$_2$O$_3$ band gap energy [11]. The band gaps of NiO–In$_2$O$_3$ co-loaded TiO$_2$ samples were 3.06 and 3.04 for 1 and 2 wt.% NiO-contents, respectively. Evidently, there was a gradual decrease in the TiO$_2$ band gap energy with NiO-loading.

Fig. 8(b) shows PL emission spectra of the samples. The spectra of all the samples are similar and show broad peaks in the range of 530–560 nm when excited at a wavelength of 532 nm. When compared with the band gap of TiO$_2$, the broad symmetric peaks appeared at around 536 nm confirmed that emission is not rising due to TiO$_2$ band edge excitation [20]. Therefore, PL signals attributed to the transition of electrons from the oxygen vacancies to TiO$_2$ valance band. The PL intensity is enfeebled in In$_2$O$_3$ sample and further reduced in NiO–and In$_2$O$_3$ promoted TiO$_2$ samples. The gradual decrease of PL intensity suggests that photo-generated electrons/holes ($e^-/h^+$) are separated efficiently [18]. This established that Ni and In have improved the mobility of charges with suppressed recombination rates.

3.2. Photocatalytic CO$_2$ reductions with H$_2$O and H$_2$ reductants

Two blank tests were performed; one for irradiation without any catalyst and the other in the presence of a catalyst without light irradiation. The carbon containing products was not detected without irradiation or photocatalyst. This confirmed that photocatalysts were cleaned and carbon containing products (CH$_4$, CO) were produced during CO$_2$ reduction only. The effect of In-loading (wt.%) on the TiO$_2$ photocatalytic activity for CO$_2$ reduction with H$_2$O in CO and CH$_4$ production is presented in Fig. 9(a). Pure TiO$_2$ has smaller CO$_2$ reduction efficiency, but is
considerably enhanced in the TiO₂ samples loaded with In. In-loaded TiO₂ samples has effectively promoted CO₂ methanation with an optimum of 3% In-contents. Therefore, 3% In-loaded TiO₂ is the most effective catalyst over which amount of evolved CH₄ reached to 249 μmole g⁻¹ after 2 h of irradiation time, significantly higher than the pure TiO₂. This enhancement in TiO₂ photoactivity of CH₄ production during CO₂ reduction was due to In₂O₃/TiO₂ mesoporous structure and hindered charges recombination rate by In–metal. At excess amount of In-loading, lower CH₄ yield can be attributed to the formation of charge recombination centers over the TiO₂ surface [11].

Fig. 9(b) presents the effect of different amounts of NiO-loading (1–3% NiO) on the TiO₂ photoactivity for selective CO₂ methanation using H₂O as a reductant. In all the cases, CH₄ was detected as the main product with a smaller amount of CO. The TiO₂ photoactivity for CO₂ methanation was reached to maximum by loading 2% NiO, then gradually decreased at higher NiO-loading. It is evident that NiO is more efficient than In₂O₃ for CO₂ reduction and maximum CH₄ production over 2% NiO/TiO₂ observed was 307 μmole g⁻¹ catal. after 2 h of irradiation time. The yield of CH₄ over NiO/TiO₂ was 1.23 fold higher than In₂O₃/TiO₂ and 3.4 fold the amount produced over the pure TiO₂. The reduced in TiO₂ photoactivity at NiO-loading above 2% was probably due to the recombination centers over the TiO₂ surface. Previously, we have reported the similar observations during CO₂ reduction with H₂ in a monolith photoreactor with CO as the main product [29].

