Research Article

Preliminary Assessment of Oxidation Pretreated Hastelloy as Hydrocarbon Steam Reforming Catalyst

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The potential of oxidation pretreated Hastelloy tube as a hydrocarbon steam reforming catalyst was assessed using tetradecane, toluene, and naphthalene as model compounds. Surface characterization showed that Fe_2O_3, Cr_2O_3, MoO_3, and NiO were formed on the surface of the alloy after oxidation at $1000°C$ for 2 hours. Catalytic evaluation showed good activity and stability with tetradecane while lower activity with increased rate of carbon formation was observed with naphthalene.

1. Introduction

The increase in energy demand coupled with the continuous decrease in supply of fossil derived fuels resulted in a series of energy price increases and threatened the energy security of several non-oil producing countries. In addition, pollutants produced from fossil fuel utilization were identified to contribute to global warming. One of the proposed solutions for these problems is using biomass as an alternative source of energy.

Hydrogen, when combined with oxygen, can be a source of electricity and heat. Through thermal gasification, biomass is converted into H_2, CO, CO_2, steam, and hydrocarbons (including tar). Gasification is usually followed by catalytic reforming of these hydrocarbons to optimize the utilization of biomass. Catalytic steam reforming (1), an endothermic reaction, is widely applied in the industrial production of hydrogen. To produce more H_2, CO produced from the reforming step is utilized and converted to additional H_2 through water-gas shift (WGS) reaction (2) to increase the yield of H_2. If intended for fuel cell application, methanation (3) is normally done to adjust the CO content of the gas depending on the fuel cell requirement. Consider

$$C_nH_m + nH_2O \longrightarrow nCO + (n + 0.5\,m)\,H_2 \quad \Delta H > 0 \quad (1)$$

$$CO + H_2O \longleftrightarrow CO_2 + H_2 \quad \Delta H° = -44\,kJ/mol \quad (2)$$

$$CO + 3H_2 \longleftrightarrow CH_4 + H_2O \quad \Delta H° = -201\,kJ/mol \quad (3)$$
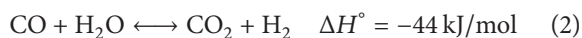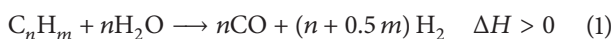
This process will convert the hydrocarbon into a gas mixture composed of CO, CO_2, CH_4, and H_2. For simple hydrocarbons, tetradecane is often used as a model compound while toluene and naphthalene are used as aromatic hydrocarbon model compounds [1–3]. As for the mechanism involved, Rostrup Nielsen proposed that the hydrocarbon molecules are adsorbed on the surface of the catalyst, its terminal carbon selectively attacked by successive α-scissions generating C_1 species. These C_1 species can then react with O_2 coming from steam or stay adsorbed on the active site and be transformed to other products [4]. If the relative rates of C_1 species generation and carbon oxidation are not balanced, carbon deposition occurs [5].

At present, supported nickel catalysts are favored over the expensive and rare noble-based catalysts for hydrocarbon steam reforming. However, supported nickel catalysts are easily deactivated by carbon accumulation that can block the catalyst active sites, disintegrate catalyst particles, and plug the reactor [6, 7]. To produce a nickel-based catalyst that prevents carbon formation and/or deposition, several support materials, different dopants for the support material [8–10], preparation techniques [11, 12], and metal combinations [13] were investigated to produce an efficient, rigid, and economically feasible steam reforming catalyst.

Our previous works showed the effectiveness of Ni-based catalysts with proper additives and supports on dry reforming [14–16] and partial oxidation [17, 18]. In order to prevent carbon deposition, a strong interaction between Ni

and support oxides is required. We have proposed oxidation treatment of Ni-containing alloys in order to produce well dispersed and strongly interacted nickel particles with adjacent oxide lattice. A preliminary study on the oxidation of Ni-containing SUS304 alloy showed the development of steam reforming activity with oxidation pretreatment [19]. The application of commercially available Ni-containing alloy tubes was proposed for small on-site reforming reactors that could be used for biomass gasification. Screening tests done on several Ni-containing alloys revealed that oxidation pretreatment resulted in the formation of mixed metal oxides which consequently enhanced the catalytic activity of the alloys toward hydrocarbon partial reforming [18].

In this paper, the application of preoxidized Ni-containing alloys as steam reforming catalysts for hydrocarbons generated via biomass gasification was evaluated. Oxidation pretreatment was done for 2 reasons, to

    (a) disperse the catalytically active component on the surface of the alloy tube; and

    (b) form a layer of metal oxides that would promote the reaction and retard catalyst deactivation.

Furthermore, the strong Ni-to-support interaction provides the alloy with good mechanical strength and thermal stability.

