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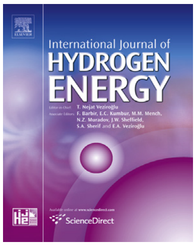

Hydrogen production from pyrolysis catalytic reforming of cellulose in the presence of K alkali metal

Jun Zou [a], *Haiping Yang* [a,*], *Zhiwei Zeng* [a], *Chunfei Wu* [b,**], *Paul T. Williams* [c,***], *Hanping Chen* [a]

[a] *State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan, 430074, China*
[b] *School of Engineering, University of Hull, Hull, HU6 7RX, UK*
[c] *Energy Research Institute, The University of Leeds, Leeds, LS2 9JT, UK*

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ABSTRACT

The inherent alkaline metals in biomass material are known to be volatile during biomass pyrolysis. However, there are very limited works about the investigation of the influence of alkaline metal on hydrogen production from downstream catalytic reforming of pyrolysis vapors. In this study, the influence of volatile K inside the cellulose sample was investigated in terms of hydrogen production and catalyst stability using a two-stage fixed-bed reaction system in the presence of a Ni/Al_2O_3 catalyst. When the content of K in the cellulose sample was increased from 0 to 15%, the deposition of K on the surface of the reacted catalyst was kept constant at around 0.5 wt.% in terms of the weight of the catalyst. The life time test shows that hydrogen production was around 28 (mmol g^{-1} cellulose) for each experiment, when the catalyst was reused 5 times using the pure cellulose sample. However, the hydrogen production was significantly reduced to 22 (mmol g^{-1} cellulose) after the catalyst was reused 5 times with the 2.5% K/cellulose sample. X-Ray Fluorescence analysis shows that the reduce hydrogen production might be ascribed to the increase of the K deposition on the surface of the reused catalyst.

Introduction

Biomass is an important energy resource and is largely available in the world [1]. With the increasing concern of using fossil fuels resulting in greenhouse gases emission and energy security issues, more attentions have been focused on using biomass, which is a renewable and sustainable resource. In addition the utilization of biomass is a CO_2 neutral process [2]. There are several routes to converting biomass into energy and fuels [3–11]. Thermochemical process is a promising technology, and has attracted many attentions [12–17]. Furthermore, hydrogen is an ideal energy carrier in the future energy system, since the combustion of hydrogen only generates water, and hydrogen powered fuel cells has very high energy efficiency [18]. Therefore, hydrogen production from biomass gasification has been extensively investigated [16,17]. The introduction of catalyst has been reported as a key factor

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* *Corresponding author*. Tel.: +86 27 87542417.
** *Corresponding author*. Tel.: +44 1133432504.
*** *Corresponding author*. Tel.: +44 1133432504.
E-mail addresses: yhping2002@163.com (H. Yang), c.wu@leeds.ac.uk (C. Wu), p.t.williams@leeds.ac.uk (P.T. Williams).

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to enhance the process efficiency and hydrogen production [16,19,20].

However, there are many challenges for hydrogen production from catalytic biomass gasification. For example, biomass has high alkali metal content, which could evolve out at high temperature and causes corrosion and agglomeration issues [21]. Many studies have been carried out on the release of alkali metals during biomass thermal conversion. Patwardhan et al. [22] studied the biomass ash and discovered that the major constituents in biomass ash are silica, potassium, calcium, magnesium and sodium, and potassium occupies a large proportion in addition to silica. The alkali metals including potassium have been reported to largely affect biomass gasification process in terms of product yield [23,24]. In general, the presence and release of alkali metals have impacts on both primary biomass pyrolysis and the secondary reforming reactions [25–27]. For example, Shimada's team [28] researched the effect of alkali metal chlorides and alkaline earth metal chlorides on pyrolysis via thermal analysis and isothermal pyrolysis, and found that even a small amount of inorganic salts could change the surface molecules reactivity in crystalline cellulose and significantly influence the product yield. Among of the alkali metal and alkaline earth metal, it is well known that potassium salts have considerable effects on the pyrolysis behavior of cellulose [29,30]. However, it is reported that when the KCl concentration in organic salts-impregnated cellulose sample was higher than 0.08 mmol g^{-1} cellulose (i.e. 0.3 wt.%), no clear effect of salts was obtained on the production of low molecular weight compounds [22].

At present, introducing catalyst into the process of thermal-chemical conversion of biomass has been largely studied for enhancing hydrogen [16,31,32]. In particular, there are many investigations about producing hydrogen from two-stage pyrolysis-catalytic steam reforming of biomass [16,32]. The two-stage biomass thermo-chemical conversion process has advantages of easily controlling of the catalytic reforming stage, where direct contacts between catalyst and pollutants from biomass char and ashes are avoided and the used catalyst is easier to be separated and regenerated, compared with single-stage gasification by mixing catalyst and raw biomass.

