

Catalytic Activity of Oxidation Pretreated Hastelloy for Methanol Steam Reforming

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Hastelloy, a Ni containing alloy, was investigated to improve its catalytic activity on bio-oil steam reforming by oxidation pretreatment. Methanol as the major composition of bio-oil was used as a model compound. The untreated Hastelloy presented low methanol conversion with high selectivity of methane. After oxidation pretreatment, the Hastelloy showed good activity towards methanol steam reforming. The Cr and Mn promoters on the surface increased with the increase of oxidation temperature, resulting in the improvement of steam reforming activity. The Ni alloy appeared after pretreatment and controlled the oxidation state of Ni, leading to the decrease of methanation. The oxidation pretreatment at 1273 K provided the highest catalytic performance, but the agglomeration apparently occurred. The scales on the surface combined together when the oxidation was longer than two hours. Therefore, the optimal oxidation pretreatment condition was at 1273 K for two hours.

1. Introduction

Nowadays, the global warming has been brought as a major issue. A determinacy of the global warming is the increase of CO₂ in atmosphere which is mainly emitted from the combustion of fossil fuel such as petroleum oil, natural gas and coal. Concern on this issue has led to the growth of alternative energy, especially H₂ energy. Recently, H₂ fuel has been applied in vehicles to replace fossil fuel usage. As a result, H₂ demand increases significantly; hence, the H₂ production improvement must be studied.

According to green production, H₂ source must be from biomass. However, the solid biomass is not suitable for storage and transportation. A liquid form of biomass, bio-oil is produced from biomass pyrolysis in biorefinery processes. After pyrolysis of biomasses such as beech wood, spruce wood, olive husk and hazelnut shell, methanol apparently appears as a component of these bio-oils (Demirbas, 2007). Moreover, additional methanol is used to improve bio-oil properties. Therefore, methanol was selected as the model compound of bio-oil.

To produce H₂, the conventional reaction, steam reforming, is operated in various industries. Noble metal catalysts with supports exhibit high activity and stability. Due to high price of these catalysts, the low cost catalysts such as nickel and nickel oxide are widely employed in industrial scale. Moreover, nickel base catalysts have been studied to incorporate with several promoters (e.g. Cr, Fe, Zn, and Cu), resulting in the catalytic performance improvement. In the case of methanol steam reforming, three main reactions including methanol steam reforming (Eq(1-2)) and water gas shift (Eq(3)) usually occur. However, methane is possibly produced from syngas product via methanation reaction.



Nickel also exists in commercial alloys which are used in several works. The nickel containing alloys including Hastelloy, Superinvar, Stainless steel and Inconel have been investigated as the catalytic structure for H_2 production. The supercritical water conditions were operated to achieve reforming activity without using external catalysts (Yu et al., 1993). Additionally, several studies revealed that high temperature oxidation pretreatment is an alternative way to improve the catalytic activity at normal operating conditions of reforming (Tagawa et al., 2013, De la Rama et al., 2014). Tagawa et al. (2013) evaluated the catalytic activity of the nickel containing alloy for partial oxidation reaction. The oxidation pretreated Hastelloy provided the highest catalytic performance and this improvement might be the effect of the minor metal containing in the alloy. The Hastelloy also offered the highest steam reforming activity when compared with the others (De la Rama et al., 2014). In this study, the steam reforming of bio-oil using methanol as model compound was investigated. The untreated Hastelloy and oxidation pretreated Hastelloy were employed as a catalyst. The catalytic activity evaluation and the morphology were studied with the effect of oxidation temperature and time. The optimal pretreatment condition was provided and this condition will be guidance for further study.

2. Experiment

2.1 Experimental set-up

Chapter 2 Oxidation pretreatment and catalytic activity evaluation were studied by using the same experimental setup as shown in Figure 1. The experimental equipment including evaporator, electrical furnace and condenser was employed. The feed gas streams were controlled by mass flow meters. Commercial Hastelloy tubes having an outer diameter of 0.635 cm were cut at 50 cm long. The prepared tube was held inside a quartz tube reactor which has an inner diameter of 1.0 cm. The reactor was controlled temperature by electrical furnace, and the oxidation and reactions occurred on the outer surface of Hastelloy inside reactor.

