

# Partial Oxidation Catalysts Derived from Ni Containing Alloys for Biomass Gasification Process

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Preparation of partial oxidation catalysts for post treatment of bio-waste gasification process is proposed. Oxidized metal alloys containing nickel, which can be expected to have strong interaction between nickel and support oxides with high dispersion were used in the partial oxidation of model compounds of bio-waste gas. Commercial metal alloy tube was used as a catalyst precursor because tube wall catalyst can provide enough space to accommodate deposited carbon without plugging the reactor. Metal alloy tube was calcined under oxygen flow at 1273 K for 2 h. Then partial oxidation at 1003 K was conducted with model reactants such as tetradecane, toluene, or naphthalene and thiophene diluted in toluene. Activity with tetradecane decreased as: Hastelloy > Superinvar > SUS304 > Inconel, naphthalene and thiophene caused deactivation but dilution could slow down the deactivation process. The activity was suspected to depend mainly on the nickel content of the alloy. In addition, Fe, Co and Mo might have significant effect on the activity. The long term (5 days) activity of Hastelloy is higher with toluene than with tetradecane.

## 1. Introduction

Gasification of biomass and bio-waste is one of the essential technologies for a sustainable society. In order to obtain synthesis gas, a catalytic reforming process is performed after non-catalytic gasification of solid biomass. National Institute for Environmental Studies, Japan is proposing a compact gasification process for producing hydrogen from wood wastes and paper wastes which involves thermal biomass gasification followed by biogas reforming (Kawamoto et al., 2009). In theory, gasification will completely convert the biomass to CO and H<sub>2</sub>; however, CO<sub>2</sub>, H<sub>2</sub>O, hydrocarbons, S containing compounds, tar and char are also being produced in practice. Tar, mainly composed not only of aliphatic hydrocarbons but also of polycyclic aromatic hydrocarbons (Wang et al., 2005), usually block and corrode the pipes. Depending on the gasification process, such as steam gasification or pure oxygen gasification, catalytic steam reforming, dry reforming (CO<sub>2</sub> reforming) or partial oxidation is then performed. Thus reforming catalyst should be specifically designed for these reaction conditions. Ni-based catalysts were reported to almost eliminate tar, however, carbonaceous deposits and sintering of catalyst particles still lead to catalyst deactivation. Carbonaceous residue deactivates the catalyst by covering its active surface, blocking the pore, disintegrating the catalyst and plugging of reactors. Different forms of carbon and coke are produced depending on the type of reactions, catalysts, feeds and reaction conditions.

In our previous studies, Ni based catalysts have been effective both under dry reforming conditions with continuous (Takano et al., 1996a) and periodic (Promaros et al., 2007) reactors as well as partial oxidation with packed bed (Ito et al., 1999) and MCFC type reactors (Tagawa et al., 2001). Selection of support materials, additives and arrangement of vacant space to accommodate temporal carbonaceous compounds were essential (Takano et al., 1996a). Catalytic properties are greatly affected by the metal-support interaction and could be rendered in the different stages of catalyst preparation. In preparing catalysts for hydrogen related reactions (Tagawa and Okada, 1999), oxidation of alloys is considered in providing an optimum dispersion and morphology of the catalyst (Chikamatsu et al., 1995). In the case of Mg<sub>2</sub>Cu alloy, high temperature oxidation in O<sub>2</sub> provided mixed oxides of MgO and CuO, which showed activity on the selective hydrogenation of C18 esters (Chikamatsu et al., 1994.).

