

Tailoring performance of La-modified TiO₂ nanocatalyst for continuous photocatalytic CO₂ reforming of CH₄ to fuels in the presence of H₂O

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ABSTRACT

Photo-induced CO₂ reforming of CH₄ in the presence of H₂O over La-modified TiO₂ nanoparticles in a continuous flow photoreactor has been investigated. The structure and properties of the catalyst samples, synthesized by a sol-gel method, were systematically characterized by XRD, Raman, SEM, TEM, CO₂-TPD, TGA, N₂-sorption, XPS, UV-Vis DRS and PL spectroscopy. The crystallite size was reduced while, BET surface area and basicity were increased due to the presence of La₂O₃. The La-modified TiO₂ nanocatalysts were tested under different catalyst loading, irradiation time, reaction temperature and type of reductants. The main products detected over La/TiO₂ catalysts during photo-induced CO₂-CH₄ reaction system were CO, H₂ and C₂H₆. The amount of CO produced over 5 wt.% La/TiO₂ was 9.6 fold more the amount of CO produced by pure TiO₂. When H₂O was added to the CO₂-CH₄ reaction system, the yield of CO increased 37 fold higher over 5 wt.% La/TiO₂ compared to TiO₂. The enhanced photocatalytic performances can be attributed to the synergistic effect of La₂O₃ for CO₂ adsorption with hindered charge recombination rate by La³⁺ and appropriate redox potentials. The photocatalytic turnover productivity (PTOP), calculated for the first time, presented amounts of products evolved with the photon energy consumption. The highest PTOF number achieved for CO production using the CO₂-CH₄-H₂O reaction system was 3.83 fold higher than PTOF achieved in CO₂-CH₄ reaction system. However, PTOF for the production of H₂ and C₂H₆ in CO₂-CH₄ system was 1.2 and 2.1 fold higher than the CO₂-CH₄-H₂O reaction system, respectively. The stability test revealed prolonged life time of La/TiO₂ in cyclic runs for dynamic CO₂-CH₄ conversion to fuels in the presence of H₂O than using only CO₂-CH₄ reaction system. Therefore, CO₂-CH₄ could efficiently be converted to fuels over a La/TiO₂ catalyst while the addition of H₂O could promote both photoactivity and stability.

1. Introduction

Global warming effects due to rapid development of the modern society, primarily CO₂ greenhouse gas emitted due to large amounts of fossil fuels consumption, is getting considerable attention around the world [1]. Recycling of CO₂, as the safest and cheapest carbon source, has bilateral advantages in view of the alleviating greenhouse gas and supply of some useful chemicals and fuels. Among all, CO₂ conversion by photo-catalysis process has been considered as prospective routes to reutilize CO₂ due to its potential economics and environment friendly process [2,3]. For the first time, in 1979, Inoue et al. [4] pioneered photocatalytic CO₂ reduction by water to CH₃OH, HCOOH, HCHO, CH₃COOH and CH₄ over different semiconductor materials such as TiO₂, ZnO, WO₃, CdS and SiC. In spite of excessive efforts have been established over the past three decades, the activity, selectivity and stability of many semiconductors in CO₂ reduction applications is

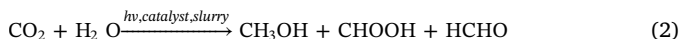
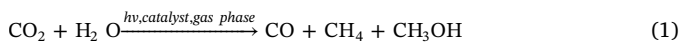
dependent on the type of reducing agent, contents of photo-catalyst composite and photoreactor system [5,6].

Since 1980s the use of H₂O as a reducing agent for photocatalytic CO₂ reduction over various heterogeneous materials has attracted considerable interest [7,8]. Using the gas phase system, CO₂ with water vapors can be converted to CO, CH₄ and CH₃OH as the potential products as explained in Eq. (1). However, slurry system promoted the production of CH₃OH, HCHO and CHOOH during CO₂ reduction with H₂O as explained in Eq. (2) [9]. In this perspective, production of CH₄ from photo-reduction of CO₂ with water vapors over Fe/TiO₂ [10], photo-reduction of CO₂ with H₂O to liquid products (CH₃OH, HCHO) over CeO/TiO₂ [11], use of Ag-MgO/TiO₂ for the production of CH₄ from CO₂ and water in gas phase system [12], Fe-doped CeO for CO and CH₄ production from CO₂ and water vapors [13], production of CO from CO₂-water vapors over Ag/CdS [14], Ag/TiO₂ nanorods [15], V and W co-doped TiO₂ in internally illuminated monolith reactor [16],

