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Hydrogen production from an ethanol reformer via thermal management over various catalysts

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Abstract

This study carried out hydrogen production by reforming of ethanol. In this experiment the parameters were, including ethanol supply rate, O_2/EtOH (Oxygen/Ethanol molar ratio), catalysts (Fe, Co, Ni, Pt, Pd, Rh and Ru), and the reforming temperature was provided with heat re-circulation, H_2+CO concentration were analyzed. First, for this system the commercialized catalysts was adopted to a suitable range of flow rate. The experimental results indicated that the optimal (H_2+CO) concentration of 43.41% can be obtained by using rhodium (Rh). Additionally, in this system the reforming performance of Rh and Ru catalysts with energy-saving methods were compared against its original system. The experimental results obtained demonstrated that the conversion efficiency of ethanol, concentration of hydrogen and carbon monoxide, could be enhanced by means of heat insulation and heat recycling. The reforming performance satisfactorily was greater by using Ru catalyst than that by Rh catalyst.

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1. Introduction

Since the dawn of the twenty first century, a worldwide concern has been the energy crisis. It greatly impacts the international economy and future life of human, including the transportation and the social stability of countries. With the economies rapidly rising, energy consumption demands to increase. It is a primordial issue for the researchers to urgently discover alternative energy. In the proximate decades, the fossil fuel will remain as the primary source of energy supplying. Hydrogen stands as a promising future energy. Heat and water are contained in the hydrogen combustion, without threatening to the environment. Hydrogen could be produced from bio-fuels, such as ethanol, colza oil. Even though carbon dioxide will be generated in the process of hydrogen production, nonetheless it is of use for the plant in the oxygenic photosynthesis. If this alternative energy is used effectively, global carbon dioxide emission could be reduced in the nearest future. Moreover, coal cleaning, fuel cell and fuel reforming technology could reduce the counter effects of traditional fuel on the environment. It has become a worldwide discussed issue nowadays.

Mattos et al. [1] analyzed by using the catalysts of Pt/Al_2O_3, Pt/ZrO_2, Pt/CeO_2 and $Pt/Ce_{0.50}Zr_{0.50}O_2$, the partial oxidation of ethanol with different supports. The results showed that the support is a priority on the products distribution of the partial oxidation of ethanol. A lower oxygen exchange capacity leads to a higher production of ethoxy species. With the CeO_2 and $Ce_{0.5}0Zr_{0.50}O_2$ supports, the higher oxygen exchange capacity precedes the formation of acetate species. Silva et al. [2] carried out hydrogen production through partial oxidation of ethanol on Rh/CeO_2 catalyst with a water–gas shifting reactor for reducing CO concentration. The results showed that hydrogen production from partial oxidation reaction is seriously affected by the reaction temperature.

Cavallaro et al. [3] employed 5% Rh/Al_2O_3 catalyst for optimizing an auto-thermal reforming of bio-ethanol for the production of syngas for fuel cell application. The experimental results explained that, under $O_2/EtOH$ ratio of 0.6, it mostly had a tendency to form CH_4 and CH_3CHO. Under higher $O_2/EtOH$ ratio, the oxidation phenomena caused the decrease of hydrogen production. Benito [4] investigated the ethanol steam reforming with different active phases (Ni, Cu and Co) supported on zirconia labeled. Among the catalysts, Ni and Co are highly active, with large selectivity to hydrogen at 700 ^oC. Particularly, catalyst Co illustrates the excellent stability after a 60 h operation, hydrogen production being close to that estimated by thermodynamic equilibrium. Rodrigues et al. [5] experimented with catalyst of nickel alumina washcoating on a honeycomb monolith for the ethanol partial oxidation under very low residence time. The catalyst achieved good dispersion of γ -Al_2O_3 and NiO over the cordierite surface and could be efficient to the ethanol dehydrogenation reaction at low temperatures. It is also favorable to augment hydrogen production because of its activity for reforming at higher temperatures. Moharana et al. [6] inspected the publications on ethanol reforming for hydrogen production. They stated that ethanol is a promising future bio-fuel because of its high hydrogen content, no toxicity, ease of storage and handling safety. Ethanol also possesses the advantage that the CO_2 produced during steam reforming reaction is equal to the CO_2 required for plant growth, and thus provides a perfect cycle for CO_2 consumption. Theoretically, no net CO_2 production is liberated into the environment.