However, most of the current works about the effect of alkali metals on biomass thermo-chemical conversion are focused on biomass pyrolysis, or on catalytic reforming of model compounds of biomass fuel gas. For example, Eom et al. [33] examined the catalytic effects of essential minerals on biomass pyrolysis and reported that K showed great promoting effect of low molecular compounds. It is noted that K had been investigated as catalyst promoter to enhance hydrogen production from biomass gasification or catalytic reforming of hydrocarbons. For example, Guan et al. [34] impregnated various concentrations of K on calcined scallop shell catalyst and revealed that potassium promoted the catalytic activity of catalyst in terns of H_2 generation in the steam reforming of tar. Addition of potassium to a Ni-based catalyst resulted in the increase of hydrogen production from biomass thermo-chemical conversion [34,35]. The negative effect of the presence of alkali metal on hydrogen production from biomass thermo-chemical conversion has been reported by Wu et al. [36] who found that H_2 content decreased from 35.1 to 26.7% when alkali metal vapors exposed over catalyst for 17 h during the catalytic reforming of biomass fuel gas.

Since there are very limited studies about the influence of release of alkali metals from biomass pyrolysis on the catalytic reforming of pyrolysis vapors for hydrogen production, this work aims to understand the effect of K resulted from biomass pyrolysis on hydrogen production. Different amounts of K were loaded in the biomass sample, which was pyrolyzed in a first-stage reactor. The produced pyrolysis vapors were catalytic reformed in the presence of a Ni/Al_2O_3 catalyst in a second-stage reactor. In particular, the stability of catalyst in terms of hydrogen production from K-impregnated biomass was studied by reusing the catalyst several times.

Experiment materials and methods

Materials and catalyst preparation

Cellulose (Sigma–Aldrich Co., Ltd., microcrystalline powders of 20 μm particle size) was used as a reprehensive material for biomass sample. Results of the proximate analysis (TGA2000: Las Navas, Spanish) and ultimate analysis (elemental analyser: EL-2, Vario Germany) of the cellulose are listed in Table 1. It shows that the volatile content in cellulose is very high (up to 95.68 wt.%) while the ash content can be neglected (0.02 wt.%). Biomass samples used in this work containing different amounts of K were prepared by impregnation method. A certain amount of KCl (analytically pure, Sinopharm Chemical Reagent Co., Ltd.) and cellulose were added to deionized water, kept stirring at 80 °C for 3 h, then dried at 105 °C overnight. The concentration of K in cellulose sample is 0, 2.5, 5, 10 and 15 wt.%, respectively.

Ni/Al_2O_3 catalysts with a Ni content of 15 wt.% were prepared by a wetness impregnation method as mentioned in previous work [19]. γAl_2O_3 (analytically pure, Sinopharm Chemical Reagent Co., Ltd.) was impregnated with aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$. The catalyst precursors were dried at 105 °C for 12 h, and subsequently calcined at 800 °C for 3 h in a muffle furnace under air atmosphere. The catalysts were crushed and sieved to granules with the size ranging from 0.245 to 0.350 mm prior to experimental work.

Experimental apparatus and procedure

The experiment was carried out with a two-stage pyrolysis catalytic reforming fixed-bed system. A schematic diagram of the reaction system is shown in Fig. 1. In the first stage, biomass sample was pyrolyzed in a stainless tube reactor with internal diameter was 45 mm. The derived pyrolysis vapors were catalytic steam reformed under a second reactor tube with an internal diameter of 26 mm in the presence of the Ni/Al_2O_3 catalyst.

At the beginning of each experiment, 0.5 g Ni/Al_2O_3 catalyst, supported by quartz wool, was placed on the porous plate in the second reactor. When the second reactor was heated and stabilized at 800 °C, 1.5 g biomass sample was put into the first reactor. Fast pyrolysis of biomass sample happened in the first stage, and the volatiles including K metal (if K was impregnated into the biomass sample) were derived entering

Table 1 – Proximate and ultimate analysis of the cellulose (dry basis, wt.%).

	Proximate analysis (wt.%, db.)			Ultimate analysis (wt.%, db.)				
	Volatiles	Fixed carbon	Ash	C	H	N	S	O[a]
Cellulose	95.68	4.30	0.02	42.76	5.94	0.05	0.03	51.2

[a] The oxygen content was calculated by difference.

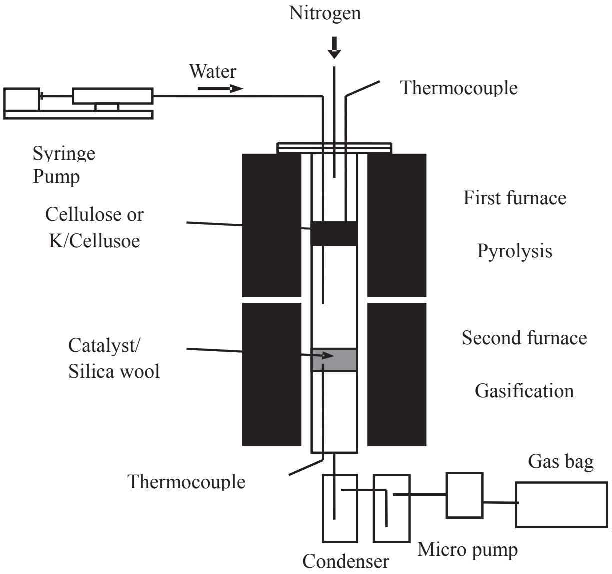


Fig. 1 – Schematic diagram of a two stage pyrolysis catalytic reforming system.

the second reactor. At the same time, water was introduced using a syringe pump into the second reactor where it became steam for catalytic reforming. When the steam content was investigated in this work, the feeding rate of water was set to 0, 0.01, 0.02, 0.1, 0.2 g min^{-1}, respectively, while the carrier gas nitrogen was kept at 150 ml min^{-1}.

