Development of a Method for Increasing BET Surface Area of Rapid Anodic Alumina Layers Used as Catalyst Supports

On-line Number 981

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ABSTRACT

The preparation of catalysts supported by anodic alumina layers have been developed and practically applied in Japan. In order to reduce the cost of these catalyst supports, we tried to use rapid anodic alumina layers, but by the former method, the value of BET surface area of these layers was too small to use as a good catalyst support. As a solution of this problem, the purpose of this work is to develop the new method for increasing the BET surface area of rapid anodic alumina layers to improve activities of these alumina layers which used as catalyst supports. For preparing these layers, aluminum plates were rapidly anodized in sulfuric acid solution to obtain porous alumina layers with about 100µm of thickness. Then, these plates were soaked in sulfuric acid solution in order to widen the pore size of these alumina layers. After that, they were soaked in hot deionized water for hydration treatment. The experimental results showed that after pore widening treatment and hydration treatment, the value of BET surface area of rapid anodic alumina layers increased from 60 (by former method) to 200 m²·g⁻¹·Al₂O₃ and, it was clarified that the alumina layer with bigger pore size has a bigger BET surface area after hydration treatment. The new method can be applied for not only rapid anodic alumina layers but also for other anodic alumina layers such as those formed in oxalic acid, chromic acid and so on.

KEYWORDS
anodic alumina layer, pore-widening treatment, BET surface area, catalyst support

INTRODUCTION

In the fixed bed reactor, it is difficult to keep reaction temperature the same throughout the radius, because the thermal conductivity of packed catalyst is low and the contact thermal resistance of catalyst is large. So, there is a wide distribution of reaction temperature in the reactor, which is called hot spots in case of an exothermic reaction. This undesirable distribution causes side reactions, makes difficult for reaction-control and damages catalysts. Moreover, the pressure drop of this kind of reactor is too high to use it at high space velocities.

To dissolve weak points of the fixed bed reactor, plate type catalyst whose catalyst layer is directly formed on the metal body of reactor wall is proposed. Various preparation methods of plate type catalyst have been reported such as anodic oxidation method, spray method, galvanizing method and leaching method of Raney alloy. The plate catalyst which prepared by anodic oxidation of alumina plates is proposed as an outstanding plate catalyst due to its high catalytic reactivity, high thermal conductivity, low pressure drop, flexibility in reactor design, light weight and so on (Murata, K., 1996). This plate type catalyst is called “alumite catalyst” and has been practically applied in Japan. To prepare a catalyst support, a commercial aluminum plate was anodized in sulfuric acid or oxalic acid solutions for several hours to form alumina layers whose thickness was about 100µm. And then, these anodic alumina layers were soaked in hot water and heated in air for increasing BET surface area. BET surface area of these alumina layers was about 170-180m²·g⁻¹ (Murata, H. et.al., 1993).
In order to reduce the production costs of alumite catalyst supports, we tried to use the rapid anodic alumina layers (Figure 1), prepared by a new rapid anodic oxidation method (Hoshino, S., 1999), for preparing alumite catalyst supports. But, by the former preparation method of alumite catalyst support (Kameyama, H., 1990), BET surface area of these layers was too small to use as a good catalyst support. Therefore, our objective was to investigate the characters of rapid anodic oxidation coating and to develop a improve method to increase BET surface area of rapid anodic alumina layers for improving the reactivity of them. Here, we focus on the process of widening pore size of anodic alumina layers by soaking them in acid solution. This process is called ‘pore-widening treatment’. And we report on our investigation into the effect of pore widening treatment on the pore size and BET surface area of anodic alumina layers as a improve method for increasing the BET surface area of them.

**Rapid anodic oxidation**

Due to values of electric current density, there are two types of anodic oxidation. One is common anodic oxidation and the other is rapid anodic oxidation of which electric current density is 300A·m⁻² and over (Keikinzoku Seihin Kyokai, 1994). In rapid anodic oxidation process, aluminum plates are anodized in sulfuric acid solution bath. The electrolyte needs to be stirred vigorously to avoid burning of anodic oxide coating. The velocity of electrolyte flux is recommended at a range from 0.3 to 3m·s⁻¹ (Hoshino, S., 1999). To compare the influence of the electrolyte temperature and electrolysis time on common and rapid anodic oxidation, the anodic oxidation was prepared in the sulfuric acid solution at concentration of 15 wt%, from 273 to 293K. The electric current density was varied from 100 to 1000A·m⁻². The electrolysis time was varied from 0.25 to 16h. The relationship between film thickness and the anodizing time is shown in Figure 2. (The detail will be reported in another paper.). It shows that the rapid anodic oxidation can be carried at room temperature (293-298K) and the formation period of alumina films are remarkably shorter than those of common anodic oxidation for the same film thickness, which is the reason that rapid anodic alumina layers were chosen as new alumite catalyst supports.
EXPERIMENTAL

The flow sheet of the proposed catalyst support preparation used rapid anodic alumina layers is shown in Figure 3. It consists of: the rapid anodic oxidation, pore widening treatment and hot water treatment.

