

Ethanol Steam Reforming for Renewable Hydrogen Production over La-Modified TiO₂ Catalyst

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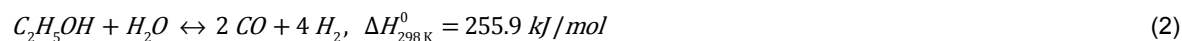
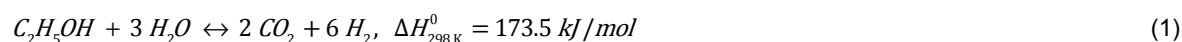
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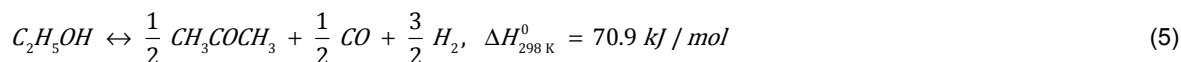
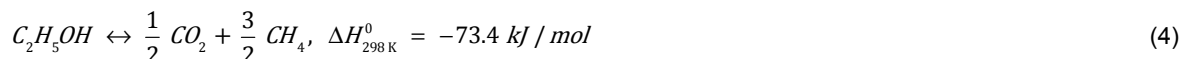
In recent years, ethanol steam reforming (ESR) has received considerable attention as a promising route for cleaner H₂ production. This process could be industrially advantageous, ideally yielding 6 moles of H₂ per mole of ethanol reacted. The major drawbacks of the process are the endothermic nature of the reaction and presence of CO₂ in the product. At low temperatures (below 500 °C), side reactions that yield alternative products such as acetic acid, acetaldehyde and ethylene are favoured. Besides promoting ESR, higher temperatures make the process costly for an industrial development while promoting CO, CO₂ and coke formation, which is the main cause of catalyst deactivation. In this study, a series of La-loaded TiO₂ catalysts were prepared by an impregnation-co-precipitation method, La being a well-known inhibitor of CO and CO₂ formation. Catalytic ethanol steam reforming was conducted in a tubular fixed bed reactor operated at 1 atm, 500 °C and an ethanol/water molar feed ratio of 10:1. The influence of La-loading on inhibiting coke formation and selectivity towards hydrogen formation by ethanol steam reforming has been investigated. The catalytic performance of La-loaded TiO₂ catalyst was found to be considerably higher when compared to the pure TiO₂. At 10 % La loading, ethanol conversion of ~27.5 % was achieved with a H₂ mole fraction of 0.53. Significant amounts of valuable products such as CH₄ and C₂H₄ were also detected in the product mixture. More importantly, CO was not detected over La-loaded TiO₂ catalyst, which confirmed its ability for minimizing coke formation. This development has confirmed improved efficiency of La/TiO₂ catalyst toward renewable hydrogen production.

1. Introduction

In recent years, steam reforming of hydrocarbons such as glycerol (Patcharavorachot et al., 2014), giant reed (Toscano et al., 2014), methane (Panagakos, 2015) and biomass material (Daltro et al., 2014) have been investigated. However, ethanol steam reforming has received considerable attention as a promising source of hydrogen (H₂) production (Zeng et al., 2016). Ethanol steam reforming (ESR) has the industrial advantage of theoretically producing 6 mole of hydrogen per mole of ethanol reacted. Furthermore, ESR allows for the direct utilization of carbon dioxide (CO₂) in various renewable biomass feed stock for ethanol production. Bio-ethanol production process has the advantage of being carbon-neutral because CO₂ produced from the fermentation reaction is recyclable for biomass growth (Deluga et al., 2004).

The major drawbacks to ESR are related to high endothermic nature of the steam reforming reaction Eq(1) and the occurrence of concurring side reactions, the most important of which are; ethanol partial reforming reaction Eq(2), ethanol decomposition reactions Eq(3)-(5), Boudouard reaction Eq(6), the reverse water-gas-shift (WGS) reaction Eq(7), carbon monoxide (CO) reduction Eq (8) and CO₂ reduction Eq(9).





The extent of these competitive reactions influences the selectivity of the ESR process, modifying the ethanol and water equilibrium conversions. Carbon formation is favored by reaction Eq(6), Eq (8) and Eq(9). The consequent deactivation of ESR catalysts due to coke deposition constitutes a serious limit in the industrial ESR reaction development and application. Moreover, the other reactions listed, either produce CO or CO₂ which contributes to green-house gas (GHG) emissions. According to thermodynamic analysis of feasible reactions, reactions of Eq(2) to Eq(9) are favored by same operation conditions that favor the main ESR reaction, Eq(1). The consequent deactivation of ESR catalysts due to carbon deposition limits the industrial application of the ESR process due to costs related to inability of recycle. Hence, for achieving industrially relevant ethanol conversions at relatively moderate temperatures, the use of a catalyst with high activity for ESR and selectivity towards hydrogen is required. Furthermore, the catalyst should offer good stability through inhibition of coke formation (Liu et al., 2015b).

