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Catalytic steam reforming of biomass-derived tar for hydrogen production with $K_2CO_3/NiO/\gamma$-Al_2O_3 catalyst

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Abstract−A major problem of using Ni-based catalysts is deactivation during catalytic cracking and reforming, lowering catalytic performance of the catalysts. Modification of catalyst with alkali-loading was expected to help reduce coke formation, which is a cause of the deactivation. This paper investigated the effects of alkali-loading to alumina-supported Ni catalyst on catalytic performance in steam reforming of biomass-derived tar. Rice husk and K_2CO_3 were employed as the biomass feedstock and the alkali, respectively. The catalysts were prepared by a wet impregnation method with γ-Al_2O_3 as a support. A drop-tube fixed bed reactor was used to produce tar from biomass in a pyrolysis zone incorporated with a steam reforming zone. The result indicated that $K_2CO_3/NiO/\gamma$-Al_2O_3 is more efficient for steam reforming of tar released from rice husk than NiO/γ-Al_2O_3 in terms of carbon conversion and particularly hydrogen production. Effects of reaction temperature and steam concentration were examined. The optimum temperature was found to be approximately 1,073 K. An increase in steam concentration contributed to more tar reduction. In addition, the K_2CO_3-promoted NiO/γ-Al_2O_3 was found to have superior stability due to lower catalyst deactivation.

Key words: Biomass Gasification, Tar Reforming, Alkali Metal, Ni-catalyst, K_2CO_3

INTRODUCTION

Due to the worldwide concern about the depletion of fossil fuels and environmental problems associated with the use of these sources, renewable energy sources are getting increased attention. Biomass is considered as a potential source of renewable energy. Different conversion processes offer production of heat, electricity and synthetic fuels from biomass feedstock. Gasification is one of the promising processes in terms of conversion efficiency and lower environmental impacts [1]. Gaseous product of the gasification can be used directly as a clean fuel or a feedstock for other fine-chemical manufacturing such as methanol synthesis. Nowadays, there is an increasing interest in hydrogen fuel because it is a clean fuel for future and creates almost no pollution [2]. In addition, growth in fuel cell technology points out how important hydrogen production is in the future. Renewable lignocellulosic biomass can be used as an alternative feedstock for hydrogen production. Two technologies that have been explored are steam gasification and catalytic steam reforming of pyrolysis oil. The gasification of biomass typically encounters one major problem of tar formation [3-5]. Tar is undesirable because of various problems associated with condensation, formation of tar aerosols and polymerization to form more complex structures, which cause problems in process equipments as well as engines and turbines used in application of producer gas [6]. Catalytic steam reforming of biomass-derived tar is attractive because it can not only remedy the tar problem but also increase the hydrogen yield [7,8].

Several Ni-based catalysts have been found to be very effective in terms of tar reforming and tar elimination [9-12]. The major problem in using Ni-based catalysts is the deactivation due to coke formation. This coke is caused by dehydrogenation of some hydrocarbon derivatives in the tar product. Addition of alkali or alkaline-earth metal oxide has been reported to be able to suppress the coke deposition on Ni-catalysts [13,14]. A number of researches have been devoted to the studies of catalytic effect on steam reforming of tar-model compounds, e.g., toluene and naphthalene [6,15-20]. There have been few works using real tar from biomass. Therefore, this paper was to study the catalytic effect on steam-reforming of real tar derived from fast pyrolysis of biomass using a drop-tube fixed-bed reactor. Rice husk was chosen to represent biomass feedstocks. Ni-catalysts were prepared using a wet impregnation method with γ-Al_2O_3 as a support. The advantage of K_2CO_3 addition onto NiO/γ-Al_2O_3 was investigated in terms of improvement in gas composition, in particular hydrogen yield, and catalyst lifetime [29,30]. In addition, temperature and steam concentration were also varied to perceive their influences on gas composition and tar conversion.

EXPERIMENTAL SECTION

1. Materials and Catalysts Preparation

Rice husk obtained from the National Corn and Sorghum Research Center, Thailand, was used as a biomass raw material. The sample was sized in range 150 and 250 μm, dried at 383 K for 24 hours, and then stored in desiccators. Table 1 summarizes proximate and ultimate analyses of the rice husk.

