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HYDROGEN PRODUCTION FROM GASIFICATION OF PALM KERNEL SHELL IN THE PRESENCE OF Fe/CeO$_2$ CATALYSTS

(Penghasilan Hidrogen daripada Pengegasan Isirung Kelapa Sawit dengan Kehadiran Mangkin Fe/CeO$_2$)

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Abstract

Biohydrogen is a renewable source of clean fuel and energy which can be derived from biomass. One of the suitable candidate as a source of biomass is palm kernel shell (PKS). Our initial work shows that biohydrogen may be produced from PKS in the presence of zeolite supported catalysts. The potential of using cerium oxide (CeO$_2$) supported catalysts for the production of biohydrogen from PKS is explored in this work using 2.5 – 10 % Fe loading. The catalysts were prepared by incipient wetness impregnation method and calcined at 500 ^{o}C for 16 h. The physicochemical properties of these catalysts were characterized using BET and XRD. The catalysts were tested in dry and steam gasification of PKS at 700 ^{o}C using PKS feeding rate of 2 g h^{-1} under N$_2$ atmosphere with biomass to catalyst ratio of 3:1 (wt/wt). Steam to biomass ratio of 3.5:1 (wt/wt) was used in steam gasification reaction. The gaseous products were analyzed using an on-line gas chromatography equipped with thermal conductivity detectors (TCD) and fitted with Molsieve 5A and Hayesep Q columns. Result shows that 2.5 % Fe/CeO$_2$ gave the highest hydrogen production in both the dry and steam gasification of PKS.

Keywords: biohydrogen, palm kernel shell, ceria supported catalysts, gasification

Abstrak

Biohidrogen adalah sumber bahan api yang boleh diperbaharui daripada sumber biomas. Isirung kelapa sawit (PKS) merupakan salah satu sumber biomas yang sesuai digunakan umtuk tujuan ini. Kajian awal menunjukkan biohidrogen boleh dihasilkan daripada PKS dengan menggunakan mangkin berpenyokong zeolite. Dalam kajian ini, muatan mangkin 2.5 – 10 % logam Fe berpenyokong cerium oksida (CeO$_2$) digunakan untuk meningkatkan penghasilan biohidrogen daripada PKS. Pemangkin disediakan menggunakan kaedah pengisitepuan pembasahan permulaan dan dikalsinkan pada suhu 500 ^{o}C selama 16 jam. Sifat fizikal kimia pemangkin ini dianalisa menggunakan teknik BET dan XRD. Kereaktifan mangkin untuk penghasilan biohidrogen diuji dalam pengegasan kering dan berstim pada suhu 700 ^{o}C dengan PKS diperkenalkan pada kadar 2g h^{-1} dan nisbah PKS kepada pemangkin adalah 3:1 (wt/wt). Nisbah stim kepada PKS 3.5: 1 (wt/wt) telah ditetapkan dalam eksperimen pengegasan berstim. Gas yang telah dihasilkan telah dianalisa menggunakan kromatograf gas yang dilengkapi pengesan konduktiviti termal (TCD) serta tiub Molsieve 5A dan Hayesep Q. Keputusan kajian menunjukkan penghasilan hidrogen yang maksimum dicapai dengan kehadiran mangkin 2.5 % Fe / CeO$_2$.

Kata kunci: biohidrogen, tempurung kelapa sawit, mangkin berpenyokong CeO$_2$, pengegasan

Introduction

The hiking prices of petroleum fuel and growing issues on environmental impact, particularly emission of greenhouse gases draw world's attention to the biomass as an alternative energy. The possible utilization of biomass to produce bio-fuels such as bioethanol and biohydrogen makes biomass a critically important source of sustainable energy future. The production of hydrogen rich gas from renewable biomass is being promoted as the fuel for the future since it has higher engine efficiencies and zero emission.

Biomass can be reformed to hydrogen through gasification technology where it converts lignocellulosic biomass to gaseous products such as H$_2$, CO, CO$_2$, CH$_4$ and light hydrocarbons. Traces amount of char, ash and tar are also produced during biomass gasification. However, the formation of tar and char create severe problems in the operation of gas engine such as corrosion, burning difficulties and internal deposition.