The outlet products passed through two condensers where the liquid products were collected. Finally, the noncondensable gases were cleaned, dried and collected with a gas bag. Each experiment was conducted for about 40 min to ensure the reaction completed and all the products were collected. Experiments were repeated to ensure the reproducibility of the results.

Products analysis and characterization

The non-condensed gases were analyzed by dual-channel gas chromatography (microGC 3000A, Agilent Technologies, America) with thermal conductivity detectors: (a) Column A was molecular sieve 5A (MS-5A, Ar as carrier gas) for the separation of H_2, N_2, CO, CH_4; (b) Column B (PorapakQ-PPQ, He as carrier gas) for the detection of CO_2, C_2H_6, C_2H_4, C_2H_2. Each sample was measured for three times at least to get the average value. In this work, all the gas yields were reported on the base of 1 g of pure cellulose.

The reacted catalysts were analyzed by temperature-programmed oxidation (TPO) using a thermogravimetric analyzer (STA409, Netzsch, German) to detect the properties of the cokes deposited on the surface of the reacted catalysts. The fresh and reacted catalysts were characterized by X-Ray Diffraction (XRD, X'Pert PRO, PANalytical B.V, Netherlands) and X-Ray Fluorescence (XRF, EAGLE III, EDAX Inc, America) to determine the presence and the state of metals. A high resolution scanning electron microscope (SEM, Quanta 200, FEI, America) was used to investigate the surface morphology of the catalysts.

Results and discussions

Influence of water addition

Mass balance of experiments with different water injection rates

Fig. 2 shows the yields of gases produced using 2.5% K-cellulose under different water feeding rates. When the Ni/Al_2O_3 catalyst was added into the gasification process with the water feeding rate of 0.01 g min^{-1}, the yield of hydrogen increased sharply from 14.2 to 20.9 (mmol g^{-1} cellulose) compared with 2.5% K-cellulose gasification without catalyst; in addition the gas yield also significantly increased from 0.47 to 0.77 (g g^{-1} cellulose), indicating that the Ni/Al_2O_3 was efficient for promoting hydrogen and gas productions.

With the increase of steam injection rate, more gases were produced since the reaction between steam and derived pyrolysis compounds were enhanced, in addition the yields of CO_2 and H_2 increased while the yield of CH_4 reduced. It is suggested that Ni/Al_2O_3 may promote the steam reforming of

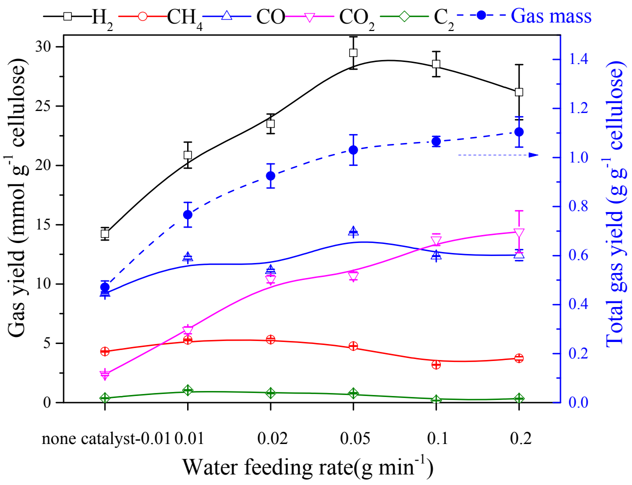


Fig. 2 – Gas productions under different water feeding rates (biomass sample is cellulose containing 2.5% K).

tar (Reaction 1), water gas shift reaction (Reaction 2) and methane steam reforming (Reaction 3), when the water injection rate was increased.

$$CH_xO_y + (2-y)\ H_2O \leftrightarrow CO_2 + (2 + x/2-y)H_2 \quad \text{(R1)}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \text{(R2)}$$

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad \text{(R3)}$$

The yield of hydrogen reached a maximum number of 29.5 (mmol g^{-1} cellulose) when the water feeding rate was 0.05 g min^{-1}. Then the H_2 yield decreased slightly as the water feeding rate was further increased. It seems that an optimal water feeding rate between 0.05 and 0.1 g min^{-1} was required for the production of hydrogen in this work. Garcia's co-workers [37] reported that steam promoted the stability of catalyst by prohibiting catalyst deactivation. However, Wu and Williams [17] indicated that extra water weaken the decomposition of large molecular compounds and resulted in a lower hydrogen production. And in their work about tyres gasification [38], the water feeding rate had significant effect on hydrogen production, excessive water feeding rate decreased both the concentration and potential production of hydrogen.

XRD analysis of fresh and reacted catalysts under different water feeding rates

The XRD analysis to the fresh un-reduced Ni/Al_2O_3 catalyst shows that Ni–Al spinel phase ($NiAl_2O_4$) is the main crystal compound in the catalyst (Fig. 3). NiO phase is difficult to be identified might be due to the NiO particles are too small to be detected. Regarding the reacted catalysts resulted from experiments with different water feeding rates, Ni crystal phase was obtained. The presence of Ni is ascribed to the reduction of catalyst under the reducing environment (CO and H_2) during the thermo-chemical conversion of biomass. Meshari et al. [39] proposed that the reduction of NiO-catalyst could be conducted during propane steam reforming. It is suggested that the catalyst without pre-reduction could be used in the gasification process for hydrogen production from biomass, in order to simplify the procedure and decrease the cost of catalyst pretreatment.

