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

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In recent years, ethanol steam reforming (ESR) has received considerable attention as a promising route for cleaner H\textsubscript{2} production. This process could be industrially advantageous, ideally yielding 6 moles of H\textsubscript{2} per mole of ethanol reacted. The major drawbacks of the process are the endothermic nature of the reaction and presence of CO\textsubscript{2} 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, CO\textsubscript{2} and coke formation, which is the main cause of catalyst deactivation. In this study, a series of La-loaded TiO\textsubscript{2} catalysts were prepared by an impregnation-co-precipitation method, La being a well-known inhibitor of CO and CO\textsubscript{2} 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 TiO\textsubscript{2} catalyst was found to be considerably higher when compared to the pure TiO\textsubscript{2}. At 10 % La loading, ethanol conversion of ~27.5 % was achieved with a H\textsubscript{2} mole fraction of 0.53. Significant amounts of valuable products such as CH\textsubscript{4} and C\textsubscript{2}H\textsubscript{4} were also detected in the product mixture. More importantly, CO was not detected over La-loaded TiO\textsubscript{2} catalyst, which confirmed its ability for minimizing coke formation. This development has confirmed improved efficiency of La/TiO\textsubscript{2} catalyst toward renewable hydrogen production.

1. Introduction

In recent years, steam reforming of hydrocarbons such as glycerol (Patcharavorachot et al., 2014), giant read (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 (H\textsubscript{2}) 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 (CO\textsubscript{2}) in various renewable biomass feed stock for ethanol production. Bio-ethanol production process has the advantage of being carbon-neutral because CO\textsubscript{2} 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 CO\textsubscript{2} reduction Eq(9).

\[\text{C}_2\text{H}_5\text{OH} + 3 \text{H}_2\text{O} \leftrightarrow 2 \text{CO}_2 + 6 \text{H}_2 \quad \Delta H_{298K}^0 = 173.5 \text{ kJ/mol} \quad (1)\]
\[\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O} \leftrightarrow 2 \text{CO} + 4 \text{H}_2 \quad \Delta H_{298K}^0 = 255.9 \text{ kJ/mol} \quad (2)\]

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\[ C_2H_5OH \leftrightarrow CO + CH_4 + H_2, \quad \Delta H_{298K}^0 = 50.1 \text{ kJ/mol} \]  \hspace{1cm} (3)

\[ C_2H_4OH \leftrightarrow \frac{1}{2} CO_2 + \frac{3}{2} CH_4, \quad \Delta H_{298K}^0 = -73.4 \text{ kJ/mol} \]  \hspace{1cm} (4)

\[ C_2H_3OH \leftrightarrow \frac{1}{2} CHCOCH_3 + \frac{1}{2} CO + \frac{3}{2} H_2, \quad \Delta H_{298K}^0 = 70.9 \text{ kJ/mol} \]  \hspace{1cm} (5)

\[ CO \rightarrow \frac{1}{2} CO_2 + \frac{1}{2} C, \quad \Delta H_{298K}^0 = -86.2 \text{ kJ/mol} \]  \hspace{1cm} (6)

\[ CO_2 + H_2 \rightarrow CO + H_2O, \quad \Delta H_{298K}^0 = 41.2 \text{ kJ/mol} \]  \hspace{1cm} (7)

\[ CO + H_2 \rightarrow C + H_2O, \quad \Delta H_{298K}^0 = -131.3 \text{ kJ/mol} \]  \hspace{1cm} (8)

\[ CO_2 + 2 H_2 \rightarrow C + 2 H_2O, \quad \Delta H_{298K}^0 = -90.1 \text{ kJ/mol} \]  \hspace{1cm} (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 CO_2 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 H_2 (> 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, CeO_2 was reported as an efficient material for selective steam reforming of ethanol for hydrogen production (Soykål et al., 2012). Recently, Lanthanum (La) has been reported as an efficient metal to give higher selectivity and stability to TiO_2 in the production of hydrocarbons (Liu et al., 2015a). While previously, TiO_2 supported catalyst, Ni/ Ce-TiO_2 (Ye et al., 2008) has been studied, up to now, limited reports are available on the introduction of La-loaded TiO_2 for selective ESR towards hydrogen production with improved stability.

In this study, La-loaded TiO_2 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 CO_2 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, CO_2 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 N_2 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 C₁−C₆ 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 C₁−C₂, C₃−C₅ compounds and light gases (H₂, O₂, N₂, CO).