2. Experiment

2.1. Ni-Containing Alloy Oxidation Pretreatment and Surface Characterization. Commercially available Ni-containing alloy tubes (outer diameter: 1/4 in, length: 35 cm), Inconel 600, Inconel 601, Hastelloy, Superinvar, and SUS304, were used in this study. Using a benchtop apparatus (Figure 1) the alloy tube was inserted into a quartz tube, placed inside an electrically heated furnace, and oxidized at 1000°C for 2 hours in O_2. The temperature of the furnace was programmed to rapidly increase to 1000°C within 30 minutes, maintain the temperature at 1000°C for 2 hours, and gradually cool to room temperature.

Characterization of the most catalytically active alloy was performed by scanning electron microscope (SEM) coupled with an energy dispersive X-ray spectrometer (EDX).

2.2. Catalytic Tests Using Different Hydrocarbon Model Compounds. To evaluate the catalytic activity and stability of oxidation pretreated Ni-containing alloy tubes as steam reforming catalysts, reactions were conducted using tetradecane, toluene, and naphthalene as model compounds for biomass gasification. Categorically, tetradecane was used to evaluate the performance of the catalyst when used with simple and straight-chained hydrocarbons, toluene for aromatic hydrocarbons, and naphthalene for polyaromatic hydrocarbons. To monitor the reactions, effluent gas samples were collected and analyzed by gas chromatography coupled with a thermal conductivity detector (GC-TCD). Specifically, production rates of CO, CO_2, H_2, and CH_4 were determined every 30 minutes during the screening tests. Reactions were conducted with 140 μmol/s of steam and 36 μmol/s N_2 carrier gas, automatically fed into the reactor at 730°C, hereafter
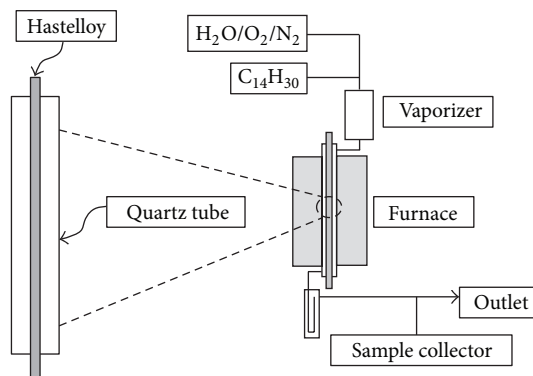

FIGURE 1: Diagram of the benchtop apparatus used in the experiment.

referred to as standard reaction condition. Tetradecane and toluene were, respectively, pumped into the reactor at 1 μmol/s and 2 μmol/s, while 100 : 1 naphthalene-toluene was fed at 2.10 μmol/s. In cases where low or unstable catalytic activities were displayed during the screening reactions, higher reaction temperatures were applied. Using the suitable reaction temperature, long term reactions were conducted to observe the catalyst's activity and stability. Since H_2 can also be produced by the competing reaction hydrocarbon cracking, CO was used as an indicator of steam reforming reaction.

Mass-balance, in terms of carbon (4), calculations were done to estimate and compare the amount of carbon formed during the reactions. A carbon mass balance of less than 1.0 indicated the formation of carbon. Consider

$$\text{C-balance} = \frac{\left(w\text{CO} + x\text{CO}_2 + y\text{CH}_4\right)}{\left(zn\text{C}_n\text{H}_m\right)}, \qquad (4)$$

where w, x, y, and z is the stoichiometric coefficient in the balanced chemical reaction.

3. Results and Discussions

3.1. Catalytic Activity Tests

3.1.1. Screening Test. After the oxidation pretreatment step, the applicability of Ni-containing alloys as steam reforming catalyst was tested using tetradecane (Table 1), a straight-chained hydrocarbon model. Catalytic activity, as indicated by CO production rate, can be arranged as Hastelloy > Superinvar > Inconel-600 > Inconel-601, SUS304. Inconel-601 and SUS304 did not show any activity towards steam reforming which was not observed when both alloys were applied to tetradecane partial oxidation [18]. Among the tested alloys, Hastelloy showed the highest activity for tetradecane steam reforming reaction (5) done with a 1 μmol/s of hydrocarbon feed rate at standard reaction condition; thus it was subjected to further evaluation. Consider

$$\text{C}_{14}\text{H}_{30} + 14\text{H}_2\text{O} \longrightarrow 29\text{H}_2 + 14\text{CO} \qquad (5)$$

Table 1: Production rates of primary gas produced via tetradecane steam reforming over preoxidized Ni-containing alloys[*].

Alloy	Production rate (μmol/s)[**]		
	CO	H_2	CH_4
Inconel-600	2.75	24.4	1.13
Inconel-601	0	2.23	1.63
Hastelloy	7.45	21.5	0.99
Superinvar	2.76	9.44	1.44
SUS304	0	0.73	0.74

[*]Refer to Tagawa et al. (2013) [18] for the chemical composition of tested alloys; [**]data were collected after 120 minutes.