The catalysts used in this investigation are K_2CO_3/γ-Al_2O_3, NiO/γ-

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Table 1. Proximate and ultimate analyses of rice husk

Proximate (%, as received)	
Moisture	9.02
Volatile matter	51.57
Fixed carbon	15.86
Ash	23.55
Ultimate (%, dry and ash free)	
Carbon	41.66
Hydrogen	5.93
Nitrogen	0.88
Oxygen*	51.53

*By difference

Al_2O_3, and $K_2CO_3/NiO/\gamma\text{-}Al_2O_3$. The $K_2CO_3/NiO/\gamma\text{-}Al_2O_3$ catalyst (Ni =9 wt%, K=9 wt%) was prepared by the wet impregnation method. The $\gamma\text{-}Al_2O_3$ particles, average diameter of 150 μm in size, were immersed in an aqueous solution of Nickel(II)nitrate hexahydrate, $Ni(NO_3)\cdot 6H_2O$, followed by drying. Consequently, the prepared catalyst was calcined at 873 K for 2 hours. A specific amount of potassium was then impregnated using the same procedure with an aqueous solution of potassium carbonate, K_2CO_3, followed by drying and further calcining at 573 K for 1 hour.

2. Drop-tube Fixed Bed Reaction

The experiments to examine the catalytic effect were carried out in a drop-tube fixed bed reactor. The schematic diagram of the experimental apparatus is illustrated in Fig. 1. The catalyst of 1.7 g, approximately 1 cm in height, was placed as a fixed-bed section in the outer tube (diameter of 25 mm). Biomass sample was introduced by dropping into the inner tube (diameter of 11 mm), in which quartz wool was packed for gas/solid separation at its lower end. The rice husk, approximately 120 mg, was placed and held in a tubular sample holder, which was connected to the top end of the inner tube. Atmospheric N_2 was supplied into the inner tube at 30 ml/min while N_2 mixed with H_2O (steam) 50%v/v was fed into the outer tube at 120 ml/min. After a steady temperature of the reactor was attained, the sample was dropped onto the quartz wool bed (inner tube) and underwent fast pyrolysis under N_2 atmosphere. Volatiles were immediately forced by the carrier gas to be swept away from the solid residue and flew through the catalyst bed (outer tube) where steam reforming took place. Temperatures of the reactor both pyrolysis and reforming zones were consistently the same and kept at 1,073 K throughout all experiments with different catalysts. In case of the parametric studies, temperature was varied from 873 K to 1,173 K and steam concentration was altered from 50% to 70%v/v.

