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SHORT COMMUNICATION

PREPARATION OF $Pd/Al_2O_3/Al$ CATALYSTS FOR CO REMOVAL

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Abstract – Aluminum was carefully anodized, then palladium salts were supported on its Al_2O_3 surface layer by ion-exchange. CO 3.76 vol% contained in the air can be eliminated at around 200 °C. Both anodization conditions and the nature of the precursor solutions affect catalyst nature, particularly the pH value of the precursor solutions. The pH value of the solution suitable for supporting active components is 5-6. Palladium, which is present as Pd^{2+} and Pd^{4+} after calcination, distributes uniformly on the support surface which had a honeycomb structure.

Key words : Metal Support, Monolith, Pd Catalyst, CO Oxidation

INTRODUCTION

Monolithic catalysts have played a critical role in exhaust control and have gained an increasing share of the catalyst market [Cybuski et al., 1994; Irandust and Anderson, 1988]. However, there are still some problems to be solved, e.g., binding strength between honeycomb carrier and adhesive layers as well as high cost of platinum metal usage.

Aluminum anodization has been an advanced technique conventionally applied for dyeing, errosion-resisting etc. [Diggle and Downie, 1969]. Recently it has been used for host materials to prepare magnetic recording mediator, optical devices [Masuda and Fukuda, 1995] or catalyst substrates [Hönicke, 1983]. Hönicke prepared $V_2O_5/Al_2O_3/Al$ catalysts for partial oxidation of 1,3-butadiene [Hönicke, 1987]. Preparation of noble metal catalysts loaded on such metal carrier has not been found. No studies on the effect of anodization and noble metal loading on catalyst activity have been reported. Herein we have prepared Pd catalysts supported on such supports and discuss the effects of preparation conditions on the catalyst structure and catalytic performance for CO oxidation.

EXPERIMENTAL

Commercial aluminum wires were rinsed to obtain a purified surface with acetone solvent or basic solution. Careful control of anodization conditions is necessary to produce an alumina layer suitable for supporting palladium. Anodization can be carried out under the following conditions: in 10 wt% H_2SO_4 solution at 13 °C, 20 v (d.c.) for 1 hour and aluminum plate as counter electrode. Because the alumina layer is grown out on aluminum itself having high mechanic strength and thermal conductivity as a metal core, a high binding strength between alumina and aluminum core can be reached. After being anodized, aluminum wires were rinsed with distilled water and impregnated in $(NH_4)_2PdCl_4$ aqueous solution for a certain period. No high temperature at which drying and reducing is required. The catalysts were calcined at 400 °C. A flow containing 99.95 % hydrogen was used for reduction of the catalysts. Pd loading amount in the catalyst ranges only below 1.0 wt%.

Catalysts were evaluated in a fixed-bed glass microreactor (i.d. 8 mm) connected with on-line GC 1102 with 5A molecular sieve columns and TCD. The feed gas is air containing CO 3.76 % (by volume). Pd concentrations were detected by Shimadzu AAS (Atom Adsorption Spectroscopy). SEM and EDAX were carried out on Hitachi JEOL 1200 EM. XPS data were obtained on a USA PHI 550 Electron Energy Spectrometer.

RESULTS AND DISCUSSION

In Table 1 is shown the effect of the current density of anodization on the catalytic activity. Catalytic activity for CO oxidation increased with the current density quickly at first, then slowly from 600 mA/cm^2, finally by nothing between 800-1,200 mA/cm^2. Variations in the electrolyte temperature and anodizing period showed a similar effect on the catalytic performance. According to anodization theory, there is an equation concerning such anodization conditions [Diggle and Downie, 1969],

$$D = D_0 - k \cdot f(c,T) \cdot t \tag{1}$$

Table 1. Effect of current density on catalytic activity for CO oxidation

No. of catalyst	Current density (mA/cm^2)	LOT (°C)
1	4	255
2	200	222
3	600	211
4	800	205
5	1200	205

Note : LOT light-off temperature ; Anodized in 10 % H_2SO_4 aqueous solution at 20 v, 13 °C for 1 h, except at 10 v in No. 1 catalyst ; $(NH_4)_2PdCl_4$ as precursor, Calcined at 400 °C for 5 h.

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Table 2. Relation between pH of impregnating solution and catalytic performance

No. of catalyst	pH	LOT (°C)	Depth of Pd distribution (12 μm)
01	5-6	198	15
02	2	364	4
03	9	313	6

Note: see in Table 1

in which D refers to the practical depth of the porous oxide layer; D_0 the theoretical depth of the oxide layer depending on current density, electrolyte temperature and anodization period; and $k \cdot f(c, T) \cdot t$ as the dissolution rate of porous oxide. From the equation, it can be concluded that the carrier must be treated appropriately to get a good catalyst with high catalytic activity and good binding strength because the factors are closely related each other and the catalytic activity seems to be dependent on the oxide layer thickness.

