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Novel surface pretreatment for metal structured catalyst

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ABSTRACT

The novel surface pretreatment is successfully developed to strengthen the adherence of catalyst via the oxidative formation of the uniform metal oxide layer on the metal substrate, which plays an important role as a binder between metal substrate and catalyst layer. The developed pretreatment method can be applied without regard to shape and composition of metal support. The surface pretreated metal structured catalysts are adopted to the natural gas steam reforming, showing a CH_4 conversion of 82% and stability for 120 h at high GHSV of 31,000 h^{-1}, while conventional metal structured catalysts quickly deteriorates.

1. Introduction

In general chemical processes, the conventional packed bed reactor with pellet catalysts has some barriers which are attributed to heat and mass transfer limitation due to low thermal conductivity of ceramic support and diffusional resistance into the pellet resulting in the low effectiveness factor ($\eta = 0.03$) [1]. The part of available active metal on the surface of pellet catalyst participates in reaction and becomes low efficient because of the internal mass and heat transfer resistance. Ultimately, it has been supplemented by using excess pellet catalysts which cause the increase of reactor volume, pressure drop, channeling and slow response time [2]. Hence, the metal structured catalysts such as monolith, metal foam and mesh have been investigated as an alternative to conventional packed bed reactor [3]. Previous works have reported that it is possible for the reactors with metal structured catalyst to be compact and lightweight on system and increase space-time yields by the enhancement of heat and mass transfer between the catalyst and metal structure carrier [4,5]. It has been verified by the authors that the heat flux in the monolithic bed reactor was higher than that in the packed bed reactor under the same degree of temperature gradient from the furnace wall to the catalyst bed [6]. In addition, our investigation was proved by means of the comparative experimental studies using either the metal monolith or pellet catalysts [7]. Generally speaking, metal structured carriers with different geometric surface area exhibit the difference in heat and mass transfer characteristics affecting the catalytic performance [8]. No matter what the shape, however, the metal structured catalysts need to tackle the detachment of catalyst layer and deterioration of catalyst due to the difference of thermal expansion coefficient between the metal substrate and ceramic catalyst layer and the catalyst sintering at high reaction temperature, respectively [9].

Researchers have focused on developing the pretreatment of substrate to improve the adherence between metal substrate and catalyst layer. In particular, FeCralloy material has been applied for the metal structured carrier because it is favorable to the Al_2O_3 layer formation on the FeCralloy surface by heat treatment. The formed Al_2O_3 layer enhances the adherence between the metal substrate and catalyst layer [10,11]. Fig. 1(a) demonstrates the fact that the conventional pretreatment makes irregular metal oxide layer on the metal substrate which has the coated Al_2O_3 layer easily peeled off [12]. It was confirmed by means of SEM image of Al_2O_3 coated FeCralloy substrate. There are two ways to resolve this problem. One approach is the coating of Al_2O_3 thin layer which provides large surface area as a support for the uniform active metal distribution and good cohesion within the catalysts by a variety of methods such as sol–gel route, slurry coating and chemical vapor deposition in Fig. 1(b) [13]. It is expected that the coated Al_2O_3 thin layer is strongly linked between the irregular metal oxides on the metal substrate. The other is the formation of uniform Al_2O_3 layer to adhere strongly between the catalyst layer and the metal substrate. Meille [14] dealt with the various pretreatments of the substrate including anodic oxidation, thermal oxidation and chemical treatment through the review concerning the catalyst deposition on structured surfaces.

We have developed a proprietary way for the uniform Al_2O_3 layer formation on the metal substrate by a controlled oxidative method. Hence, the present study evaluates the catalytic activity