3.1.2. Tetradecane Steam Reforming.

Based on the screening test results, the long term reaction experiment done using Hastelloy was performed which showed that it was able to maintain a stable activity for 48 hours followed by a gradual deactivation as suggested by the slow but continuous decline in CO production rates (Figure 2). The decrease in the production rates of CO_2 and H_2 further supports this inference. Further, the experimental H_2/CO production ratio was higher than the theoretical H_2/CO (Figure 3) which indicated the occurrence of H_2 producing side-reactions. Based on CH_4 and CO_2 detected in the effluent gas it was possible that tetradecane cracking and WGS reactions were simultaneously taking place with the main reactions. In terms of H_2 production, these side-reactions would produce additional H_2 but methane decomposition (6) also produces carbon which could lead to catalyst deactivation. Correspondingly, a decline in carbon balance (Figure 3) started after the 48th hour of the experiment. Based on this, the catalyst was most likely deactivated by carbon deposition. Consider

$$CH_4 \longrightarrow C + 2H_2 \quad \Delta H^\circ = 75.6 \, kJ/mol \qquad (6)$$
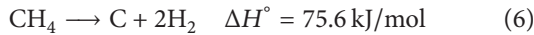
3.1.3. Toluene Steam Reforming.

When the catalytic potential of preoxidized Hastelloy in steam reforming was evaluated using toluene (2 μmol/s), an aromatic hydrocarbon model compound, it was assumed that toluene reacts with water to produce H_2 and CO (7) or H_2 and CO_2 (8) and are both occurring at nearly an equal rate (Figure 4). Also, the catalyst sustained a stable reaction for 72 hours as illustrated by its CO production rate. The large difference between the experimental and theoretical H_2/CO (Figure 5) ratio is a consequence of the combined H_2 produced through (7) and (8). Concurrently, additional H_2 was also generated by WGS and toluene cracking (9) [20]. During the reaction, carbon formation also took place as depicted by Figure 5. Carbonaceous deposits were probably formed from benzene (Figure 6) [21], the primary product of toluene decomposition [22], or through thermal toluene decomposition (10) [20]. Consider
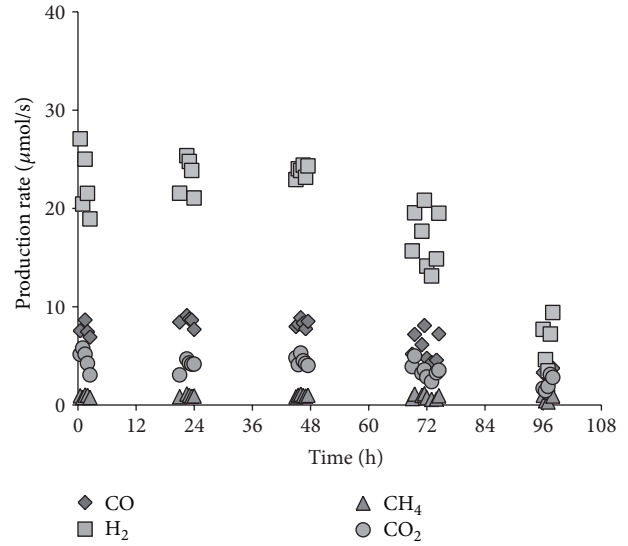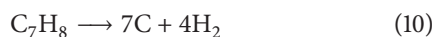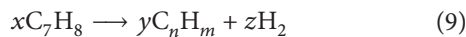
$$C_7H_8 + 7H_2O \longrightarrow 7CO + 11H_2 \qquad (7)$$

$$C_7H_8 + 14H_2O \longrightarrow 7CO_2 + 18H_2 \qquad (8)$$

$$xC_7H_8 \longrightarrow yC_nH_m + zH_2 \qquad (9)$$

$$C_7H_8 \longrightarrow 7C + 4H_2 \qquad (10)$$

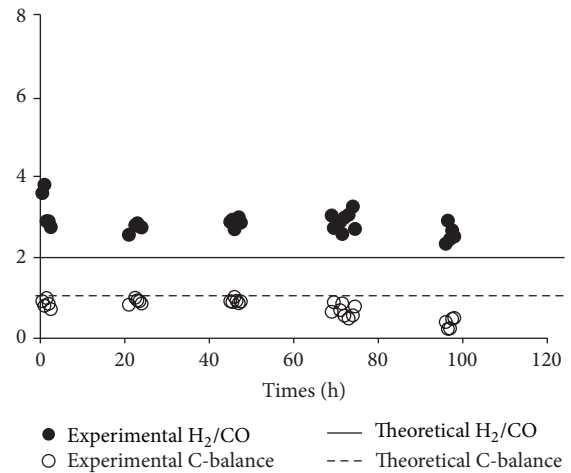Figure 2: Tetradecane steam reforming over oxidation pretreated Hastelloy.