It is evident from the above discussion that NiO is the most efficient to enhance TiO₂ photoactivity for selective CO₂ methanation. Efficient adsorption and desorption process over Ni active sites has attributed to the improved photoactivity. This can be explained based on thermodynamics, as the electrons would be trapped efficiently, if the reduction potential of metal is more positive than
the semiconductor (e.g. TiO$_2$) conductance band [21]. As the redox values of both NiO and In$_2$O$_3$ are lower than the CB of TiO$_2$ ($-0.50$ V), thus electron can effectively be transferred toward these metals to prolong their lifetime [17]. Moreover, as the potential of Ni$^{2+}$/Ni ($-0.23$ V) is lower than the In$^{3+}$/In ($-0.33$ V), thus more electrons would be transferred toward NiO which could result in higher photocatalytic activity for CO$_2$ reduction.

Fig. 10 shows the efficiency of NiO-promoted In$_2$O$_3$/TiO$_2$ catalysts for the photocatalytic CO$_2$ reduction by H$_2$O reductant at different irradiation times (0–8 h). Using all types of photocatalysts, CH$_4$ and CO were detected as the major CO$_2$ reduction products with smaller amount of ethane (C$_2$H$_6$). Fig. 10(a) shows production of CH$_4$ versus irradiation time over pure TiO$_2$ and NiO-promoted In$_2$O$_3$/TiO$_2$ samples. For the pure TiO$_2$, lower CH$_4$ production was detected over the entire irradiation time due to the fast recombination of photo-generated electron–hole pairs. However, loading In$_2$O$_3$ into TiO$_2$ effectively promotes CO$_2$ methanation reaction and continuous CH$_4$ production detected even after 8 h of irradiation time. However, NiO-promoted In$_2$O$_3$/TiO$_2$ photocatalysts found very efficient for CO$_2$ methanation and rate of CH$_4$ formation was faster with the increase of NiO-loading.

The optimal amount of NiO-loading was determined to be 1 wt.% NiO in 3 wt.% In$_2$O$_3$/TiO$_2$ catalyst that exhibited the maximum photocatalytic activity. In NiO-promoted In$_2$O$_3$/TiO$_2$ catalyst, CH$_4$ production activity was obviously enhanced compared to In$_2$O$_3$/TiO$_2$ and pure TiO$_2$ over the entire irradiation time. This has confirmed higher photoactivity and stability of this catalyst for the selective CO$_2$ methanation reaction. The excess NiO-loading may develop charge recombination centers and/or shielded TiO$_2$ surface active sites [17]. The highest CH$_4$ yield rate observed for the NiO-In$_2$O$_3$/TiO$_2$ sample was 1920 µmole g$^{-1}$, 2 folds more than the amount produced over In$_2$O$_3$/TiO$_2$ and increased 6.5 times more than the pure TiO$_2$. This implied that the NiO-promoted In$_2$O$_3$/TiO$_2$ catalysts had a much lower recombination rate of charges (e$^-$/h$^+$), attributed to the excited carriers transfer, resulting in enhanced CH$_4$ production.

Fig. 10(b) shows production of CO during CO$_2$ reduction by H$_2$O versus irradiation time over the NiO-loaded In$_2$O$_3$/TiO$_2$ samples. Evidently, the photocatalytic behavior of all the catalysts over the irradiation time is similar to CH$_4$ production. However, CH$_4$ formation was 4-folds higher than the amount of CO produced over NiO-In$_2$O$_3$/TiO$_2$ under the same operating conditions. It could be seen that surface area and crystal sizes are almost the same in In$_2$O$_3$/TiO$_2$ and NiO-In$_2$O$_3$/TiO$_2$ samples. However, the photoactivity of single ion and co-doped ions are entirely different in both CO and CH$_4$ production. Therefore, it is postulated that suppressed recombination rate, in the presence of Ni and In co-metal ions, has contributed effectively to the enhancement of CO$_2$ reduction efficiency. The yield of C$_2$H$_6$ production in gas phase over the irradiation time under UV-light irradiation can be observed in Fig. 10 (c). Over TiO$_2$, smaller amount of C$_2$H$_6$ was produced and gradually increased using 3 wt.% In$_2$O$_3$ and 0.5% Ni–3% In$_2$O$_3$/TiO$_2$ catalysts. The amount of C$_2$H$_6$ production was continuous over the entire irradiation time, which confirmed prolonged photoactivity and stability of these catalysts. The other products detected in smaller amounts over Ni–In loaded TiO$_2$ catalysts were ethylene (C$_2$H$_4$), propylene (C$_3$H$_6$) and propane (C$_3$H$_8$). Similar observations were reported previously [11].