2. Experimental set-up and method

A purposely built ethanol reformer was designed including peripherals of a reactor, a spark providing system, a fuel supply system, gas sampling system and temperature control system. Experimental set-up can be found in Fig. 1. The fuel supply system was constituted of air and ethanol supply unit. Air was manipulated by a mass flow meter; ethanol was kept in a tank pushed by a pressurized N_2 (6 kg/cm^2), controlled by flow meters. The gas analysing device was a gas

chromatography (Agilent 6850 GC) for determining the gas composition. The catalytic converter consists of the dimensions of 60mm in diameter, 50mm in length, fabricated of metallic substrate with mesh of 100 cells/in^2. The catalysts utilized were Fe, Co, Ni, Pt, Pd, Rh and Ru supported on Al_2O_3, and the catalyst specifications are listed in Table 1.
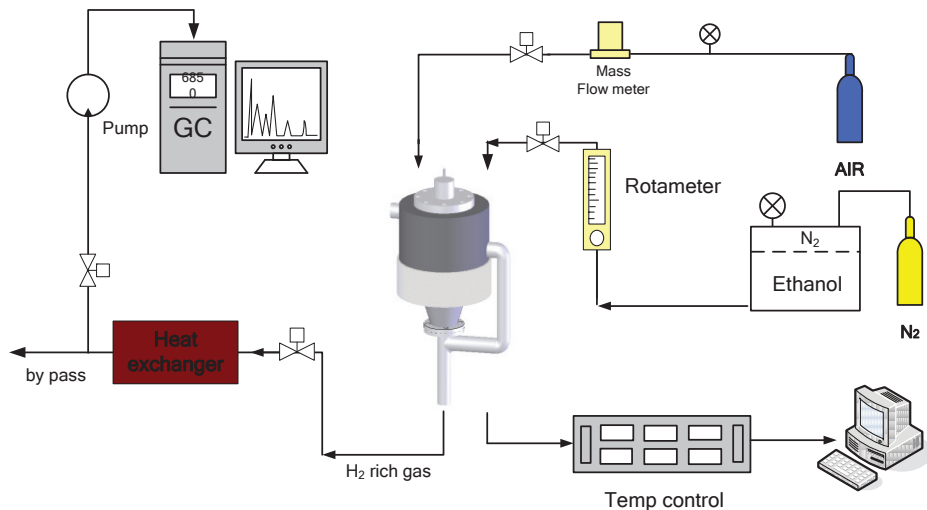

Fig. 1 Experimental set-up

Table 1 Specifications of the catalyst

Catalysts	Fe, Co, Ni, Pt, Pd, Rh, Ru
Washcoat	Al_2O_3
D × L(mm^2)	Φ60.0x50.0
Wt (%)	6
Loading density（g/ft^3）	50
Mesh（Cell/in^2）	100

The parameters consisted of ethanol supply rates of 16.97, 22.63 and 28.29 cc/min, O_2/EtOH ratio of 0.5–1.0. Appropriate quantity of air was delivered to the system for partial oxidation of fuel to supply heat of reaction for reforming. In the reforming processes, as the O_2/EtOH was significantly low, it not only obstructed the activity of the catalyst but also lacked of oxidation and consequently induced the low operating temperature. However, overly high O_2/EtOH ratio, it might provoke oxidation of H_2 and CO to form H_2O and CO_2 and would also lead to high temperature to damage the catalyst. Therefore, the fuel supply was regulated by an appropriate ratio of air and hydrocarbon fuel, before being directed into the reaction chamber for reforming.
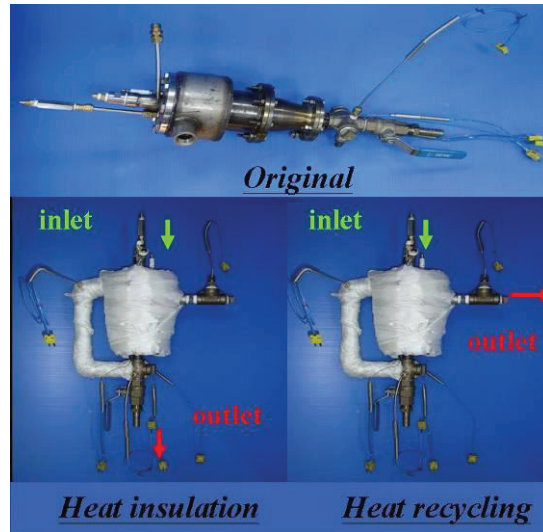
Fig. 2 Energy saving reformer for ethanol reforming