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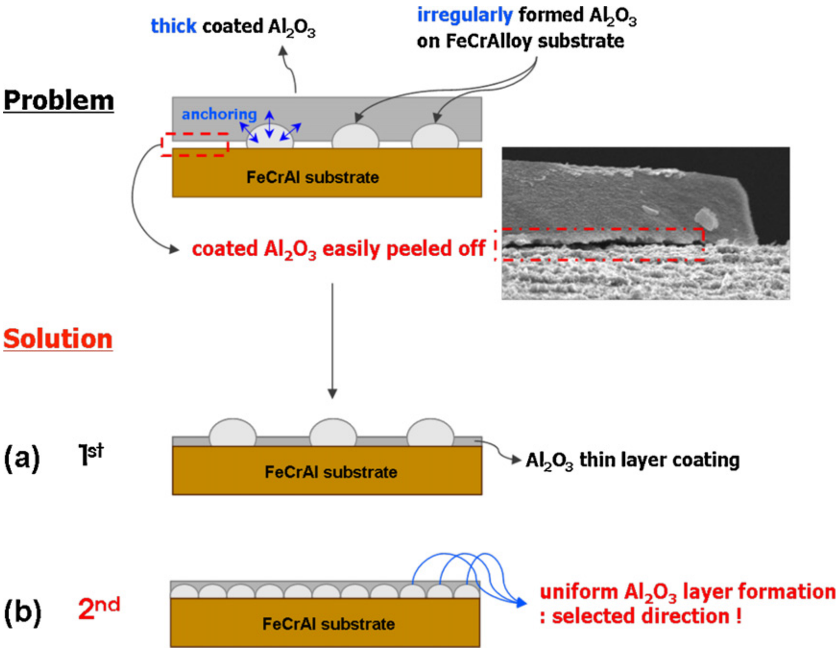

Fig. 1. Schematic diagram of the problem-solving sequence; (a) Al_2O_3 thin layer coated metal substrate and (b) uniform Al_2O_3 layer formation on the metal substrate.

of metal structured catalyst with the suggested pretreatment in natural gas steam reforming (NGSR) for H_2 production as compared to metal structured catalyst without the pretreatment.

2. Experimental

2.1. Preparation of metal structured catalyst

FeCralloy monolith, foam and mesh were used as metal structured carriers. FeCralloy monolith was prepared by rolling a flat metal strip and a corrugated strip in the same way of previous works [6,7]. FeCralloy foam with 580 μm pore size and 19 mm thickness was supplied by Alantum (Germany) and used by cutting round in diameter of 21 mm. Also, FeCralloy mesh was the product with size of #30 from Fiber Tech Corporation in Korea.

Each prepared metal structured carriers was rinsed with acetone in ultrasonic bath for 30 min and then pre-calcined at 900 °C after the developed surface treatment. Pre-calcined structured carriers were coated with 10 wt% Al_2O_3 sol followed by 15 wt%$Ni/MgAl_2O_4$ catalyst wash-coating and then calcined at 600 °C for 3 h under air. The Al_2O_3 sol solution prepared by dissolving boehmite (DISPERAL P2, SASOL) in deionized water was dip-coated twice and then calcined at 900 °C for 6 h under air. For the preparation of stable Al_2O_3 sol solution, the behavior of viscosity and pH was observed in Al_2O_3 sol solutions with various Al_2O_3 content of 5–20 wt%. The viscosity and pH was measured by Sine-wave Vibro viscometer (SV-10, Korea A&D Corp.) in vibration type and a pH meter (model 720A+, Orion) at 26 °C, respectively. The catalyst slurry was prepared as a mixture of 15 wt%$Ni/MgAl_2O_4$ catalyst powder, boehmite and deionized water in the weight-ratio of 1:4:1 and stirred for 3 days. The 15 wt%$Ni/MgAl_2O_4$ pellet catalyst with a large surface area (25.8 m^2/g) and a metallic surface area (2.7 m^2/g) was prepared by impregnation method. The catalyst was wash-coated repeatedly up to the loaded catalyst amount of 2.0 g.

2.2. Characterization

BET was carried out to measure the surface area of catalyst in BELSORP-Max (BEL Japan, Inc.) by the N_2 adsorption at −196 °C. The metallic surface area was measured by H_2-chemisorption through the pulse technique in BEL-METAL-3 (BEL Japan, Inc.). The sample of 50 mg was reduced in H_2 flow at 700 °C for 1 h and purged at 700 °C for 1 h in He flow and then cooled to 50 °C. A 20% H_2/Ar gas was pulsed into the catalyst when the Ni surface was saturated. The surface morphology and composition of metal substrate were identified by scanning electron microscopy (SEM, HITACHI S-4700) and energy dispersive spectrometry (EDS, Horiba 7200-H), respectively.