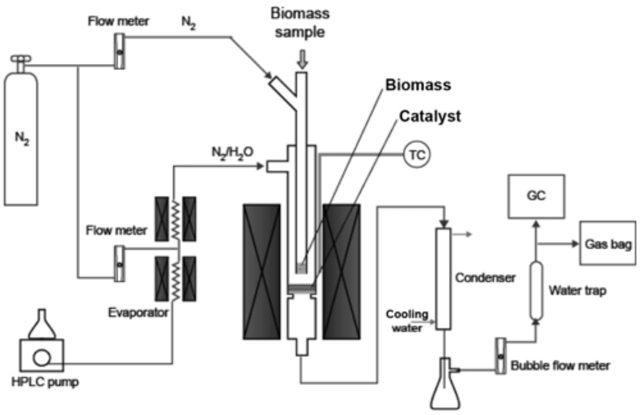


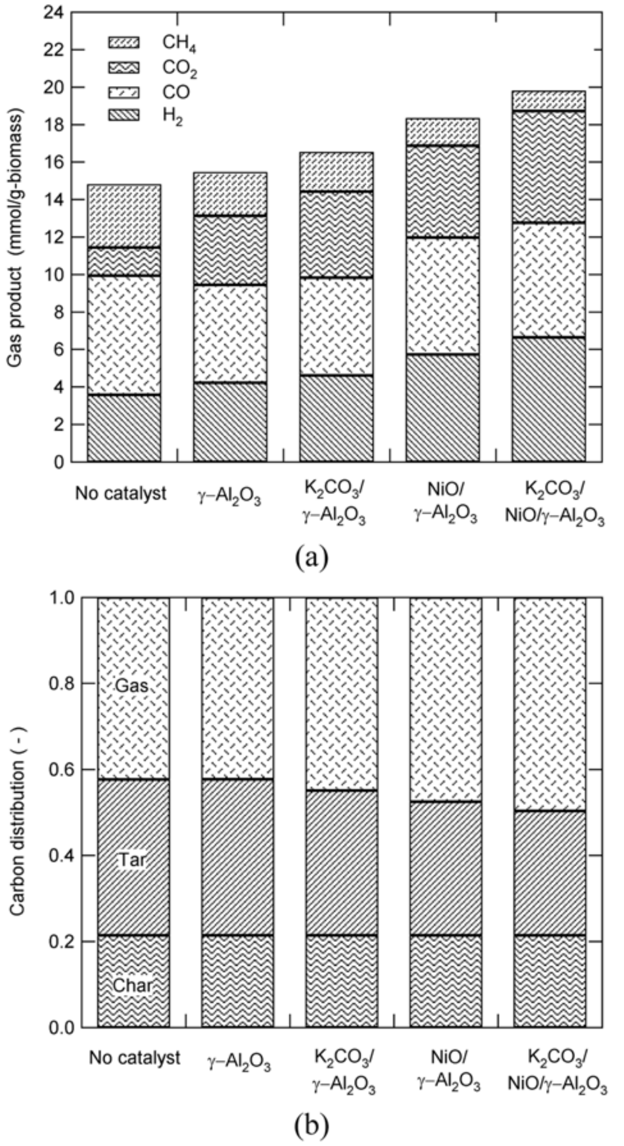
Fig. 1. Experimental apparatus.

In each experiment, vapor product from the reactor was cooled by a double-pipe condenser. Liquid product and tar were separated from the effluent in an ice trap. After water was eliminated by a silica-gel filter, gas was collected in gas-sampling bags and analyzed by micro gas chromatography (Agilent 3000A). The composition of gaseous products was determined, consisting of hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), and methane (CH_4). The flow rate of outlet gas was assumed to be equivalent to inlet carrier gas since the amount of gas produced from biomass sample was negligible. Consequently, the gas yield can be determined from total gas collected and gas composition. The amount of solid residue after the reaction was weighted after drying overnight and subjected to the CHN analyzer. Quantitative measurement of tar is difficult due to the very low amount of tar produced in this reactor system. The amount of tar was represented by the carbon conversion to tar, which was calculated from carbon balance explained later. Additionally, the CHN analyzer was used to determine carbon content of used catalysts, indicating the amount of carbon deposition.

RESULTS AND DISCUSSION

1. Catalytic Performance of Various Catalysts

The prepared catalysts, including $K_2CO_3/\gamma\text{-}Al_2O_3$, $NiO/\gamma\text{-}Al_2O_3$, and $K_2CO_3/NiO/\gamma\text{-}Al_2O_3$, were tested at 1,073 K with steam concentration of 50%v/v. The catalytic effects on steam reforming of tar from rice husk were explored by means of comparing results to that obtained from no-catalyst condition. The results with support, $\gamma\text{-}Al_2O_3$, were also taken into consideration to ensure the catalytic effects resulted from the loading metals. Fig. 2 shows the catalytic performance of various catalysts in terms of gas products and carbon conversion from steam reforming of tar. It is noted that char was isolated from the reforming reaction section. Thus the carbon conversion to char did not change unless the reaction temperature was changed. Carbon conversion to tar was determined by subtraction of carbon in gas and carbon in char from the total carbon in the rice husk. As can be seen, the total gas productivity increased and the carbon conversion to tar decreased when catalysts were presented in the outer-tube bed. Even the $\gamma\text{-}Al_2O_3$ alone was also observed to give a slight increase in the total gas yield and a noticeable change in gas composition. The reason might be that $\gamma\text{-}Al_2O_3$ is porous and has high surface area, resulting in some expected catalytic behavior of such a kind of support. However, it was likely not an active catalyst for reforming of tar because the carbon conversion to tar was found to be comparable to that obtained in no catalyst condition. The presence of either K_2CO_3 or NiO was observed to ameliorate steam reforming of tar, leading to higher gas production and lower conversion to tar. The result also emphasized superior performance of NiO over K_2CO_3. From the comparison between $NiO/\gamma\text{-}Al_2O_3$ and $\gamma\text{-}Al_2O_3$, the tar yield obviously decreased while total gas yield increased, in particular H_2, CO, and CO_2. On the contrary, CH_4 became lower. This showed that NiO effectively catalyzes steam reforming of hydrocarbon (tar) to produce light-gaseous