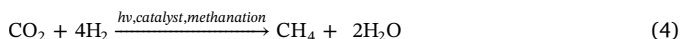
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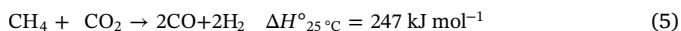
g-C₃N₄/Ag/TiO₂ composite catalyst for the production of CO and CH₄ from CO₂-water [17], production of CO from CO₂-water using g-C₃N₄/N/TiO₂ catalyst [18] and g-C₃N₄/Cu/TiO₂ for the production of CH₃OH, HCHO and HCOOH from CO₂ in slurry system [19], have been reported. However, lower yield rates with trivial selectivity have been reported as H₂O is a weak, hardly reducible reductant.



Recently, hydrogen has been employed for the photocatalytic CO₂ reduction to CO and CH₄ through reverse water gas shift (RWGS) reaction and CO₂-methanation reaction as explained in Eqs. (3) and (4), respectively. Thermodynamically, H₂O reduction potential to generate H₂ is lower ($E_{\text{red}}^0 = 0$ eV) than the standard CO₂ reduction potential to produce 'CO₂' ($E_{\text{red}}^0 = -1.9$ eV) [20]. Hence, H₂O is not a competent reducing agent and H₂O photoreduction to H₂ proceeds more preferably compared to CO₂ reduction. Using H₂ as a reductant for CO₂ photoreduction would possibly be a more realistic approach. Photocatalytic RWGS reaction of CO₂ reduction to CO by H₂ over Ag/TiO₂ NWs [21], Ag/TiO₂ and NiO-In₂O₃/TiO₂ [22] nanocatalysts has been reported with improved yield rate and selectivity. Therefore, photocatalytic CO₂ reduction with H₂ through RWGS reaction is potentially viable to produce fuels at higher yield rates with improved selectivity.



In the past few years, great efforts have been made in recycling dangerous greenhouse gases e.g., CH₄ and CO₂ to synthesis gas (CO, H₂) through dry reforming process as explained in Eq. (5).



The CO₂ and CH₄ reforming, also called dry reforming of methane (DRM), is recognized as an interesting route to simultaneously convert two kinds of greenhouse gases. The major hindrance in the utilization of DRM is the endothermic process which requires higher input energy for the reactants to be converted to useful chemicals [23]. The use of photo-technology would break the thermodynamic barriers of the reaction, thus a promising route for direct CO₂ photo-reduction with CH₄ to fuels [24]. However, photo-induced CO₂-CH₄ reaction yielding useful chemicals is a more challenging task as both CO₂ and CH₄ are stable molecules. Therefore, efficient and selective photocatalytic system for enhanced CO₂ reforming of CH₄ to fuels is vigorously sought.

More recently, researchers have started working on photocatalytic CO₂ reforming of CH₄, to fuels over different semiconductor photocatalysts [25,26]. However, only few have reported successful production of CO and H₂ as main products with smaller amounts of hydrocarbons while using UV-light. In this context, in 2004, pioneering work on photocatalytic CO₂ reduction with CH₄ was reported by Shi et al. [27] using Cu/CdS-TiO₂/SiO₂ photo-catalyst. The reaction was performed in a cell type photoreactor at different reaction temperatures and oxygenated compounds reported were C₂H₆, CH₃COOH, CH₃COCH₃ and CO. Later, photo-reduction of CO₂ with CH₄ was reported with the production of CO and H₂ as the main products over the ZrO₂ catalyst [28]. Another work, Ga₂O₃ was investigated for photocatalytic CO₂ reduction with CH₄ under UV-light irradiations. The products detected were CO, H₂ and C₂-C₄ hydrocarbons with reaction temperature 314–673 K [29]. Similarly, CO₂ reforming of CH₄ was reported over Pt-loaded TiO₂ catalyst, CO and H₂ were identified as the main products [30]. In another development CO₂ photo-reduction by CH₄ over MMT-loaded TiO₂ catalyst with the production of CO and hydrocarbons was developed. [31]. Photocatalytic transformation of CO₂ and CH₄ system was investigated over TNTs modified by Au and Rh. The main products detected were CO and H₂ but in smaller

amounts, although employing high reaction temperature [32].