![Fig. 10. Effect of NiO-promoted In$_2$O$_3$/TiO$_2$ catalysts for CH$_4$, CO and C$_2$H$_6$ production of photocatalytic CO$_2$ reduction with H$_2$O vapors at various Ni-loading and irradiation times under UV-light irradiations: (a) CH$_4$ evolution, (b) CO evolution and (c) C$_2$H$_6$ production.](image-url)
In addition to NiO and In2O3 loaded TiO2 catalysts, understanding the effects of reductants (H2, H2O) on CO2 reduction efficiency is essential. The effects of H2O and H2 reductants on the amounts of CO and CH4 formation during CO2 reduction over 1% NiO–3% In2O3/TiO2 catalyst is presented in Fig. 11. By replacing reductant H2O with H2, the selectivity was shifted from CH4 to CO, where, the production of CO was significantly increased. It is apparent from the results that reducing agent has contributed significantly to enhance CO2 reduction process and product selectivity. In the case of H2, CO production was prominent over the entire irradiation time. Alternatively, by using H2/H2O reductants simultaneously, performance of NiO–In2O3/TiO2 catalyst for CH4 production was entirely different. In the beginning, CH4 yield rate was noticeable, but gradually deteriorated, whereas, the amount of CO produced was more than the yield of CH4 after 6 h of reaction time. Firstly, there was more H2O adsorbed over the catalyst which has favored larger CH4 production, but gradually decreased, probably, more H2 adsorption over the time.

The higher CO2 reduction efficiency in the presence of H2 could be explained based on the adsorption–desorption competitions between the reactants. Generally, since the interfacial contact rates between water vapors and catalyst surface are less formidable than H2 and the catalyst surface [22]. Therefore, the lower yield rate using H2O vapors could be due to less competition between CO2 and H2O than H2. Besides, H2O is not efficient reductant for CO2 reduction because of their reduction potential difference. Therefore, H2 is more favorable as a reductant for photocatalytic CO2 reduction compared to CO, but a higher CH4 selectivity could be achieved using H2O reductant.

Recently, it has been reported that CO2 was firstly converted to CO and then transformed to CH4 over TiO2 based photocatalysts [22,30]. Therefore, using H2O as a reductant, it can be acted as an electron donor and CO was finally converted to CH4. In the presence of H2, number of photogenerated electrons used in CO2 reduction and H+ were similar to that of photogenerated holes consumed by H2 oxidation, resulting in selective CO production [31]. On the other hand, it was probably due to the reduction potential difference of reductants and products as discussed in Section 3.3. Photocatalytic CO2 reduction by H2 to the selective CO formation could be further explained based on reverse water gas shift (RWGS) reaction. Previously, we have investigated photocatalytic CO2 reduction to CO over different co-loaded TiO2 nanocatalysts in a batch and continuous mode of monolith photocatalyst [21,32,33]. Therefore, it can be established that CO would be a major CO2 reduction product via RWGS reaction using a cell type or a monolith photoreactor operated in a batch or continuous mode of operation.

