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# 主 論 文 の 要 旨

論文題目 STUDY ON HYDROCARBON REFORMING CATALYST FOR BIOMASS GASIFICATION PROCESS DERIVED BY PREOXIDATION OF NICKEL CONTAINING ALLOYS
(ニッケルを含む合金の酸化により誘導されるバイオマスガス化プロセス用の炭化水素改質触媒に関する研究)

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## 論 文 内 容 の 要 旨

In this thesis, the feasibility of commercially available nickel-containing alloys was evaluated as reforming catalysts by oxidation pretreatment. The aim was to reform tar by-products obtained from biomass gasification process. Using tetradecane as a model compound, steam reforming, dry reforming and partial oxidation were conducted. The experiment was conducted over several commercially available alloys using steam, carbon dioxide and oxygen as reforming gases. Based on the results obtained from the screening studies, 2 alloys were further evaluated as dry reforming catalysts. SUS304 and Kovar were respectively chosen due to its relatively lower cost and high catalytic activity. The main goal of this research is to provide a robust, low-cost and readily available dry reforming catalyst for small, on-site reforming operations. Oxidation pretreated nickel-containing alloys (Fig. 1) have several advantages for this application, which include the formation of basic metal oxide layer that acts as a substrate for dispersed nickel, reaction promoter, and carbon formation retardant. All of these are important when developing a good dry reforming catalyst.

In general, Figure 1 illustrated that the formed oxide matrix was assumed to be a mixture oxides of basic components such as Fe and Cr which acted as a support for the active components. Ni should be one of the active components and several elements such as Co and Mo were expected to function as promoters or co-catalysts. Since Ni particles were finely dispersed and able to maintain a strong interaction with the support matrix, Ni were hardly sintered to form large particle that could act as nucleating sites for carbonaceous deposits.

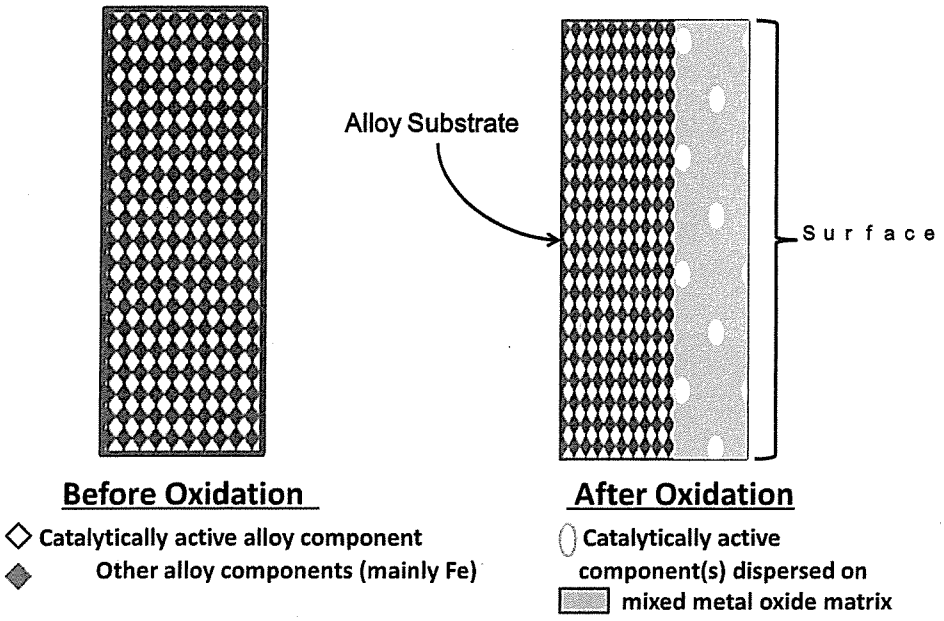


Figure 1. Simplified illustration of the surface of a preoxidized Ni-containing alloy

In Chapter 1, the aim and the objective of this thesis were summarized along with the present issues involved in global energy supply and technology. Further, the developments and potential of biomass derived energy were also discussed. Hydrocarbon reforming was highlighted as a means of improving the efficiency and marketability of biomass gasification.

Chapter 2 discussed the screening tests done using 6 commercially available alloys tubes. This chapter is composed of 3 paper published by the authors which respectively presented the data on partial oxidation, steam reforming, and dry reforming using several model compounds. The mixed oxides formed after oxidation pretreatment and catalytic activity displayed by the alloys were correlated. SUS304 and Kovar were selected for further evaluation in terms of tetradecane dry reforming.

Chapter 3 presented the dry reforming activity of preoxidized SUS304 (1000°C, 120 min) at different reaction temperatures and $CO_2$ flow rates using tetradecane as the model compound. The results showed that preoxidized SUS304 displayed high reaction rate and good resistant against carbon formation even at low reaction temperature (≤700°C) by using high $CO_2$ flow rates (42 and 70 μmol/s). Nickel, probably as NiO, might be the active component while the trivalent- metal oxide $Cr_2O_3$ prevented the formation of carbon by improving the mobility of active oxygen species thus promoting its reaction with the hydrocarbon fragments to form CO and $H_2$. Another notable feature of preoxidized SUS304 is the formation of $Fe_2O_3$, a basic metal oxide that promotes the adsorption and dissociation of $CO_2$. Further work is needed to develop and characterize the catalyst before it can be commercially applied. The maximum performance of pretreated SUS304 was roughly 3 times as much as that of the untreated SUS304.

In Chapter 4, the feasibility of preoxidized Kovar as a dry reforming catalyst was discussed. In addition to nickel, Kovar also contains cobalt which was also identified to be catalytically active towards dry reforming reaction. Conducting the oxidation pretreatment at different temperatures revealed that at temperatures >700°C, a separate

layer is formed on the surface of the alloy tube. Characterization done by XRD and SEM-EDS showed that the performance of Kovar as a dry reforming catalyst is significantly influenced by 3 factors: the oxidation state of iron, thickness of iron oxide ($Fe_3O_4$) layer, and mechanical stability of the formed metal oxide matrix. Among the tested preoxidation temperatures, optimum activity was observed with Kovar preoxidized at 700 °C. In the future, catalyst pretreatment and reaction parameter optimization should be conducted to maximize the potential of Kovar as a dry reforming catalyst.

The data gathered confirmed the author's hypothesis on the application of oxidation on rendering commercially available Ni-containing alloys catalytically active towards dry reforming reaction. It was also deduced that oxidation temperature significantly affects the activity, stability, and mechanical robustness of the catalyst.

Some of the developed catalysts are now under further evaluation in the biomass gasification plant located in the "National Institute for Environment Studies" in Tsukuba, Japan for steam reforming reactions of tar produced by wood waste steam gasification. The next generation of this biomass gasification pilot plant is to operate with pure oxygen equipped with electrochemical oxygen purification system where the primary gasification process produces high temperature carbon dioxide. The developed catalysts are expected to play an important role in converting tar derived from biomass gasification into CO and $H_2$ via dry reforming reaction.

This study presented promising preliminary data on the potential of preoxidized SUS304 and Kovar as dry reforming catalysts. Further research on alloy based catalysts may also provide other researchers an alternative catalyst preparation that would circumvent the common problems encountered with supported metal catalysts.