From Fig. 3, it is interesting to note that a sharp peak related to the diffraction of NiO was obtained at 43.3° for the reacted Ni/Al_2O_3 catalyst used in the experiment with a water injection rate of 0.2 g min^{-1}. It is suggested that higher steam partial pressure made it easier to oxidize Ni particles. The promotion of NiO formation has been reported by Li et al. [40], who investigated the influence of steam on the phase change of Ni nanoparticles with TiO_2 as catalyst support using in-situ environmental TEM. They found that the Ni particles were oxidized at 600 °C under an atmosphere containing 5% water, 9% H_2 and 86% N_2.

Fig. 3 shows a low crystallinity of potassium in the catalyst, which is consistent with other studies where K was loaded on the surface of catalyst before experiments [41–44]. Millar et al. [45] have reported that in the presence of water, alkali ions can form hydroxylic species. Therefore, it is unlikely that K could exist in a form of oxide state under the reducing conditions and in the presence of water [43]. The sharp diffraction peak of the reacted Ni/Al_2O_3 catalyst with the water injection rate of 0.2 g min^{-1} demonstrated that the crystallinity of NiO was largely increased more water injection. And the formation of NiO would respond for the decreasing of the activity of catalyst at higher steam flow, and lead to the lower hydrogen yield (as shown Fig. 2).

Temperature programme oxidation of catalysts related to different water injection rates

After each experiment with a different water injection rate, the reacted catalyst was analyzed by temperature programmed

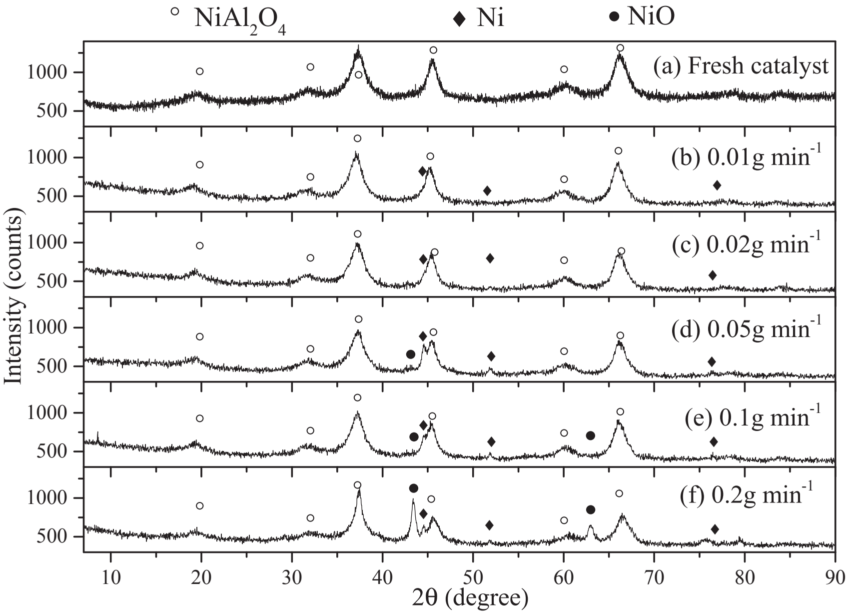


Fig. 3 – XRD spectra of the fresh and reacted catalysts: the influence of steam addition.

oxidation (TPO) (Fig. 4). The weight increase from 300 °C may be due to the oxidation of metallic Ni, since Ni crystal was observed from the XRD analysis (Fig. 3). When the water feeding rate was 0.02 or 0.05 g min^{-1}, higher mass increase was observed in the TPO analysis. This is consistent with that larger amount of Ni was observed on the reacted catalyst related to water feeding rate of 0.02 or 0.05 g min^{-1} (Fig. 3(c), (d)).

The mass decrease at about 500 °C was due to the combustion of deposited coke on the surface of the reacted catalyst. Since XRD results show that the diffraction of graphite carbons is not observed, amorphous carbon might be deposited on the reacted catalyst. Overall, the coke deposition on the reacted catalyst after catalytic thermochemical conversion of biomass was very small (less than 1 wt.% of the mass of catalyst). In relation to the hydrogen production and the availability of active Ni sites, 0.1 g min^{-1} water feeding rate was selected for the studies about the influence of K addition on hydrogen production and catalyst stability in this work.

Influence of K content on hydrogen production from pyrolysis catalytic reforming of biomass

Mass balance using biomass containing different amounts of K

As shown in Fig. 5, when 2.5% K was added into the cellulose sample, the yields of H_2 increased slightly from 27.7 to 28.5 (mmol g^{-1} cellulose), and CO yield increased from 10.6 to 12.4 (mmol g^{-1} cellulose), while the yield of CH_4 decreased from 5.2 to 3.2 (mmol g^{-1} cellulose). It seems that compared with untreated cellulose, adding a small amount of K promoted the production of hydrogen, carbon monoxide and the total gas. It has been reported that a small addition of alkali chlorides accelerated the release of small-molecule gases during biomass pyrolysis [28]. In addition, the addition of K might promote the reforming of hydrocarbons [24], which can contribute to the production of H_2 through reforming reactions. And similar phenomenon was found by Wang et al. [46,47], they studied the effect of alkali metal on the catalytic reforming of bio-oil.