Rapid anodic oxidation

Aluminum plates (JIS H4000-A1050, purity of 99.5%, thickness of 0.5 mm) were pretreated in 20 wt% NaOH aqueous solution for 1 min and 30 wt% HNO₃ aqueous solution for 3 min. Then, they were anodized in 15 wt% sulfuric acid solution at 293 K and at electric current density of 500 A·m⁻² for about 60 min to form porous alumina films with film thickness about 100 µm in two outer surfaces of aluminum plates. After anodizing, these rapid anodic alumina layers (RAAL) were washed with water, naturally dried and then heated at 623 K for 1 h to remove residual sulfuric acid.

Pore widening treatment (PWT)

Rapid anodic alumina layers of which film thickness is about 100 µm were soaked in sulfuric acid solution at concentration of 15 to 25 wt%, at temperature between 283 and 303 K for soaking period from 30 to 75 minutes. After soaking in acid solution, they were washed with deionized water, naturally dried and calcined at 623 K for 1 h in air.

Hot water treatment (HWT)

These rapid anodic alumina layers were soaked in deionized water at 358 K for 2 h. Then, they were washed with deionized water, naturally dried for over 6 h at room temperature. And then, they were calcined at 773 K for 3 h in air. This process is called ‘hot water treatment’.

Measurement method

The thickness of alumina films was measured by the eddy current probe method (ANOTECH-T3.3B). BET surface area and the pore size distribution of anodic alumina layers were analyzed by a nitrogen adsorption method (COUNTER SA 3100). Micrographs of these catalyst supports were taken with an FE-SEM (HITACHI S-4500).

RESULTS AND DISCUSSION

Effects of PWT time

To investigate the effects of PWT time on the pore size and BET surface area of rapid anodic alumina layers, we used RAAL which was prepared by above mentioned method; soaked them in 15
wt % sulfuric acid solution at 298K for soaking period varied from 30 to 75 minutes. After pore-widening treatment, the pore size, BET surface area and film thickness of these alumina layers were measured. The change of pore size distribution with increasing PWT time is shown in Figure 4. The variation of film thickness is shown in table 1. One part of these pore widened layers was soaked in hot water, calcined at 773K for 3h in air for hot water treatment and then, BET surface area of these layers was measured. The effects of PWT time on BET surface area of all samples are shown in Figure 5.

Table 1. The change of film thickness with PWT time

<table>
<thead>
<tr>
<th>PWT time [min]</th>
<th>0</th>
<th>30</th>
<th>45</th>
<th>60</th>
<th>75</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film thickness [µm]</td>
<td>100</td>
<td>100</td>
<td>95</td>
<td>92</td>
<td>78</td>
</tr>
</tbody>
</table>

Figure 4 shows that the peaks of pore radius distribution of these alumina layers increased from about 8nm to about 17.5nm with increasing of PWT time. It is clear that the pore size of a sample, which is soaked in acid solution for a longer time, is bigger than that is soaked for shorter time. As shown in Figure 5, BET surface area of alumina layers after PWT changed lightly with increasing PWT time; but, after HWT, BET surface area of those increased rapidly with increasing PWT time. The values of BET surface area of alumina layers after PWT and HWT increased from about 60 to 170m²g⁻¹-Al₂O₃ for the treating time varied from 0 to 75min. It means that the longer PWT time is, the bigger BET surface area obtains. But, as the undesirable results, film thickness of theses layers decreased with PWT time as shown in table 1. The thickness of these layers decreased slightly from 0 to 60min but remarkably at 75min. According to the results in Figure 4 and Figure 5, we recognized that an alumina layer with bigger pore size had a higher BET surface area after HWT. The variation of the pore size with increasing of PWT time was also observed with FE-SEM. The pictures of the surface of alumina layers after PWT for 0 to

![Figure 4. Effects of PWT time on the pore size](image1)

![Figure 5. Effects of PWT time on BET surface area](image2)

![Figure 6. Surface of anodic alumina layers after PWT](image3)
60 min is shown in Fig. 6; and the pore size and thickness of pore wall are shown in table 2.

**Table 2.** The variation of Pore size and thickness of pore wall with increasing PWT time

<table>
<thead>
<tr>
<th>PWT time [min]</th>
<th>Pore size [nm]</th>
<th>Thickness of pore wall [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>13-16</td>
<td>30-33</td>
</tr>
<tr>
<td>30</td>
<td>23-25</td>
<td>21-25</td>
</tr>
<tr>
<td>60</td>
<td>27-33</td>
<td>17-23</td>
</tr>
</tbody>
</table>

The observation results show that the pore size became bigger and bigger while the thickness of pore wall became thinner and thinner with increasing of PWT time. It means that the dissolution of alumina layers occurred from inside of the pore of alumina layers.

**Effects of PWT temperature**

The effects of PWT temperature on pore size and BET surface area of rapid anodic alumina layers are also investigated. In this case, the pore-widening treatment was performed in 15 wt% sulfuric acid solution for constant period of 60 minutes while, the temperature of sulfuric acid solution was varied from 283 to 303K. After pore-widening treatment, one part of these layers was soaked in hot water, calcined at 773K for 3h in air. The result of the effects of PWT temperature on pore size distribution is shown in Figure 7. The effect of PWT temperature on BET surface area of alumina layers before and after HWT is shown in Figure 8. The variation of film thickness is shown in table 3.