Figure 3: H_2/CO ratio and carbon balance of tetradecane steam reforming over oxidation pretreated Hastelloy.

3.1.4. Toluene-Naphthalene Steam Reforming.

To investigate the effects of polyaromatic hydrocarbons (PAH) on the catalytic activity of oxidation pretreated Hastelloy, naphthalene was dissolved in toluene and used as hydrocarbon feedstock. When steam reforming was performed on toluene-naphthalene, 100 : 1 molar ratio at 2.10 μmol/s, a stable but low activity was observed under standard reaction condition (Figure 7) with a relatively high amount of carbon formed when compared to that of pure toluene. To prevent the reactor from being plugged with carbon, the reaction was conducted at 900°C. Since steam reforming is an endothermic reaction, increasing the temperature was expected to promote the reaction. As shown in Figure 8, with the exception of CH_4, production rates were roughly tripled when the reaction was conducted at 900°C. However, catalytic activity started to decline shortly after 24 hours (Figure 8); thus the experiment
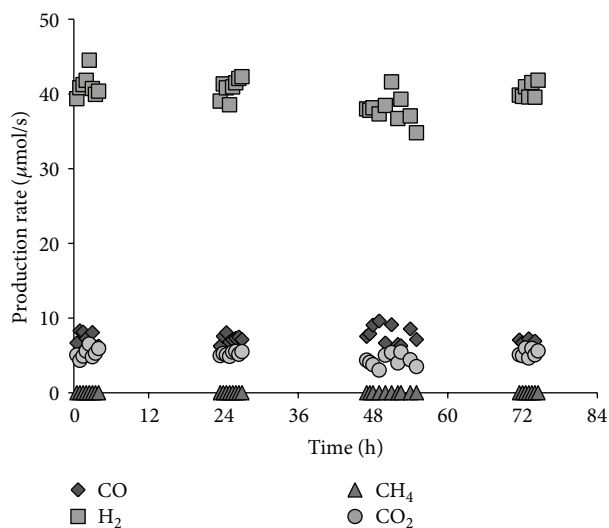
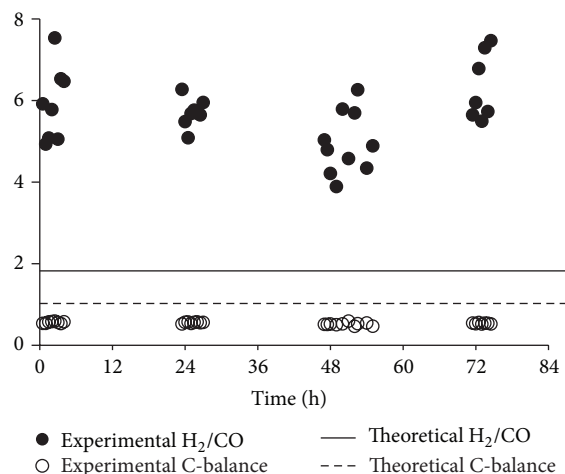FIGURE 4: Toluene steam reforming over oxidation pretreated Hastelloy.

FIGURE 5: H_2/CO ratio and carbon balance of toluene steam reforming over oxidation pretreated Hastelloy.

FIGURE 6: Simplified decomposition scheme of toluene and naphthalene [21].
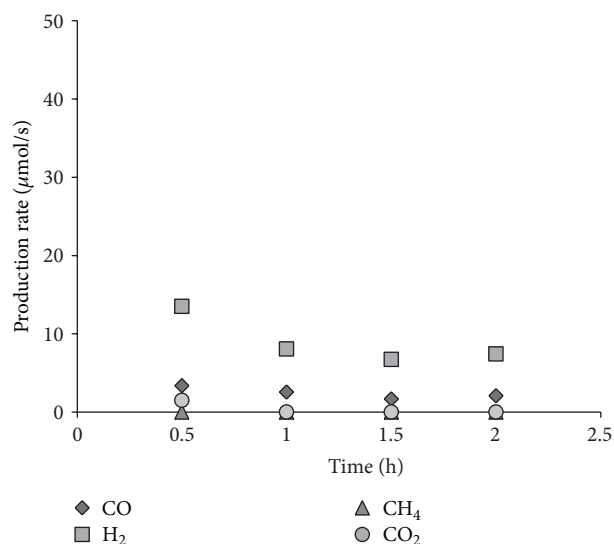
FIGURE 7: Toluene-naphthalene (100 : 1) steam reforming over oxidation pretreated Hastelloy.
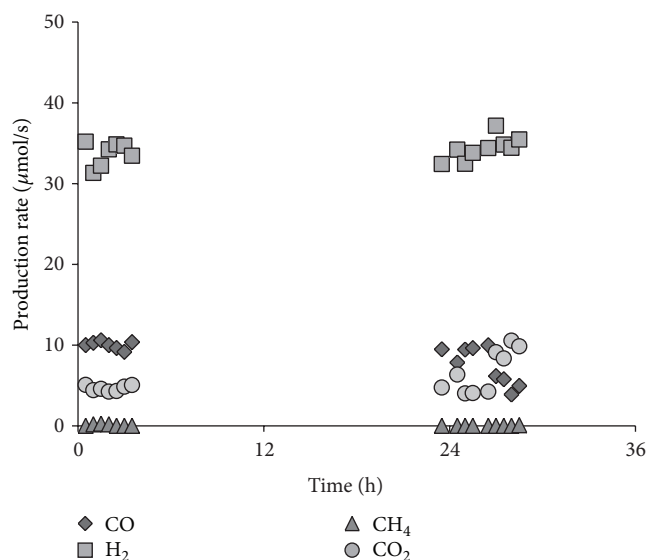
FIGURE 8: Toluene-naphthalene (100 : 1) steam reforming over oxidation pretreated Hastelloy at 900°C.