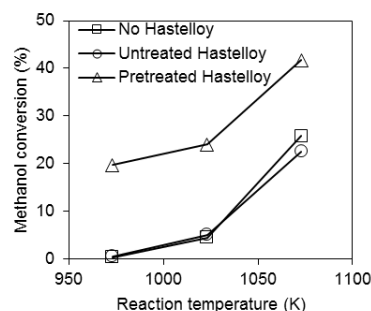
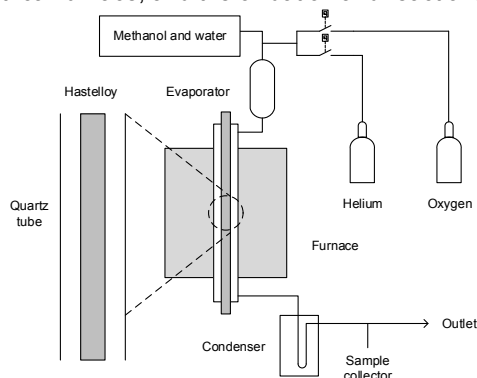


Figure 1: Schematic diagram of the experimental setup

Figure 2: Methanol conversion after one hour reaction for different systems

2.2 Oxidation pretreatment and characterization

Chapter 3 Pure oxygen was fed at 30 ml/min to oxidize the outer surface of Hastelloy for the pretreatment. The oxidation pretreatment conditions were varied in terms of temperature and time as summarized in Table 1. In the characterization, Hastelloy was cut at 1.5 cm long and compressed in order to be fit in the analyzers. The samples, prepared Hastelloy, were placed at the middle of reactor for oxidation pretreatment. The characterization was examined by scanning electron microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS) and X-ray Diffraction (XRD). SEM photographs was specified the magnification level of 1,200 times.

Table 1: Oxidation pretreatment conditions

Temperature (K)	Time (h)
1073 - 1273	2
1273	1 - 4

2.3 Catalytic activity evaluation

Methanol and water were mixed using 1:1 molar ratio inside an ultrasonic bath. The well-mixed mixture was fed at 6 ml/h by a syringe pump to an evaporator which operated at 423 K. Helium at a flow rate of 30 ml/min

was employed as a carrier gas. The vaporized stream was directly fed to the reactor which was operated at a constant temperature between 973 and 1073 K for 120 min. The reaction performance were defined as shown in Eq(4-6) when q_i is molar flow rate. To monitor the reaction, the effluent gas samples were collected and analyzed by a gas chromatography coupled with a thermal conductivity detector.

$$\text{Methanol conversion (\%)} = \frac{(q_{\text{CO}} + q_{\text{CO}_2} + q_{\text{CH}_4})_{\text{Outlet}}}{(q_{\text{CH}_3\text{OH}})_{\text{Inlet}}} \times 100 \quad (4)$$

$$\text{Selectivity of } i \text{ component (\%)} = \frac{(q_i)_{\text{Outlet}}}{(q_{\text{CO}} + q_{\text{CO}_2} + q_{\text{CH}_4})_{\text{Outlet}}} \times 100 \quad (5)$$

$$\text{H}_2 \text{ yield (\%)} = \frac{(q_{\text{H}_2})_{\text{Outlet}}}{3} \frac{(q_{\text{CH}_3\text{OH}})_{\text{Inlet}}}{(q_{\text{CO}} + q_{\text{CO}_2} + q_{\text{CH}_4})_{\text{Outlet}}} \times 100 \quad (6)$$

3. Results and discussion

3.1 Catalytic activity of Hastelloy

In this study, the reaction was operated at high temperature, so the thermal decomposition was possibly present. The untreated Hastelloy and oxidation pretreated Hastelloy were evaluated their activity in order to study the effect of oxidation pretreatment. In thermal decomposition investigation, the reaction occurred inside the quartz tube reactor without catalyst. As shown in Figure 2, the untreated Hastelloy and the thermal decomposition provided the similar results respectively at low methanol conversion. Meanwhile, higher methanol conversion was apparently achieved with the oxidation pretreated Hastelloy at 1273 K for two hours. Moreover, the gas production rates from the reaction at 1023 K and an hour is reported. In the study of thermal decomposition, H₂ and CO were mainly produced with low methane production (0.02 μmol/s). However, the large amount of CH₄ (0.26 μmol/s) appeared in the product stream for the untreated Hastelloy. The untreated Hastelloy is obviously active for the methanation, converting syngas to methane. After oxidation, the Hastelloy produced much higher H₂ production rates with higher CO₂ and lower CH₄ selectivity. According to Eq(2), the presence of CO₂ showed that the steam reforming activity occurred, and the H₂ was highly produced, achieving 18.92% of H₂ yield. Consequently, the methanol steam reforming only occurred over the pretreated Hastelloy, while the untreated Hastelloy is active for the methanation. It should be noted that our reaction system was operated under atmospheric pressure. The H₂ yield in this study was lower than those reported in literatures using Ni containing alloy catalyst (Taylor et al., 2003) which operated the system under super critical water conditions.