**Table 3.** Variation of film thickness of alumina layers with increasing of PWT temperature

<table>
<thead>
<tr>
<th>PWT temperature [K]</th>
<th>Before Treating</th>
<th>283</th>
<th>288</th>
<th>293</th>
<th>298</th>
<th>303</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film thickness [µm]</td>
<td>100</td>
<td>100</td>
<td>99</td>
<td>97</td>
<td>92</td>
<td>60</td>
</tr>
</tbody>
</table>
Figure 7 shows that the peaks of pore radius distributions of these alumina layers increased from about 8nm to about 22nm with increasing of PWT temperature from 283 to 333K. As the same as the above mentioned results, Figure 8 shows that BET surface area of alumina layers after only PWT changed lightly with increasing PWT temperature; however, after HWT, BET surface area of those increased remarkably with increasing PWT temperature. The values of BET surface area of alumina layers after PWT and HWT increased from about 60 to 202m²g⁻¹-Al₂O₃ according to the variation of treating temperature from 288 to 303K. It means that, the higher PWT temperature is, the bigger BET surface area obtains. As the results of dissolution of alumina, film thickness of these layers remarkably decreased at PWT temperature of 303K as shown in table 2. We also recognized that an alumina layer with bigger pore size had a higher BET surface area after HWT.

The variation of pore size distribution

The variation of pore radius distribution of RAAL due to each process is showed in Figure 9. In case of PWT in 15 wt% sulfuric acid solution at 303K for 60min and HWT at the regular condition, the peak of pore radius distribution changed from about 8nm to about 22nm and after HWT, it moved to 2nm even if, the alumina layers was soaked in acid solution or not. The change of the shape of pores of RAAL before and after HWT and calcining at 773K was observed with FE-SEM. The observation results show that the shape of pores changed from cylinder to granular shape as shown in Figure 10.

Changes of pore size and film thickness of anodic alumina layers have been explained by the dissolution of alumina into acid solution. Two theories about the dissolution of alumina layer have been proposed. One is shortening theory and the other is pore widening theory. Diggle et.al. (1969) advanced the pore shortening theory that only the surface of alumina layer is dissolved into acid solution. Nagayama et.al. (1983) propounded the pore widening theory that alumina layer is dissolved into acid solution from inside the pore of alumina layer. Our experimental results showed the dissolution of alumina layers occurred from inside of the pores as the pore widening theory. But, we could not explain the remarkable decrease of film thickness with only pore widening theory. Therefore, we could not deny the shortening theory; and we think that the dissolution of alumina into acid solution occur not inside the

![Figure 9. Change of the pore size with PWT and HWT](image-url)

**Figure 9.** Change of the pore size with PWT and HWT

**Figure 10.** Change of pore shape with and without
pore but also on the surface of alumina layers.

The mechanism of hydration of anodized thin alumina layer has been clarified by Koda et.al. When anodized alumina is soaked into hot water, the alumina is hydrated and the volume is increased. Then, the pores of alumina layer are filled with hydrated alumina in a short time (Murata, K. 1996). The effect of HWT on BET surface area of anodized alumina layer has been reported by H. Kameyama et.al. (1995). However, the relationship between the pore size and BET surface area has not reported. In this work, we found that an anodized alumina layer with bigger pore has higher BET surface area after HWT, and it can be explained as illustrated in Figure 11. In the case of Non-PWT, when we soaked the alumina layer into hot water, the hydration reaction occurred around the pore mouth and stopped when the pore mouth was filled fully even if, the deeper parts were still empty. Therefore, the amount of hydrated alumina was still small and after calcining, the value of BET surface area increased not so much. In the other hand, after PWT, the pore became bigger, the hydration reaction occurred deeper, therefore, the amount of hydrated alumina became bigger; and after calcining, the value of BET surface area increased significantly.

CONCLUSION

A method was developed for increasing BET surface area of the rapid anodic alumina layers by soaking these alumina layers into acid solution after anodizing for pore widening treatment. The value of BET surface area increased from about 60 to about 200 m²·g⁻¹·Al₂O₃ after soaked them into hot deionized water and then calcined at 773K for 3h. It is known that alumina layers with bigger pore have higher BET surface area. However, the thickness of alumina layer decreases with increasing of PWT time or temperature, therefore, it is necessary to choose a reasonable condition for preparing the suitable catalyst support.

The effect of PWT on alumite catalyst support not only for increasing BET surface area but also for increasing the dispersion of catalyst metal (T. Take at.al., 2003) and for prevention of the detachment of anodic alumina layers from base metal(Tran,T.P.et.al., 2001). The pore widening treatment process is applied not only for rapid anodic alumina layers but also for common sulfuric, oxalic anodic oxidation coating or so on to improve their catalyst activation.

REFERENCES

Murata, K.; Preparation of Plate Type Catalyst and Design of Tube Wall Reactors, Doctoral Thesis, Tokyo University of Agriculture and Technology, Japan, 1996


