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Photocatalytic Carbon Dioxide and Methane Reduction to Fuels over La-Promoted Titanium Dioxide Nanocatalyst

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Selective photocatalytic carbon dioxide (CO_2) reforming of methane (CH_4) to carbon monoxide (CO) and hydrocarbons over lanthanum loaded titanium dioxide (La/TiO_2) nanoparticles has been investigated. TiO_2 nanoparticles (NPs) with different La-loadings were synthesised using sol-gel method. The catalysts were characterised using X-ray diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM) and Photoluminescence (PL) spectroscopy. Pure crystallite and anatase phase TiO_2 with hindered charge recombination were detected in the La-loaded TiO_2 samples. The products obtained were mainly CO, followed by ethane (C_2H_6) and traces of propane (C_3H_8). Pure TiO_2 was favourable for CO evolution, while La-loaded TiO_2 samples promoted hydrocarbons formation. The 2 wt% La/TiO_2 photocatalyst conferred the maximum C_2H_6 yield of 492.8 µmole/g-cat at CO_2/CH_4 feed ratio 1.0 and irradiation time 2 h. The enhanced photocatalytic performance can be attributed to efficient reactant adsorption with hindered charge recombination rate in the presence of La-metal.

1. Introduction

Global warming effects due to the greenhouse gases, primarily carbon dioxide (CO_2) and methane (CH_4) emitted due to fossil fuels combustion and human activities is getting a lot of attention (Yang et al., 2016). Among the carbon capture and sequestration processes, conversion of CO_2 with CH_4 is particularly interesting because it is a promising route for direct conversion of both greenhouses gases into fuels (Tahir et al., 2015). The CO_2 reforming of CH_4 also called dry reforming is an endothermic process, requires higher input energy to be reduced to chemicals. The use of photo-technology is a promising strategy for the photocatalytic conversion of CO_2 and CH_4 to fuels under normal operating conditions (Gusain et al., 2016). However, efficient and selective photocatalytic system for enhanced CO_2 reforming of CH_4 to fuels is vigorously sought.

Among the semiconductor materials, titanium dioxide (TiO_2) is the most widely studied photocatalyst due to its numerous advantages such as low cost and excellent chemical and thermal stability (He et al., 2016). TiO_2 have poor photocatalytic activity due to the fast recombination of photo-generated charges. Loading metals into the lattice of TiO_2 can alter the morphology and structure to overcome the problems. Different metals such as Ni (Tahir et al., 2016), Cu (Gonell et al., 2016), Ag (Kong et al., 2013) and Au (Mei et al., 2013) have been investigated by various researchers to promote TiO_2 photoactivity and selectivity during photocatalytic CO_2 reduction applications.

Among the various metals for modification of TiO_2, the use of basic oxide is considered as efficient way to promote CO_2 adsorption. In recent years, rare-earth metals are typically investigated for the modification of TiO_2 structure to enable the increment of surface oxygen vacancies. Cerium dioxide (CeO_2) was reported as an efficient material for selective photocatalytic CO_2 reduction to fuels (Liu et al., 2016). CeO_2 loaded into g-C_3N_4 remarkably enhanced photocatalytic activity for CO_2 reduction to CO and CH_4 (Li et al., 2016). The introduction of rare earth elements or their oxide into TiO_2 semiconductor are expected to utilise both the basic property for CO_2 activation and could improve photo activity for the trapping electrons over the TiO_2 surface. La has been reported as an efficient metal for selective photocatalytic CO_2 reduction with

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H_2O to CH_4 (Liu et al., 2015). The enhanced and selective photoactivity of La-loaded photocatalyst was due to higher CO_2 adsorption because of its surface basicity with proficient charge separation.

It is anticipated La-promoted TiO_2 catalyst would be appreciable to enhance photocatalytic CO_2 reduction with CH_4 to selective fuels. In this study, the photoactivity of different La-loaded TiO_2 catalysts were examined for selective CO_2 photoreduction with CH_4 to fuels under normal operating conditions. The photocatalytic reaction mechanism was analysed based on the experimental results.