The constitution of energy conservation, including heat insulation and heat recycling systems, on reforming were also analyzed in this study. The results were compared against the original one. The experimental set-ups are illustrated in Fig. 2, respectively. In the heat insulation system, the outer surface was insulated with glass fibre to minimize heat loss; for the heat recycling system, the high temperature reformate gas stream was re-circulated into the gas jacket over the outer surface of the reformer.

3. Relative calculations

The study carried out the reforming of ethanol for hydrogen production on energy saving reformer over various catalysts. The parameters employed were O_2/EtOH and conversion efficiency. They were calculated by equations (1)-(2), respectively.

(1) O_2/EtOH (Oxygen/Ethanol molar ratio)

$$O_2 \Big/ EtOH = \frac{\dot{n}_{O_2}}{\dot{n}_{C_2H_5OH}} = \frac{\dfrac{\rho_{O_2} \times \dot{V}_{O_2}}{M_{O_2}}}{\dfrac{\rho_{C_2H_5OH} \times \dot{V}_{C_2H_5OH}}{M_{C_2H_5OH}}} \qquad (1)$$

$$C_2H_5OH\ convesion\ = \left(\frac{moles\ of\ C_2H_5OH\ consumed}{moles\ of\ C_2H_5OH\ introduced} \right) \times 100\% \qquad (2)$$

4. Results and discussion

4.1. Effect of ethanol supply rate with commercialized catalyst

In this study, the experiments of ethanol reforming for hydrogen production by partial oxidation (POX) reaction were carried out with commercialized catalyst. The experimented parameters included O_2/EtOH ratio of 0.5-1, ethanol flow rate of 16.97, 22.63 and 28.29cc/min. The reformate gas concentration and temperature were measured and analyzed to investigate the operating parameters for the best hydrogen production with various catalysts. Figs. 3-4 show the effect of O_2/EtOH ratio on the produced H_2+CO concentration and catalyst bed temperature. In these figure, it could be found that H_2+CO concentration and reaction temperature increased with increasing ethanol flow rate before peak value; after the peak, H_2+CO concentration decreased with increasing O_2/EtOH ratio, and peaking at O_2/EtOH ratio of 0.75.
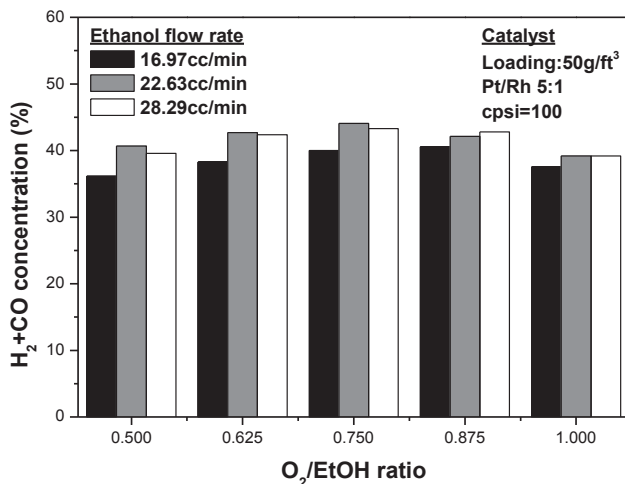