Anodized aluminum substrate itself showed no activity in the blank experiments. The effect of pH value of metal salts solution on the catalytic activity is shown in Table 2. It is clear that strong acidity or basicity of impregnating solution shows a negative effect on catalyst performance when $(NH_4)_2PdCl_4$ is precursor. From the view of adsorption dynamics of oxide pellets in aqueous solution and polarization theory, it can be explained that adsorption amounts of metal ions decrease greatly with an increase of acidity or basicity. When in acid solution, adsorption of metal ions follows the reaction, as shown in Eq. (2):

$$\text{Al-O-H}+M^{n+} \leftrightarrow \text{Al-O-M}+H^{+} \quad n: \text{metal ion charge number} \qquad (2)$$

Obviously, ion-exchange decreases with increasing acidity of the solution due to the equilibrium shift; when in basic solution, the surface of the carrier mostly exists as Al-O^- which makes the $PdCl_4^{2-}$ ions apart due to the ion charge effect with the increasing basicity. It can be proved by SEM and EDAX data that shallower distribution and lower loading of Pd are formed in the catalysts made in basic or strong acid solutions than in a weak acid one. Thus, the pH of the impregnating solution affects the adsorption greatly. In short, good catalyst is not only related to the anodization but also to the competitive adsorption of metal ions during impregnation.

The catalysts were characterized by XPS, SEM, EDAX. The XPS results show that the palladium states in the catalyst are Pd^{2+} and Pd^{4+} after calcination according to the binding energy data of $Pd_{3d\,5/2}$ and PdO, PdO_2 standard spectra, shown in Table 3. In the experimental range, palladium mainly distributes uniformly on the surface within ca. 10 μm depth around.

Table 3. XPS data of the catalysts

	Pd/Al (Atomic ratio)	Binding $Pd_{3d\,5/2}$	Energy (eV) Al_{2p}	O_{1s}
Catalyst	1:33	337.4	73.8	532.6
PdO	–	336.1	–	–
PdO_2	–	337.7	–	–

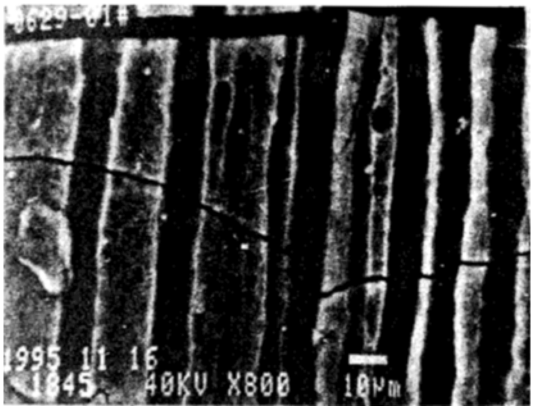

Photo 1. SEM micrograph of Al_2O_3/Al support.

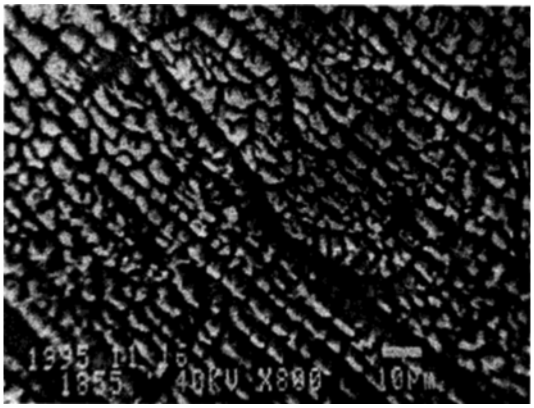

Photo 2. SEM micrograph of the surface of Pd/Al_2O_3/Al catalyst.

To investigate the surface structure, an SEM image was made as seen in Photos 1 and 2. The support surface features a honeycomb structure (Photo 1). The catalyst structure is different from the support one, shown in Photo 2. The catalyst surface presented many terraces on a series of parallel and uniform microchannels. No strip phenomena occurred during all the testing.

With anodized aluminum as a support, palladium catalysts with loading lower than 1.0 wt% were prepared and exerted good catalytic activity for CO elimination at around 200 °C. Both anodization conditions and the nature of the precursor solutions affect catalyst property, especially the pH of the precursor solution. The palladium states in the catalyst are Pd^{2+} and Pd^{4+} after calcination, and they are distributed uniformly on the supported surface featuring a honeycomb structure. Thus, a new preparation method of supported noble metal catalysts was explored and it proved to be successful.

REFERENCES

Cybuski, A. and Monlijn, J. A., "Monoliths in Heterogeneous Catalysis", *Catal. Rev. Sci. Eng.,* **36**(2), 279 (1994).

Diggle, J. W., Downie, T. C. and Goulding C. W., "Anodic Oxide Films on Aluminum", *Chem. Rev.,* **69**(3), 365 (1969).

Hönicke, D., "Formation of an Al_2O_3-coated Catalyst with a Metallic Core by Anodic Oxidation of Aluminum", *Applied*

Catal., **5**, 179 (1983).

Hönicke, D., "Partial Oxidation of 1,3-Butadiene on $V_2O_5/Al_2O_3/$ Al-coated Catalysts: Effects of Pore Lengths on Product Selectivities", *J. Catal.,* **105**, 19 (1987).

Irandust, S. and Anderson, B., "Monolithic Catalysts", *Catal. Rev. Sci. Eng.,* **30**(3), 341 (1988).

Masuda, H. and Fukuda, K., "Ordered Metal Nanohole Arrays Made by a Two Step Replication of Honeycomb Structures of Anodic Alumina", *Science,* **268**(9), 1466 (1995).