was terminated to prevent the possible plugging of the reactor which could damage it. It was deduced from Figure 8 that the presence of a PAH (naphthalene) in the hydrocarbon feedstock decreased the activity while the tendency to form carbon was increased. The collected data were consistent with the findings of Coll et al. [23]. Furthermore, it was assumed that naphthalene forms carbon in a similar manner with toluene (Figure 6) but is relatively easier because of its 2-ringed structure [24].

3.1.5. Comparison of Reactivity. The complexity of the hydrocarbon is hypothesized to be the primary factor that affects its reactivity. Particularly, an increase in the number of aromatic rings in the compound's structure results in a lower reaction rate. Using CO as an indicator of steam reforming reaction, preoxidized Hastelloy displayed activity for both simple and aromatic hydrocarbons (Figure 9). Tetradecane
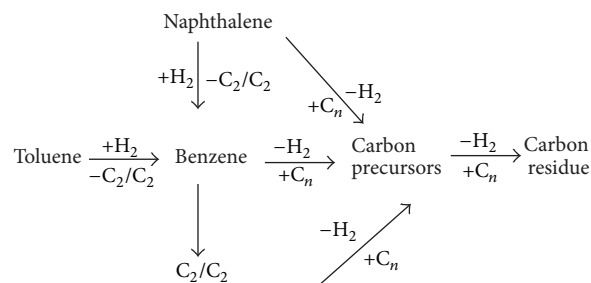
and toluene showed similar reactivity with an average CO production rate of 8 μmol/s, while naphthalene was the least reactive. Straight-chained hydrocarbons, like tetradecane, when subjected to hydrocarbon cracking will produce significantly shorter and simple hydrocarbons that are relatively more reactive than longer and complex hydrocarbons, thus preventing the excessive accumulation of hydrocarbon fragments that may eventually be converted to carbonaceous deposits. Conversely, aromatic hydrocarbons will dominantly produce benzene [22] that will eventually be converted to carbon. Consequently, as the number of aromatic rings in the hydrocarbon increases so is its probability to form carbon. Based on the collected data, despite the small difference in their reactivity, toluene displayed a higher tendency to form carbon than tetradecane (Figure 10). Also, the quantity of carbon formed during tetradecane steam reforming started to increase after 48 hours while that of pure toluene remained stable. It may be possible that the type of carbon formed varied depending on the composition of the hydrocarbon feedstock. Specifically, it was inferred that filamentous carbon was formed during tetradecane steam reforming while pyrolytic-type carbon was formed with toluene and naphthalene [6, 7]. Carbon filaments deactivate the catalyst by encapsulating the active metal particle. However, this does not happen at high H_2/CO or H_2O/hydrocarbon ratios [7] which was the condition used in this study; thus, the catalyst was able to remain active and stable for 48 hours. Within 48 hours, it was deduced that the amount of filamentous carbon that accumulated on the surface of the catalyst was sufficient enough to plug the pores leading to its gradual deactivation. Filamentous carbon formation which displaced the metal particles on the catalyst surface could have possibly exposed more nucleating sites which consequently led to more carbon being formed (Figure 10). Further, a constant carbon formation was observed in the case of aromatic hydrocarbons, toluene and naphthalene. This implied that the rate of hydrocarbon cracking that produces the carbon precursors was not affected by the catalyst. On the other hand, the continuous formation of pyrolytic carbon led to the encapsulation of the catalyst particles [7] and eventually to its deactivation.