Catalytic gasification of biomass helps to decompose tar and heavy hydrocarbon in the product gas streams at a lower temperature. In fact, the application of catalyst not only functions as tar abatement, but it also plays a significant role in promoting high content of product gases [1]. Despite of having significant activities as water gas shift (WGS) catalysts and in hydrocarbon reforming, Fe-based catalysts also facilitate in biomass steam gasification. This is explained by the capability of Fe to crack tar produced in the product stream which is similar to the capability of dolomite [2].

To avoid catalyst deactivation, different promoters or supports are added to the catalyst precursor. In our previous work, Zeolite Beta (BEA) supported catalysts were used as a catalyst and the result indicated a significant performance in producing H$_2$ from steam gasification of PKS [3]. This work presents further catalyst development using Cerium Oxide (CeO$_2$) as the catalyst support due to its redox properties and ability to promote metal-ceria interaction [4]. Tomishige and co-workers [5] investigated various oxide supports and supported metal catalysts for gasification of cellulose at 550 $^{\circ}$C and reported that the highest yield of CO and H$_2$ were achieved using CeO$_2$ as support while the lowest conversion was found on Al$_2$O$_3$ and SiO$_2$. Thus, this work aims to study the effect of Fe loading on CeO$_2$ on the production of H$_2$ in dry and steam gasification of PKS.

Materials and Methods

Chemicals and raw materials

Palm kernel shell (PKS), the biomass feedstock for gasification reaction was collected from Felda Nasaruddin Plantation in Perak. The PKS was first dried at 110 $^{\circ}$C for 4 h before they were ground and sieved to 500 µm. The ultimate and proximate analyses of PKS are displayed in Table 1.

Table 1. Ultimate and Proximate analysis of PKS

Ultimate analysis (%)	
C	49.65
H	6.13
N	0.41
S	0.48
O	43.33
Proximate analysis (%wt wet basis)	
Volatile matter	81.03
Fixed carbon	14.52
Ash	4.44

Catalyst loading with range 2.5 – 10 wt% Fe/CeO$_2$ were prepared using incipient wetness impregnation method with Cerium oxide (CeO$_2$) as the catalyst support. CeO$_2$ (Sigma Aldrich, 99.9 %) was first calcined at 500 °C for 16 hr. Next, the required amount of Fe(NO$_3$)$_3$.9H$_2$O (Merck, 98 %) was dissolved in sufficient amount of deionized water followed by addition of CeO$_2$ to the metal salt solution while stirring. The slurry formed was left for 4 hr and then dried at 120 °C for 16 hr. Finally, the prepared catalysts were calcined at 500 °C for 16 hr. The prepared catalysts were crushed and sieved to <250 μm. The catalysts are denoted as xFe/CeO$_2$, where x represents the amount of Fe loading e.g. 2.5Fe/CeO$_2$ is 2.5wt % of Fe was loaded on cerium oxide.

Characterization of catalysts
N$_2$ adsorption-desorption isotherm (Micromeritics ASAP 2020) was used to determine the surface area, pore size and pore volume of the catalyst. The samples were degassed in vacuum at 200 °C for 4 hr prior to the measurement. Powder X-Ray Diffraction (XRD) pattern of the catalysts was obtained using a Bruker D8 Advance diffractometer with a radiation sources of Cu-Kα to identify their crystal structures. The reducibility measurement of the catalysts was conducted on a Thermo Electron TPDRO 1100 analyser. The sample was reduced in a stream of 5 %H$_2$/N$_2$ at a heating rate of 20 °C to reach a final temperature of 1000 °C.

Gasification of PKS
Both dry and steam gasification reaction of PKS were performed at 700 °C in a two staged reactors. The biomass samples were placed in the first reactor and a catalyst sample was held in placed by quartz wool in the second reactor with biomass to catalyst mass ratio of 3:1. The reactor system was purged with N$_2$ at 100 ml min^{-1} before both reactors were heated to 700 °C at a heating rate of 150 °C/hr. Then, the PKS was introduced at feeding rate of 2 g hr^{-1} under N$_2$ atmosphere. Water was introduced by liquid pump when the temperature of the first reactor reached 700 °C, where it was instantly evaporated at the elevated temperature and then carried to the reactor by N$_2$ flow. The steam to biomass (S/B) ratio was 3.5. The outlet gases passed through a condenser prior to analysis with online gas chromatography (Agilent 7890A) equipped with two thermal conductivity detectors (TCD) and a flame ionization detector (FID). H$_2$, CO and CO$_2$ were measured using TCD detectors fitted with Molsieve 5A and Hayesep Q column, while CH$_4$ and C$_2$ hydrocarbons were analyzed using FID detector fitted with HP-AL/S and DB-1 columns.