Ethanol conversion and selectivity towards various products is greatly dependent on physicochemical properties of the catalysts, active metal and promoters. The noble metal catalysts with high selectivity to H₂ (> 80 %) are; Rh, Ru, Pd and Ir, while transition metal catalysts are; Ni, Co and Cu (Contreras et al., 2014). The order of activity for these metals is Ru > Rh > Ni ~ Ir > Pt > Pd (Hou et al., 2015). Despite the high activities and low tendency to carbon deposition of the noble metals, costs and limited availability of these metals hinders widespread industrial application. Transition metals have shown more promise due to their relative low cost. However, transition metals are more susceptible to coking and deactivate more rapidly than the noble metals. On the other hand, introduction of rare earth metals and their oxides into catalyst support could improve both activity and stability. The rare-earth metals are typically investigated to enable the increment of surface oxygen vacancies. In this perspective, CeO₂ was reported as an efficient material for selective steam reforming of ethanol for hydrogen production (Soykal et al., 2012). Recently, Lanthanum (La) has been reported as an efficient metal to give higher selectivity and stability to TiO₂ in the production of hydrocarbons (Liu et al., 2015a). While previously, TiO₂ supported catalyst, Ni/Ce-TiO₂ (Ye et al., 2008) has been studied, up to now, limited reports are available on the introduction of La-loaded TiO₂ for selective ESR towards hydrogen production with improved stability.

In this study, La-loaded TiO₂ catalysts were prepared and evaluated for hydrogen production via ESR using a fixed bed reactor. The effects of La addition on the coke formation inhibition through reduction of CO and CO₂ production are critically evaluated. Although, La is not known to be a good promoter when compared to both noble and transition metals, its addition could greatly reduce CO, CO₂ and coke formation in ESR.

2. Experimental Section

2.1 Experimental Set-Up and Procedure

The laboratory set up reported in Figure 1 consisted of a feed, reaction and analysis section. The feed to the reactor was a gas mixture of water (steam), ethanol and nitrogen (carrier gas). The ESR reactions were carried out at atmospheric pressure in a borosilicate glass tube with an internal diameter of 8 mm and length of 29 cm. The fixed bed reactor was placed in a horizontal tube furnace which was monitored by a programmable temperature controller. Reaction temperature was gauged by measuring the temperature of the catalyst bed using a coaxial K thermocouple. Catalyst weight was 0.5 g diluted in quartz, catalyst to inert ratio of 1:1. The catalyst was heated to reaction temperature under N₂ flow, then the water/ethanol mixture was let

into the reactor to carry out the catalytic test. The operative conditions used in the experimental tests are reported in Table 1. The analysis section consisted of an online GC (Agilent 6890N network GC system) for gas samples and an offline GC (Agilent 7820A GC system) for liquid samples. Online GC was equipped with two columns; a flame ionization detector (FID) and a thermal conductivity detector (TCD). FID detector was connected with an HP-PLOT Q capillary column (Agilent, length 30 m. ID 0.53 mm, film 40 μm) for separation of C_1 - C_6 hydrocarbons, alcohols and oxygenated compounds. The TCD detector was connected to UCW982, DC-200, Porapak Q and Mol Sieve 13 X columns for detection of C_1 - C_2 , C_3 - C_5 compounds and light gases (H_2 , O_2 , N_2 , CO).