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

Table 1: Operation conditions used in the experimental tests

<table>
<thead>
<tr>
<th>Condition</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction temperature (ºC)</td>
<td>500</td>
</tr>
<tr>
<td>Pressure (atm.)</td>
<td>1</td>
</tr>
<tr>
<td>Feed molar ratio (S/E)</td>
<td>10 : 1</td>
</tr>
<tr>
<td>N₂ flow rate (ml/min)</td>
<td>40</td>
</tr>
</tbody>
</table>

2.2 Catalysts Synthesis and Characterization

La-loaded TiO₂ microparticles (TiO₂ MPs) were prepared by impregnation method. Anatase TiO₂ in powder form was used, while La was obtained from Lanthanum (III) nitrate hexahydrate (La-(NO₃)₃·6H₂O). La-loading was varied from 5-15 %. Typically, 1 g of TiO₂ was mixed with an appropriate amount of La-(NO₃)₃·6H₂O 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 ºC for 12 h. The dried cake was ground and calcined under air flow in a furnace at 500 ºC 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- Kα radiation (λ = 1.54 Å). 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 CO₂ ratio, the following formula was used for calculations:
Conversion$_{\text{ethanol}}$ (%) = \( \frac{\text{mol of ethanol converted}}{\text{mol of ethanol fed}} \times 100 \)  

(10)

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

(11)

\[ H_2 \text{ Yield} \text{ (\%)} = \frac{\text{mol of } H_2 \text{ produced}}{6 \times \text{mol of ethanol fed}} \times 100 \]  

(12)

\[ \text{Yield}_i \text{ (\%)} = \left( \frac{\text{no. of } C \text{ atoms}}{2} \times \text{moles of } i \text{ produced} \right) \times 100 \]  

(13)

\[ \frac{CO_2}{CO} = \frac{F_{\text{out}}^{\text{CO}_2}}{F_{\text{out}}^{\text{CO}} + F_{\text{out}}^{\text{CO}_2}} \]  

(14)

3. Results and Discussion

3.1 Catalyst Characterization

The XRD patterns of pure TiO$_2$ MPs and 10 % La-modified TiO$_2$ MPs (Figure not shown) revealed pure anatase and crystalline phase of TiO$_2$ calcined at 500 °C. In the case of La-modified TiO$_2$, TiO$_2$ persisted its original reflection while smaller peak of La was also appeared, which has confirmed its dispersion over TiO$_2$. The structure and morphology of 10 % La/TiO$_2$ 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 TiO$_2$ 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/TiO$_2$ (a) SEM image at 1 μm scale, (b) SEM image at 100 nm scale](image)

3.2 Catalytic Ethanol Steam Reforming

The effect of La-loading on the performance of TiO$_2$ catalyst for ethanol conversion has been investigated and results are depicted in Table 2. Evidently, significantly ethanol conversion could be seen using La/TiO$_2$, yet, this conversion is not much appreciable when compared to literature. However, these respective conversions show marked improvement when compared to pure TiO$_2$ sample. With a 27.5 % conversion, 10 % La loading shows appreciable activity for the TiO$_2$ 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>
<thead>
<tr>
<th>Catalyst</th>
<th>Ethanol Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>0.54</td>
</tr>
<tr>
<td>5 % La/ TiO$_2$</td>
<td>11</td>
</tr>
<tr>
<td>10 % La/ TiO$_2$</td>
<td>27.5</td>
</tr>
<tr>
<td>15 % La/ TiO$_2$</td>
<td>24</td>
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</table>
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$_2$H$_4$). This can be attributed to a shift in selectivity of the catalyst from CO to hydrocarbons and promotion of ethanol partial steam reforming (C$_2$H$_5$OH $\leftrightarrow$ 2 CH$_4$ + H$_2$) and ethanol dehydration (C$_2$H$_5$OH $\rightarrow$ C$_2$H$_4$ + H$_2$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](image1)

![Figure 4: The effect of time and La-loading on H$_2$ selectivity and CO$_2$/COx ratio during ESR process](image2)

While keeping the reaction temperature constant at 500 ºC, La-loaded catalyst performance was gauged by varying reaction time to investigate the H$_2$ selectivity and CO$_2$/COx ratio. Figure 4 shows the H$_2$ selectivity and CO$_2$/COx ratios at different times and for different La-loading of TiO$_2$ MPs catalysts. Since CO yield was zero, the CO$_2$ to COx 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 (CO $\rightarrow$ ½ CO$_2$ + ½ C), which is favored at temperatures below 700 ºC, 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 TiO$_2$ MPs were prepared and their performance for ethanol steam reforming to hydrogen was investigated. It was observed that La-loaded TiO$_2$ samples gave much higher yield rate for hydrogen production at 500 °C and atmospheric pressure. Although, the activity of La/TiO$_2$ 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 CO$_2$ decomposition reaction would contribute to coke formation. Furthermore, carbon (C) is balanced by the production of CH$_4$ and C$_2$H$_4$, 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, CO$_2$ and subsequently coke formation.

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