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A Novel Method to From Well-adhered $\gamma$-Al$_2$O$_3$ Coating in 316L Stainless Steel Microchannels

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Abstract

A method to enhance the adherence of Al$_2$O$_3$ coating with AISI 316L metallic substrate was proposed in this study. The substrate was aluminized by pack cementation at 850°C for 10 h, and then oxidized at 900°C for 10 h, subsequently, the Al$_2$O$_3$ whiskers formed uniformly. The suspension mixing 3μm $\gamma$-Al$_2$O$_3$ powder, alumina sol, PVA and water was directly applied to the microchannels pretreated by above mentioned aluminizing and oxidation method by dip coating. And then the sample was dried and calcined at 600°C for 2 h to form $\gamma$-Al$_2$O$_3$ coating in the microchannel. The morphology and phase composition of the coating were characterized by X-ray diffraction (XRD), energy dispersive spectrometer (EDS), scanning electron microscope (SEM). The adhesion between the substrate and coating was tested by ultrasonic vibration. The results showed that aluminized treatment could effectively improve the adhesion, and the mass-loss rate of the coating was only 1.24%. The main pore size of the coating was between 30 Å and 100 Å. The coating has no cracks, and possessed with high specific surface area, 234 m$^2$/g.

Keywords: 316L metallic substrate; Aluminized pretreatment; $\gamma$-Al$_2$O$_3$; Suspension; Dip coating; Adhesion

1. Introduction

Microchannel reactors are commonly used for conducting heterogeneous catalytic reactions such as Fischer Tropsch synthesis. Micro-packed beds of powder catalysts can sometimes be used [1-3], but in general, a very thin layer of catalyst that sticks to the reactor wall is preferred, because of mass and/or heat transfer improvement [4-6]. Success of such reactors depends on the formation of an adherent and uniform support layer on the microchannels. The pretreatment of the substrate to coat is gaining more and

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more importance because it allows to increase the adherence of the catalytic layer and thus the life time of the structured catalyst. In most of the studies, aluminum containing metallic substrates have been used in order to take advantage of the formation of an Al2O3 layer on the surface of the substrate on thermal treatment at high temperature. For aluminum-free substrate, a primer coating can be used to form a thin layer of alumina which can enhance the adherence of the subsequent washcoat [7]. However, the combinationability of the washcoat was still difficult to ensure.

The study proposed a novel aluminizing pretreatment method to further enhance the adherence of Al2O3 layers on aluminum-free stainless steel.

2. Experimental

Micro-structured plates made of AISI 316L stainless steel, containing 32 channels 500μm deep and 500μm wide on only one plate side were used. The proposed washcoating process consisted of substrate pretreatment and coating deposition.

2.1. Substrate pretreatment

Firstly, a 316L plate was cleaned in 5% NaOH alkaline and then 30% HNO3 acidic solution, and was then ultrasonically rinsed in acetone for 30min to remove oil, primary oxidation and superficial impurities. Secondly, the plate was packed in the aluminizing agent which is powders mixing Al, NH4Cl and Al2O3 with a certain proportion, and then aluminized at 850°C for 10h. The aluminized layer with 30μm thickness was formed. Thirdly, the plate was heated up to 900°C with a ramp rate of 3°C/min and oxidized for 10h. Uniform Al2O3 whiskers were grew up on the surface of the metallic substrate. The process was called as aluminizing pretreatment.

Another plate was pretreated by immersing in HCl and HNO3 mixed solution to increase the surface roughness for comparison, which was called as acid pretreatment in the following context.

2.2. Coating deposition

The boehmite sol was prepared by adding aluminum hydroxide powder to a 0.4 wt. % HNO3 aqueous solution, PH value of which was controlled to 3.5. The sol was stirred to ensure uniformity and then aged for 2 days. Then, the boehmite sol was mixed with the 4 wt. % PVA and stirred for 2 h and resulted in alumina sol. The γ-Al2O3 suspension was prepared by dispersing commercial γ-Al2O3 powder (3μm) and PVA in the alumina sol to form coating slurry. After vigorous stirring at room temperature, the suspension was suitable for deposition and applied to the microchannels pretreated by above mentioned aluminizing and oxidation method by dip coating, dried at room temperature and calcined at 600°C for 2 h.

The coating on the acid treated substrate was prepared in two steps: (i) boehmite primer deposition: applying the alumina sol to the microchannels, drying and calcined at 600°C for 5 h to form primer coating. (ii) dip-coating in the alumina suspension: same process with the aluminized substrate.