The feasibility of surface oxidized Ni containing alloys as hydrocarbon partial oxidation catalyst was investigated in this study. When alloys are subjected to oxidation pre-treatment, the less noble metal component gets oxidized first and forms a protective metal oxide scale. As a reforming catalyst, the metal oxide scale is hypothesized to function both as a support material and a reaction precursor while preventing carbon formation. In addition, the catalytically active metal was predicted to be highly dispersed on the metal oxide matrix to provide bigger surface area and promote catalyst activity. Further, a strong interaction between the support material and the dispersed metal is also hypothesized to provide good resistance towards Ni migration which will cause whisker-like carbon formation. Tetradecane, toluene, naphthalene, and thiophene were selected as model compounds of biomass gasification products and used to evaluate the catalytic activity of the alloys for hydrocarbon reforming through partial oxidation. We would like to propose the oxidation of metal alloys containing nickel, which can be expected to yield strong interaction of nickel and support oxides with high dispersion. We used metal alloy tube as a catalyst precursor because tube wall catalyst can provide enough space to accommodate deposited carbon without plugging the reactor (Takano et al., 1996b).

## 2. Experimental

Figure 1 shows the apparatus used for the alloy oxidation treatment and partial oxidation reactions. It consists of an evaporator, a quartz tube (inner diameter: 1cm), an electrically heated furnace and a temperature control system. The alloy tube was inserted into the quartz tube and placed in the middle of the heated furnace. The outer surface of the alloy tube was used as a catalyst. The upper end of the quartz tube was connected to the feed inlet while the lower end was connected to a gas sampling valve and a condenser. Surface oxidation of alloy (outer diameter: 1/4 in, length: 35 cm), was conducted using oxygen at 1003 K for 2 h. Of the 35 cm tube length, approximately 15 cm was at the isotherm region of the furnace. The temperature was programmed to rapidly increase to 323 K and then to 1003 K within 30 min. After the 2 h oxidation process, the temperature was gradually decreased to room temperature. Table 1 shows the composition of the tested alloys. Commercial alloys containing nickel such as SUS304, Inconel 600 and 601, Superinvar and Hastelloy were selected. Fe is also commonly contained as balance metal.

Partial oxidation reaction using gaseous oxygen was conducted after oxidation pre-treatment of the alloy tube. The catalytic activity was compared in terms of CO production rates. All throughout the experiment, the model reactant (tetradecane and toluene) was automatically pumped into the reactor through a vaporizer at a rate of 1.06  $\mu\text{mol/s}$  along with  $\text{N}_2$  flow of 36.3  $\mu\text{mol/s}$ ; naphthalene and thiophene were dissolved into toluene and used. Partial oxidation of tetradecane:



was conducted at 1003 K with  $\text{O}_2$ ; 7.5  $\mu\text{mol/s}$ . These were referred as the standard reaction conditions in the remaining parts of this paper. Long term reaction was also performed to test the stability of the catalyst. Specifically, the catalysts which showed the highest CO production rate were used for this purpose using the corresponding flow rates used in the screening test. For both steps, GC-TCD (GL Sciences GC-3200) was used to quantify  $\text{H}_2$ , CO,  $\text{CO}_2$  and  $\text{CH}_4$  in the product gas using Ar as carrier gas.

## 3. Results and Discussions

### 3.1 Screening of catalysts

Results of screening test under standard conditions at 30 min are compared in Table 2 as initial activities. Rate of formation [ $10^{-6} \times \text{mol/s}$ ] over alloys pretreated in  $\text{O}_2$  at 1003K for 2h were presented. Rate of CO production represented partial oxidation activity. As shown in Table 2, the activity at 30 min decreased as; Hastelloy > Superinvar > SUS304 > Inconel with respect to CO production rate; while, Superinvar > SUS304 > Hastelloy > Inconel with respect to  $\text{H}_2$  production rate. The theoretical  $\text{H}_2/\text{CO}$  value is 15/14, thus the excess in production of hydrogen in the case of Superinvar suggested either complete oxidation of CO to  $\text{CO}_2$  or decomposition of reactant to form coke deposits. The orders were almost the same at 120 min, however, the rate of CO production increased in the cases of Hastelloy (3.88 to 7.18 [ $10^{-6} \times \text{mol/s}$ ]), Superinvar (3.82 to 6.51) and SUS304 (3.63 to 6.74). This suggested the gradual development of new active site during oxidation reaction in addition to initial active site produced by the oxidation pretreatment. The production of methane did not strongly depend on catalysts which suggested the non-catalytic thermal decomposition of tetradecane. Since the highest activity was observed on Hastelloy, details of catalytic behavior of Hastelloy on partial oxidation of various reactants were further investigated.