(a)

(b)

Fig. 2. Performance of various catalysts in steam reforming of rice husk-derived tar with respect to (a) gas production and (b) carbon conversion (reaction temperature of 1,073 K and steam of 50%v/v).

compounds. On the other hand, K_2CO_3 performed as a less active catalyst for steam reforming of tar when it was loaded onto the γ-Al_2O_3 support. This is attributable to conceivable formation of some stable phases between K_2CO_3 and alumina. Addition of K_2CO_3 was incentive when it was loaded to the NiO/γ-Al_2O_3, since further improvement was observed in terms of both total gas production and tar conversion. The greater amount of H_2 and CO_2 in this case compared with that in the case of NiO/γ-Al_2O_3 is ascribed to the water-gas shift reaction efficiently enhanced by K_2CO_3. The finding figures out the beneficial interaction between NiO and K_2CO_3. The possible mechanism of NiO and K_2CO_3 involving in steam reforming of hydrocarbon is listed as follows [21,22].

$$xNiO+C_xH_y\rightarrow xCO+\frac{y}{2}H_2+xNi \tag{1}$$

Table 2. Carbon deposition on used catalysts

Catalysts	Carbon deposition (wt%, dry basis)
γ-Al_2O_3	2.31
K_2CO_3/γ-Al_2O_3	1.82
NiO/γ-Al_2O_3	3.74
K_2CO_3/NiO/γ-Al_2O_3	0.50

$$xNi+C_xH_y\rightarrow x(Ni\cdots C)+yH \tag{2}$$

(Ni···C: surface active C species)

$$Ni+H_2O\rightarrow Ni^{\delta+}\cdots O^{\delta-}+2H \tag{3}$$

($Ni^{\delta+}\cdots O^{\delta-}$: surface mobile oxygen species)

$$H+H\rightarrow H_2 \tag{4}$$

$$Ni\cdots C+H_2O\rightarrow Ni+CO+H_2 \tag{5}$$

$$Ni\cdots C+K_2CO_3\rightarrow Ni^{\delta+}\cdots O^{\delta-}+2K+2CO \tag{6}$$

$$Ni\cdots C+Ni^{\delta+}\cdots O^{\delta-}\rightarrow 2Ni+CO \tag{7}$$

$$2K+2H_2O\rightarrow 2KOH+H_2 \tag{8}$$

$$CO+H_2O\rightarrow CO_2+H_2 \tag{9}$$

$$2KOH+CO_2\rightarrow K_2CO_3+H_2O \tag{10}$$

A number of previous studies reported about catalytic effects of K_2CO_3 on gasification of char or carbon. The presence of NiO on γ-Al_2O_3 prospectively induced the formation of more carbon in forms of coke in comparison with γ-Al_2O_3 alone. Such carbon or coke would be active carbon species which are promptly reacted with K_2CO_3 to produce more gas product. Table 2 shows amount of carbon deposition on used catalysts. It is clear that the presence of K_2CO_3 significantly decreased the carbon deposition on the catalysts. This could explain why K_2CO_3/NiO/γ-Al_2O_3 gave admirable performance in catalytic reforming of tar as well as hydrogen production. Compared to the condition with no catalyst, the tar was reduced from 36.2% to 28.9% (carbon-based conversion) and hydrogen was increased from 24.1% to 33.5%v/v. Such an improvement was observed even using a small amount of catalyst with considerably short contacting time. Therefore, the K_2CO_3/NiO/γ-Al_2O_3 is considered as an effective catalyst in hydrogen production from biomass gasification.