2. Experimental

2.1 Catalyst preparation and characterisation

La-modified TiO_2 nanoparticles were synthesised using controlled sol-gel method. 15 mL of titanium tetra iso-propoxide was mixed in 45 mL of 2-propanol and stirred for 30 min in a 250 mL round bottom flask. The hydrolysis process was conducted by adding drop-wise 10 mL of 1 M acetic acid dissolved in 15 mL 2-propanol. The mixture was vigorously stirred for 24h at room temperature. Subsequently, lanthanum nitrate ($LaNO_3$ H_2O), dissolved in isopropanol, was added and stirred for another 6 h until a clear sol was obtained. The sol was dried in the oven at 80 °C for 24 h under air flow, then calcined in a muffle furnace at a rate of 5 °C min^{-1} up to 500 °C for 5 h. Un-doped TiO_2 nanoparticles were also prepared using similar procedure.

The crystalline structure of the catalysts was ascertained by X-ray diffraction (XRD) recorded on a powder diffractometer (Bruker Advance D8, 40 kV, 40 mA) using a Cu Kα radiation source in the range of $2\theta = 10$ - 80° with a step size of 0.05° and counting time of 5 s. The surface morphology was examined using field emission scanning electron microscopy (FE-SEM JEOL model JSM-6700F, Japan). Photoluminescence (PL) spectra of samples were recorded on a Raman Spectrophotometer (HORIBA Scientific) with a 325 nm emitting laser as an excitation source.

2.2 Photoactivity testing

The reactor consists of a stainless steel cylindrical vessel with a length of 5.5 cm and total volume of 150 cm^3. An amount of 25 mg powdered photocatalyst was evenly introduced inside the cylindrical stainless steel chamber, equipped with a quartz window, for passing light irradiations using a 200 W Hg lamp as a UV light source. Compressed CO_2 (99.999 %) and CH_4 (99.999 %) were regulated by mass flow controllers (MFC). The two gasses passed through the reactor for 30 min to saturate the catalyst and to purge the reactor prior to the start of the experiment. Inlet and outlet valves were closed and the pressure inside the photoreactor was maintained at atmospheric pressure. The batch experiment was initiated by turning on the lamp for a duration of 2 h. The temperature inside the reactor was controlled using a temperature controller and maintained at 100 °C.

The products were analysed using an on-line gas chromatograph (GC-Agilent Technologies 6890 N, USA) equipped with a thermal conductivity detector (TCD) and a flame ionised detector (FID). The TCD detector was connected to UCW982, DC-200, Porapak Q and Mol Sieve 5A columns while the FID detector was connected with a HP-PLOT Q capillary column.

3. Results and discussion

3.1 Characterisation analysis of catalysts

Figure 1(a) presents the XRD patterns of the pure TiO_2 and 2 wt% La-doped TiO_2 samples. No rutile phase is detected, suggesting that the crystalline anatase phase of TiO_2 is formed at 500 °C. The XRD patterns of the La-modified TiO_2 samples are similar to those of pure TiO_2. The signals corresponding to La is not observed possibly due to low amount of La-loading, which is below the detection limit of XRD, or the La-species are highly dispersed over the TiO_2 surface. Similar observations have been reported previously (Liu et al., 2015).

Photoluminescence (PL) analysis is an effective way to investigate optic characteristics of semiconductor nanomaterials, in particular, information about the surface oxygen vacancies and separation of photo-generated charges. Figure 1(b) shows the PL emission spectra of the pure TiO_2 and La-modified TiO_2 nanocatalysts excited at a wavelength of 325 nm. It is noticeable that the emission spectra of the La/TiO_2 sample are similar to those of the pure TiO_2, where the maximum intensity could be seen at a wavelength of 550 nm. This PL signals can be attributed to the transition of electrons from the oxygen vacancies to TiO_2 valance band. The PL intensity is decreased significantly in La/TiO_2 compared to the pure TiO_2 sample. This is evidently due to the introduction of defects sites over the TiO_2 surface by La, resulting in hindered recombination of photo-generated charges (Khalid et al., 2012). PL measurements suggest that the lower the PL intensity the higher would be the photo-activity of nanocatalysts.