The yield rates comparison of the products during photocatalytic CO2 reduction using H2O, H2 + H2O and H2 reductant over different photocatalysts are presented in Fig. 12 and the results are summarized in Table 2. It could be seen that type of reductant exhibits a significant influence on the photocatalytic activity of catalyst and selectivity of products. The CH4 production rate was lower over the pure TiO2 but significantly increased using NiO and In2O3 based TiO2 co-catalysts. In particular, with the same photocatalyst (1% NiO–3% In2O3/TiO2), different amounts of CH4 yield rate and selectivity were achieved with different reductant. Using H2O reductant, maximum CH4 yield rate achieved was 240 µmol·g−1·h−1 and selectivity 80%. This amount of CH4 production was 1.45 fold higher than using H2 + H2O reductant and 1.15 folds more than using H2 reductant. However, CO was the major product using H2 reductant and maximum yield rate detected was 243 µmol·g−1·h−1 with selectivity 53%. The total production rate (CO2 + CH4) of 451 µmol·g−1·h−1 was achieved using H2 reductant, a 1.28 fold more than using H2 + H2O reductant and 1.5 times larger than using H2O reductant. Therefore, H2 is the more efficient reductant for CO2 conversion to both CO and CH4 over NiO and In2O3 based TiO2 co-catalysts. Yet, the higher selectivity for CH4 production could be achieved using H2O as a reductant.

In order to investigate the performance of CO2 photoreduction with H2 and or H2O reductants over NiO and In2O3 loaded TiO2 photocatalysts the results are compared with the work reported by various researchers. CO2 reduction with H2O to CO was reported after 3.5 h during gas phase CO2 reduction in a batch mode operation with a maximum yield of 14.73 µmol after 12 h irradiation time [34]. Over I/TiO2 and Cu–I/TiO2, a CO yield rate of 3.9 and 12 µmol·g-catal.−1 was reported after 3.5 h during gas phase CO2 reduction in a batch mode operation [35]. Similarly, photocatalytic CO2 reduction with H2O to CH4 over different photocatalysts such as CH4 yield of 100.22 ppm cm−2·h−1 over MgO/TNTs [36], rGO–Pt/TNTs with CH4 yield rate of 10.96 µmol·m−2 [37], CH4 yield rate of 23.10 µmol·g-catal.−1 after 480 min over 3-D Au/TiO2 nanoparticles [38] and a CH4 production of 184 µmol·g-catal.−1 after 24 h over Zn–Cu promoted TiO2 has been reported [39]. A comparison study between previous reports and current study revealed higher performance of TiO2 catalysts loaded with Ni and In metals for selective CO and CH4 production using H2O and/or H2 reductants in the same type of photocatalyst system.

**Fig. 11.** Effect of H2 and H2/H2O reductant for the production of CH4 and CO during CO2 reduction over 1% Ni–3% In2O3/TiO2 at different irradiation times.

**Fig. 12.** Production rate of CO and CH4 over different types of reductants and photocatalysts: (a) CO2 + H2O with TiO2, (b) CO2 + H2O with 3% In2O3/TiO2, (c) CO2 + H2O with 1% NiO–3% In2O3, (d) CO2 + H2 with 1% NiO–3% In2O3/TiO2, and (e) CO2 + H2 with 1% NiO–3% In2O3/TiO2.
Eqs. (8)–(10) divulged production of CO and CH4 through utilization of H2O and/or H2 reductant. The reductant was adsorbed on the catalyst surface, then the electron (e−)–holes (h+) pairs are produced. Due to the short lifetime, they can recombine immediately or can be trapped by the doped metal to participate in oxidation and reduction process. The reactions in Eqs. (1)–(10) may express the pathways of CO2 photoreduction to CO and CH4.

