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A Pt/Alumina Catalyst Coated on Aluminum Thin Plate for Oxidation Reaction on Heat Transfer Surface

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In order to give catalytic activity to heat transfer surface, aluminum plate was treated by anodization, γ-alumina coating and Pt-impregnation. Prepared catalysts showed a substantial activity for the oxidation of acetone and also showed good thermal conductivity

To give a catalytic activity on heat transfer surface is an interesting theme in chemical industries, in the area of oxidation reaction or chemical heat pump engineering, in which it is eagerly needed to promote chemical reaction and heat transfer simultaneously. Metallic aluminum has high thermal conductivity but it is known as an inadequate support for Pt or other catalysts. Anodic oxidation of aluminum is widely known and applied in many areas of surface treatment, to stabilize and/or coloring the surface, or to make a non-conductive film of electrolytic capacitor, etc.[1] On the other hand, M. Yamada et al.[2] reported the effect of anodic oxidation on controlling porosity or morphology of aluminum oxide and studied catalytic activities of the oxidized films stripped from the aluminum base. Here, we report a new method to improve the surface area and catalytic activity by γ-alumina coated on anodized aluminum surface.[3] In this procedure, we aimed at making a stable alumina support on heat transfer surface of aluminum and obtained considerably good results.

Catalysts were prepared as follows, and summarized in Table 1. Surface-oxidized aluminum base (SAB): Aluminum foil modified by anodic oxidation which was commercially produced for the production of electrolytic capacitor was treated at 350 °C in air for 1 h (SAB-1). Alternatively, aluminum foil (99.99%, 0.12 mm in thickness) was cut to 40 cm^2, pretreated in 5 mol dm^{-3} NaOH and 2.8 mol dm^{-3} HNO_3 solutions and washed in deionized water and, then anodized in an aqueous solution of 2.5 wt% CrO_3, at a current density of 62 A m^{-2} at 30 C, for 6 h with stirring. This anodized aluminum foil was treated at 350 °C in air for 1 h (SAB-2, Cat.C). γ-Alumina coating: The SAB-1 and SAB-2 were soaked in a 3% aqueous solution of fiber type alumina sol (diameter of the fiber= 10 nm, length of the fiber= 100 nm, pH = 6-7, Shokubai Kasei Kogyo) for 1 min with stirring at room temperature and dried under room condition. After this soaking procedure was repeated twice, the foil was treated at 350 °C for 1 h. Pt impregnation: The SAB

or alumina-coated SAB was soaked in a 0.1% chroloplatinic acid solution whose pH was controlled by addition of NH_4OH. In this procedure, black Pt particles were deposited at once on SAB-1 and alumina-coated SAB-1 at pH 7. These Pt-deposited foils were dried at room temperature and then at 350 °C in air (Cat.A and Cat.B). On the other hand, in the cases of SAB-2 and alumina-coated SAB-2, the deposition of Pt was not obserbed even at pH 10, therefore the chloroplatinic acid solution was impregnated by gentle boiling under atomospheric pressure for 1 h at pH 10. After these Pt-impregnated foils were dried at room temperature, they were reduced in a H_2 stream at 200 °C for 2 h (Cat.E and Cat.F).

The cross-sectional surface of the SAB-2 and the surfaces of Cat.C-F were obserbed by SEM (JSM-35CF,JEOL) (Fig.1-2d). The amount of aluminum oxide produced on SAB-2 during anodization was 10 wt%, which was determined by weighing the sample before and after dissolution of oxidized film with 2 mol dm^{-3} HCl solution without generation of hydrogen. As seen in Fig.1, the thickness of anode-oxidized layer was about 10 μm. Figures 2a to 2d show that the alumina coating and the treatment with a boiling alkaline solution of chloroplatinic acid made some considerable changes in the appearance of the anodized surface. Within the limit of experimental measurement with a micrometer, the thickness of the catalyst which was treated by alumina-coating or Pt-impregnation appeared to be the same as that of base foil. It was shown that both of the alumina-coating and the treatment with a boiling solution of chloroplatinic acid during Pt impregnation influenced the BET surface area as expected from Fig.2. It is known that the surface structure of anodized aluminum is changed by a treatment with boiling water.[4] Apparent surface area of a catalyst was calculated from the weight and the shape. It was considered that little change in weight was observed during the treatment with alumina-coating and Pt impregnation. Bulk density was determined by a measuring cylinder packed with 1 g of catalyst which was cut into pieces of about 3 mm x 7 mm for catalytic reaction. Content of Pt was determined by tin(II) chloride method.[5] Catalytic activity of the oxidation of acetone (500-600 ppm in air) was measured at 200-300 °C at a space velocity between 10000 and 50000 h^{-1}, using a flow reactor made of pyrex glass tube of 28 mm. The catalysts were of thin plate shaped of 3 mm x 7 mm for Cat.A-F, and of granular shape of about 4-7 mm in diameter for D220 and D20M. One gram of catalyst was packed together with 28.3 g of quartz granules of about 1 mm in diameter, and the height of the catalyst layer in the reactor was 50 mm. Acetone was sent into a stream of preheated air from a diffusion tube whose temperature was controlled in a water bath. The concentrations of acetone before and after the reaction gas mixture that was passed through the catalyst bed were measured by GLC. Judging from the relation between SV^{-1} and conversion of acetone (20-60%), the reaction rate equation determined considering that the reactor was an integral type. The reaction rate was 1st order with respect to acetone concentration for Cat.A, B, D220,and D20M, while it was 2.5th order for Cat.E and F under the reaction conditions mentioned above.