Fig. 3 Effect of differing O_2/EtOH with fuel ratio on the catalyst outlet H2+CO concentration
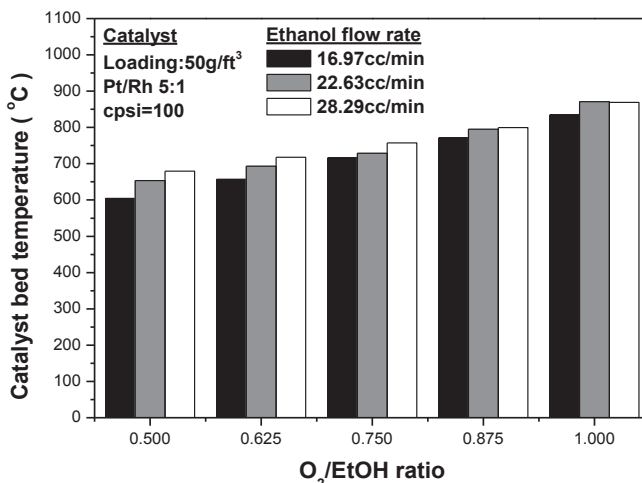

Fig. 4 Effect of differing O_2/EtOH with fuel ratio on the catalyst outlet catalyst bed temperature

At ethanol flow rate of 16.97cc/min, H_2+CO concentration was around 36.13Vol.% and 40.54Vol.% with increasing O_2/EtOH ratio, after apex at O_2/EtOH ratio of 0.875, the value decreased with increasing O_2/EtOH ratio. With the similar trend, the H_2+CO concentration for the ethanol flow rate of 22.63cc/min varied between 39.24Vol.% and 44.09Vol.% with O_2/EtOH ratio, and peaking at O_2/EtOH ratio of 0.75. Further observing the case of 28.29cc/min ethanol flow rate, H_2+CO concentration was around 39.18Vol.% and 43.30Vol.% with the peak value at 0.75 O_2/EtOH ratio. It also could be found that the H_2+CO concentration was lower than that of 22.63cc/min ethanol flow rate. Above all, the concentration increases with increasing O_2/EtOH ratio before peak because lower O_2/EtOH ratio translates to less oxygen for oxidation and reaction temperature be lower, therefore lower H_2+CO concentration produced. However, with increasing O_2/EtOH ratio after apex, the dilution effect of nitrogen in higher air flow rate caused the lower H_2+CO concentration production.

From Fig. 5, it can be found that the ethanol conversion efficiency increases with higher O_2/EtOH ratio; and at the same O_2/EtOH ratio, higher conversion efficiency of ethanol is obtained as the flow rate increases. This is because of the increase in oxidation heat with the ethanol supply. As the O_2/EtOH is between 0.5 and 0.875, the ethanol conversion efficiency of 81.5% is achieved at ethanol flow rate of 22.63cc/min. When the O_2/EtOH is 1.0, the ethanol flow rate of 28.29cc/min can give the best conversion efficiency of 89.14%.
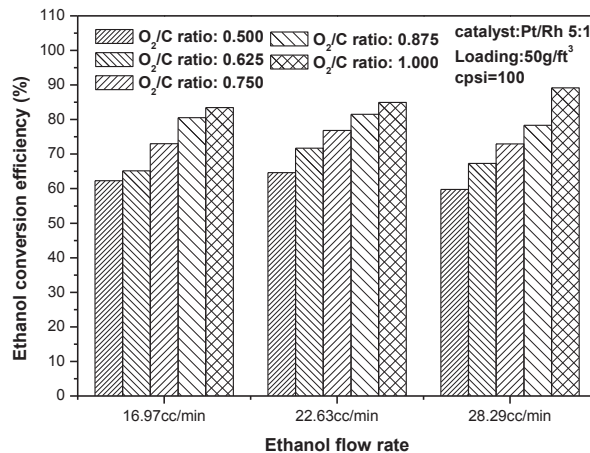

Fig. 5 Effect of O_2/EtOH on the fuel conversion efficiency under various fuel flow rate.

Further from this figure, one can find the ethanol conversion efficiency increases with increasing flow rate and O_2/EtOH ratio. The dominant factor is the reforming temperature. Suitable fuel flow rate and O_2/EtOH ratio give the higher conversion efficiency because of high temperature due to heat of fuel oxidation. However, it is not allowed because of the effects of dilution and oxidation. Over high O2/EtOH ratio would cause the oxidation of hydrogen and carbon monoxide, and the dilution effect of excess air supply.