2. Influence of Reaction Temperature

Reaction temperature is commonly a major parameter that could substantially affect reforming reaction as well as thermal decomposition. The temperature plays more influential roles in a catalytic system. The effect of temperature on steam reforming with the K_2CO_3/NiO/γ-Al_2O_3 catalyst was investigated at constant steam concentration of 50%v/v. Fig. 3 shows gas yields and carbon-based yields at different temperatures from 873 K to 1,173 K. With increasing temperature, the yield of H_2, CO and CO_2 increased while that of CH_4 decreased. The decrease in char and tar, in other words, more conversion to gas, was observed at elevated temperature. This emphasized that decomposition of biomass and reforming of tar are endothermic and accordingly favor high operating temperature [23,24].

$$\text{Fuel (biomass)}\rightarrow Char+H_2+CO+CO_2+\cdots+Tars \quad \Delta H>0 \tag{11}$$

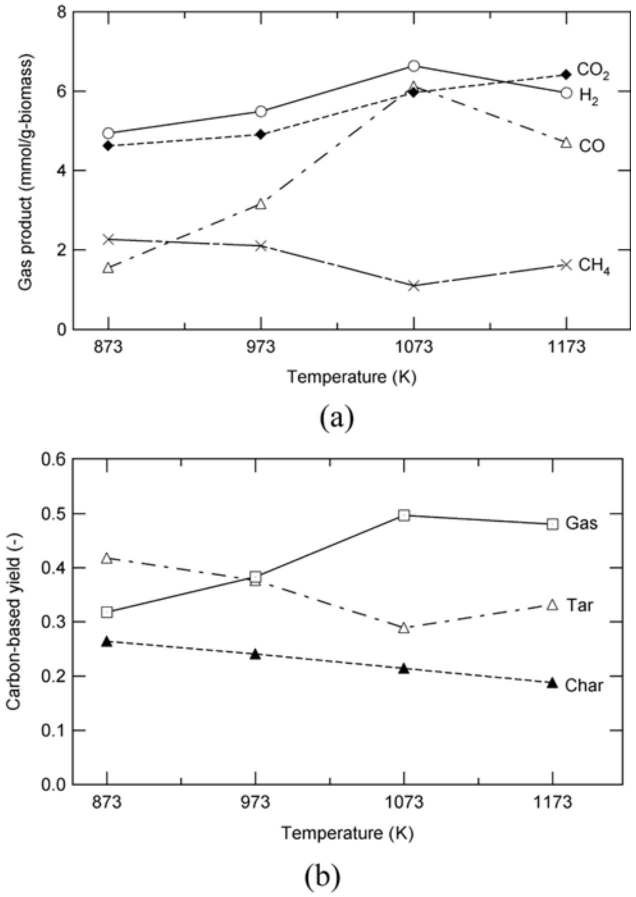


Fig. 3. Effect of reaction temperature on (a) gas production and (b) carbon conversion using $K_2CO_3/NiO/\gamma\text{-}Al_2O_3$ (steam of 50%v/v).

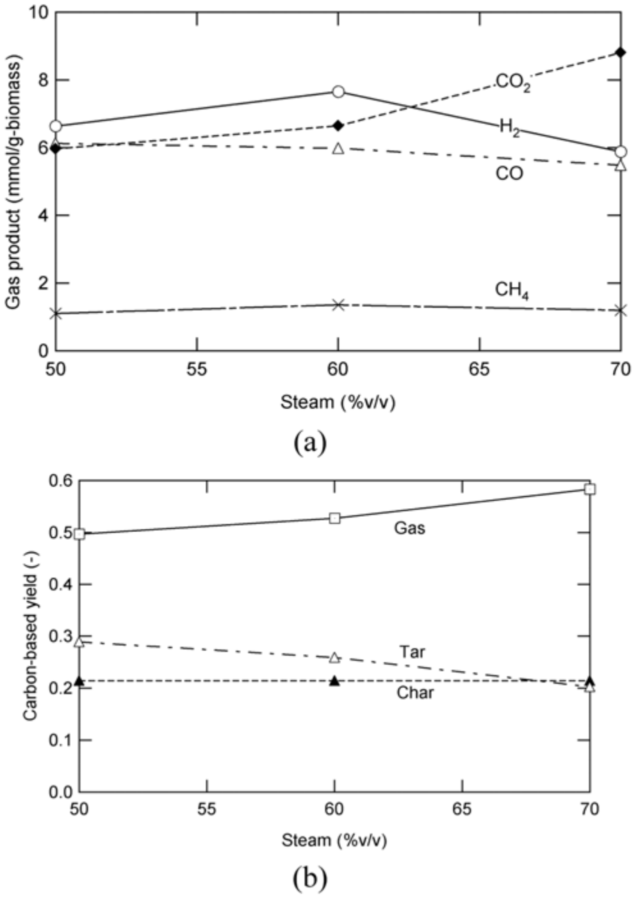


Fig. 5. Effect of steam concentration on (a) gas production and (b) carbon conversion using $K_2CO_3/NiO/\gamma\text{-}Al_2O_3$ (reaction temperature of 1,073 K).