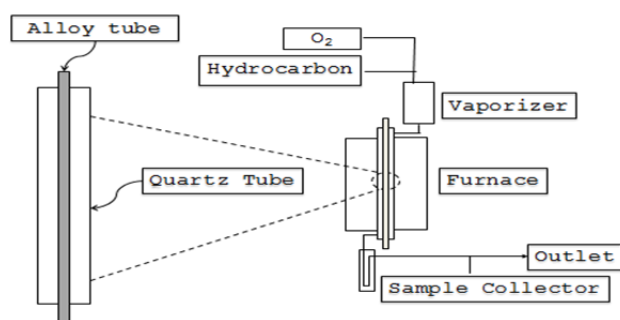


Figure 1: Experimental apparatus

Table 1: Composition of tested alloys (weight percent)

Alloy	C	Al	Co	Si	Mn	P	S	Ni	Cr	Mo	Fe
SUS 304	<0.08			<1.00	<2.00	<0.05	<0.03	10.0 ~14.0	18.0 ~20.0		Bal
Inconel 600	<0.15				<1.00			<72.0	14.0 ~17.0		6.00 ~10.0
Inconel 601		1.00 ~1.70						58.0 ~63.0	21.0 ~25.0	<1.00	Bal
Superinvar	0.07		4.00 ~6.00		0.30 ~0.40			31.0			Bal
Hastelloy	0.02		2.50	0.08				57.0	14.5 ~16.5	15.0 ~17.0	4.00 ~7.00

Table 2: Initial activity of tetradecane partial oxidation over tested catalysts

Alloy	CO	H <sub>2</sub>	CH <sub>4</sub>
SUS 304	3.63	5.58	0.941
Inconel 600	1.68	0.863	0.913
Inconel 601	1.57	0.873	0.973
Superinvar	3.82	8.13	0.519
Hastelloy	3.88	4.53	0.584

Reaction rate in  $10^{-6}$  mol/s under standard conditions

### 3.2 Reactivity of model reactants

Activity of Hastelloy was tested for model reactants such as tetradecane, toluene, naphthalene and thiophene. The long term activity of Hastelloy, which was pretreated in O<sub>2</sub> at 1003K for 2h, was tested on the partial oxidation of tetradecane. Figure 2 shows the time dependence of the reaction rate. Although initial activity was not stable in day one (~1000 min), the activity seemed to stabilize in day two with H<sub>2</sub>/CO ratio that was almost equal to the theoretical ratio. However, a considerable amount of coke was developed in day 3 which caused the reactor to be plugged.

Figure 3 shows the long term activity of Hastelloy for the partial oxidation of toluene. Instead of tetradecane, toluene ( $2.09 \times 10^{-6}$  mol/s) was reacted with O<sub>2</sub> ( $7.63 \times 10^{-6}$  mol/s). A stable activity was observed for more than 4 days. Considerable amount of CO<sub>2</sub> was also observed but the rate of methane formation was negligible. Based on these observations, it was deduced that toluene might be more reactive than tetradecane and total oxidation was preferred over thermal decomposition to form methane.

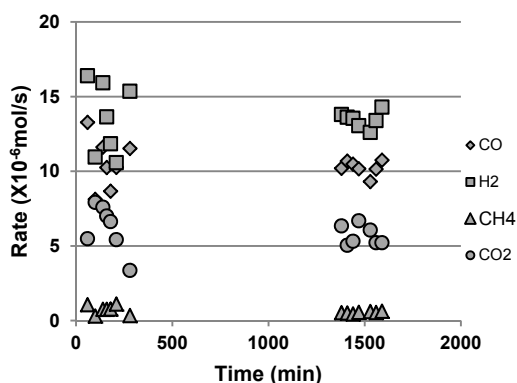


Figure 2: Partial oxidation of tetradecane over pre-oxidized Hastelloy under standard reaction conditions.