2.3. Characterization of the coated samples

The prepared samples were characterized by SEM images (Electron Scanning Microscope EVOMA from Zeiss), XRD analyses (D/mx2550V), EDS analyses (X-MAX50), BET analyses (Mecromeritics2010, using the N2 absorption technique). The coating adhesion was measured by
ultrasonic adhesion test. The coated samples were immersed in acetone solution, and treated in an ultrasonic bath for 30 min. The weight loss was measured to evaluate the adhesion between the coating and substrate.

3. Results and discussion

3.1. Morphology characterization

The surface morphologies of the pretreated stainless steel substrate were shown in Fig.1. It was found that the aluminized surface uniformly formed Al$_2$O$_3$ whiskers through oxidation at high temperature, as shown in Fig.1 (a), which greatly increases the specific surface area of the oxidized layer. The acid treated surface had many etched holes, as shown in Fig.1 (b), improving the surface roughness and then adherence of the coating with the substrate.

![Fig. 1. The morphology of (a) aluminized surface; (b) acid treated surface](image)

Figure 2 showed the morphology of coatings in the microchannels with different pretreatment method. The coating on the stainless steel substrate through aluminizing treatment has no crack, as shown in Fig.2(a), whereas, a small amount of cracks exist in the coating by acid pretreatment, subsequently, these cracks will reduce the adhesion obviously.

![Fig. 2. Morphology of coating by different pretreatment (a) aluminizing treatment; (b) acid treatment](image)

From Fig. 3(a), it can be seen that the coating has high pore volume and grain growth uniformity. The composition of the coating was $\gamma$-Al$_2$O$_3$ from the XRD analysis results, as showed in Fig.3(b).
3.2. BET surface area

From the BET analysis results, as shown in Fig.4, the main pore size of the coating was between 30 Å and 100 Å. The coating possessed with high specific surface area, 234 m²/g, and good pore connectivity.

3.3. Coating adherence

The ultrasonic vibration test results were listed in Table 1. The coating on the substrate through aluminizing pretreatment has lowest weight loss, which has good adherence with the stainless steel substrate compared with that through acid pretreatment and Ref.[8,9].

Table 1. Results of adhesion test

<table>
<thead>
<tr>
<th>Samples</th>
<th>Carrier load /mg.plate⁻¹</th>
<th>Weight loss %</th>
</tr>
</thead>
<tbody>
<tr>
<td>The coating by aluminizing pretreatment</td>
<td>94.0</td>
<td>1.24</td>
</tr>
<tr>
<td>The coating by acid pretreatment</td>
<td>90.0</td>
<td>3.9</td>
</tr>
<tr>
<td>Reference[8]</td>
<td>91.6</td>
<td>2.52</td>
</tr>
<tr>
<td>Reference[9]</td>
<td>24.7</td>
<td>3.1</td>
</tr>
</tbody>
</table>

3.4. Catalytic performance

The catalyst coating on the microchannel plate was tested for Fischer Tropsch synthesis (FTS). The catalytic activity in microreactor was measured in terms of CO conversion and product selectivity. The temperature was maintained at 493 K and the pressure at 2 MPa. CO conversion decreased from 33.2% to 30.3% when GHSV increased from 12000 h⁻¹ to 21000 h⁻¹. The catalyst exhibited a high C₅+ selectivity and a low CH₄ selectivity under the high GHSV. The CH₄ selectivity decreased to 11.6% with the GHSV
increased to 21000 h$^{-1}$. And the C$_5^+$ selectivity increased to 79.8%. The C$_5^+$ productivity was about 0.847 gC$_5^+$g$^{-1}$cat h$^{-1}$.

4. Conclusions

In this paper, a method to improve the adherence of Al$_2$O$_3$ coating with AISI 316L metallic substrate was proposed. The uniform Al$_2$O$_3$ whiskers formed on the 316L stainless steel surface after the proposed aluminizing and the oxidation process. And the coating applied on the aluminized surface by dip coating was verified to have high adhesion by ultrasonic vibration tests. The aluminized treatment could effectively improve the adhesion between the γ-Al$_2$O$_3$ coating and aluminum-free metallic substrate.

The coating were characterized by X-Ray diffraction (XRD), energy dispersive spectrometer (EDS), scanning electron microscope (SEM), and BET analysis. The results showed that the main pore size of the coating was between 30 Å and 100 Å. The coating has no cracks, and possessed with high specific surface area, 234 m$^2$/g.

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References


Biography

Li Zhang received her Ph.D. degree in 2004 from Tianjin university, and now is a professor from East China University of Science and Technology. Her research focuses on microreactor technology for Fischer-Tropsch synthesis.