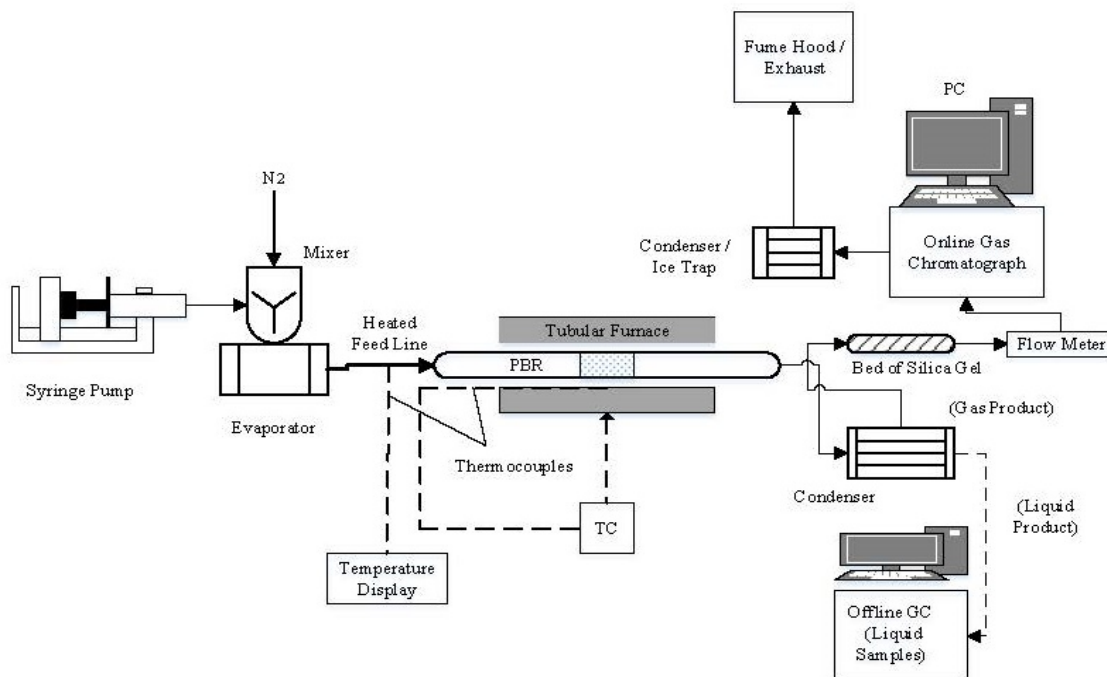


Figure 1: Schematic of Experimental Apparatus of Ethanol Steam Reforming for Hydrogen Production

Table 1: Operation conditions used in the experimental tests

Condition	Value
Reaction temperature ($^{\circ}\text{C}$)	500
Pressure (atm.)	1
Feed molar ratio (S/E)	10 : 1
N_2 flow rate (ml/min)	40

2.2 Catalysts Synthesis and Characterization

La-loaded TiO_2 microparticles (TiO_2 MPs) were prepared by impregnation method. Anatase TiO_2 in powder form was used, while La was obtained from Lanthanum (III) nitrate hexahydrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$). La-loading was varied from 5-15 %. Typically, 1 g of TiO_2 was mixed with an appropriate amount of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in 50 mL of deionized water and stirred in a beaker at 250 rpm for 1 h. The slurry formed was dried in an oven at $110\text{ }^{\circ}\text{C}$ for 12 h. The dried cake was ground and calcined under air flow in a furnace at $500\text{ }^{\circ}\text{C}$ for 5 h. Finally, the calcined powder was finely ground and sieved. The crystalline phase was investigated using powder X-ray diffraction (XRD; Bruker D8 advance diffractometer, 40 kV and 40 mA) with Cu- $\text{K}\alpha$ radiation ($\lambda = 1.54\text{ \AA}$). The morphology was estimated using scanning electron microscopy (SEM) carried out with JEOL6390 LV SEM instrument.

2.3 Quantitative Analysis

To quantitatively evaluate ethanol conversion, product selectivity, product yield and CO_2 ratio, the following formula was used for calculations:

$$\text{Conversion}_{\text{ethanol}} (\%) = \frac{\text{mol of ethanol converted}}{\text{mol of ethanol fed}} \times 100 \quad (10)$$

$$\text{Selectivity}_{\text{species}} (\%) = \frac{\text{number of mol of gas species}}{\text{sum of mols of all gas species}} \times 100 \quad (11)$$

$$\text{H}_2 \text{ Yield} (\%) = \frac{\text{mol of H}_2 \text{ produced}}{6 \times \text{mol of ethanol fed}} \times 100 \quad (12)$$

$$\text{Yield}_{\text{C}_{\text{product}}} \text{ i} (\%) = \frac{(\text{no. of C atoms}) \times (\text{moles of i produced})}{2 \times (\text{moles of Ethanol fed})} \times 100 \quad (13)$$

$$\frac{\text{CO}_2}{\text{CO}_x} = \frac{F_{\text{CO}_2}^{\text{out}}}{(F_{\text{CO}_2}^{\text{out}} + F_{\text{CO}}^{\text{out}})} \quad (14)$$

3. Results and Discussion

3.1 Catalyst Characterization

The XRD patterns of pure TiO₂ MPs and 10 % La-modified TiO₂ MPs (Figure not shown) revealed pure anatase and crystalline phase of TiO₂ calcined at 500 °C. In the case of La-modified TiO₂, TiO₂ persisted its original reflection while smaller peak of La was also appeared, which has confirmed its dispersion over TiO₂. The structure and morphology of 10 % La/TiO₂ MPs sample was analyzed using scanning electron microscopy (SEM), as shown in Figure 2. Figure 2 (a) shows uniform and spherical particle size. Evidently, La-modified TiO₂ has micro-particles which can easily be observed as being spherical in structure and uniform in size as depicted in Figure 2 (b).