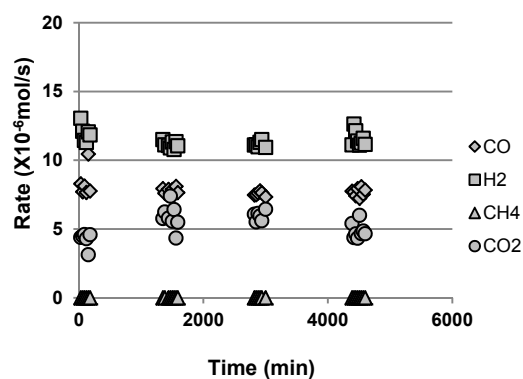


Figure 3: Partial oxidation of toluene over pre-oxidized Hastelloy under standard reaction condition

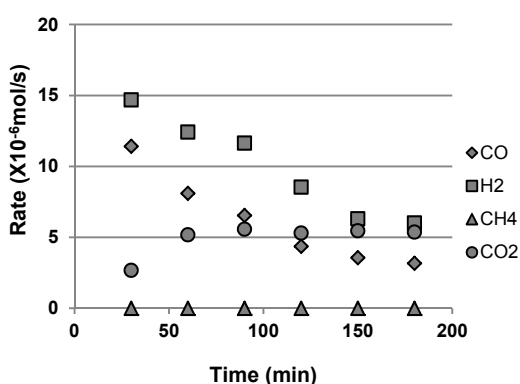


Figure 4: Partial oxidation of naphthalene dissolved in toluene (1/50) over pre-oxidized Hastelloy under standard reaction condition

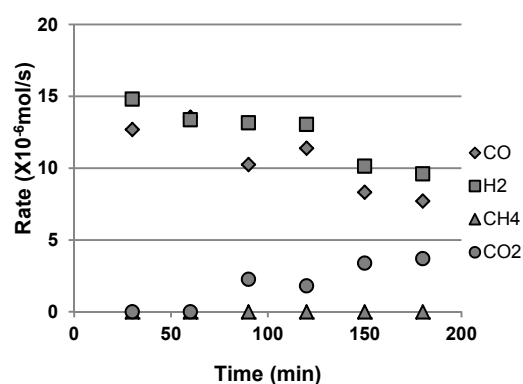


Figure 5: Partial oxidation of naphthalene dissolved in toluene (1/100) at 1173 K over pre-oxidized Hastelloy under standard reaction conditions

Further, the effect of naphthalene on the partial oxidation of toluene was tested. Figure 4 shows the results when naphthalene  $5.7 \times 10^{-8}$  mol/s and toluene  $2.09 \times 10^{-6}$  mol/s were pumped into the reactor. The initial activity was strongly affected by naphthalene and the catalyst was deactivated at 3h, but thermal decomposition ( $\text{CH}_4$  production) and complete oxidation was not so affected by naphthalene. When the reaction was conducted at higher temperature (1173 K) and lower concentration ( $2.84 \times 10^{-8}$  mol/s), results shown in Figure 5 suggested that deactivation caused by naphthalene is not so strong as was observed in Figure 4. Although the activity decreased gradually, the catalyst remained active at 3 h. Thus, the selection of reaction conditions is effective in reducing the deactivation effect of naphthalene.

