

Research Article

Evaluation of Preoxidized SUS304 as a Catalyst for Hydrocarbon Reforming

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Received 10 July 2013; Accepted 1 August 2013

Academic Editors: R. Gonzalez-Olmos, S. K. Kurunthachalam, and D. Sun

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The feasibility of oxidation pretreated SUS304 alloy tube as a hydrocarbon reforming catalyst was investigated. It was hypothesized that preoxidation resulted in the dispersion of the active component and the formation of mixed metal oxides on the surface of the alloy which consequently rendered the alloy tube catalytically active towards reforming reaction. Oxidation pretreatment was done in O₂ at 1000°C for 2 hours followed by a catalytic evaluation at 730°C for 2 hours. Tetradecane was used as a model compound for steam, partial oxidation, and CO₂ reforming experiments. According to the collected XRD pattern, α -Fe₂O₃ and Cr₂O₃ were formed after oxidation pretreatment. In addition, SEM-EDX analysis showed a very rough surface composed of oxygen, chromium, iron, and nickel. Catalytic evaluation of the sample displayed activity towards partial oxidation and CO₂ reforming which led to the conclusion that oxidation pretreated SUS304 alloy tube has a potential as a catalyst for partial oxidation and CO₂ reforming of hydrocarbons. However, the varying activity observed suggested that each reforming reaction requires a specific formulation and morphology.

1. Introduction

Fossil fuel, the world's major source of energy, is rapidly depleting as a result of the continuous increase in demand [1] and the decline in oil discoveries [2]. In addition, fossil fuel production and utilization lead to several environmental problems. As an alternative, biomass-derived energy is being developed to lessen greenhouse gas emissions as well as sustain the world's growing oil demand. Biomass as a fuel source offers the advantages of being CO₂ neutral. Furthermore, this alternative energy resource can also provide energy security, especially to non-oil-producing countries.

Hydrogen is one of the most attractive energy sources that can be derived from biomass. It is a clean source of energy with water as its sole product upon consumption. The general process in producing hydrogen from biomass involves biomass gasification followed by syngas reforming. In theory, gasification will completely convert biomass to CO and H₂. In practice, by-products such as tar, hydrocarbons, char, sulfur-containing compounds, CO₂, and H₂O are also produced [3]. Hydrocarbon by-products are then subjected to reforming reaction which increases the efficiency of this

technology. Tar, mainly composed of polycyclic aromatic hydrocarbons, was reported to be almost eliminated when using Ni-based catalysts during hydrocarbon reforming [4]. However, carbonaceous deposits and sintering of catalyst particles still lead to catalyst deactivation. Carbonaceous residues deactivate the catalysts by covering the active surface, blocking the pores, disintegrating the catalysts, and plugging the reactors. Depending on the type of reaction, catalyst, feedstock, and reaction conditions, different kinds of carbon and coke can be formed.

Among the catalysts used for hydrocarbon reforming, Ni-based catalysts are widely preferred due to the high availability and low cost of nickel [5]. Various supports, promoters, and dopants are widely utilized and studied to create rigid and selective catalyst. Several support materials had been tested, for example, SiO₂, Al₂O₃, ZrO₂, MgO, olivine, and MgAl₂O₄ [6–13]. In our previous studies, Ni-based catalysts have been effective both under dry reforming conditions [14, 15] and partial oxidation conditions [16, 17]. Selection of support materials and additives and arrangement of vacant space to accommodate temporal carbonaceous compounds are essential [14]. In addition, metal particle size, metal

dispersion, and catalytic activity are some of the properties that are important in designing effective catalysts. These properties are greatly affected by the interaction between the active component and the support material, which could be controlled in the different stages of catalyst preparation [18].

Further, it was reported that the high temperature oxidation of Mg₂Cu alloy resulted in the formation of MgO and CuO, which rendered the alloy catalytically selective towards C18 ester hydrogenation [19, 20]. In this study, the feasibility of surface oxidized SUS304, an austenitic alloy (10–14% wt Ni, 18–20% wt Cr, and balance Fe), as hydrocarbon reforming catalyst was investigated. This research is pioneered on the application of oxidized Ni-containing alloys as a reforming catalyst. It was hypothesized that oxidation pretreatment will result in the formation of mixed metal oxides and the dispersion of the catalytically active component on the metal oxide matrix. The metal oxides formed on the surface of the alloy functioned as a support material, reactor promoter, and retard carbon formation. In addition, the dispersed catalytically active component was predicted to maintain a strong interaction with the support material which consequently made it resistant towards metal migration, a precursor of whisker-like carbon formation.