2.3. Catalytic test

The natural gas steam reforming (NGSR) reaction was carried out at 700 °C under atmospheric pressure. Before the reaction, the catalyst was reduced in 10%H_2/N_2 at 700 °C for 1 h. Reactants were fed with steam to carbon (S/C) ratio of 3 and the space velocity (SV) was 15,000–31,000 h^{-1}. Effluents were analyzed with an on-line micro gas chromatograph (Agilent 3000) equipped with a TCD detector. For comparison, 15 wt%$Ni/MgAl_2O_4$ pellet and conventional metal structured catalyst were used as references. The conventional metal structured catalyst was applied the thermal pre-treatment.

3. Results and discussion

3.1. Surface pretreatment

As aforementioned, the surface pretreatment such as anodic oxidation, thermal oxidation and chemical treatment was carried out to obtain the uniform metal oxide layer with increasing the surface roughness on the metal substrate [14]. It is favorable to the strong interaction between metal oxide layer and coated catalyst layer. In the case of FeCralloy substrate, Al_2O_3 oxide layer was formed by thermal treatment because Al diffusion is faster than other compositions of Fe and Cr [10]. It is worth noting that the Al_2O_3 layer formed on the FeCralloy substrate is compatible with Al_2O_3 sol coating. Furthermore, uniform Al_2O_3 layer with large surface area on the metal substrate combines well with the catalyst layer. In the conventional thermal treatment, however, the morphology and composition of surface metal oxide layer is mainly

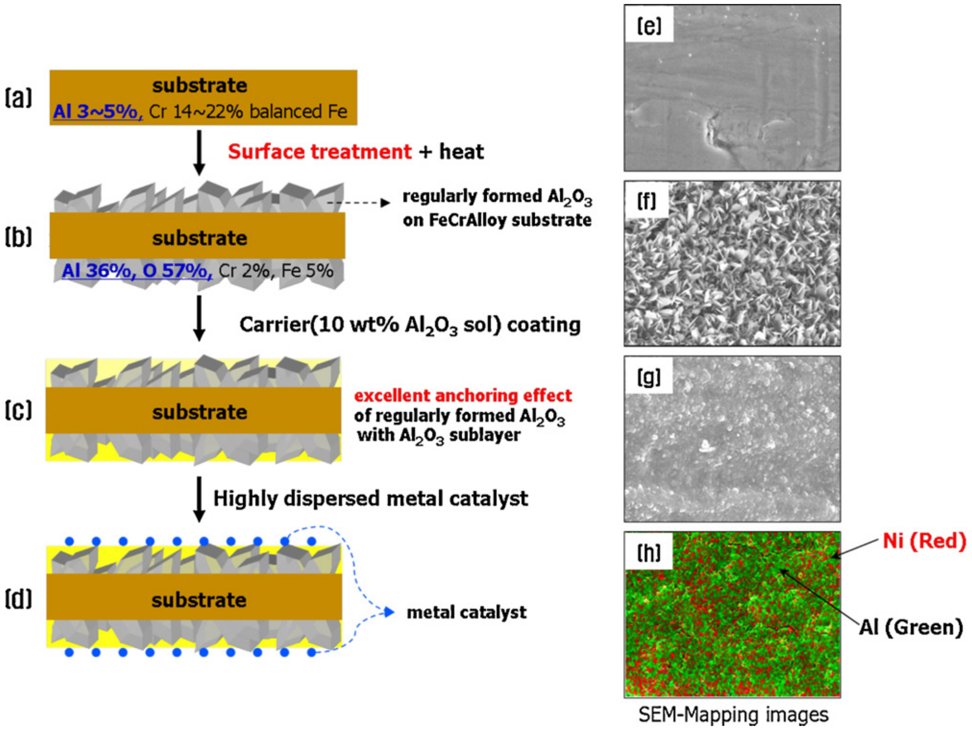

Fig. 2. Schematic drawing of the suggested method for catalyst coating (a–d) and corresponding SEM images obtained from experiments (e–h); fresh FeCralloy metal substrate, metal substrate after surface pretreatment, Al_2O_3 sol-coated metal substrate, and metal catalyst-coated metal substrate, respectively (from top to bottom).

affected by the heating temperature and time, resulting in the agglomeration of oxide layer at high heating temperature for a long time. Besides, it is also difficult to form the even oxide layer on the metal substrate irrespective of the shape and composition of metal structured carrier. It is essential, therefore, to develop the versatile surface pretreatment for the formation of uniform metal oxide layer on the surface of metal structured carrier regardless of shape.