With the increasing of K addition, the yield of hydrogen reduced. A minimum of total gas yield (~1.0 g g^{-1} cellulose) was obtained with the K addition of 5%. With the further increase of K addition to 15%, the total gas yield was slightly increased to 1.05 (g g^{-1} cellulose). Patwardhan et al. [22] studied the pyrolysis of cellulose with different amounts of K addition. It is reported that the increase of KCl addition to the cellulose sample showed a small influence on the production of low molecular hydrocarbons. Therefore, the addition of K to the cellulose sample may mainly affect the catalytic reforming reactions in the second stage, it not only affect the reforming of volatile, but the activity of catalysts.

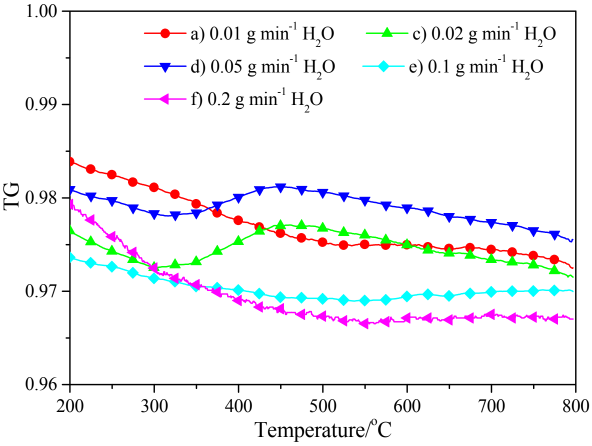


Fig. 4 – TGA results of the reacted catalysts with different water injection rates.

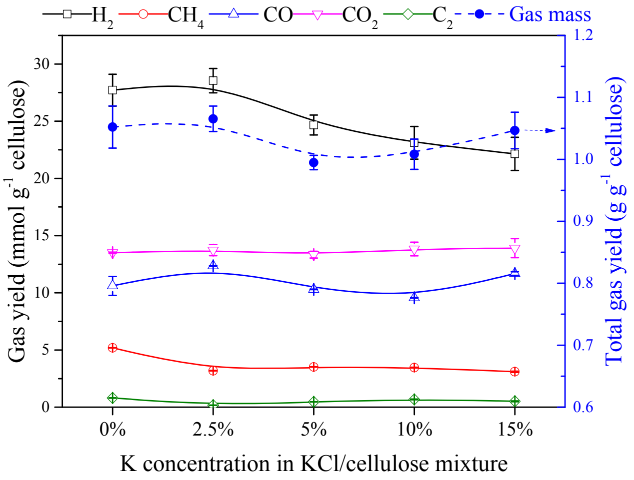


Fig. 5 – Influence of K concentration on gas productions.

As shown in Fig. 5, it is demonstrated that excessive amount of K suppressed the activity of Ni/Al_2O_3 for hydrogen production. It is suggested that the catalytic sites responsible for hydrogen production reactions such as water gas shift reaction were deactivated in the presence of excessive K. Further discussion can be seen in Section Analysis of the reacted catalysts from thermo-chemical conversion of cellulose with different amounts of K addition.

Analysis of the reacted catalysts from thermo-chemical conversion of cellulose with different amounts of K addition

The distribution of K deposited on the reacted catalyst had been determined by X-ray fluorescence. It is expected that more K vapor entered into the second reforming stage, when more K was loaded on the biomass sample. However, as shown in Table 2, it can be found that the potassium concentration attached on the surface of the reacted catalyst keeps constant at about 0.5 wt.% in relation to the weight of the reacted catalyst. It seems that the deposition of K on the surface of the reacted catalyst is corresponded to the available surface areas of the catalyst, instead of the amounts of K loaded in the cellulose sample. In addition, the XRD analysis to the reacted catalysts used with biomass samples containing different amount of K addition was carried out. The results (Fig. S1) show that the diffraction patterns are similar for the reacted catalysts used for different biomass samples, and that indicates the deposited K has the same effect on catalysts under different potassium introducing. Although the deposition of the K on catalyst surface was kept constant at about 0.5 wt.% of catalyst amount when the addition of K to cellulose were added in cellulose sample are variant. The ratio of

Table 2 – Mass balance of K and K deposition on the surface of the reacted catalyst: Influence of the amount of K addition.

K concentration in cellulose (wt. %)	K in solid char (%)	K released out (%)	K deposited on catalyst (%)	K concentration on used Ni/Al_2O_3 (wt. %)
15%	81.573	17.345	1.082	0.487
10%	82.169	16.098	1.733	0.520
5%	82.893	13.820	3.287	0.493
2.5%	82.324	10.809	6.867	0.515

residual K to the whole amount of feeding in system varies from 1.1 wt.% to 6.9 wt.%. That means the concentration of exhausted K changed from 10.9 wt.% to 5.1 wt.%, it is supposed that the spared K salts formed aerosol and weaken the contacted between volatile and catalysts when combined the data with and without Ni/Al_2O_3 catalyst. So it is the varied concentrations of exhausted K that caused the different resulting gas yields.