4.2. Hydrogen production with various catalysts

Figs. 6 and 7 show that the hydrogen-rich gas production by various catalysts as O_2/EtOH set between 0.5-1.0, flow rate at 22.63cc/min. It can be found that the difference of H_2+CO concentration

was the most obvious at O_2/EtOH ratio of 0.5; where with Fe catalyst, H_2+CO concentration was as low as about 16.88 Vol.%; however, with Rh catalyst, it gave the highest H_2+CO concentration about 40.96 Vol.%. According to these tests, Rh still gave the best reforming performance at other higher O_2/EtOH ratios.

As a whole, H_2+CO concentration increases with O_2/EtOH ratio. While, Co catalyst had the maximum difference in H_2+CO concentration, which was from 19.51 Vol.% up to 33.7 Vol.%. It indicated that the reforming performance by Co catalyst was significantly influenced by O_2/EtOH ratio, which implies the effect of the related reforming temperature. Using Rh catalyst could achieve the best H_2+CO concentration. However, the variation in production was not obvious. The H_2+CO concentration was about between 40.96 Vol.% and 44.06 Vol.%.
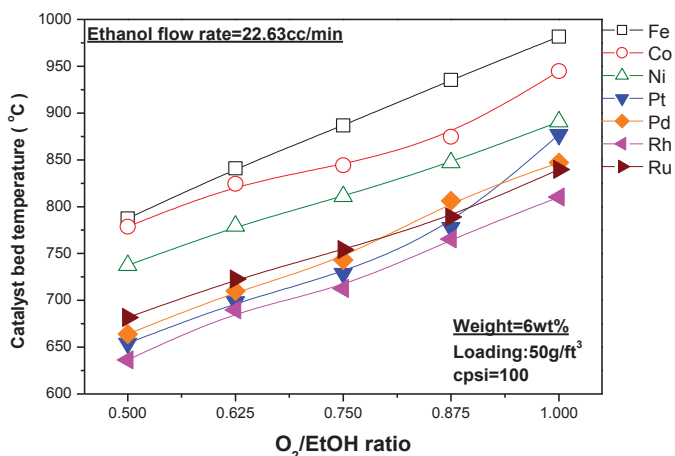

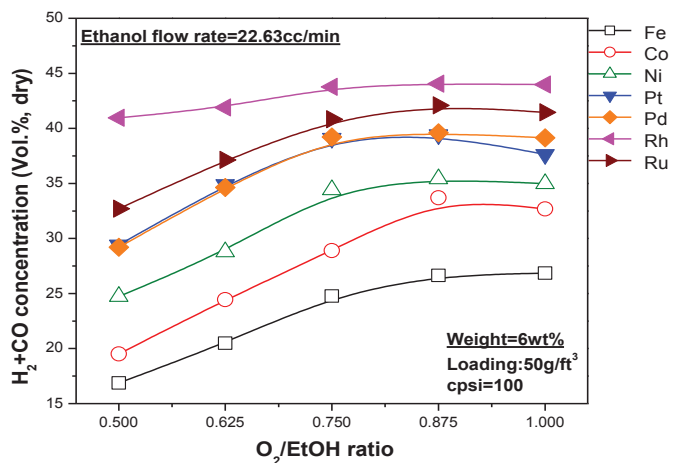Fig. 6 O_2/EtOH ratio on the catalyst bed temperature by using various catalysts

Fig. 7 O_2/EtOH ratio on the H_2+CO concentration by using various catalysts
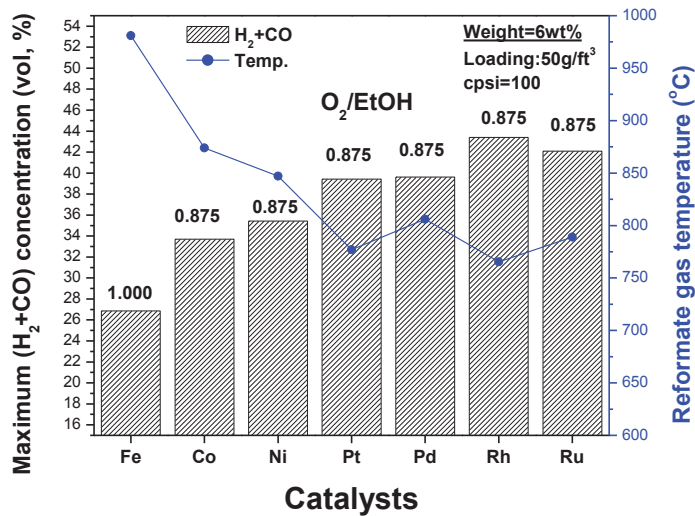
Fig. 8 The reaction of concentrated H$_2$+CO with catalyst bed temperature.