The suggested procedure for catalyst coating on the metal substrate is illustrated in Fig. 2(a–d). First of all, the metal structured carrier goes through the developed surface treatment, namely controlled oxidation, and heating at 900 °C for 6 h. The scale-like Al_2O_3 layer is regularly formed throughout the metal substrate. And then, the Al_2O_3 sublayer anchoring strongly to the metal substrate is coated by 10 wt% Al_2O_3 sol solution. In final step, active metal catalyst is highly dispersed for a good catalytic performance. These procedures were confirmed based on the data from SEM images below to the right in Fig. 2(e–h). The magnification of images is equally same (×10,000). As shown in Fig. 2(h), the Ni component and its well-distribution were identified by elemental mapping analysis (red dots). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.) It is anticipated that the scale-like Al_2O_3 layer which was uniformly formed on the FeCralloy substrate by the controlled oxidation is favorable to the adhesion of Al_2O_3 sublayer on the metal substrate [3].

Fig. 3 shows the surface morphology of prepared metal structured carriers. It is evident that the application of developed surface treatment makes the extremely uniform Al_2O_3 layer on the substrate irrespective of the shape of metal carrier. On the contrary, without the surface treatment, the metal substrate by only thermal treatment was formed irregularly agglomerated metal oxide layer in Fig. 3(e). In addition, it is observed that the Al_2O_3 layer agglomerates severely at the condition of a high heating temperature above 900 °C and a long time of 10 h in conventional thermal treatment (data not shown here).

Table 1 summaries the atomic ratio of element on the surface layer of metal structured carrier. It is confirmed that after our proprietary surface treatment, Al content of metal oxide surface layer considerably increases in comparison with the surface layer without the surface treatment. The Al content of 5.2% in fresh FeCralloy mesh increased up to 36.1% after surface treatment, while a lower Al atomic content of 21.7% was measured on the conventional thermal treatment. It is also obvious that prepared metal structured carriers with surface treatment show similar Al atomic content on the surface irrespective of shape. Based on these results, it is concluded that the suggested surface treatment can make the uniform Al_2O_3 layer on the surface regardless of the shape of metal structured carriers. It can be envisaged that the Al_2O_3 layer growth is attributed to the difference in diffusivity of metals which comprises FeCralloy surface. It seems likely that the surface treatment promotes the growth of uniform Al_2O_3 layer with a preferred diffusivity of Al.

Table 1
EDS data of prepared metal substrates.

Element (At.%)	Fresh	After developed surface treatment			After conventional thermal treatment
	Mesh	Monolith	Foam	Mesh	Mesh
Fe	63.4	5.1	6.9	5.2	24.1
Cr	18.1	2.2	3.7	2.2	8.2
Al	5.2	35.7	33.9	36.1	21.7
O	12.7	57.0	55.5	56.5	45.7