The influence of K addition on stability of catalyst

Mass balance of experiment with pure cellulose or 2.5 wt. % K/cellulose

In order to further understand the influence of K addition on catalytic performance during the thermo-chemical of biomass, the stability of catalyst was investigated by using the same catalyst for 5 times (during each cycle, fresh raw biomass material was used). Two raw samples include pure cellulose and 2.5% KCl/cellulose were used for catalyst stability test in terms of coke formation on the surface of reacted catalyst and hydrogen production.

As shown in Fig. 6(a), when the reacted catalyst was reused, the yields of H_2 and CO clearly decreased from 28.55 to 22.25 (mmol g^{-1} cellulose) and from 12.36 to 8.78 (mmol g^{-1} cellulose), respectively. While the production of CO_2 increased from 13.7 to 17.9 (mmol g^{-1} cellulose), and the yields of light hydrocarbons such as CH_4 increased from 3.19 to 3.89 (mmol g^{-1} cellulose) and C_2 yield increased from 0.18 to 0.31 (mmol g^{-1} cellulose) after the Ni/Al_2O_3 was used for thermo-chemical of K/cellulose sample for 5 times. In contrast, gas productions from thermo-chemical conversion of pure cellulose increased slightly when the catalyst was used for 5 times. For example, the total gas yield increased from 1.05 to 1.44 (mmol g^{-1} cellulose) after 5 times recycle of catalyst (Fig. 6(b)). This was due to that more Ni could be generated by the reduction of NiO after the catalyst was reused under the reducing experimental environment. The comparison between Fig. 6(a) and (b) showed clear differences in terms of gas productions, indicating that the presence of K in biomass sample has obvious negative effect on hydrogen production. Catalyst deactivation is resulted from coke deposition, metal sintering [48,49] might be responsible for the lower hydrogen and gas production when K was introduced in the biomass sample.

Analysis of the reacted catalysts used for 5 times for catalytic thermo-chemical conversion of biomass

In this section, further analysis to the reacted catalysts was carried out to explain the effect of K on catalyst deactivation during the pyrolysis catalytic steam reforming of cellulose. XRD analysis of the reused catalysts was shown in Fig. 7. It is suggested that with the increase of the reuse of the Ni/Al_2O_3, more Ni species were produced. In addition, the diffraction peak of Ni phase becomes sharper with the increase of the reusing cycle of the catalyst, indicating that metal sintering happened after each cycle of experiment. Therefore, metal sintering might be responsible for the reduction of hydrogen production when the catalyst was reused for 5 time for the K-added cellulose sample. However, similar diffraction pattern was observed for the reacted catalyst used for 5 times using the pure cellulose sample (Fig. 7(a)), compared with the reacted catalyst using the 2.5% K/cellulose sample (Fig. 7(f)). Since the hydrogen production was not reduced when the Ni/Al_2O_3

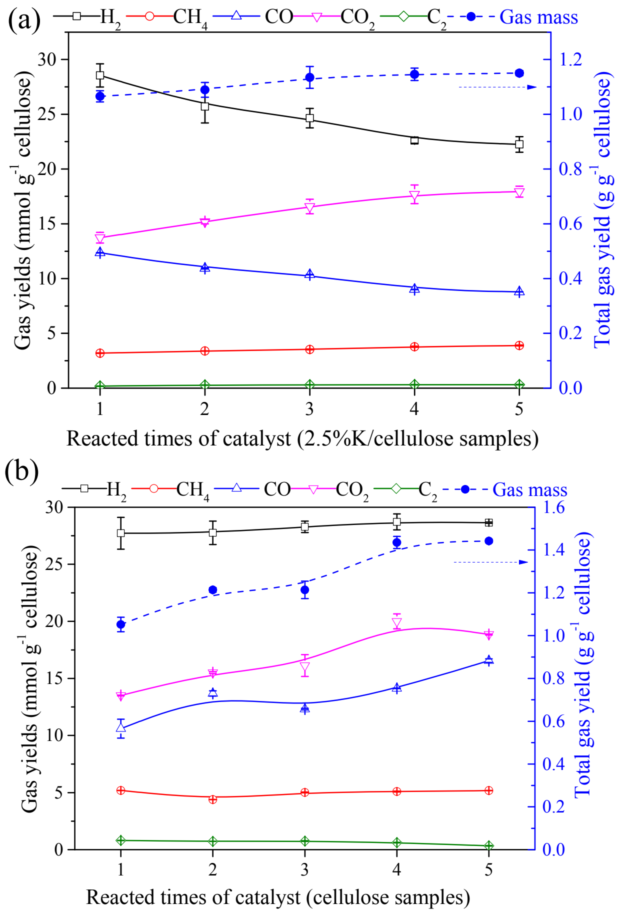


Fig. 6 – (a) Gas productions from 2.5% K/cellulose sample for the life time tests. (b) Gas productions from pure cellulose for the life time tests.