The effect of thiophene on the partial oxidation of toluene was also investigated. Figure 6 shows the results when thiophene  $2.78 \times 10^{-10}$  mol/s was dissolved in  $2.09 \times 10^{-6}$  mol/s toluene under  $\text{O}_2$  flow of  $7.32 \times 10^{-6}$  mol/s at 1003 K. The initial activity was not affected by thiophene. Gradual deactivation was observed for 2 h, while immediate deactivation occurred with higher concentration of thiophene. When the reaction was conducted at a higher temperature (1123 K) as shown in Figure 7, the activity during the second day was decreased to half of the initial activity, and deactivation was observed to slow down in three days. As observed with naphthalene, thermal decomposition ( $\text{CH}_4$  production) and complete oxidation was also not largely affected by thiophene. Figure 8 shows the material balance during the reaction shown in Figure 7. The time course of material balance is almost same as that of reaction rate (Figure 6). As the activity decreased gradually with time, both carbon balance and hydrogen balance decreased below 1. This suggests the gradual deposition of the carbonaceous materials or heavy hydrocarbons on the catalyst surface; oxidation of hydrogen to water was also suggested from the decrease of hydrogen balance. Both polycyclic aromatic compounds and sulfur containing compounds were detected in the actual biogas collected from the thermal gasification of wood, thus the concentration of those compounds should be maintained to be as low as possible in order to prevent catalyst deactivation.

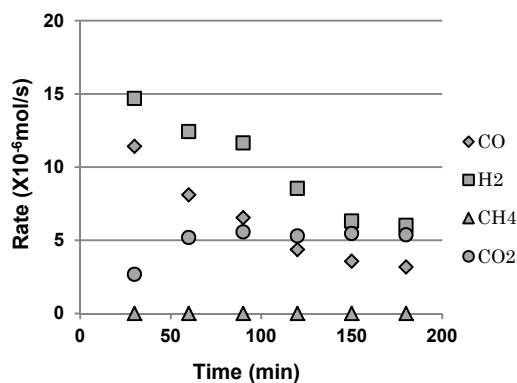


Figure 6: Partial oxidation of thiophene dissolved in toluene (1/10000) over pre-oxidized Hastelloy under standard reaction conditions at 1003 K

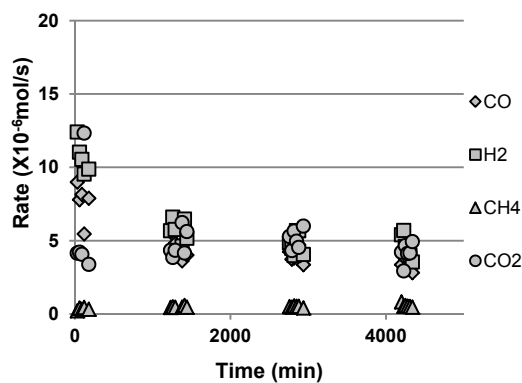


Figure 7: Partial oxidation of thiophene dissolved in toluene (1/10000) over pre-oxidized Hastelloy under standard reaction conditions at 1173 K

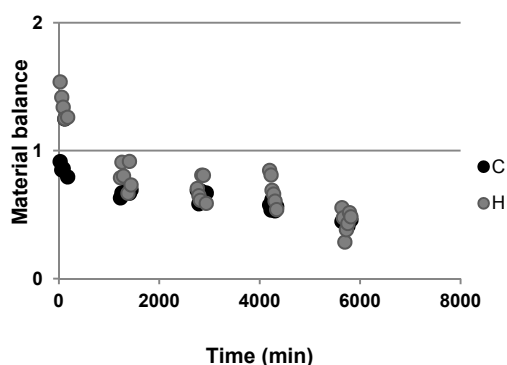


Figure 8: Material balance of partial oxidation of thiophene dissolved in toluene (1/10000) over pre-oxidized Hastelloy in the case of Fig. 7.