3.2 Morphology of the oxidation pretreated Hastelloy

Figure 3 shows SEM photographs of the untreated Hastelloy and the oxidation pretreated Hastelloy. The appearance of the untreated surface was clearly smooth (Figure. 3a). After pretreatment, the small scales were formed over the surface as shown in Figure. 3b-3f, leading to the increase of the roughness and surface area (Fischer et al., 2008). Increasing surface area after pretreatment improved the catalytic activity of Hastelloy.

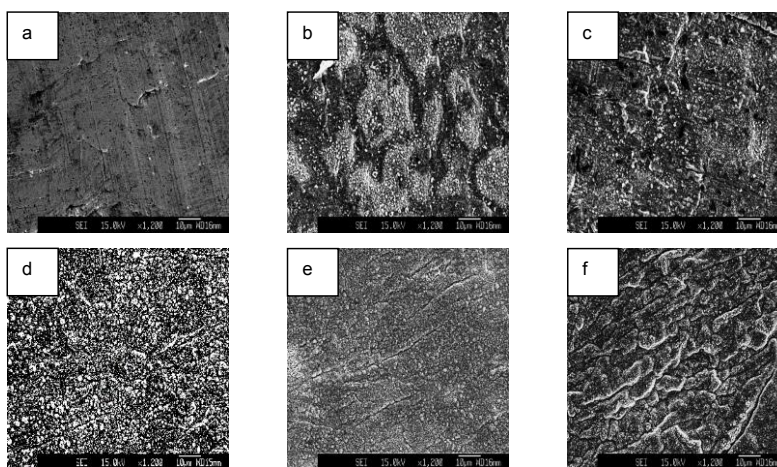


Figure 3: Scanning electron micrographs for (a) Hastelloy, the oxidation-pretreated Hastelloy for two hours at (b) 1073 K, (c) 1173 K and (d) 1273 K and the oxidation pretreated Hastelloy at 1273 K for (e) 1 h and (f) 4 h

According to the EDS results, the metal compositions of the untreated Hastelloy were 57.1% of Ni, 11.9% of Cr and 17.0% of Mo. After oxidation pretreatment at 1273 K for two hours, the main active component, Ni, was reduced to 11.4%, while Cr and Mn increased up to 60.1 and 19.9%, respectively. At this oxidation temperature, most of metals were reactive and movable according to Tamman temperature (Baker, 1982). Cr and Mn strongly moved to the surface, so the main metals after pretreatment are Ni, Cr and Mn. In several studies, Cr and Mn are promoters of steam reforming and water gas shift catalysts (Sekizawa et al., 1998). Cr and Mn promoted dispersion of the active site and the oxygen vacancy, resulting in the improvement of the stability, activity of catalysts and CO₂ selectivity and the decrease of coke formation. Therefore, the presence of Cr and Mn improved the activity of steam reforming and water gas shift. In Figure 4, the XRD patterns of the untreated Hastelloy and the pretreated Hastelloy is reported. Ni metal which is active for methanation reaction (Yan et al., 2013) was the main peak of the untreated Hastelloy, leading to the presence of methanation reaction. After oxidation, the Ni peak was reduced, and the several small unknown peaks appeared at 2θ between 55 and 70 degree. These unknown peaks were possibly the peaks of Ni alloys which controlled the oxidation state of Ni (Tagawa et al., 2013), resulting in the increase of steam reforming activity and the decrease of methanation.

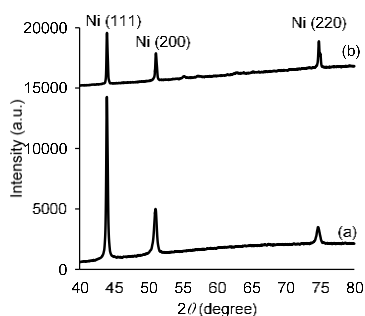


Figure 4: XRD spectra of (a) the untreated Hastelloy and (b) the oxidation pretreated Hastelloy

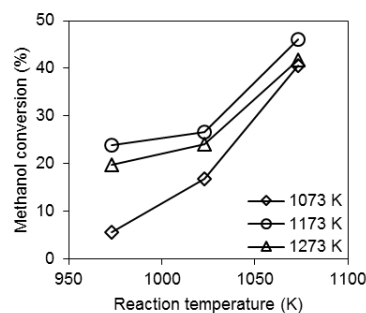


Figure 5: Effect of oxidation pretreatment temperature on methanol conversion after an hour reaction (pretreatment time = 2 h)

3.3 Effect of oxidation pretreatment temperature

In the previous sections, the oxidation pretreatment successfully activated the catalytic performance of Hastelloy by the increase of surface area and the presence of promoters on the surface. The catalytic activity improvement was affected by the oxidation temperature and the influence of oxidation temperature was revealed in this study.