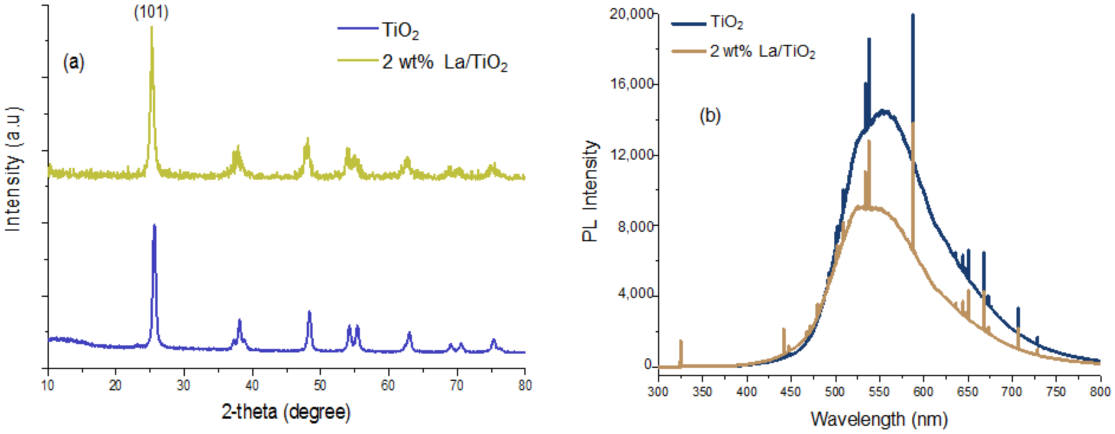

Figure 1: (a) XRD patterns of TiO_2 and 2 wt% La-loaded TiO_2 samples; (b) Photoluminescence (PL) spectra of TiO_2 and La-loaded TiO_2 nanoparticles

Figure 2 exhibits the morphology of pure and modified TiO_2 samples. The uniform and spherical nanoparticles of TiO_2 are obvious in Figure 2(a). This is probably due to the controlled growth of TiO_2 crystal lattice using the modified sol-gel method. The effect of La-loading on TiO_2 NP morphology is presented in Figure 2(b). The morphology of La-loaded TiO_2 samples are similar with the un-doped TiO_2 NPs. TiO_2 NPs are much smaller in La-loaded TiO_2 sample compared to pure TiO_2. This is possibly due to the reduced crystallite sizes of TiO_2 in the presence of La, as a consequence of agglomerated particles.

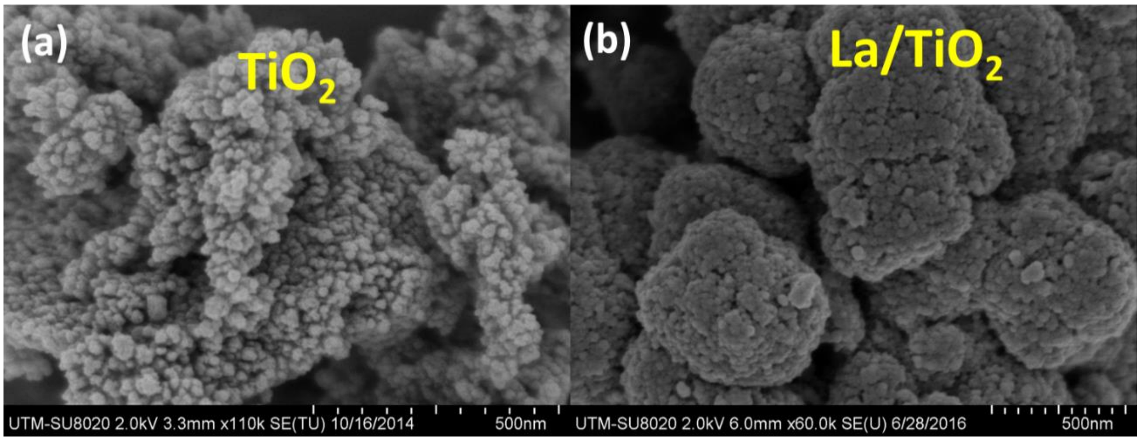

Figure 2*: FE-SEM image of TiO_2 and 2 wt% La/TiO_2 samples: (a) SEM image of TiO_2 NPs, (b) SEM image of 2 wt% La/TiO_2 nanoparticles*

3.2 Photocatalytic CO_2 reduction with CH_4

Initially, blank experiments are conducted to confirm products formed are due to photoreduction of CO_2 and CH_4 only. Experiments were conducted in a gas phase system at 100 °C and irradiation time 2 h. In all types of catalysts, carbon containing compounds were not detected in the reaction system without reactants or light irradiations. Any carbon containing compounds produced were derived from CO_2 photo-reduction with CH_4 during photocatalysis process.