### 3.3 Characterization of catalyst

XRD spectra were of Hastelloy catalyst before and after the oxidation pre-treatment was collected. From the untreated and pre-treated alloy tube, 1-2 cm was cut and pressed into plate prior to XRD analysis. The XRD pattern of the untreated sample in Figure 9 shows no trace of oxide materials including nickel oxide. The sample after standard pre-treatment ( $T=1003$  K) showed small peaks which were too small to identify. Therefore pre-treatment was conducted at 1273K. Figure 10 shows the XRD spectra after oxidation pre-treatment at 1273 K. The small peaks observed when pre-treatment was conducted at 1003 K were enhanced when sample pre-treatment was done at 1273 K. Oxide peaks of component materials such as CrO and CoO as well as mixed oxide of NiMoSiO and NiMoFeO were observed. It is worth noting that apparent peak of NiO was not observed although the original alloy is 57% composed of nickel (Table 1). This shows that large particles of NiO which caused coking were initially not present in the catalyst surface. Thus NiO should be finely dispersed in the oxide matrix or contained as mixed oxide. With standard treatment at 1003 K, these oxide particles were deduced to be very small resulting into dispersed active sites on the surface of oxidized alloy.

### 3.4 Discussion

The screening test showed that partial oxidation activity decreases as: Hastelloy > Superinvar > SUS304 > Inconel, which seemed to depend mainly on the nickel content of alloy. However, this order does not coincide with nickel content of the catalyst: Inconel > Hastelloy > Superinvar > SUS304 (Table 1). Table 1 and XRD results suggested that Fe, Co and Mo, which formed oxide phase or mixed oxide phases, could have significantly affected the activity of the catalyst. Although partial oxidation and reforming active site might be highly composed of nickel, the activity should also be controlled by the additional components of the alloy.

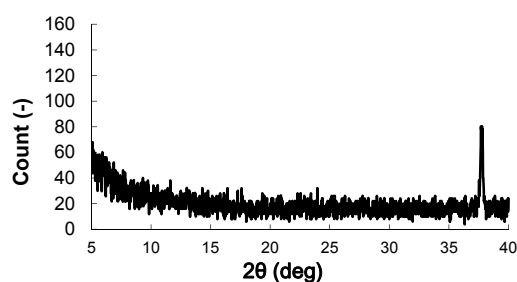


Figure 9: XRD of untreated Hastelloy

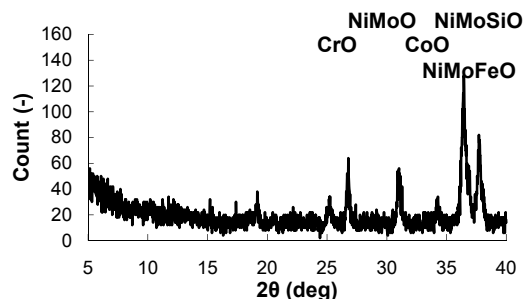


Figure 10: XRD of pre-treated Hastelloy (1273 K in O<sub>2</sub> for 2h) before used in the reaction

These oxides were assumed to function as: 1) a source of activate oxygen to enhance partial oxidation activity, and 2) disperse and keep nickel particles in its ideal small size as to prevent the accumulation of carbon whisker. The remarkable high activity of Hastelloy and Superinvar suggested the importance of the Co component. During the long term reaction, catalyst deactivation by carbon deposition suggested that gradual reduction of nickel by product gas (CO and H<sub>2</sub>) which resulted in larger Ni particles to form through sintering which provided active sites for carbon deposition. Biogas containing polycyclic aromatic compounds and sulfur containing compounds deactivated the catalyst. However they do not deactivate decomposition and total oxidation activity which suggested that the active site for these side reactions were different from active site of partial oxidation. Dilution of poisonous compounds and operation at higher temperature is also suggested to be effective in slowing down the deactivation process. Thus, high temperature oxidation of Ni containing alloy can provide effective catalyst for biogas partial oxidation. Also, other alloy components such as Co are also effective in enhancing and maintaining the activity of the catalyst. Finally, the utilization of commercial alloy tube will make it easy to design catalyst bed for onsite small size gasification plant for biowaste.

### Acknowledgement

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