The ubiquitous TiO₂ is mainly employed as a photo-catalyst in CO₂ reforming of CH₄, but the production rate was not much appreciable. Significant research has been conducted on developing efficient photocatalysts, while the use of basic oxide in TiO₂ modification is considered as one prospect to promote CO₂ adsorption. In recent years, rare-earth metals are typically investigated for the modification of TiO₂ structure to enable the increment of surface oxygen vacancies [33]. In this regard, CeO₂ was reported as an efficient material for selective photocatalytic CO₂ reduction with H₂O to fuels [34]. Similarly, CeO₂ loaded into g-C₃N₄ remarkably enhanced photocatalytic activity for CO₂ reduction by H₂O to CO and CH₄ [35]. Recently, photocatalytic hydrogen production from formic acid over Au-loaded La₂O₃/TiO₂ with enhanced yield and selectivity has been reported [36]. Thus, the introduction of rare earth elements or their oxide into TiO₂ semiconductor are expected to utilize both the basic property for CO₂ activation and could improve photo activity for the trapping electrons over the TiO₂ surface.

Due to the unique electronic configuration and spectral characteristics, lanthanum (La) is considered as the best dopant for modifying crystal structure, optical properties and surface adsorption of TiO₂ [37,38]. Li et al. [39] reported the use of La as an efficient metal for selective photocatalytic CO₂ reduction with H₂O to CH₄ under UV-light. The enhanced and selective photo-activity of La/TiO₂ photo-catalyst was due to higher CO₂ adsorption because of its surface basicity with proficient charge separation. Therefore, it is anticipated that La-promoted TiO₂ catalyst would be appreciable to enhance photocatalytic CO₂ reduction with CH₄ to selective fuels. In addition, introducing H₂O into CO₂-CH₄ system would conceivably be a more attractive approach to improve photo-activity and products selectivity. This is because H₂O can be helpful for CO₂ reduction and CH₄ oxidation due to the generation of hydrogen ions and hydroxyl radicals [39]. Thus, photocatalytic CO₂ reduction with CH₄ in the presence of H₂O would be a potentially workable approach to produce more fuels at higher yield rates and improved selectivity. Up to now there is no report on photocatalytic CO₂ reduction with CH₄ in the presence of rare earth oxides or rare earth element modification.

In the present study, selective photocatalytic conversion of CO₂ with CH₄ and H₂O over La-modified TiO₂ nanocatalysts was examined. The samples were synthesized by sol-gel single step method and were characterized by XRD, Raman, SEM, BET, TEM, XPS, CO₂-TPD, UV-Visible and PL spectroscopy. The La-doped TiO₂ catalyst was further investigated in the presence of different La-contents in a continuous flow photoreactor system. The effect of operating parameters such as reductant type, irradiation time and reaction temperature on the photocatalytic activity of La/TiO₂ catalyst is critically investigated. Specifically, the effect of H₂O in the CO₂-CH₄ reaction system is explored to investigate its influence on the catalyst activity, products selectivity and stability in a continuous flow photoreactor system. More importantly, for the first time photocatalytic turnover productivity (PTOP) is introduced for measuring the amount of products evolved based on the specific surface area and amount of photons energy. The stability test was analyzed in cyclic runs in a continuous flow photoreactor to investigate the active life of catalyst. In addition, the photocatalytic reaction mechanism in the presence of different reducing systems based on the experimental results was also proposed.

2. Experimental

2.1. Catalyst preparation

La-modified TiO₂ nanoparticles were synthesized using controlled sol-gel method. Typically, 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 dropwise 10 mL of 1 M acetic acid dissolved in 15 mL 2-propanol. The mixture was vigorously stirred for 24 h at room temperature.

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