Results and Discussion
Catalysts characterization
The N$_2$ adsorption- desorption isotherms of the CeO$_2$ support shows a Type III isotherm according to IUPAC classification system which indicates that the CeO$_2$ is a non-porous materials. Table 2 shows the BET surface area of the CeO$_2$ based catalysts. The surface area increases with increasing of Fe loading. This shows that the loading of Fe metal provides additional nucleation sites which contribute to the higher surface area [6].

Table 2. The surface area of Fe/CeO$_2$ catalysts

Catalysts	CeO$_2$	2.5Fe/CeO$_2$	5Fe/CeO$_2$	7.5Fe/CeO$_2$	10Fe/CeO$_2$
Surface area (m^2/g)	4.2	5.0	5.2	5.6	6.4

The X-ray diffractograms of CeO$_2$ based catalysts are shown in Figure 1. All samples show four significant diffraction peaks at 2θ= 28.6°, 33.1°, 47.6°, 56.4° which correspond to the (111), (200), (220) and (311) planes of cubic CeO$_2$ (81-0792 JCPDS file). It is observed that the peak heights slightly decrease with increasing loading of Fe on the CeO$_2$ support. Appearance of a small peak corresponding to the hexagonal hematite iron oxide, Fe$_2$O$_3$ (02-0919 JCPDS file) is only detected in 10Fe/CeO$_2$ catalyst which indicates that the Fe$_2$O$_3$ are finely dispersed on the surface of CeO$_2$ at lower loading of Fe. However, the absence of diffraction peaks has been suggested to be attributed to the Fe$_2$O$_3$ phase where Fe was substituted in the CeO$_2$ lattice leading to formation of a solid solution of iron-cerium oxide [7].
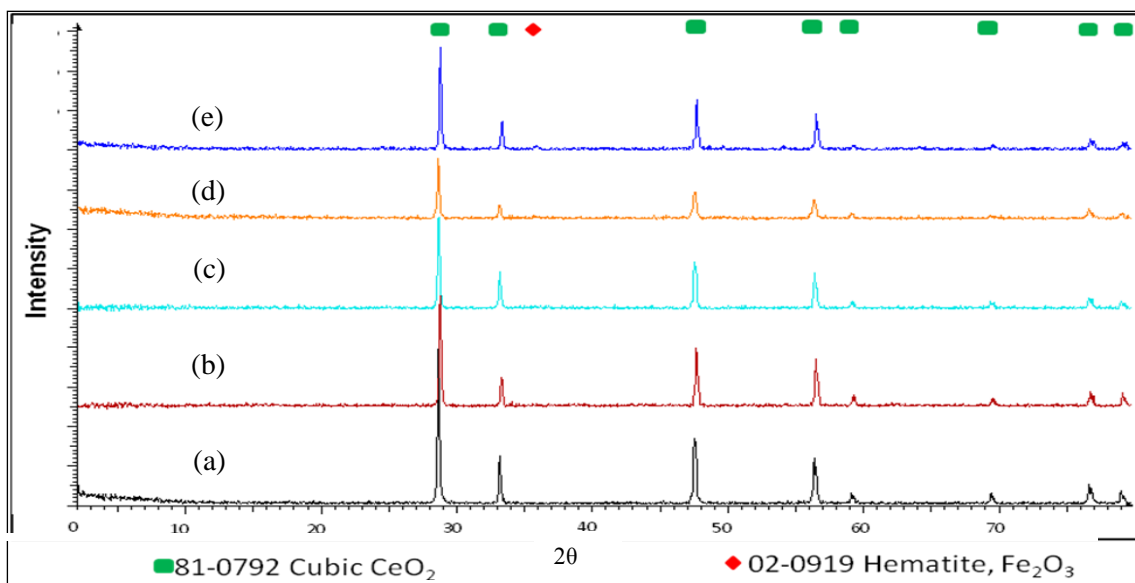
Figure 1. X-Ray diffraction patterns of (a) CeO₂ support, (b) 2.5Fe/CeO₂, (c) 5Fe/CeO₂, (d) 7.5Fe/CeO₂ and   (e) 10Fe/CeO₂