3.2. Characterization of Catalyst after Oxidation Pretreatment.
The collected SEM micrograph of the preoxidized Hastelloy (Figure 11(b)) showed a rough and perforated surface while that of the unoxidized sample was relatively smooth (Figure 11(a)). Generally, a linear correlation existing between roughness and surface area is assumed [25]; thus, it was inferred that oxidation pretreatment increased the surface area of Hastelloy. Further, corrosion studies conducted on different types of Hastelloy also reported the same morphological change [26, 27] and that although temperature, time, and O_2 partial pressure determine the composition and thickness of the formed metal oxide scale, Cr_2O_3 phase was always formed [27]. The paper published by Park et al. [27] stated that after oxidation ($\approx$755°C, <2 h, $\approx$25 Pa pO_2), only Cr_2O_3 was detected in the scale formed which was contrary to the data collected from this study. Particularly,
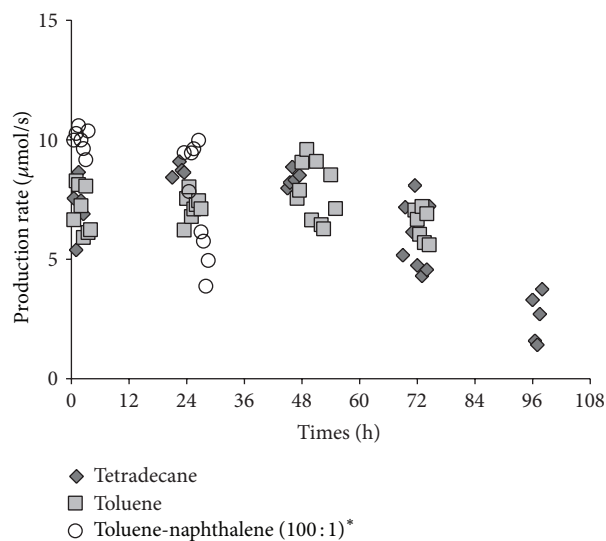

FIGURE 9: CO production rates of steam reforming performed over preoxidized Hastelloy using different hydrocarbon model compounds. *Reaction was performed at 900°C.
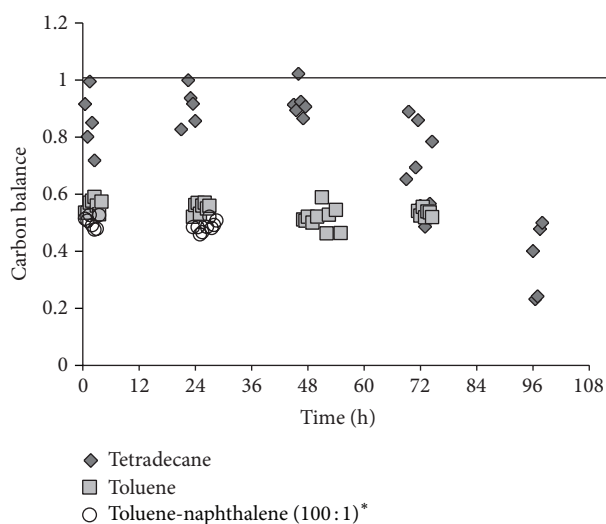

FIGURE 10: Carbon balance of steam reforming performed over preoxidized Hastelloy using different hydrocarbon model compounds. *Reaction was performed at 900°C.

EDX analysis estimated the components of the metal as oxides scale (Figure 11(b)) at 56.5% wt Cr_2O_3, 7.7% wt Fe_2O_3, 24.7% wt NiO, and 11.1% wt MoO_3. Our previously collected XRD pattern also revealed the formation of complex metal oxides, namely, NiMoSiO and NiMoFeO [18]. It was inferred that the higher oxidation temperature (1000°C) and longer duration (2 h) used in this study resulted in the formation of various metal oxides.

As a catalyst, the pitted but well adhered surface would enhance the contact between the active site and the reactants without compromising the mechanical strength of the catalyst. It is also interesting to note that supported Fe_2O_3 are commercially available as WGS catalysts and are often

Metal	Weight (%)	K-ratio
Cr	13.90	0.1389
Fe	4.75	0.0496
Ni	51.02	0.4957
Mo	13.19	0.0962
C, Si, Mn, Co, W	17.14	

(a)

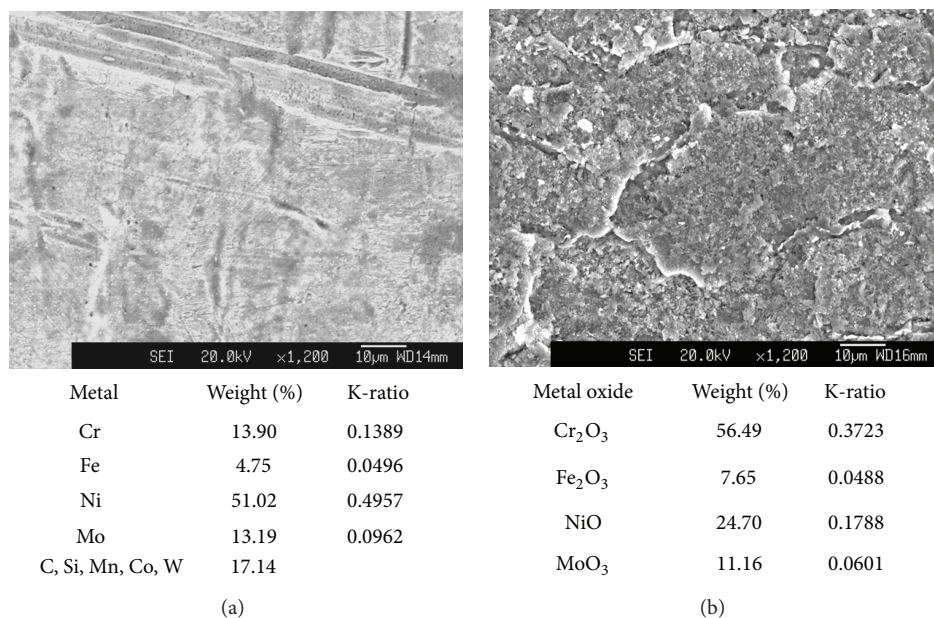| Metal oxide	Weight (%)	K-ratio
Cr_2O_3	56.49	0.3723
Fe_2O_3	7.65	0.0488
NiO	24.70	0.1788
MoO_3	11.16	0.0601