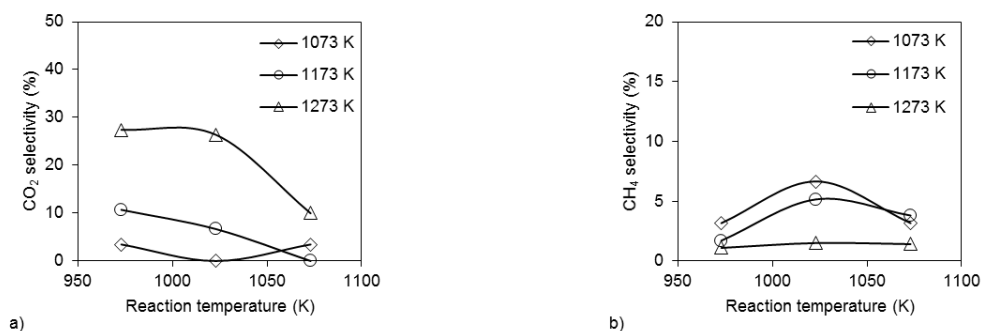


Figure 6: Effect of oxidation pretreatment temperature on selectivity of (a) CO₂ and (b) CH₄ after an hour reaction (pretreatment time = 2 h)

In Figure 5, the highest methanol conversion appeared when using oxidation pretreatment at 1173 K followed by 1273 K and 1073 K. With respect to the selectivity, CO₂ and CH₄ selectivity as shown in Figure 6 were considered as the activity of steam reforming and methanation reactions, respectively. When increasing the oxidation temperature, CO₂ selectivity (Figure 6a) increased, while CH₄ selectivity (Figure 6b) decreased. Thus, the increase of oxidation temperature resulted in the improvement of steam reforming activity and the suppression of methanation reaction. The images of SEM for the samples from various oxidation temperatures are shown in Figs. 3b-d. The formation of scale increased with the oxidation temperature, and the scales

completely covered the surface when the oxidation temperature was beyond 1173 K. At oxidation temperature of 1073 K, the convex surface with scales appeared only at some parts of Hastelloy as shown in Figure 3b, resulting in the lower surface area. However, the surface of Hastelloy when being oxidized at 1273 K (Figure 3d) strongly appeared the agglomeration, leading to the decrease of the surface area. Therefore, the surface area of the pretreated Hastelloy at 1173 K was approximately larger than the others, leading to the best conversion. In addition, the metal compositions were examined by EDS are summarized in Figure 7. When increasing the oxidation temperature, Cr and Mn increased but Ni significantly decreased. The compositions of Cr and Mn promoters on the surface increased with increasing the oxidation temperature. Active phase of Ni was highly distributed and promoted by Cr and Mn; therefore, the steam reforming activity was improved.

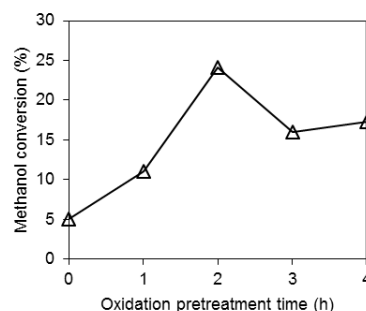
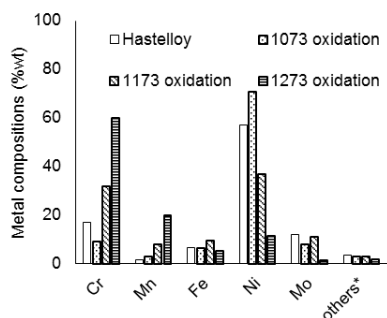


Figure 7: Metal composition on catalyst surface of Hastelloy with oxidation pretreatment at different temperatures (in percent weight) *others include Al, Si, Co, Zr and Sn (pretreatment time = 2 h)

Figure 8: Effect of oxidation pretreatment time on methanol conversion after an hour reaction at 1023 K (oxidation pretreatment temperature = 1273 K)

The oxidation temperature affects the surface area and the surface composition of promoters. The largest surface area appeared at the oxidation temperature of 1173 K, leading to the highest conversion. Meanwhile, the highest steam reforming activity occurred when the oxidation was performed at 1273 K. Therefore, the oxidation pretreatment of 1273 K was recommended in order to achieve the highest performance of methanol steam reforming.