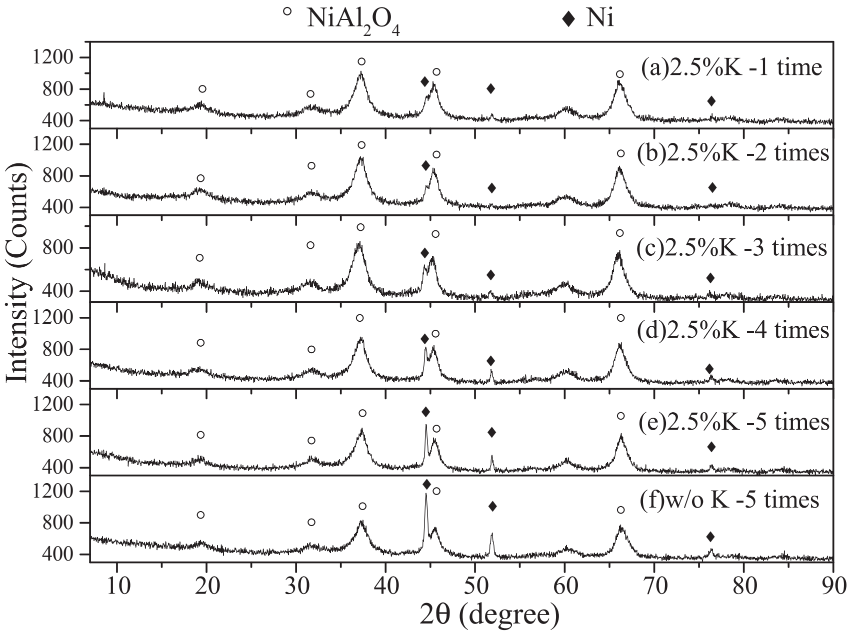


Fig. 7 – XRD spectra of the reacted catalysts from life time tests.

was reused 5 times for the pure cellulose sample, there might be other factors other than metal sintering contributing to the catalyst deactivation during the stability tests of thermochemical conversion of biomass.

TPO-FTIR analysis were carried out to the reacted catalysts resulted from the stability tests, and the results were shown in Fig. 8. There were two stages of carbon oxidation including a lower temperature region (~400 °C) for the oxidation of amorphous carbon and a higher temperature region (~700 °C) for the oxidation of graphite carbons (e.g. filamentous carbons).

From Fig. 8(b), it seems that the release of CO_2 at higher temperature (~700 °C) was enhanced for the reacted catalyst used 5 times with the pure cellulose sample, compared with the 2.5% K/cellulose sample. The fraction of amorphous carbons deposited on the surface of the reacted catalyst seems

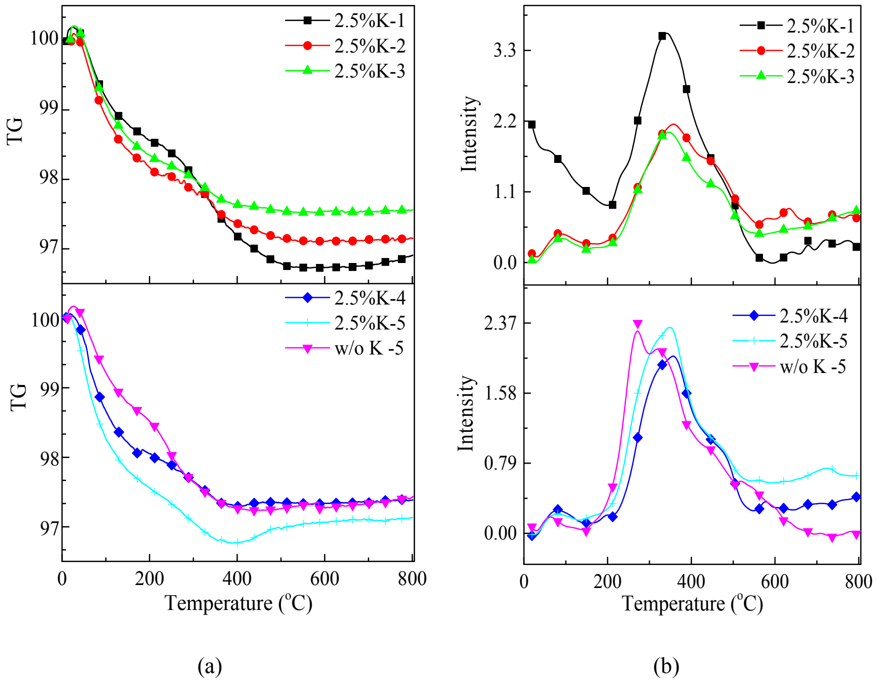


Fig. 8 – TPO-FTIR analysis of the reacted catalysts from life time tests and cellulose only sample: (a) TGA-TPO result; (b) CO_2 signals from the FTIR analysis.

