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Tailoring performance of La-modified TiO_2 nanocatalyst for continuous photocatalytic CO_2 reforming of CH_4 to fuels in the presence of H_2O

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ABSTRACT

Photo-induced CO_2 reforming of CH_4 in the presence of H_2O over La-modified TiO_2 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, CO_2-TPD, TGA, N_2-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 La_2O_3. The La-modified TiO_2 nanocatalysts were tested under different catalyst loading, irradiation time, reaction temperature and type of reductants. The main products detected over La/TiO_2 catalysts during photo-induced CO_2-CH_4 reaction system were CO, H_2 and C_2H_6. The amount of CO produced over 5 wt.% La/TiO_2 was 9.6 fold more the amount of CO produced by pure TiO_2. When H_2O was added to the CO_2-CH_4 reaction system, the yield of CO increased 37 fold higher over 5 wt.% La/TiO_2 compared to TiO_2. The enhanced photocatalytic performances can be attributed to the synergistic effect of La_2O_3 for CO_2 adsorption with hindered charge recombination rate by La^{3+} 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 PTOP number achieved for CO production using the CO_2-CH_4-H_2O reaction system was 3.83 fold higher than PTOP achieved in CO_2-CH_4 reaction system. However, PTOP for the production of H_2 and C_2H_6 in CO_2-CH_4 system was 1.2 and 2.1 fold higher than the CO_2-CH_4-H_2O reaction system, respectively. The stability test revealed prolonged life time of La/TiO_2 in cyclic runs for dynamic CO_2-CH_4 conversion to fuels in the presence of H_2O than using only CO_2-CH_4 reaction system. Therefore, CO_2-CH_4 could efficiently be converted to fuels over a La/TiO_2 catalyst while the addition of H_2O could promote both photoactivity and stability.

1. Introduction

Global warming effects due to rapid development of the modern society, primarily CO_2 greenhouse gas emitted due to large amounts of fossil fuels consumption, is getting considerable attention around the world [1]. Recycling of CO_2, 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, CO_2 conversion by photo-catalysis process has been considered as prospective routes to reutilize CO_2 due to its potential economics and environment friendly process [2,3]. For the first time, in 1979, Inoue et al. [4] pioneered photocatalytic CO_2 reduction by water to CH_3OH, HCOOH, HCHO, CH_3COOH and CH_4 over different semiconductor materials such as TiO_2, ZnO, WO_3, 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 CO_2 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 H_2O as a reducing agent for photocatalytic CO_2 reduction over various heterogeneous materials has attracted considerable interest [7,8]. Using the gas phase system, CO_2 with water vapors can be converted to CO, CH_4 and CH_3OH as the potential products as explained in Eq. (1). However, slurry system promoted the production of CH_3OH, HCHO and CHOOH during CO_2 reduction with H_2O as explained in Eq. (2) [9]. In this perspective, production of CH_4 from photo-reduction of CO_2 with water vapors over Fe/TiO_2 [10], photo-reduction of CO_2 with H_2O to liquid products (CH_3OH, HCHO) over CeO/TiO_2 [11], use of Ag-MgO/TiO_2 for the production of CH_4 from CO_2 and water in gas phase system [12], Fe-doped CeO for CO and CH_4 production from CO_2 and water vapors [13], production of CO from CO_2-water vapors over Ag/CdS [14], Ag/TiO_2 nanorods [15], V and W co-doped TiO_2 in internally illuminated monolith reactor [16],

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g-C_3N_4/Ag/TiO_2 composite catalyst for the production of CO and CH_4 from CO_2-water [17], production of CO from CO_2-water using g-C_3N_4/N/TiO_2 catalyst [18] and g-C_3N_4/Cu/TiO_2 for the production of CH_3OH, HCHO and HCOOH from CO_2 in slurry system [19], have been reported. However, lower yield rates with trivial selectivity have been reported as H_2O is a weak, hardly reducible reductant.

$$CO_2 + H_2O \xrightarrow{hv,catalyst,gas\ phase} CO + CH_4 + CH_3OH \quad (1)$$

$$CO_2 + H_2O \xrightarrow{hv,catalyst,slurry} CH_3OH + CHOOH + HCHO \quad (2)$$

Recently, hydrogen has been employed for the photocatalytic CO_2 reduction to CO and CH_4 through reverse water gas shift (RWGS) reaction and CO_2-methanation reaction as explained in Eqs. (3) and (4), respectively. Thermodynamically, H_2O reduction potential to generate H_2 is lower ($E^o_{red} = 0$ eV) than the standard CO_2 reduction potential to produce $^{\cdot}CO_2^-$ ($E^o_{red} = -1.9$ eV) [20]. Hence, H_2O is not a competent reducing agent and H_2O photoreduction to H_2 proceeds more preferably compared to CO_2 reduction. Using H_2 as a reductant for CO_2 photoreduction would possibly be a more realistic approach. Photocatalytic RWGS reaction of CO_2 reudction to CO by H_2 over Ag/TiO_2 NWs [21], Ag/TiO_2 and NiO-In_2O_3/TiO_2 [22] nanocatalysts has been reported with improved yiled rate and selectivity. Therefore, photocatalytic CO_2 reduction with H_2 through RWGS reaction is potentially viable to produce fuels at higher yield rates with improved selectivity.

$$CO_2 + H_2 \xrightarrow{hv,catalyst,RWGS} CO + H_2O \quad (3)$$

$$CO_2 + 4H_2 \xrightarrow{hv,catalyst,methanation} CH_4 + 2H_2O \quad (4)$$

In the past few years, great efforts have been made in recycling dangerous greenhouse gases e.g., CH_4 and CO_2 to synthesis gas (CO, H_2) through dry reforming process as explained in Eq. (5).