3.4 Effect of oxidation pretreatment time

It was reported that both temperature and time have influence on the surface morphology (Maaz et al., 2007). Therefore, the oxidation time was investigated to find the optimal condition which presented the high active phase with low effect of agglomeration. In this study, the reaction was operated at 1023 K.

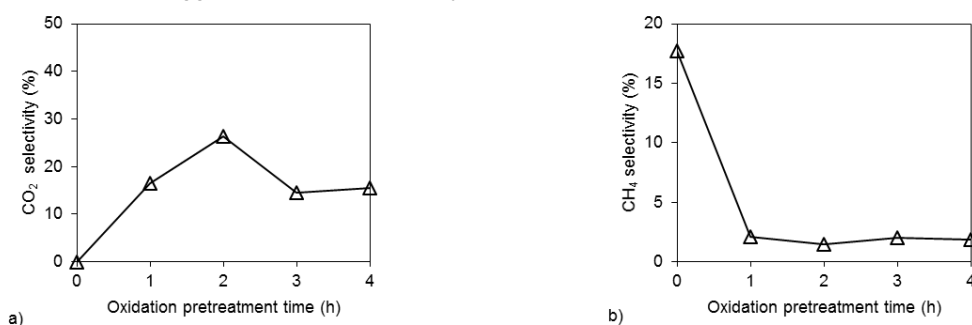


Figure 9: Effect of oxidation pretreatment time on selectivity of (a) CO₂ and (b) CH₄ after an hour reaction at 1023 K (oxidation pretreatment temperature = 1273 K)

Methanol conversion (Figure 8) and selectivity of CO₂ (Figure 9a) were increased with increasing pretreatment time up to two hours. Further increase of pretreatment time resulted in the decrease of methanol conversion and CO₂ selectivity. As shown in Figure 9b, CH₄ selectivity was lower than 5% selectivity when oxidation time was longer than one hour. The highest catalytic performance in terms of conversion and selectivity was obtained by the Hastelloy with two hours oxidation pretreatment. With respect to the SEM images, the agglomeration did not appear on the surface of Hastelloy after oxidation for an hour as shown in Figure 3e. The surface was similar to the Hastelloy surface when oxidized for two hours (Figure 3d), but the oxide scales

did not cover the surface completely. On the other hand, the agglomeration strongly occurred when oxidizing Hastelloy for four hours as shown in Figure 3f. The scales combined together and formed as the large convex surface. Consequently, the surface area relatively decreased, resulting in the loss of active surface. The agglomeration significantly presented when oxidation pretreatment time was longer than two hours. According to the EDS results, the main metal composition after oxidation was similar when oxidation time was longer than two hours. The promoters, Cr and Mn were lower when being oxidized for an hour, leading to incomplete activation. Therefore, the optimal oxidation time was two hours which provided the highest catalytic performance.

4. Conclusion

In this study, the untreated Hastelloy which has the activity of methanation was activated to be a catalyst for methanol steam reforming by the oxidation pretreatment. The Hastelloy provided higher conversion and CO₂ selectivity after oxidation at 1273 K for two hours. The oxide scales were formed after pretreatment, resulting in the relatively larger surface area. The alloy of Ni formed after oxidation controlled the oxidation state of Hastelloy which promoted the steam reforming activity and suppressed methanation. Cr, Mn and Ni were the main metals on the oxidation pretreated Hastelloy surface. Cr and Mn promoters increased with the oxidation temperature, leading to the improvement of the catalytic activity. Consequently, the oxidation at 1273 K provided the highest catalytic activity of steam reforming. However, the agglomeration apparently occurred at this oxidation temperature, resulting in the loss of active area. With respect to the oxidation time, one hour oxidation did not activate the catalytic surface completely which presented lower composition of the promoters. Meanwhile, the pretreatment over two hours strongly appeared the agglomeration which combined the scales together. Thus, two hours oxidation was the suitable condition to activate the Hastelloy which provided the highest catalytic performance. The suitable pretreatment condition for Hastelloy was the oxidation at 1273 K for two hours.

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