The effects of La-loading on the activity of TiO_2 for CO_2 reduction with CH_4 to CO, C_2H_6 and C_3H_8 are presented in Figure 3(a). Pure TiO_2 registers smaller amounts of hydrocarbons but is more favourable for CO formation. The trends of CO and hydrocarbons formation were different with various La-loading. The amount of CO slightly decreases in 1 wt% La/TiO_2, but surge as La-loading increases to 3 %. The effects of La-loading onto TiO_2 performance for CO_2 photo-reduction with CH_4 to hydrocarbons (C_2H_6 and C_3H_8) are obvious compared to the pure TiO_2 sample. Higher hydrocarbons (C_2H_6 and C_3H_8) were detected over all types of La-loaded TiO_2 photo-catalysts with marginal effects conferred by 1 wt% and 2 wt% loading.

The yield of C_2H_6 was much higher compared to C_3H_8. Photocatalytic CO_2 reduction with H_2O to CH_4 has been reported using La-loaded TiO_2 photo-catalyst (Liu et al., 2015). It was detected that La was favourable for selective CH_4 production until 2 wt%, but over 5 wt% smaller amount of CH_4 was evolved. In the current study, photocatalytic CO_2 reforming of CH_4 is favourable for formation of C_2H_6 hydrocarbon fuels.

The products selectivity over un-doped and 2 wt% La-doped TiO_2 samples is presented in Figure 3(b). CO selectivity of 92.64 % was detected over pure TiO_2, which was decreased to 70.64 % in 2 wt% La-loaded TiO_2 samples. The selectivity of C_2H_6 evidently increased to 28.91 % over 2 wt% La/TiO_2 sample. These observations have confirmed that La is favourable for selective photocatalytic CO_2 and CH_4 conversion to hydrocarbon fuels. Introducing La into TiO_2 could effectively promote CO_2 and CH_4 adsorption over the TiO_2 surface which ultimately converted to CO and hydrocarbons. Enhanced photo-activity was evidently due to hindered charges recombination rate as evidenced in PL analysis.

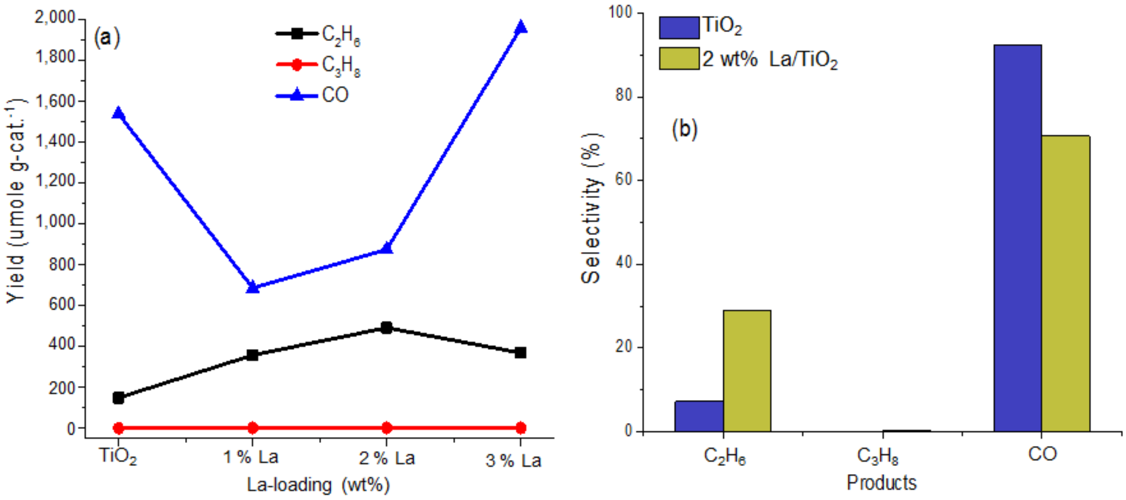

Figure 3: (a) Effect of La loading onto the photoactivity of TiO_2 NPs for CO_2 reduction with CH_4 to CO and hydrocarbons at 100 °C, irradiation time 2 h and CO_2/CH_4 feed ratio 1.0.; (b) products selectivity over TiO_2 and 2 wt% La/TiO_2 catalyst