As discussed in Figs.6-7, it showed that the heat release of ethanol oxidation was enough to the reaction needed. Over excess air supply would lead to high temperature and reduction of hydrogen and carbon monoxide concentrations due to the effects of oxidation and dilution. Fig. 8 shows overall observations, the sequence of the catalysis effect on the syngas production was Rh＞Ru＞Pt＞Pd＞Ni＞Co＞Fe. Especially by using Rh catalyst, the best reforming performance was achieved under all the tested O$_2$/EtOH ratios. It indicated that Rh catalyst has good selectivity for hydrogen.

4.3. Hydrogen production with using heat recycling

In this experiment, the ethanol flow rate was set as 22.63cc/min according to the results summarized before. The effect of O$_2$/EtOH ratio on the (H$_2$+CO) concentration by using original system, heat insulation and heat recycling with Rh=6wt% and Ru=6wt% catalysts was investigated.

The O$_2$/EtOH ratio of 0.5-1.0 was used for the original system to study the effect of the parameters. The reaction temperature was higher due to less heat loss if the energy-saving methods were employed. However, the temperature on the catalyst should be taken into consideration, namely, it should prevent the too high temperature to damage the catalyst. Therefore, the O$_2$/EtOH ratio was set between the range of 0.5-0.75 as the energy-saving methods were adopted.

As shown in Table 2, one can find a better H$_2$+CO concentration could be obtained by using Rh catalyst. H$_2$+CO concentration was improved about 2~3% by energy saving methods with different O$_2$/EtOH ratios; where at O$_2$/EtOH ratio of 0.75, the best H$_2$+CO concentration was achieved around 46.15Vol%. In contrast, the improvement of H$_2$+CO concentration by Ru catalyst could be obtained around 6~10% with the apex of 44.41Vol% at O$_2$/EtOH ratio of 0.75. Further in this figure, it also demonstrated that H$_2$+CO concentration increased with O$_2$/EtOH ratio in the tested range. Moreover, it could be found that the application of heat insulation and heat recycling could give better results than that of original system, especially under low O$_2$/EtOH ratio, or in the condition by using Ru catalyst.

Table 2 O_2/EtOH on H_2+CO concentration in reformate gas by using energy saving methods

O_2/EtOH	H_2+CO concentration Vol.%					
	Original system		Heat insulation		Heat recycling	
	Rh/Al_2O_3	Ru/Al_2O_3	Rh/Al_2O_3	Ru/Al_2O_3	Rh/Al_2O_3	Ru/Al_2O_3
0.50	40.69	32.37	41.71	37.55	43.89	42.15
0.625	42.27	37.26	42.78	40.92	45.53	44.13
0.75	44.04	38.28	44.45	42.26	46.15	44.41
0.875	44.68	40.66	na	na	na	na
1.00	44.59	41.77	na	na	na	na

Ethanol flow rate=22.63mL/min, Weight=6wt%, loading: 50g/ft3, CPSI=100

5. Conclusions

This study of hydrogen production from ethanol reformer with various catalysts showed that a better reforming effect of the noble metal catalyst can be achieved under low temperature condition. It also proved that better hydrogen selectivity can be reached with the noble metal. The best H_2+CO concentration was produced by Rh catalyst. Analysis sequence of the catalysis effect on the syngas production was $Rh > Ru > Pt > Pd > Ni > Co > Fe$. In addition, although better hydrogen yield and selectivity could be obtained by using Rh catalyst, in general hydrogen production was quite undetected even with the combination of energy saving method. Nonetheless, the adoption of energy saving method and the use of Ru Catalyst contributed to greatly improve the reforming efficiency.

Acknowledgements

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