Tetradecane was selected as a model compound because it is a simple and pure straight-chained hydrocarbon. This allowed the fundamental reactions to be observed without the possibility of catalyst deactivation by sulfur poisoning. Since SUS304 is a temperature resistant alloy, oxidation was performed at 1000 °C in O₂ to facilitate metal oxide formation. In accordance to the by-product gases produced during biomass gasification, steam reforming (1), partial oxidation (2), and dry (CO₂) reforming (3) were conducted to evaluate the catalytic activity of surface oxidized SUS304:



2. Materials and Methods

2.1. Experimental Apparatus. Figure 1 shows the apparatus used for oxidation and reforming experiments, composed of a vaporizer, a quartz tube reactor (inner diameter: 1 cm), an electrically heated furnace, and a temperature control equipment. The alloy tube was inserted into the quartz reactor and placed into the middle of the furnace. The upper end of the reactor was connected to the vaporizer, while the lower end was connected to the gas sampling valve and to a condenser.

2.2. Oxidation Pretreatment. SUS304 tubes (outer diameter: 1/4 in, length: 35 cm) used in this study were manufactured by Sumikin & Nippon Steel. Surface oxidation was conducted in O₂ at 1000 °C for 2 hours. Using the temperature control equipment, the temperature was programmed to rapidly increase to 1000 °C within 30 minutes, made stable for 2 hours, and gradually cooled to room temperature.

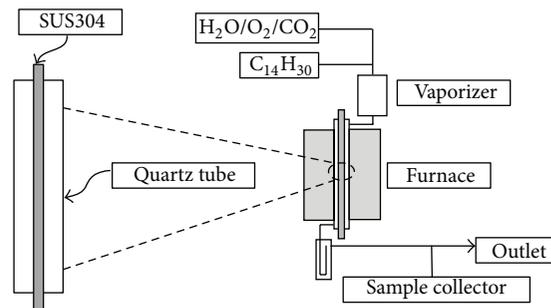


FIGURE 1: Diagram of the reaction apparatus.

2.3. Characterization. From the middle part of the alloy tube, approximately 1 cm was cut, pressed, and analyzed through X-ray diffraction (XRD) and scanning electron microscopy (SEM). The formation and identification of metal oxides by XRD profiling was done using RINT-2500TTR with CuK α (50 kV, 100 mA, $\lambda = 1.54$) as X-ray source. Morphological and compositional analyses were done by a scanning electron microscope with an energy dispersive X-ray detector or SEM-EDX (JSM-6330F).

2.4. Catalytic Activity Evaluation. The catalytic activity of the surface oxidized alloy was compared in terms of CO production rates during steam reforming, partial oxidation, and CO₂ reforming of tetradecane. All reforming reactions were performed at 730 °C for 3 hours with tetradecane automatically pumped into the reactor through a vaporizer at a rate of 1 $\mu\text{mol/s}$. Stoichiometric molar ratios of H₂O, O₂, and CO₂ were, respectively, fed into the reactor. These reaction conditions were referred to as standard reaction condition hereafter.

After determining the type of reforming reaction having the highest CO production rate, a long term reaction was performed using the suitable standard condition. This was conducted to observe the stability of the catalyst.

Primary product gases (CO₂, CO, H₂, and CH₄) were quantitatively monitored using a gas chromatograph integrated with a thermocouple detector or GC-TCD (GL Science GC-3200) with Ar as carrier gas.

3. Results and Discussion

3.1. Catalyst Characterization. Based on the XRD patterns shown in Figure 2, SUS304 is a single phase solid solution of γ -Fe, having a face centered cubic (fcc) crystal lattice. In addition, the 2-hour oxidation pretreatment resulted in the formation of mixed metal oxides, α -Fe₂O₃ and Cr₂O₃, on the surface of the alloy tube. Visual inspection of the alloy tube also showed that SUS304 had lost its metallic luster; instead, its surface became dark gray in color.