$$C_nH_m + nH_2O \rightarrow nCO + \left(n + \frac{1}{2}m\right)H_2 \qquad \Delta H>0 \quad (12)$$

However, most gas yield showed opposite trends and tar conversion was dropped when the temperature rose beyond 1,073 K to 1,173 K. This is attributable to the inevitable deactivation of catalyst by thermal sintering at such a high temperature [25]. Fig. 4 shows SEM images of the surface of fresh $K_2CO_3/NiO/\gamma\text{-}Al_2O_3$ and used catalysts at different temperatures, 1,073 K and 1,173 K. It was observed that the surface of spent catalyst differed from the fresh one. Using the catalyst at 1,173 K obviously gave a substantial change on the surface in comparison with that at 1,073 K. This would be evidence of the extensive deactivation undergone due to significant sintering and densification of the Ni structure.

3. Influence of the Steam Concentration

The effect of steam concentration on catalytic performance was examined in the same manner as in the previous section. The steam concentration was varied, 50%v/v, 60%v/v and 70%v/v, by adjusting the flow rate. The reaction temperature was kept at 1,073 K for all experiments. Results of gas production and carbon conversion versus steam concentration are shown in Fig. 5. It was observed

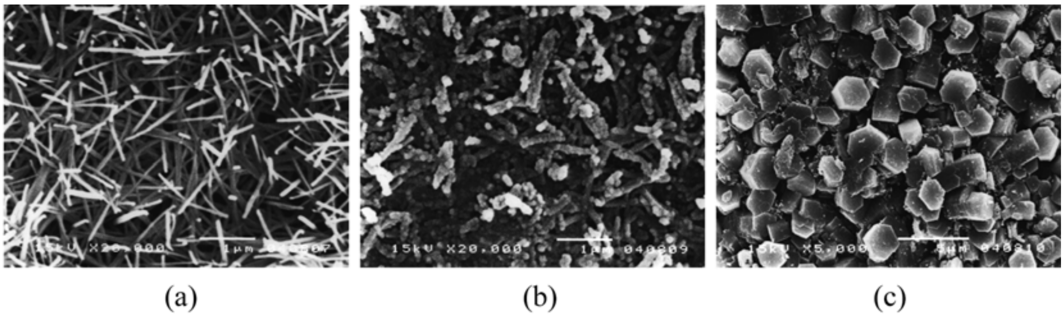
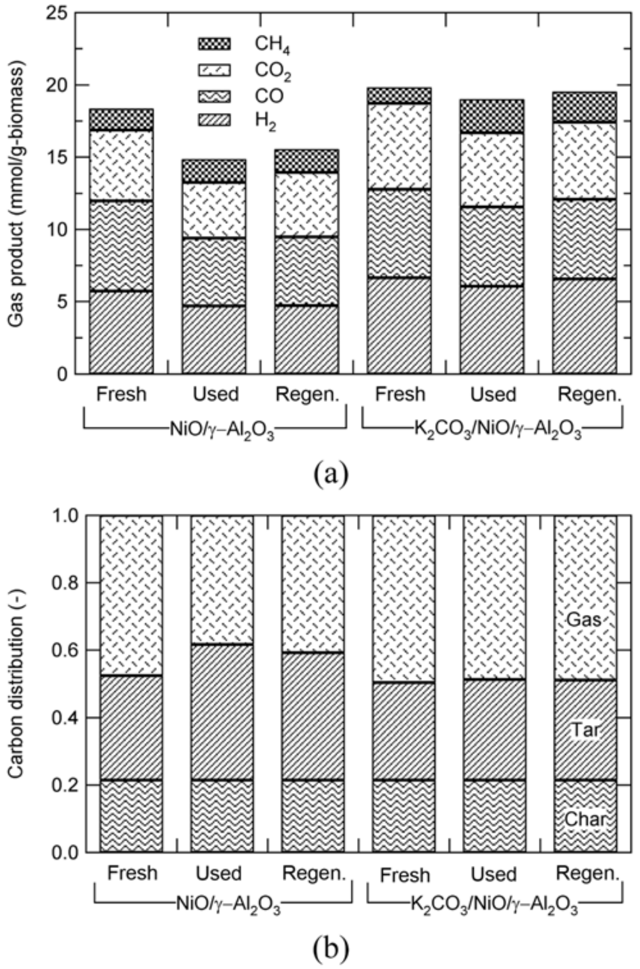