\[
\begin{align*}
\text{TiO}_2 & \rightarrow e_{cb}^+ + h_{vb}^- \\
\text{In}^{3+} + e_{cb}^- & \rightarrow \text{In}^{3+} - e_{cb}^+ \\
\text{Ni}^{2+} + e_{cb}^- & \rightarrow \text{Ni}^{2+} - e_{cb}^+ \\
\text{H}_2 \text{O} + h^+ & \rightarrow \text{OH} + \text{H}^+ \\
\text{H}_2 \text{O} + \text{OH} + 3\text{h}^+ & \rightarrow 3\text{H}^+ + \text{O}_2 \\
\text{H}_2 + 2\text{h}^+ & \rightarrow 2\text{H}^+ \\
\text{CO}_2 + e^- & \rightarrow \text{CO} \\
\text{CO}_2 + e^- & \rightarrow \text{CO}^+ + \text{H}^+ \\
\text{CO}_2 + e^- & \rightarrow \text{CO}^+ + \text{H}^+ \\
\text{C} + \text{H}^+ + e^- & \rightarrow \text{CH}_2 \rightarrow \text{CH}_3 \rightarrow \text{CH}_4
\end{align*}
\]

Eqs. (1)–(3) reveal photo-excited electron–hole pair production and their trapping by Ni and In–metals, thus increasing the lifetime of charges to precede oxidation and reduction process. The holes are used for oxidation of H2O and/H2 as explained in Eqs. (4)–(6). CO2 reduction by electrons is illustrated in Eq. (7). Reactions in Eqs. (8)–(10) divulged production of CO and CH4 through utilization of H+ ions and electrons (e−). Therefore, it could be seen, that CO2 was firstly converted to CO by reduction reaction, whereas CO should pass through various steps to be ultimately converted to CH4. The some of the formed CO when desorb from the surface, will no longer be contributing to CH4 formation.

As the photocatalytic activity is closely related to the band structure of photocatalysts as well as the redox potential, the enhanced photocatalytic mechanism for NiO–In2O3/TiO2 can be explained by the scheme presented in Fig. 13. Under the light irradiations, VB electrons of TiO2 excited to CB creating holes in VB. Without In2O3 or NiO metals, these charges recombine back and only a fraction of electrons and holes participate in reduction and oxidation process, thus, TiO2 shows a quite low photocatalytic activity. When In2O3 or NiO metals were loaded on TiO2 surface, CB electron of TiO2 can transfer to these metals which cause electron–hole pair separation. Furthermore, more electrons could be trapped if the metal reduction potential is more positive than the CB of TiO2. As the redox values of both NiO and In2O3 are lower than the CB of TiO2 (0.50 V), thus electron can effectively be transferred toward these metals to prolong their lifetime [17]. Moreover, as the potential of Ni2+/Ni (0.23 V) is lower than In3+/In (0.24 V), thus more electrons would be transferred toward NiO which could result in higher photocatalytic activity for CO2 reduction than In2O3. The production of CH4 as the main product over both types of catalysts could be explained based on TiO2 conduction band potential. Since the reduction potential of CO2/CH4 (0.24 V) is less than the conductance band of TiO2 (0.5 V), the reaction was more favorable to generate methane efficiently. In the case of CO2 reduction with H2, CO was produced in significant amount. As the potential difference of H2/H+ (0 V) and CO (−0.48 V) are more appropriate compared to CO2/CH4 (−0.24 V), resulting CO as the main product. On the other hand, a potential difference of H2O/H+OH (+2.32 V) and CO2/CH4 (−0.24 V) were favorable for

### Table 2
Summary of products produced during photocatalytic CO2 reduction with H2O and/or H2 reductants using TiO2 and metal-loaded TiO2 catalysts.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Reductant</th>
<th>Yield ratea (μmole g−1 h−1)</th>
</tr>
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<tbody>
<tr>
<td>TiO2</td>
<td>H2O</td>
<td>37</td>
</tr>
<tr>
<td>3% In2O3/TiO2</td>
<td>H2O</td>
<td>118</td>
</tr>
<tr>
<td>0.5%NiO–3%In2O3–TiO2</td>
<td>H2O</td>
<td>218</td>
</tr>
<tr>
<td>1.0%NiO–3%In2O3–TiO2</td>
<td>H2O</td>
<td>240</td>
</tr>
<tr>
<td>2.0%NiO–3%In2O3–TiO2</td>
<td>H2O</td>
<td>197</td>
</tr>
<tr>
<td>1.0%NiO–3%In2O3–TiO2</td>
<td>H2</td>
<td>208</td>
</tr>
<tr>
<td>1.0%NiO–3%In2O3–TiO2</td>
<td>H2O + H2</td>
<td>166</td>
</tr>
</tbody>
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<table>
<thead>
<tr>
<th></th>
<th></th>
<th>Selectivityb (%)</th>
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<tbody>
<tr>
<td>CH4</td>
<td>CO</td>
<td>Total</td>
</tr>
<tr>
<td>67</td>
<td>33</td>
<td>100</td>
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<td>54</td>
<td>100</td>
</tr>
<tr>
<td>47</td>
<td>53</td>
<td>100</td>
</tr>
</tbody>
</table>