The SEM micrograph of the untreated SUS304 (Figure 3(a)) displays a smooth surface, while that of the oxidized tube (Figure 3(b)) reveals a very rough surface with no distinguishing shapes between oxides of iron and chromium. Table 1 shows the surface composition of

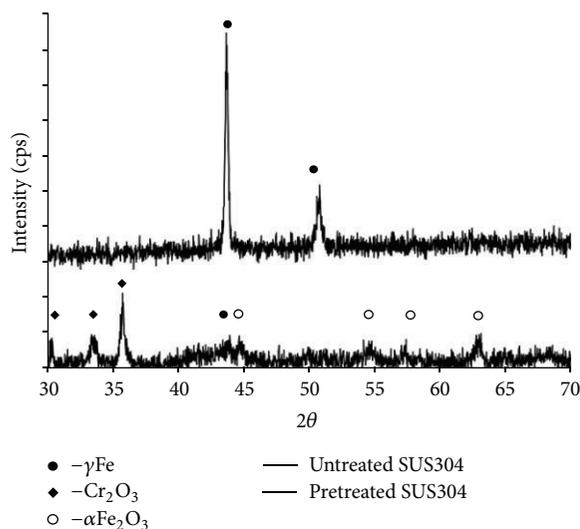


FIGURE 2: X-ray diffraction data of SUS304 before and after oxidation pretreatment at 1000°C for 2 h in O₂.

the sample before and after the oxidation pretreatment as well as the amounts of the identified oxides calculated based on the atomic composition of the sample after oxidation. The atomic composition of the unoxidized sample reflected that of an austenitic alloy. When the marked area in Figure 3(b) was further magnified (Figure 3(c)) and subjected to EDX analysis (Table 1), oxygen (56.27 atomic%) was also detected in addition to Fe, Cr, and Ni. The detection of oxygen implied that oxidation pretreatment led to the formation of an oxide layer. The relative amounts of the formed oxides were calculated stoichiometrically based on the obtained data. However, to clearly present and compare the changes in the abundance of Fe, Cr, and Ni, their respective amounts were recalculated after subtracting that of oxygen from the total sample composition. The calculated data shows that Cr surface concentration increased, thus, the formed surface oxide layer was mostly composed of Cr₂O₃ followed by Fe₂O₃ and, lastly, NiO. It was expected for the oxides of Fe and Cr to be easily and abundantly formed since both were added to the alloy with the main purpose of forming a protective oxide layer under oxidizing conditions. The mechanism and kinetics involved in the oxide formation under the applied condition are currently in progress. Although the collected XRD profile after the oxidation pretreatment showed peaks for Fe₂O₃ and Cr₂O₃, it did not show NiO peaks. The increase in Ni content and detection of NiO (8.64 wt%) on the metal oxide surface by EDX indicated that oxidation pretreatment resulted in dispersed nickel oxide with very small crystalline sizes.

3.2. Catalytic Activity Evaluation. To evaluate the catalytic activity as well as the compatibility of oxidation pretreated SUS304, it was tested in steam reforming, dry reforming, and partial oxidation of C₁₄H₃₀ for 2 hours at 730°C.

Based on the CO production rate, there was no apparent catalytic activity during steam reforming reaction (Figure 4).

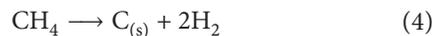
TABLE 1: Composition of SUS304 before and after oxidation at 1000°C for 2 h in O₂ as measured by SEM-EDX.

Element	Atomic%		Oxide	Weight%*
	Unoxidized	Oxidized		
Cr	20.07	51.29	Cr ₂ O ₃	50.36
Fe	73.11	39.75	Fe ₂ O ₃	41.00
Ni	6.82	8.96	NiO	8.64

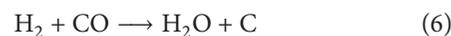
* Calculated from EDX data.

Conversely, CH₄ and H₂ production rates were stable. These observations suggested that tetradecane cracking was favored over tetradecane steam reforming. Another implication is that at 730°C not enough energy was supplied to the system to promote the reforming of tetradecane. Specifically, the Cl species generated from tetradecane was not able to react with the O₂ derived from the dissociation of H₂O_(g), as suggested by Melo and Morlanés [18].