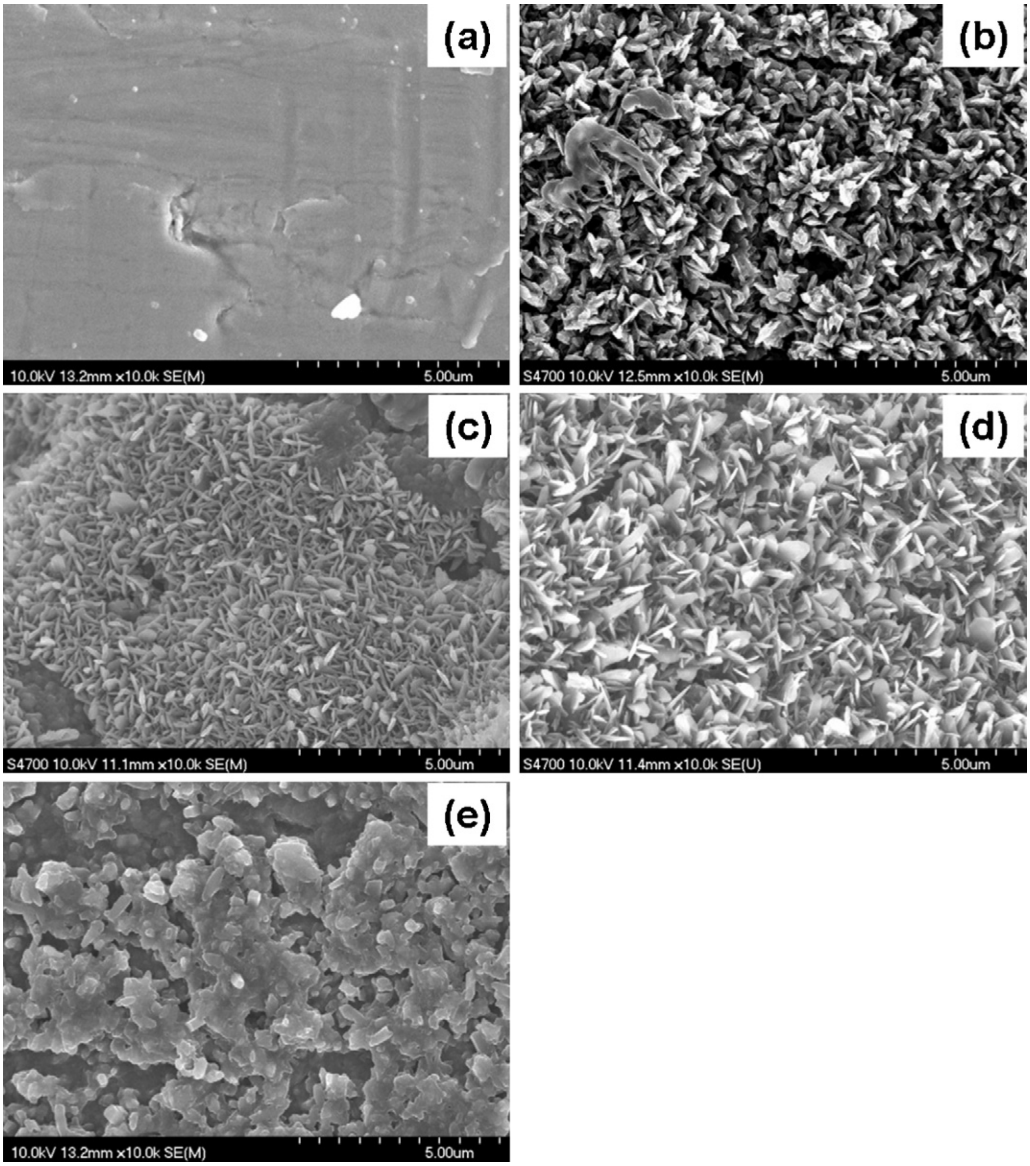

Fig. 3. SEM images of (a) the fresh FeCralloy substrate, and FeCralloy substrates prepared, (b) monolith, (c) foam and (d) mesh with surface treatment, and (e) mesh without surface treatment.

3.2. *Al_2O_3 sublayer coating*

The Al_2O_3 sublayer was coated using boehmite (AlOOH) as a precursor in Al_2O_3 sol solution. It strongly combines the catalyst layer with metal oxide layer formed on the metal substrate and also plays an important role as a support to improve good dispersion and cohesion of catalytic species [15]. Accordingly, it is also required to prepare a stable Al_2O_3 sol solution. In general, the pH value, boehmite amount and aging time of Al_2O_3 sol solution are key variables for the preparation of stable Al_2O_3 sol solution. In the case of the pH value, it can be controlled by the addition of HNO_3 or CH_3COOH which results in the repulsive interaction between the Al_2O_3 particles charged positively owing to the adsorption of H^+ ion of acid [16,17]. Jia et al. has been reported that the solution pH between 4.0 and 6.0 is optimum to obtain the stable Al_2O_3 sol solution [12]. It was accounted for the reason why sol solution with high pH value above 6.5 increases the viscosity to be hard of complete coating, while sol solution with low pH value below 3.5 is very strong acidic to decrease the oxidation layer of FeCralloy surface.