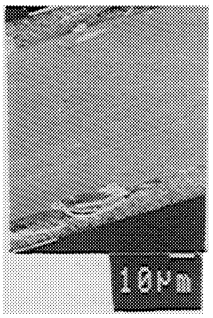
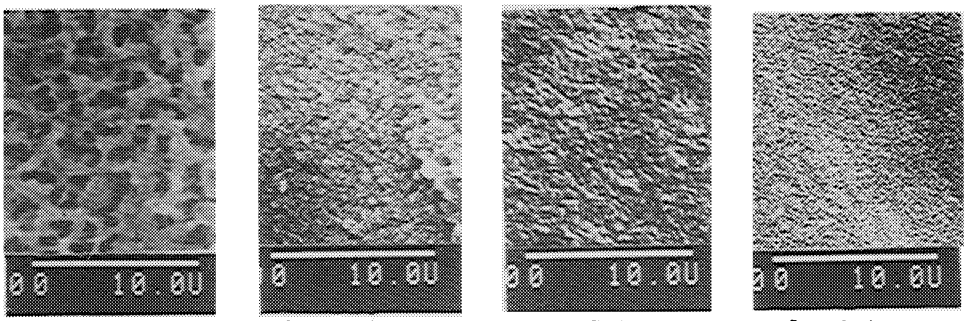


Fig.1. Cross section of SAB-2.



a: Cat.C b: Cat.D c: Cat.E d: Cat.F

Fig. 2. Surface of catalysts.

Table 1. Catalysts and their physical properties

Catalyst	A	B	C	D	E	F	D220[c]	D20M[d]
Aluminum base	SAB-1		SAB-2					
γ-Alumina coating		o[a]	o			o	Pt/alumina[b]	
Pt-impregnation	o[a]	o			o	o		
Surfacearea								
BET/m^2g^{-1}	1.2	1.5	3.5	4.9	37	56	150	13.4
apparent / $10^{-2}m^2g^{-1}$	2.9	1.7	0.78	0.77	0.76	0.77	0.16	0.26
Thickness / mm	0.07	0.07	0.103	0.108	0.107	0.107	4.0	0.34
Bulk density/g cm^{-3}	0.14	0.20	0.33	0.33	0.34	0.35	0.22	0.69
Pt /10^{-2}g-Pt g-Cat^{-1}	1.16	1.16			0.21	0.35	0.23	0.29

a) Catalyst was treated by γ-Alumina coating or Pt impregnation.
b) Commercial Pt/Al_2O_3 oxidation catalyst.
c) Ball-shaped, 4 mm diameter; Japan Engelhard.
d) Honeycomb-shaped, 0.34 mm thick; Japan Engelhard.

Table 2. Conparison of reaction rate for 600ppm-acetone and activation energy

Catalyst		A	B	E	F	D220	D20M
Reaction Rate							
based on catalys volume	200 °C		157	201	406	492	544
/ mol $m^{-3}h^{-1}$	300 °C	39.6	1570	2520	3900		8980
based on catalyst wight	200 °C		78.6	59.1	116	224	78.8
/ mol $kg^{-1}h^{-1}$	300 °C	283	786	741	1120		1300
based on BET surface area	200 °C		524	16.2	20.6	14.9	58.8
/ mol $m^{-2}h^{-1}$	300 °C	236	5240	203	200		970
based on apparent surface	200 °C		4.62	7.78	15.1	140	30.3
/ mol $m^{-2}h^{-1}$	300 °C	0.98	46.2	97.5	145		500
based on weight of Pt	200 °C		6.78	28.1	33.1	97.2	27.2
/ mol g-$Pt^{-1}h^{-1}$	300 °C	2.44	67.8	353	319		448
Activation energy / kcal mol^{-1}			12.6	12.6	12.6		16.3

The reaction rates for a concentration of acetone of 600 ppm based on different mode of normalization were listed in Table 2 together with the activation energies measured between 200 °C and 300 °C. Untreated SAB-1, Cat.C and D were not active under these conditions, and this fact means that the catalytic activity was due to the presence of Pt. Furthermore, comparing Cat.A with B, and Cat.E with F, alumina coating shows substantial improving effects on catalytic activity. From a standpoint of using the catalyst as heat transfer surface, the activity based on apparent surface area is very important. On this point, it is considered that Cat.F showed a fairly good result. On the other hand, BET surface area and the amount of Pt on catalyst seems not to affect on the activity directly. Especially in the case of Cat.E and F, the dispersion of Pt is considered to be as high as those of commercial catalysts in contrast with the cases of Cat.A and B. The study on relation between surface state of catalyst and reaction kinetics is under way. Thermal conductivity of anodized aluminum was measured for the samples, G and H, prepared under the same conditions as in the case of Cat.C and D, respectively, from a raw aluminum foil of 3 mm in thickness. The measured values were 82 and 105 kcal $m^{-1}h^{-1}K^{-1}$ for G and H, respectively. The conductivity of Aluminum is known to be 181 kcal $m^{-1}h^{-1}K^{-1}$. Apparently oxidized film of 10 μm on aluminum surface somewhat decreases the thermal conductivity, but this degree of decline in conductivity is not crucial for the usage as the surface of a heat exchanger. Thus, the catalysts prepared by the present methods are expected to be applicable to catalytically active heat transfer surface. We are now investigating on this possibility by constructing a reactor having functions of both catalyst and heat exchanger.

References

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