The catalyst was active towards the partial oxidation of tetradecane as shown in Figure 5. Also, the production of CH₄ suggested the occurrence of tetradecane cracking; thus, the produced H₂ and CO are lower than the theoretical values in (2). It was also observed that as H₂ production increased, CH₄ production decreased. This inverse relationship was interpreted to be the effect of CH₄ decomposition (4), which was also reported to be the primary route of carbon formation. It was also assumed that the surface morphology and composition of the catalyst were continuously changing during the 2-hour reaction as shown in the patterns observed from the production rates of the gases:



When subjected to dry reforming (Figure 6), the increasing CO production rate suggested an increasing activity as the experiment progressed. Between 0.5 h and 1.0 h, H₂ increased, while CH₄ decreased, after which both remained stable. Based on (4), the observed CO and H₂ production rates were lower than what was theoretically expected. The generation of water also suggested the occurrence of the reverse water-gas shift reaction (RWGS) as referred to in (5), a reaction that simultaneously occurs during CO₂ reforming [21]. Other suspected sources of water were the cited reactions in (6) and (7) which are also responsible for the formation of carbon at low temperature [21]. This, together with RWGS, led to low CO and H₂ production and an H₂/CO ratio of less than 1. Further, the stable CH₄ production indicated that tetradecane cracking simultaneously took place but at a comparatively lower rate than CO₂ reforming reaction. Lastly, the surface morphology and composition of the catalyst were deduced to continuously change as the reaction progressed as suggested by the collected data:



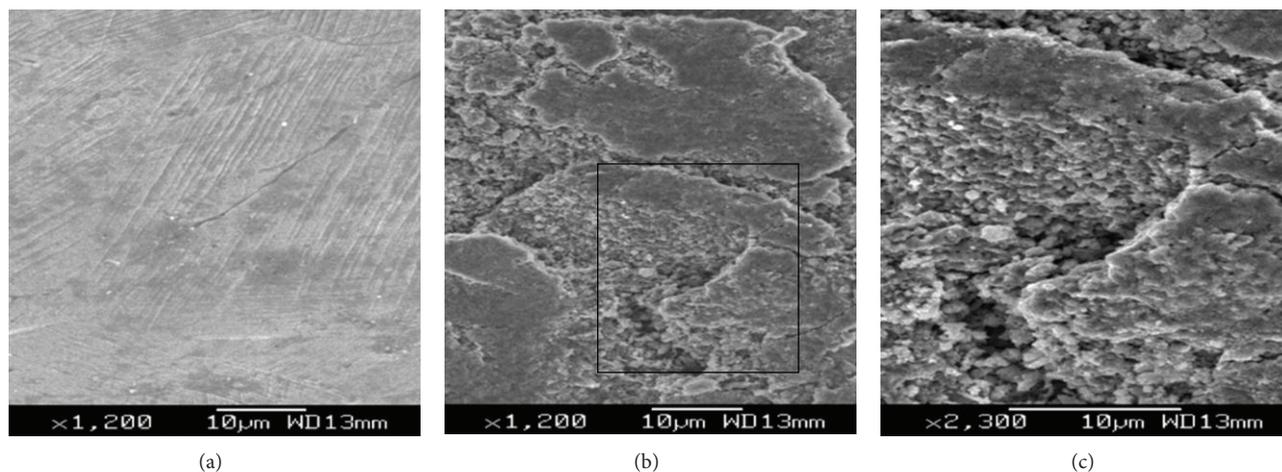


FIGURE 3: Micrographs of SUS304 showing the morphologies of (a) untreated, (b) pretreated, and (c) portion of pretreated sample subjected to elemental analysis.

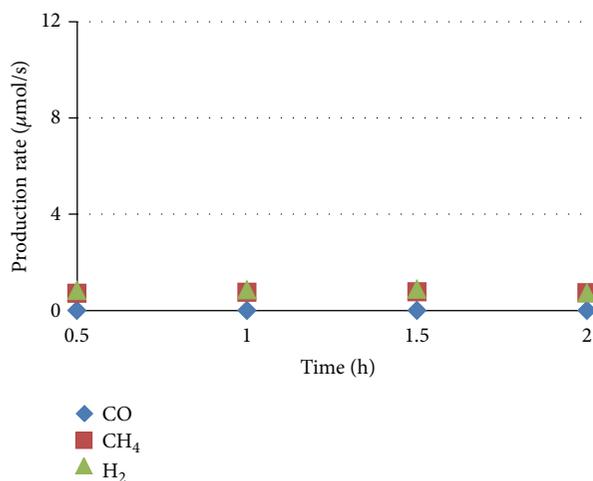


FIGURE 4: Production rate of primary gas products during tetradecane steam reforming at standard reaction condition over preoxidized SUS304.