Fig. 4. SEM micrographs of the surface of (a) the fresh $K_2CO_3/NiO/\gamma\text{-}Al_2O_3$ (b) the used $K_2CO_3/NiO/\gamma\text{-}Al_2O_3$ at 1,073 K and (c) the used $K_2CO_3/NiO/\gamma\text{-}Al_2O_3$ at 1,173 K.



(a)

(b)

Fig. 6. Comparison of catalytic stability with respect to (a) gas production and (b) carbon conversion (reaction temperature of 1,073 K and steam of 50%v/v).

that H_2 and CO_2 increased while CO decreased with increasing the concentration from 50%v/v to 60%v/v. CO_2 increased gradually and CO continuously decreased at higher steam concentration. The reduction of tar was obviously enhanced by higher steam concentration. However, a continuous increase in steam concentration unexpectedly diminished the hydrogen yield. This observation is consistent with that reported in the literature [26,27]. In this case, the similar reason could be considered to explain the influence of steam concentration. For a specific value of steam concentration, the reactions involving with H_2 production could attain equilibrium condition and consequently H_2 product reached its maximum. Despite the improvement of tar reduction, the significant drop in H_2 yield makes the excess addition of steam unsuitable in the present experimental condition over the $K_2CO_3/NiO/\gamma\text{-}Al_2O_3$.

4. Catalytic Stability

Once the superior performance of $K_2CO_3/NiO/\gamma\text{-}Al_2O_3$ to $NiO/\gamma\text{-}Al_2O_3$ was proven, its stability was also investigated by means of comparison between results using fresh catalyst and that using spent or used catalyst. Moreover, the used catalyst was calcined with air at 1,073 K for the purpose of regenerating the deactivated catalyst due to possible coke deposition. Fig. 6 illustrates catalytic stability of and $NiO/\gamma\text{-}Al_2O_3$ and $K_2CO_3/NiO/\gamma\text{-}Al_2O_3$ in terms of gas production and carbon conversion. In case of $K_2CO_3/NiO/\gamma\text{-}Al_2O_3$, slight differences of total gas production and carbon conversion to tar were obtained compared between the used and fresh catalysts. On the contrary, a drop in gas production and an increase in carbon in tar were obviously given in case of indicated $NiO/\gamma\text{-}Al_2O_3$. It is clear that $K_2CO_3/NiO/\gamma\text{-}Al_2O_3$ preserved its catalytic performance. Deactivation of catalysts could be due, in this case, to two reasons: carbon deposition (mainly from tar) and thermal sintering. The carbon deposited on catalysts can be eliminated by simple combustion with air. As can be seen, the regenerated catalyst did not show any significantly recovered performance. Moreover, at a relatively high temperature the carbon deposited on the surface of Ni-catalysts is easier to remove through reacting with steam [28]. Therefore, the deactivation is caused by the sintering of Ni particles. This indicated that the presence of K_2CO_3 served as a good promoter that can suppress thermal sintering of Ni-catalysts.

CONCLUSIONS

The presence of potassium to NiO/Al_2O_3 catalysts was found to improve the steam reforming of tar and hydrogen production associated with the water-gas shift reaction. An operation temperature not higher than 1,073 K was preferable in terms of catalytic performance of $K_2CO_3/NiO/\gamma\text{-}Al_2O_3$. An observation of terrible sintering at relatively high temperature, i.e., 1,173 K, results in a substantial drop in the catalytic activity. An increase in steam concentration enhances tar reforming. The excess in steam beyond 50%v/v reduces hydrogen production. The K_2CO_3 promoted Ni-catalyst, in this case $K_2CO_3/NiO/\gamma\text{-}Al_2O_3$, shows a superior performance compared to $NiO/\gamma\text{-}Al_2O_3$. The addition of K_2CO_3 could lessen the thermal sintering of Ni-catalyst.

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