3.3 Reaction mechanism

The multi-step reaction pathway of the process splits into three parts: the formation of the CO_2 radical, CH_4 oxidation and formation of CO and hydrocarbons. The feasible reaction pathway for this process is given by reactions in Eqs(1) – (6) (Tahir et al., 2015).

$$TiO_2 \xrightarrow{\text{light irradiation}} e^- + h^+ \tag{1}$$

$$La^{3+} + 3e^- \longrightarrow La^{3+}/3e^- \tag{2}$$

$$CO_2 + e^- \longrightarrow CO_2^- \xrightarrow{h^+,e^-} CO \tag{3}$$

$$CH_4 + h^+ \longrightarrow \circ CH_3 + H^+ \tag{4}$$

$$\circ CH_3 + \circ CH_3 \longrightarrow C_2H_6 \tag{5}$$

$$C_2H_6 + \circ CH_3 \longrightarrow C_3H_8 + H^+ \tag{6}$$

In the case of light irradiations, the photo-generated electrons and holes are produced over TiO_2 photocatalyst. Eqs(1) and (2) reveal photo-excited electron-hole pair production and their trapping by La-metal, resulting in prolonged lifetime of charges to precede oxidation and reduction process. The holes are used for oxidation of CH_4 while electrons are consumed by CO_2 for its reduction as explained in Eqs(3) and (4). Reactions in Eqs(5) and (6) divulged production and hydrocarbons through utilisation of CH_3 radicals and electrons in multi-step process. It demonstrates some level of selectivity for C_2H_6 production. The schematic presentation for CO_2 and CH_4 conversion to CO and hydrocarbons over La-loaded TiO_2 is presented in Figure 4. In conclusion, the overall high photocatalytic activity of La loaded TiO_2 for selective hydrocarbons productions can be attributed to higher CO_2 adsorption with hindered charges recombination rate.

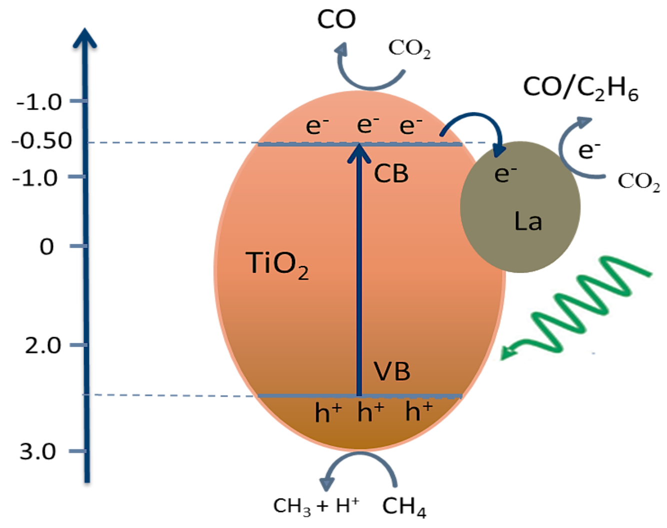

Figure 4: Schematic presentation of photocatalytic CO_2 reduction with CH_4 to CO and hydrocarbons over La-loaded TiO_2 photocatalyst.

4. Conclusions

La-loaded TiO_2 nanocatalysts were successfully synthesised for photocatalytic CO_2 reforming of CH_4. Experimental results revealed that CO_2 and CH_4 were efficiently converted to CO with appreciable amount of C_2H_6. The introduction of La into TiO_2 promotes the formation of C_2H_6 and CO as the main products. The maximum yield of C_2H_6 detected was 492.8 µmole/g-cat over 2 wt% La/TiO_2 catalyst at CO_2/CH_4 feed ratio 1.0 and irradiation time 2 h. The CO detected over La/TiO_2 catalyst was slightly decreased in 2 wt% La/TiO_2 catalyst than the amount produced over pure TiO_2 but gradually increased at higher La-loading. The significantly enhanced photoactivity of La/TiO_2 catalyst for hydrocarbons production is mainly attributed to higher adsorption of reactants and efficient separation of photo-generated electron-hole pairs. This development has confirmed that greenhouse gases (CO_2 and CH_4) can be efficiently converted to fuels using La/TiO_2 based photocatalytic system.

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