Among the three reforming reactions used to evaluate the catalytic activity of surface oxidized SUS304, catalytic activity was observed during the partial oxidation and CO₂ reforming of tetradecane. Increasing activity was observed for both partial oxidation and CO₂ reforming (Figures 5 and 6), but higher initial activity was noted during partial oxidation. At 1.5 h, the catalyst displayed higher activity for CO₂ reforming reaction. In addition, lower CH₄ was also observed throughout the CO₂ reforming experiment for 2 h.

The good activity of Ni-based reforming catalysts had been reported by several researchers as well as the positive effects of high dispersion and surface area [13]. Other components, such as Fe, were also established to stabilize nickel as well as to prevent the catalyst from being deactivated [9, 13]. Correlating these to the collected data, it was assumed that the catalytically active component was also Ni and that both Fe and Cr stabilized the Ni against sintering. Oxidation

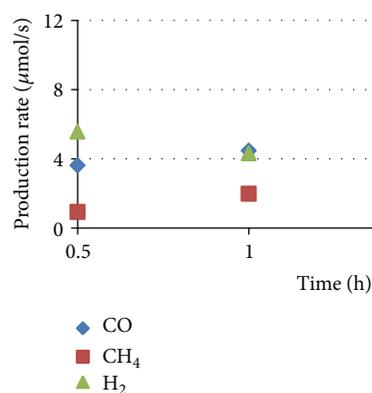


FIGURE 5: Production rate of primary gas products during tetradecane partial oxidation at standard reaction condition over preoxidized SUS304.

pretreatment was also deduced to disperse the Ni particles, thus increasing the surface area. In addition, the formed oxides functioned as a source of active oxygen that rendered the alloy catalytically active towards partial oxidation and CO₂ reforming of tetradecane. However, the varying catalytic activity observed at different types of reforming reaction suggested that each reforming reaction requires a different formulation, dispersion, and surface area.

4. Conclusion

This study evaluated the feasibility of an Ni-containing alloy SUS304 that was preoxidized at 1000 °C in oxygen for 2 hours as a catalyst for hydrocarbon reforming using tetradecane as a model compound. Sample characterization done with XRD and SEM-EDX showed that the oxide layer formed on the surface of the preoxidized sample was composed of oxides of Fe, Cr, and Ni. It was concluded that preoxidized SUS304 has a potential to be utilized as a catalyst for hydrocarbon partial oxidation and CO₂ reforming.

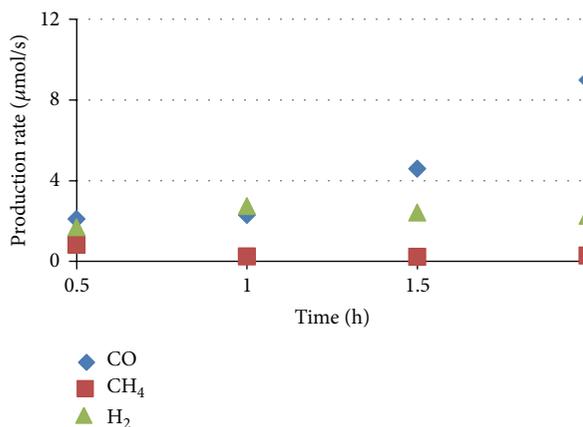


FIGURE 6: Production rate of primary gas products during tetradecane CO₂ reforming at standard reaction condition over preoxidized SUS304.

Disclosure

This is to state that all the academic affiliations of the authors are listed in the title page of the paper without any corporate or industrial affiliations with the exception of Mr. Shintaro Kawai who is presently an employee of Noritake Co., Limited, a ceramics and porcelain manufacturer. Also, all the funding sources for this study are listed in this paper professional affiliation, advisory position, patent holding, and financial holding existing between the authors and Sumikin & Nippon Steel. This form was submitted on July 19, 2013, by Sharon Rose de la Rama.

Acknowledgment

This research project was financially supported by the Ministry of Environment of Japan (K2106).

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