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \quad \Delta H^{\circ}_{25\,^{\circ}C} = 247\ kJ\ mol^{-1} \quad (5)$$

The CO_2 and CH_4 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 CO_2 photo-reduction with CH_4 to fuels [24]. However, photo-induced CO_2– CH_4 reaction yielding useful chemicals is a more challenging task as both CO_2 and CH_4 are stable molecules. Therefore, efficient and selective photocatalytic system for enhanced CO_2 reforming of CH_4 to fuels is vigorously sought.

More recently, researchers have started working on photocatalytic CO_2 reforming of CH_4, to fuels over different semiconductor photocatalysts [25,26]. However, only few have reported successful production of CO and H_2 as main products with smaller amounts of hydrocarbons while using UV-light. In this context, in 2004, pioneering work on photocatalytic CO_2 reduction with CH_4 was reported by Shi et al. [27] using Cu/CdS–TiO_2/SiO_2 photo-catalyst. The reaction was performed in a cell type photoreactor at different reaction temperatures and oxygenated compounds reported were C_2H_6, CH_3COOH, CH_3COCH_3 and CO. Later, photo-reduction of CO_2 with CH_4 was reported with the production of CO and H_2 as the main products over the ZrO_2 catalyst [28]. Another work, Ga_2O_3 was investigated for photocatalytic CO_2 reduction with CH_4 under UV-light irradiations. The products detected were CO, H_2 and C_2-C_4 hydrocarbons with reaction temperature 314–673 K [29]. Similarly, CO_2 reforming of CH_4 was reported over Pt-loaded TiO_2 catalyst, CO and H_2 were identified as the main products [30]. In another development CO_2 photo-reduction by CH_4 over MMT-loaded TiO_2 catalyst with the production of CO and hydrocarbons was developed. [31]. Photocatalytic transformation of CO_2 and CH_4 system was investigated over TNTs modified by Au and Rh. The main products detected were CO and H_2 but in smaller amounts, although employing high reaction temperature [32].

The ubiquitous TiO_2 is mainly employed as a photo-catalyst in CO_2 reforming of CH_4, but the production rate was not much appreciable. Significant research has been conducted on developing efficient photocatalysts, while the use of basic oxide in TiO_2 modification is considered as one prospect 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 [33]. In this regard, CeO_2 was reported as an efficient material for selective photocatalytic CO_2 reduction with H_2O to fuels [34]. Similarly, CeO_2 loaded into g-C_3N_4 remarkably enhanced photocatalytic activity for CO_2 reduction by H_2O to CO and CH_4 [35]. Recently, photocatalytic hydrogen production from formic acid over Au-loaded La_2O_3/TiO_2 with enhanced yield and selectivity has been reported [36]. Thus, the introduction of rare earth elements or their oxide into TiO_2 semiconductor are expected to utilize both the basic property for CO_2 activation and could improve photo activity for the trapping electrons over the TiO_2 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 TiO_2 [37,38]. Li et al. [39] reported the use of La as an efficient metal for selective photocatalytic CO_2 reduction with H_2O to CH_4 under UV-light. The enhanced and selective photo-activity of La/TiO_2 photo-catalyst was due to higher CO_2 adsorption because of its surface basicity with proficient charge separation. Therefore, it is anticipated that La-promoted TiO_2 catalyst would be appreciable to enhance photocatalytic CO_2 reduction with CH_4 to selective fuels. In addition, introducing H_2O into CO_2-CH_4 system would conceivably be a more attractive approach to improve photo-activity and products selectivity. This is because H_2O can be helpful for CO_2 reduction and CH_4 oxidation due to the generation of hydrogen ions and hydroxyl radicals [39]. Thus, photocatalytic CO_2 reduction with CH_4 in the presence of H_2O 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 CO_2 reduction with CH_4 in the presence of rare earth oxides or rare earth element modification.

In the present study, selective photocatalytic conversion of CO_2 with CH_4 and H_2O over La-modified TiO_2 nanocatalysts was examined. The samples were synthesized by sol-gel single step method and were characterized by XRD, Raman, SEM, BET, TEM, XPS, CO_2-TPD, UV–Visible and PL spectroscopy. The La-doped TiO_2 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/TiO_2 catalyst is critically investigated. Specifically, the effect of H_2O in the CO_2-CH_4 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 TiO_2 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.