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3.3. Proposed mechanism of reaction

In photocatalysis process, when photons strike over the photocatalyst surface, then the electron (e−)–holes (h+) pairs are produced. Due to the short lifetime, they can recombine immediately or can be trapped by the doped metal to participate in oxidation and reduction process. The reactions in Eqs. (1)–(10) may express the pathways of CO2 photoreduction to CO and CH4.

\[
\begin{align*}
\text{TiO}_2 & \rightarrow e_{cb}^+ + h_{vb}^- \\
\text{Ni}^{2+} + e_{cb}^- & \rightarrow \text{Ni}^{2+} - e_{cb}^+ \\
\text{H}_2 \text{O} + h^+ & \rightarrow \text{OH} + \text{H}^+ \\
\text{H}_2 \text{O} + \text{OH} + 3\text{h}^+ & \rightarrow 3\text{H}^+ + \text{O}_2 \\
\text{H}_2 + 2\text{h}^+ & \rightarrow 2\text{H}^+ \\
\text{CO}_2 + e^- & \rightarrow \text{CO} \\
\text{CO}_2 + e^- & \rightarrow \text{CO}^+ + \text{H}^+ \\
\text{C} + \text{H}^+ + e^- & \rightarrow \text{CH}_2 \rightarrow \text{CH}_3 \rightarrow \text{CH}_4
\end{align*}
\]

Fig. 13. Proposed schematic of charge transfer and reactants transformation to CO and CH4 over NiO and In2O3 modified TiO2 photocatalyst using H2O and/or H2 reductant under UV-light irradiation.
CH4 production. Therefore, both reductant and type of metals are relatively important to in photocatalytic CO2 reduction applications.

4. Conclusions

The NiO and In2O3 promoted TiO2 nanocatalysts were prepared and tested for the photocatalytic CO2 reduction using H2O and H2 reductant. The deeper insight on the reactivity and selectivity was obtained using different metals and reductant. The prepared NiO and In2O3 based TiO2 photocatalysts showed enhanced photocatalytic CO2 reduction. The formation of the nanostructure was favorable for the separation of the photo-generated charges. The porous structure of NiO–In2O3/TiO2 effectively provides reacting sites for transforming electrons to the reactants and prevents electron–hole recombination. Using H2O reductant, the photoactivity of NiO–In2O3/TiO2 catalyst was the highest for CH4 production, which exceeded 2 fold than In2O3/TiO2 and 6.5 times than the pure TiO2. The enhanced photoactivity was evidently due to hindered charges recombination rate and their efficient transfer toward Ni and In metal. On the other hand, with H2 reductant, CO was detected as the major product with appreciable amount of CH4. The total amount of products (CO, CH4) over the NiO–In2O3/TiO2 catalyst using H2 reductant was 1.5 times more than using H2O under the same operating conditions. The fundamentals derived from these experiments are useful in the design of co-catalysts and selection of reductant for production of selective fuels.

Acknowledgements

The authors would like to extend their deepest appreciation to Universiti Teknologi Malaysia (UTM), Malaysia for financial support of this research under PAS RUG (Potential Academic Staff Research University Grant).

References