In this study, boehmite of SASOL product involved in the water dispersible alumina system was used by dissolving in deionized water. It was investigated the effect of the boehmite content and aging time on the change of pH value and rheological behavior in Al_2O_3 sol solution for the optimization of boehmite content. It is because that the adhesion and coated Al_2O_3 amount depend on the viscosity which is determined by the boehmite content, aging time and solution pH [18]. Fig. 4(a) exhibits the pH value of Al_2O_3 sol solution with various boehmite contents for 140 h. All prepared Al_2O_3 sol solution maintains the constant pH value of the 4.4–4.6. In Fig. 4(b), it is observed that boehmite content has an effect on the viscosity of Al_2O_3 sol solution. The viscosity of 5 wt% and 10 wt% Al_2O_3 sol solutions exhibits no changes in the curve for the long aging time of 140 h, while that of 15 wt% Al_2O_3 sol solution increases gradually with time. Especially, in the case of 20 wt% Al_2O_3 sol solution which is not shown, the viscosity increases dramatically up to 4500 mPa s after 20 h and the sol solution is transformed into a gel state. It corresponds that high content of boehmite makes the viscous sol solution and causes the thick layer coating and crack on the surface [3,17]. According to previous reports, the dispersion or flocculation of particles is affected by the magnitude of particle–particle interaction energy and particle concentration in the colloidal suspension [19]. Furthermore,

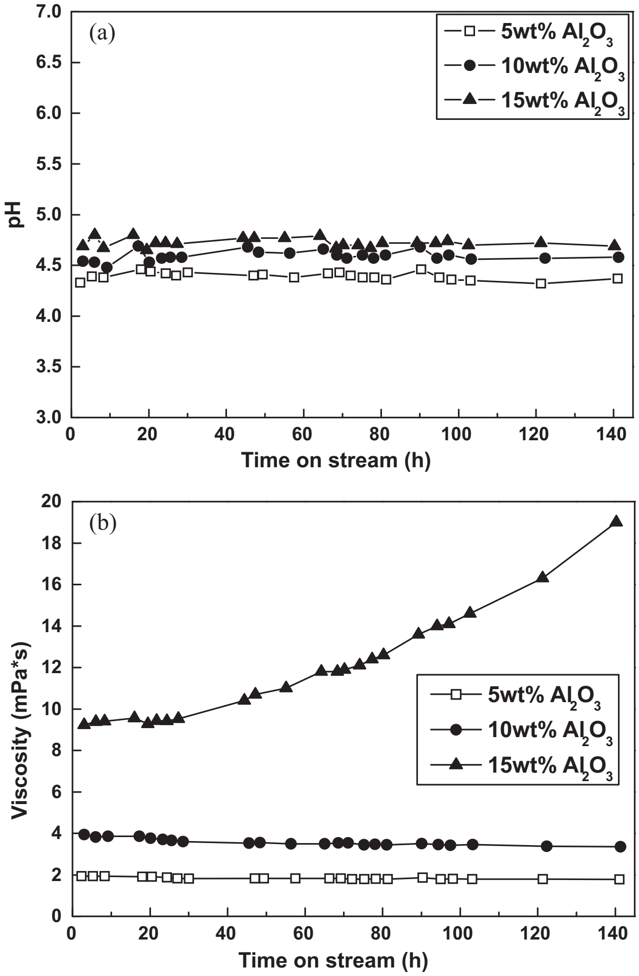

Fig. 4. Effect of Al_2O_3 content on the (a) viscosity and (b) pH of Al_2O_3 sol solution.

in boehmite system, the viscosity of the dispersion increases with increasing the interaction in the gel network which consists in the aggregation of the charged colloidal particle to form a continuous network [17]. Hence, it can be explained that the viscous solution with high content of boehmite is attributed to the increase of interaction between the particles and the formation of continuous network resulting in the gel formation. In the light of the viscosity and loading amount of Al_2O_3, we fixed the boehmite content at 10 wt% and stirred for 72 h to prepare a stable Al_2O_3 sol solution.