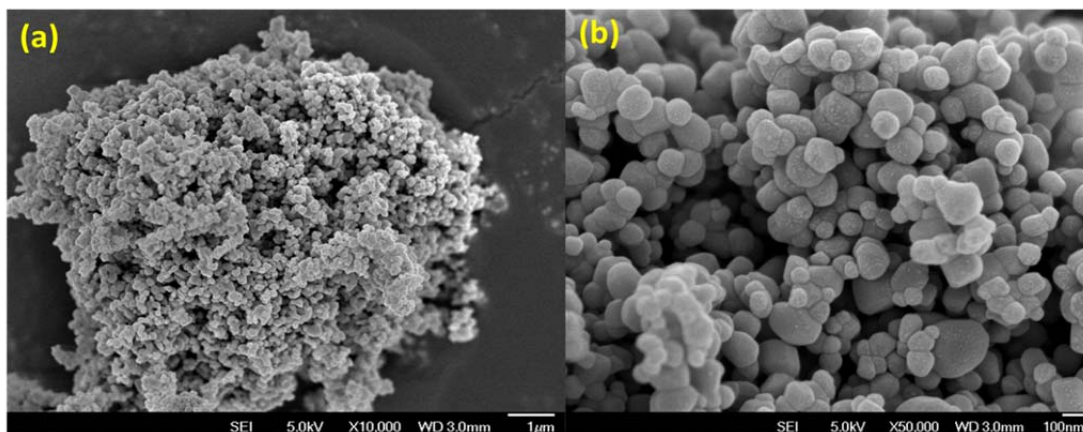


Figure 2: SEM images of 10 % La/TiO₂ (a) SEM image at 1 μm scale, (b) SEM image at 100 nm scale

3.2 Catalytic Ethanol Steam Reforming

The effect of La-loading on the performance of TiO₂ catalyst for ethanol conversion has been investigated and results are depicted in Table 2. Evidently, significantly ethanol conversion could be seen using La/TiO₂, yet, this conversion is not much appreciable when compared to literature. However, these respective conversions show marked improvement when compared to pure TiO₂ sample. With a 27.5 % conversion, 10 % La loading shows appreciable activity for the TiO₂ catalyst sample which could be further enhanced by addition of co-metals such as Rh, Pd or Ni with improved stability (Mondal et al., 2016).

Table 2: Summary of results of ethanol conversion

Catalyst	Ethanol Conversion (%)
TiO ₂	0.54
5 % La/ TiO ₂	11
10 % La/ TiO ₂	27.5
15 % La/ TiO ₂	24

Figure 3 reveals the effect of La-loading on the products yield rates. Using pure TiO_2 , smaller amount of products yield found, which were significantly increased in La-loading samples with an optimum of 10 % La-loading. More importantly, the results for respective product yield shows zero CO production. A clear decrease in the CO production due to La-addition can be observed, and this may be explained by the ability of La/TiO_2 to promote the water-gas shift reaction (Guo et al., 2009). Furthermore, there is considerable production of valuable species such as methane (CH_4) and ethylene (C_2H_4). This can be attributed to a shift in selectivity of the catalyst from CO to hydrocarbons and promotion of ethanol partial steam reforming ($\text{C}_2\text{H}_5\text{OH} + 2 \text{H}_2\text{O} \leftrightarrow 2 \text{CH}_4 + \text{H}_2$) and ethanol dehydration ($\text{C}_2\text{H}_5\text{OH} \leftrightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O}$) (Lin et al., 2015). Both ethanol conversion and H_2 yield drop when La loading is increased from 10 to 15 % due to the fact that both content and dispersion of La dictate the activity of the catalyst. La/TiO_2 activity increases with La-contents due to an increase in the number of active sites whereas dispersion decreases, hence limiting the same activity. Generally, the La content should neither be too low nor too high to avoid aggregation and sintering, similar to Ni loading in catalysis (Seo et al. 2008).