Catalytic activity

Figure 2 shows the distribution of gaseous products from dry gasification of PKS in the presence of Fe/CeO₂ catalysts with H₂ as the main products followed by CO₂ and CO while only trace amount of CH₄ was detected. Figure 2 shows that H₂ production is significantly improved when CeO₂ was used as catalyst. Incorporation of 2.5 wt% Fe to the CeO₂ support slightly increased the H₂ production but further increased in Fe loading resulted in reduction in H₂ production. However, it is also observed that increased loading of Fe resulted in an increment in CO₂ and CO produced, which indicates that the PKS undergo oxidation. In addition, the enhanced CO₂ concentration may also contribute from the oxidation of CO to produce CO₂, with reaction path as shown in Eq (1)[8].

$$CO_{ad} + O_{lattice} \rightarrow CO_2 \tag{1}$$

The maximum H₂ yield with the least formation of CO₂ and CO is obtained in the presence of 2.5 wt% Fe for both dry and steam gasification. This result may be explained in term of the formation of cubic ceria-like solid solution as corroborated in XRD pattern. The Fe-O-Ce interaction enables the formation and stabilization of small particles of mixed oxides. As this catalyst reacts, it may provide a larger number of exposed actives sites and result in higher catalytic activity [9]. It is concluded that the interaction between well dispersed Fe species and the good oxygen mobility in the Ce-Fe solid solution promotes the formation of synthesis gas. Therefore, it can be expected that the production of H₂ decreses with increasing of Fe loading.