It was identified that the Al_2O_3 sublayer was uniformly coated on the surface with surface treatment by the SEM images in Fig. 5. On the contrary, the Al_2O_3 sublayer was incompletely coated because the irregular Al_2O_3 layer on the metal substrate without surface treatment hindered from the adhesion and resulted in the formation of crack on the surface. It is obviously demonstrated by the enlarged image in Fig. 5(b). It is clear that the uniform Al_2O_3 layer by the surface pretreatment allows the even Al_2O_3 sol coating on the surface of metal structured carriers. In addition, it seems likely that irregular Al_2O_3 layer has a negative effect on the catalytic activity and stability of metal structured catalyst.

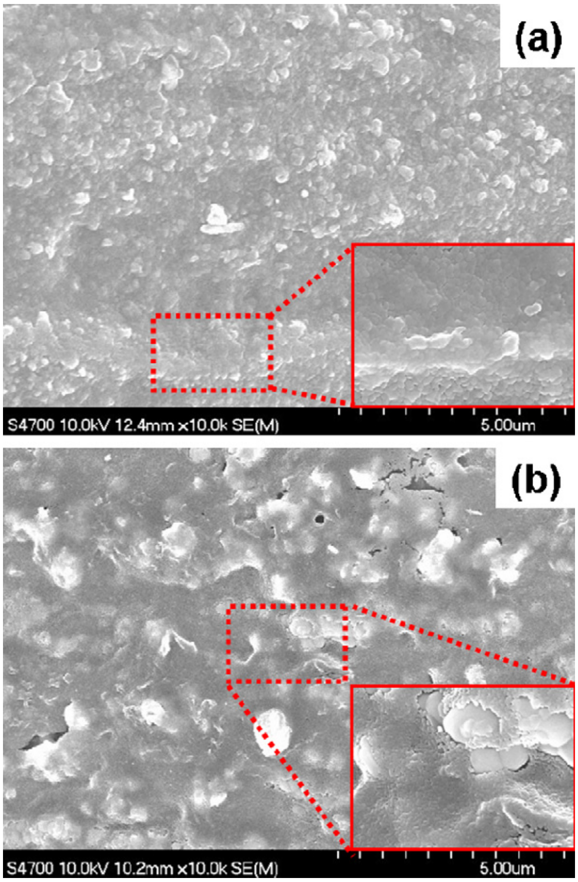

Fig. 5. SEM images of Al_2O_3 layer coated mesh substrate (a) with surface pretreatment and (b) without surface pretreatment (inserting the magnified image).

3.3. *Catalytic test in NGSR*

Fig. 6 exhibits the comparative result of catalytic activity between the pellet catalyst and monolith with surface treatment. The catalytic activity of pellet catalyst was deteriorative under severe condition with high SV from 15,000 h^{-1} to 30,000 h^{-1}, which revealed that the pellet catalyst had the heat and mass transfer limitation at high SV because of low effectiveness factor. On the other hand, the metal monolith coated with the small amount of active catalyst shows the higher CH_4 conversion than the pellet catalyst at the high SV in NGSR. In terms of temperature gradient from the wall to the catalyst bed in the furnace, it was 187 °C and 243 °C for the metal monolith and the pellet, respectively. This result is in line with previous reports that the heat transfer is more efficient in the metal monolith than the pellet catalyst [7,20]. It indicates that the metal monolith catalyst is more favorable to the H_2 production in