(b)

FIGURE 11: Scanning electron micrograph and EDX analysis of (a) unoxidized Hastelloy and (b) Hastelloy oxidized at 1000°C for 2 h.

calcined under conditions similar to steam reforming to generate Fe_3O_4 which is its catalytically active form; Cr_2O_3 is often used to stabilize and prevent iron oxide sintering [28]. As with MoO_3, it was reported to be a good promoter of Ni/Al_2O_3 steam reforming catalysts and at the same time prevent catalyst deactivation by carbon formation and sulfur poisoning [29]. It is known that the amount and size of reducible NiO, the active site, determine the activity of the catalyst. It was assumed that these metal oxides impart the same characteristics onto the pretreated Hastelloy catalyst. Currently, analyses are being performed to provide more information on the characteristics of this catalyst.

4. Conclusions

Oxidation of Ni-containing alloys at 1000°C resulted in the formation of metal oxides on the surface which rendered it catalytically active towards hydrocarbon steam reforming with Hastelloy showing the highest activity. For all model compounds, H_2 was abundantly produced both by steam reforming reaction and WGS when the reaction was performed over Hastelloy. At 730°C, tetradecane was the most reactive followed by toluene and lastly by toluene-naphthalene (100 : 1). Generally, the number of aromatic rings results in lower reactivity and higher tendency to form carbon although increasing the reaction temperature would overcome these problems. Overall, preoxidized Hastelloy showed potential as a hydrocarbon steam reforming catalyst.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

References

[1] T. J. Wang, J. Chang, C. Z. Wu, Y. Fu, and Y. Chen, "The steam reforming of naphthalene over a nickel-dolomite cracking catalyst," *Biomass and Bioenergy*, vol. 28, no. 5, pp. 508–514, 2005.

[2] B. Zhao, X. Zhang, L. Chen et al., "Steam reforming of toluene as model compound of biomass pyrolysis tar for hydrogen," *Biomass and Bioenergy*, vol. 34, no. 1, pp. 140–144, 2010.

[3] S. Bona, P. Guillén, J. G. Alcalde, L. García, and R. Bilbao, "Toluene steam reforming using coprecipitated Ni/Al catalysts modified with lanthanum or cobalt," *Chemical Engineering Journal*, vol. 137, no. 3, pp. 587–597, 2008.

[4] F. Melo and N. Morlanés, "Naphtha steam reforming for hydrogen production," *Catalysis Today*, vol. 107-108, pp. 458–466, 2005.

[5] A. W. Budiman, S. H. Song, T. S. Chang, C. H. Shin, and M. J. Choi, "Dry reforming of methane over cobalt catalysts: a literature review of catalyst development," *Catalysis Surveys from Asia*, vol. 16, no. 4, pp. 183–197, 2012.

[6] P. Forzatti and L. Lietti, "Catalyst deactivation," *Catalysis Today*, vol. 52, no. 2-3, pp. 165–181, 1999.

[7] C. H. Bartholomew, "Mechanisms of catalyst deactivation," *Applied Catalysis A*, vol. 212, no. 1-2, pp. 17–60, 2001.

[8] J. Han and H. Kim, "The reduction and control technology of tar during biomass gasification/pyrolysis: an overview," *Renewable and Sustainable Energy Reviews*, vol. 12, no. 2, pp. 397–416, 2008.

[9] S. Rapagná, H. Provendier, C. Petit, A. Kiennemann, and P. U. Foscolo, "Development of catalysts suitable for hydrogen or syn-gas production from biomass gasification," *Biomass and Bioenergy*, vol. 22, no. 5, pp. 377–388, 2002.

[10] C. Courson, E. Makaga, C. Petit, and A. Kiennemann, "Development of Ni catalysts for gas production from biomass gasification. Reactivity in steam- and dry-reforming," *Catalysis Today*, vol. 63, no. 2–4, pp. 427–437, 2000.