Both Figures 2 and 3 show that Fe loading higher than 2.5 wt% resulted in a decreased in H₂ production which could be attributed to the lack of Fe-O-Ce interactions. This trend is in agreement with those reported earlier where they proposed that lower catalytic activity of Fe-CeO₂ is due to the diffusion of Fe^{3+} into the lattice structure of Ce^{4+}, resulting in less active sites available for reaction to take place [10].
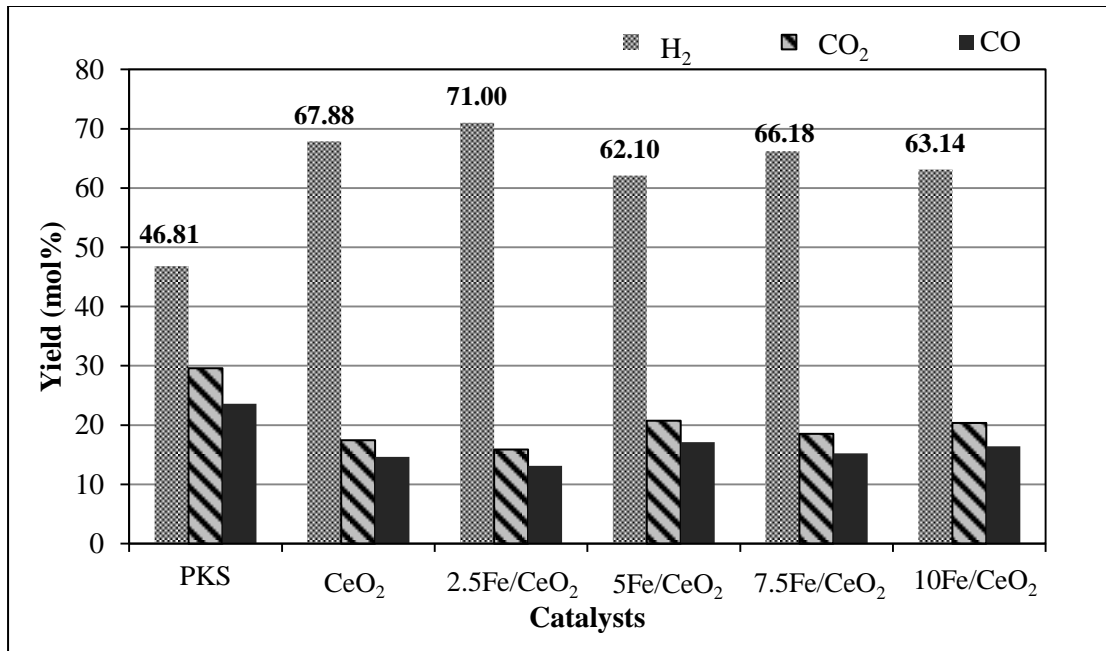
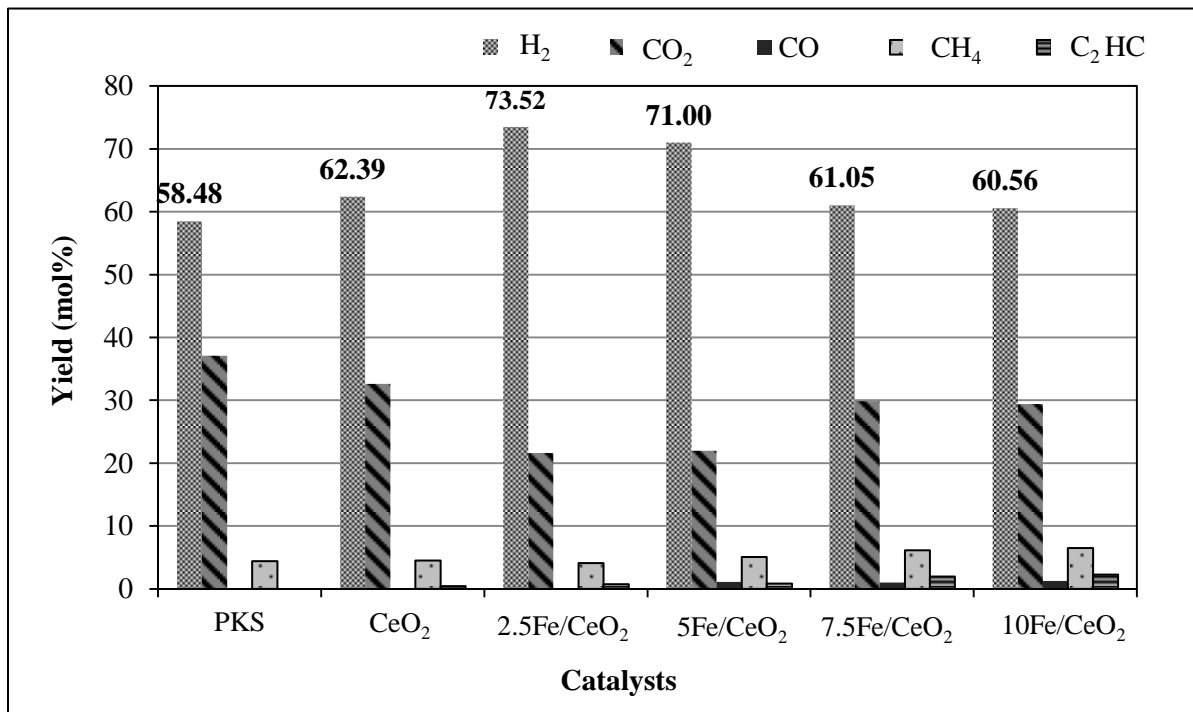Figure 2. Distribution of gaseous products from dry gasification of PKS

Figure 3. Distribution of gaseous products from steam gasification of PKS

The introduction of steam facilitates further water gas shift reactions to occur in the gasification. It has been suggested that the interaction between carbon deposits from PKS decomposition and the lattice oxygen of CeO_2 would lead to the formation of CO [11] as shown in Eq (2) which then reacts with steam to produce H_2 and CO_2, following the WGS reaction (Eq3).

$$C + O_{lattice} \rightarrow CO \qquad\qquad (2)$$
$$CO + H_2O \rightarrow H_2 + CO_2 \qquad\qquad (3)$$

Conclusion

Fe/CeO₂ catalysts with Fe loading of 2.5-10 wt% were successfully prepared and tested in PKS gasification for production of biohydrogen. Nitrogen adsorption-desorption isotherms of these catalysts show that they are Type III materials indicating that the catalysts are nonporous materials. XRD results confirmed the presence of four strong peaks of cubic Ceria and a weak peak of hexagonal hematite iron oxide, Fe_2O_3. The 2.5 wt% Fe/CeO₂ catalyst produced the maximum H_2 yield, 70% with the least formation of CO_2 and CH_4. The H_2 yield increased to 73% in steam gasification of PKS as compared to dry gasification. The favourable catalytic activity in gasification reactions may be correlated to the metal support interaction between iron species and the cubic CeO_2 solid solution. It is concluded that the H_2 yield decreases with increasing of Fe loading.

Acknowledgement

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