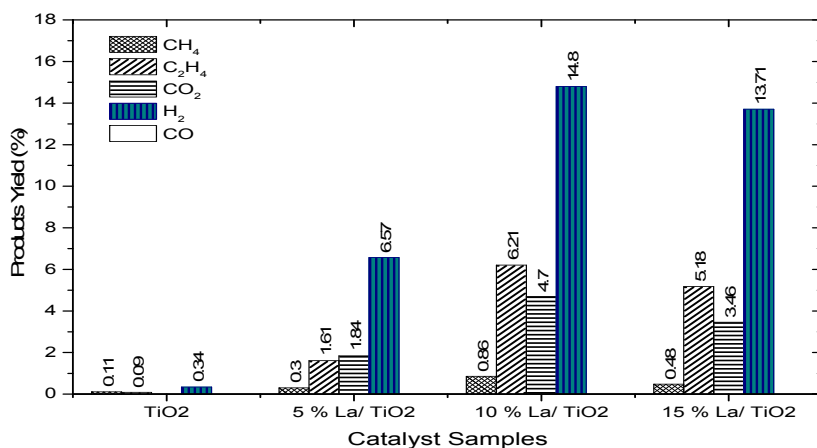


Figure 3: Effect of La-loading on the yield of different products in ethanol steam reforming

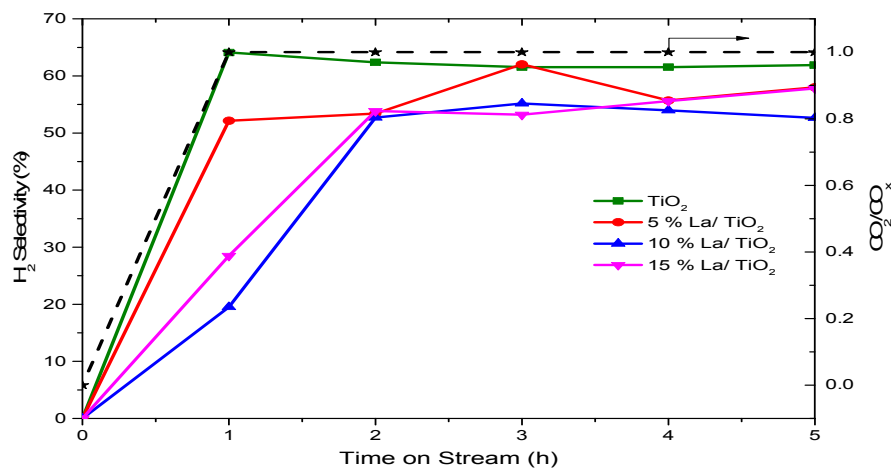


Figure 4: The effect of time and La-loading on H_2 selectivity and CO_2/CO_x ratio during ESR process

While keeping the reaction temperature constant at 500 °C, La-loaded catalyst performance was gauged by varying reaction time to investigate the H_2 selectivity and CO_2/CO_x ratio. Figure 4 shows the H_2 selectivity and CO_2/CO_x ratios at different times and for different La-loading of TiO_2 MPs catalysts. Since CO yield was zero, the CO_2 to CO_x ratio was one for all La-loading samples. H_2 selectivity was high at around 53 % and was not significantly affected by variation in La-loading into TiO_2 . CO_2 production is highest for 10 % La/TiO_2 . The high activity of this sample in ethanol conversion promotes the main ESR reaction, Eq. (1), consequently producing more of H_2 and CO_2 . Additionally, the Boudouard reaction ($\text{CO} \rightarrow \frac{1}{2} \text{CO}_2 + \frac{1}{2} \text{C}$), which is favored at temperatures below 700 °C, could be responsible for conversion of intermediate CO into CO_2 . This also revealed that La-promoted TiO_2 catalyst is more effective to enhance conversion and yield rate, rather than to promote products selectivity. Besides, La-loaded TiO_2 samples have prevented coke formation, thus prolonged the catalyst life time.

4. Conclusions

La-loaded TiO₂ MPs were prepared and their performance for ethanol steam reforming to hydrogen was investigated. It was observed that La-loaded TiO₂ samples gave much higher yield rate for hydrogen production at 500 °C and atmospheric pressure. Although, the activity of La/TiO₂ catalysts did not result in very high ethanol conversion, yet zero CO production was observed. From the list of feasible reactions, this indicates high preference toward reactions Eq(1), Eq(4) and Eq(9). Out of these, only the CO₂ decomposition reaction would contribute to coke formation. Furthermore, carbon (C) is balanced by the production of CH₄ and C₂H₄, probably from other side reactions that were not listed. From the results, it can be concluded that Lanthanum could be used in conjunction with other proven active metals of ESR to inhibit CO, CO₂ and subsequently coke formation.

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