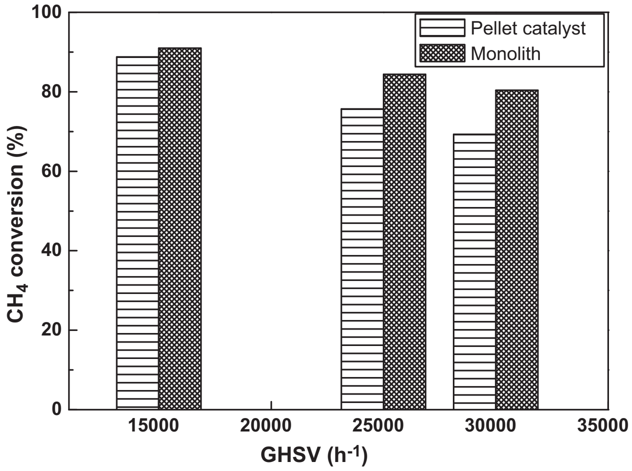

Fig. 6. Comparison of CH_4 conversion with GHSV over (a) 15 wt%$Ni/MgAl_2O_4$ pellet catalyst and (b) monolith with surface pretreatment in NGSR (reaction condition: $T = 700\,°C$, $S/C = 3.0$, after 5 h).

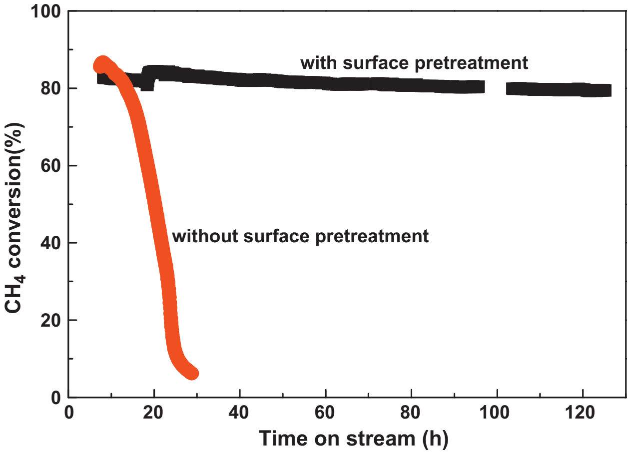

Fig. 7. Effect of surface pretreatment on CH_4 conversion with time on stream over $Ni/MgAl_2O_4$ catalyst coated monolith (a) with surface pretreatment and (b) without surface pretreatment (reaction condition: $T = 700\,^\circ C$, $S/C = 3.0$, $GHSV = 31{,}000\,h^{-1}$).

NGSR than the pellet catalyst owing to the improvement of mass and heat transfer which results from the high availability of the catalyst in the reaction and good thermal conductivity [21].

Furthermore, we investigated the effect of surface treatment on the catalytic performance. Importantly, the monolith catalyst with surface treatment showed a good stability for 120 h as compared to conventional monolith catalyst without surface treatment in Fig. 7. This result implies that the uniform Al_2O_3 layer on the metal substrate with the developed surface treatment results in a good catalytic performance by enhancing the adherence between the metal substrate and catalyst layer. In the previous reports [12,22], the increase of roughness on the metal surface facilitates the strong interaction between the coating layer and metal substrate due to providing the new coating anchoring which is a key influence factor to hinder the detachment of coating layer. As shown the SEM images in Fig. 3, it is clear that the uniform Al_2O_3 layer is formed on the FeCralloy substrate with the surface treatment. Accordingly, the uniform Al_2O_3 layer formed on the monolith with surface treatment enables the catalyst layer to combine strongly with metal substrate in our results. On the other hand, without surface treatment, the metal substrate by only thermal treatment shows the formation of irregularly agglomerated metal oxide layer which hinders the uniform catalyst coating and weakens the adherence between the metal substrate and catalyst layer. It would be likely that the catalytic deactivation of the monolith catalyst without surface treatment could happen to some extent after the long exposure to the reaction due to the week interaction between the metal substrate and catalyst layer. To prove the detachment of coating layer, we will carry out the adherence test in the near future.

4. Conclusion

We have successfully developed the novel surface treatment which makes the uniform Al_2O_3 layer on the surface of FeCralloy metal structured carrier regardless of the shape of the carriers. The formed Al_2O_3 layer enhances the adherence between the metal substrate and catalyst layer resulting in a good catalytic activity and stability in NGSR, while the structured catalysts without surface treatment becomes deactivated on the course of reaction. In conclusion, the developed surface treatment will be a promising method for the formation of uniform metal oxide layer to strengthen the adherence of catalyst layer on the metal substrate as well as to improve the catalytic activity and stability.

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