[11] J. Sehested, J. A. P. Gelten, and S. Helveg, "Sintering of nickel catalysts: effects of time, atmosphere, temperature, nickel-carrier interactions, and dopants," *Applied Catalysis A*, vol. 309, no. 2, pp. 237–246, 2006.

[12] X. Guo, Y. Sun, Y. Yu, X. Zhu, and C.-J. Liu, "Carbon formation and steam reforming of methane on silica supported nickel catalysts," *Catalysis Communications*, vol. 19, pp. 61–65, 2012.

[13] Q. Ming, T. Healey, L. Allen, and P. Irving, "Steam reforming of hydrocarbon fuels," *Catalysis Today*, vol. 77, no. 1-2, pp. 51–64, 2002.

[14] A. Takano, T. Tagawa, and S. Goto, "Carbon deposition on supported nickel catalysts for carbon dioxide reforming of methane," *Journal of the Japan Petroleum Institute*, vol. 39, no. 2, pp. 144–150, 1996.

[15] E. Promaros, S. Assabumrungrat, N. Laosiripojana, P. Praserthdam, T. Tagawa, and S. Goto, "Carbon dioxide reforming of methane under periodic operation," *Korean Journal of Chemical Engineering*, vol. 24, no. 1, pp. 44–50, 2007.

[16] M. Ito, T. Tagawa, and S. Goto, "Partial oxidation of methane on supported nickel catalysts," *Journal of Chemical Engineering of Japan*, vol. 32, no. 3, pp. 274–279, 1999.

[17] T. Tagawa, M. Ito, and S. Goto, "Combined reforming of methane with carbon dioxide and oxygen in molten carbonaceous fuel cell reactor," *Applied Organic Chemistry*, vol. 15, pp. 127–134, 2001.

[18] T. Tagawa, S. R. de la Rama, S. Kawai, and H. Yamada, "Partial oxidation catalysts derived from Ni containing alloys for biomass gasification process," *Chemical Engineering Transactions*, vol. 32, pp. 583–588, 2013.

[19] S. R. de la Rama, S. Kawai, H. Yamada, and T. Tagawa, "Evaluation of pre-oxidized SUS304 as a catalyst for hydrocarbon reforming," *ISRN Environmental Chemistry*, vol. 2013, Article ID 289071, 5 pages, 2013.

[20] C. Li and K. Suzuki, "Tar property, analysis, reforming mechanism and model for biomass gasification—an overview," *Renewable and Sustainable Energy Reviews*, vol. 13, no. 3, pp. 594–604, 2009.

[21] T. Borowiecki and A. Gołcebiowski, "Influence of molybdenum and tungsten additives on the properties of nickel steam reforming catalysts," *Catalysis Letters*, vol. 25, no. 3-4, pp. 309–313, 1994.

[22] L. Devi, K. J. Ptasinski, and F. J. J. G. Janssen, "Pretreated olivine as tar removal catalyst for biomass gasifiers: investigation using naphthalene as model biomass tar," *Fuel Processing Technology*, vol. 86, no. 6, pp. 707–730, 2005.

[23] R. Coll, J. Salvadó, X. Farriol, and D. Montané, "Steam reforming model compounds of biomass gasification tars: conversion at different operating conditions and tendency towards coke formation," *Fuel Processing Technology*, vol. 74, no. 1, pp. 19–31, 2001.

[24] A. Jess, "Mechanisms and kinetics of thermal reactions of aromatic hydrocarbons from pyrolysis of solid fuels," *Fuel*, vol. 75, no. 12, pp. 1441–1448, 1996.

[25] C. Fischer, V. Karius, P. G. Weidler, and A. Lüttge, "Relationship between micrometer to submicrometer surface roughness and topography variations of natural iron oxides and trace element concentrations," *Langmuir*, vol. 24, no. 7, pp. 3250–3266, 2008.

[26] N. Chikamatsu, T. Tagawa, and S. Goto, "Characterization of a new mixed oxide catalyst derived from hydrogen storage alloy," *Journal of Materials Science*, vol. 30, no. 5, pp. 1367–1372, 1995.

[27] J. H. Park, L. Chen, K. C. Goretta, R. E. Koritala, and U. Balachandran, "Oxidation of Hastelloy C276," in *Proceedings of the International Cryogenic Materials Conference (ICMC '02)*, vol. 48, 2002.

[28] R. Tu and T. Goto, "Oxidation of Hastelloy-XR alloy for corrosion-resistant glass-coating," *Journal of Materials Science and Technology*, vol. 19, no. 1, pp. 19–22, 2003.

[29] G. Doppler, A. X. Trautwein, H. M. Ziethen et al., "Physical and catalytic properties of high-temperature water-gas shift catalysts based upon iron-chromium oxides," *Applied Catalysis*, vol. 40, pp. 119–130, 1988.