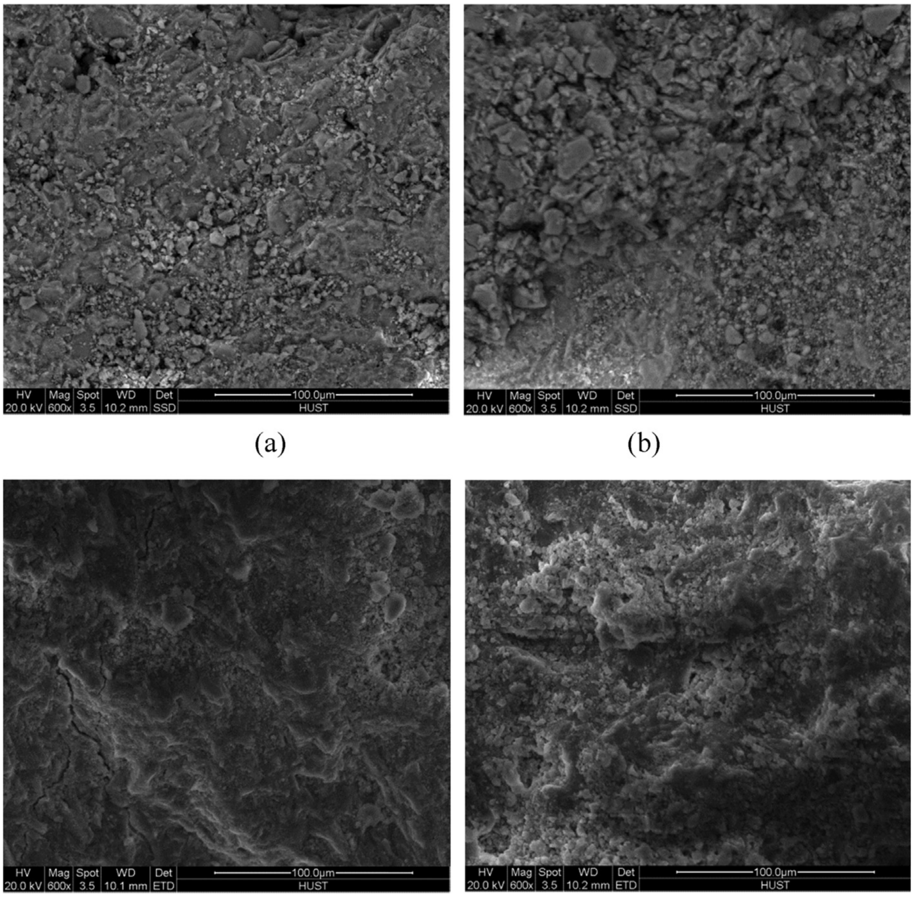
Table 3 – K deposition on the reacted catalyst: Influence of life time of catalyst.

Life time of catalyst	K concentration on used Ni/Al_2O_3 (wt. %)
5 times	2.725
4 times	1.655
3 times	1.225
2 times	1.045
1 time	0.515

slightly higher for the 2.5% K/cellulose sample compared with the pure cellulose sample. Amorphous carbons are known to encapsulate catalytic sites, and thus to reduce hydrogen production [50]. Zheng et, al. [49] reported that the carbon morphology influenced the Ni/ZrO_2 catalyst stability significantly. In addition, from Fig. 8(a), it seems that slightly higher coke deposition is observed for the reacted catalyst using 2.5% K/cellulose sample compared with the pure cellulose sample; this might result in the deactivation of catalyst in relation to a lower hydrogen production when the catalyst was reused 5 times using 2.5% K/cellulose sample.

In this work, in addition to the investigations of metal sintering and coke deposition on the surface of the reacted catalysts, the effect of K poisoning was also investigated by determining the K deposition on the reacted catalyst after each cycle of experiment. As shown in Table 3, the deposition of K was increased from 0.515 to 2.725 wt.% when the catalyst was reused for five times. The increased K deposition is suggested to result in the reduction of hydrogen production (Fig. 6(a)) from the thermo-chemical conversion of 2.5% K/cellulose during the life time test. The relation between the K deposition on the surface of the reacted catalyst and the production of hydrogen was plotted and shown in Fig. S2 (supporting information). Almost linear negative relationship is observed between the increase of the amount of K deposition on the reacted catalyst and the reduce of hydrogen production. Therefore, the poisoning effect of K on the catalyst was suggested to influence the catalyst performance significantly. However, future works about the analysis of chemical and physical properties (e.g. X-ray photoelectron spectroscopy and pore volume analysis) are required to fundamentally understand the K poisoning effect.

SEM analysis to the reused catalysts was carried out, and the results are shown in Fig. 9. It seems that agglomeration was happened on the surface of the reused catalysts, by comparing the catalyst used 5 times (Fig. 9(c)) with the fresh catalyst (Fig. 9(a)). The SEM results for the catalysts used five times are similar using two biomass samples with or without the addition of K.



(a) (b)

(c) (d)

Fig. 9 – SEM results of the catalysts: (a) fresh Ni/Al_2O_3; (b) reacted Ni/Al_2O_3 for two times with 2.5% K/cellulose; (c) reacted Ni/Al_2O_3 for five times with 2.5% K/cellulose; (d) reacted Ni/Al_2O_3 for five times with pure cellulose.

Conclusions

In this work, the influence of volatile potassium derived from the pyrolysis of cellulose biomass sample was investigated in terms of hydrogen production from catalytic thermochemical conversion in the presence of a Ni/Al_2O_3 catalyst. The following conclusions are obtained:

1) Lower water injection (<0.05 ml min^{-1}) rates may cause more carbon deposition, but too much more steam (>0.1 ml min^{-1}) might oxidized active Ni to NiO, and weaken the catalytic performance of catalysts, water feeding rate between 0.05 and 0.1 ml min^{-1} was optimal to maximize the hydrogen production.
2) Higher K amount is not good for biomass gasification for H_2 forming, but the deposition amount of potassium on catalyst has no relationship with the amounts of K loaded in the cellulose sample.
3) K addition influences the catalytic activity of Ni/Al_2O_3 during the lifetime test. H_2 yield kept stable for cellulose catalytic steam gasification with Ni/Al_2O_3 reused for 5 times, but it decreased gradually with K added.
4) The deposition of K on catalyst was increased significantly with cycle number increasing, and more filamentous carbon formed on the surface of 5 times used catalyst with K adding.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.ijhydene.2016.04.207.

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