Preparation of an Alumina-wall Tube Reactor and Its Catalytic Performance in the Steam-reforming of Methanol

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The inner wall of a narrow-bore aluminum tube was successfully oxidized to give a thin alumina wall by electrolysis. A Cu–Zn-loaded alumina-wall tube reactor afforded high performance in the steam reforming of CH_3OH to supply H_2.

The steam-reforming reaction of methanol (SRM) has attracted much attention as a promising method for a compact hydrogen production system for a fuel cell. Because of the large endothermicity of this type of reaction,[1] a packed bed reactor was found to exhibit heat-transfer limitations and temperature gradients in the reactor. This heat-transfer limitation can lead to lowered catalytic productivity. To avoid this problem, use of a wall-tube reactor is proposed.[2,3] The formation of a porous alumina thin layer on an aluminum plate by anodic oxidation is an established technique.[4] However, until now, there have been no reports on the anodic oxidation of the inner wall of a thin aluminum tube. This paper provides a first report on the anodic oxidation of a thin aluminum tube and its application to the SMR.

A straight aluminum tube, 1 m in length with 3-mm outer and 2-mm inner diameters, was used. The aluminum tube was pretreated by washing, first with benzene and then aqueous NaOH, rinsing it in distilled water, and washing it again with HNO_3 solution.

Anodic oxidation of the inner wall of the pretreated tube was carried out by inserting a Teflon-coated 0.56-mm copper wire, with the Teflon coat partially stripped off, into the tube, and this was used as a cathode electrode. The anodic oxidation was carried out by following the literature.[5] Preoxidation was achieved by circulating the electrolyte (0.6 M oxalic acid) inside the tube at a flow rate of 25 mL/min, and an electric potential of 30-V DC was applied between the cathode and aluminum tube. After the first oxidation, the inner surface was exposed to a mixture of 6.0 wt % H_3PO_4 and 1.8 wt % H_2CrO_4 at 60 °C for 15 min to remove the oxidized alumina layer. The second anodic oxidation was carried out under the same condition as above for 1–9 h. The obtained tube was washed with distilled water, and calcined at 350 °C under flowing air.

Figure 1 shows scanning electron micrograph (SEM) images of the cross section and the inner surface of the oxidized aluminum tube. Relatively uniform pores sized 20 to 30 nm were observed, and the surface area (BET, N_2) of oxidized inner wall was ca. $20 m^2/m$-tube.

As seen in Figure 2, thickness of the alumina layer increased to 40 μm linearly with increasing oxidation time up to 9 h. Oxidation time of 3 h was selected to maintain the mechanical strength of the tube.

Catalysts were prepared by the equilibrium adsorption method. An aqueous solution of 0.25 M Cu and 0.25 M Zn nitrates was introduced into the wall tube reactor. After standing
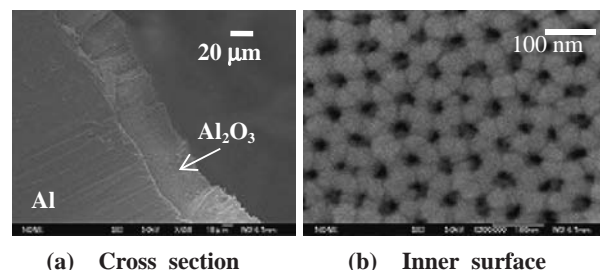

(a) Cross section　　**(b) Inner surface**

Figure 1. SEM images of the oxidized aluminum tube. Preparation conditions: constant voltage of 30-V DC at 18 °C in 0.6 M $(COOH)_2$ electrolyte for 9 h.
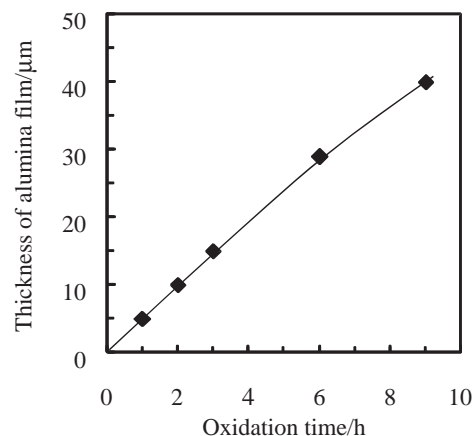

Figure 2. Relation between thickness of alumina film and oxidation time. Preparation conditions constant voltage of 30-V DC at 18 °C in 0.6 M $(COOH)_2$ electrolyte.

for 2–12 h, the solution inside the tube was drained off, followed by calcination in air flow at 350 °C for 6 h.

The reforming reaction was carried out by feeding CH_3OH together with Ar as a sweep gas at 200–300 °C, using an effective tube length of 0.8 m (heated zone). As shown in Table 1, with the bare alumina tube (Run 1), only a trace amount of DME was obtained. With a loading level of 2.8 mg/m-tube of combined weight of Cu and Zn oxides, methanol conversion of 23.9% was observed. If the catalyst adsorption time was prolonged from 2 to 12 h, the loading level increased from 2.8 to 4.5 mg/m-tube at 8 h, with an increase in CH_3OH conversion to 60.2% (Run 5). Since elongation of the catalyst loading time did not significantly increase the amount of loading, catalyst loading process was repeated as shown in Runs 6–9. With increasing repetition number, catalyst loading increased. When impregnation procedures were repeated four times, the loading level reached to 12.4 mg/m-tube, leading to methanol conver-

Table 1. Results of SRM using wall tube reactor[a]

| Run | Catalyst preparation | | | W/F^{c} /g h mol^{-1} | CH$_3$OH conv./% | H$_2$ /mmol h^{-1} | selectivity/% | |
| | Impregnation | | Catalyst | | | | | |
	time/h	repetition	weight/mg m^{-1b}				CO	CO$_2$
1[d]	0	0	0	0	0.2	0	0.0	0
2[d]	2	1	2.8	0.10	23.9	28.3	3.2	91.5
3[d]	4	1	3.3	0.12	38.7	36.8	2.1	96.5
4[d]	8	1	4.5	0.17	58.7	70.1	2.0	96.5
5[d]	12	1	4.5	0.17	60.2	70.1	2.2	97.3
6	8	1	4.5	0.17	28.2	22.7	0.3	99.6
7	8	2	6.2	0.23	78.1	62.9	0.8	99.2
8	8	3	8.3	0.31	89.8	72.3	1.3	98.6
9[e]	8	4	12.4	0.46	45.5	36.2	0.0	99.9
10	8	4	12.4	0.46	98.8	75.8	2.0	97.9
11	8	4	12.4	0.28	97.2	126	2.1	97.9
12	8	4	12.4	0.20	82.7	151	1.6	98.3
13	8	4	12.4	0.15	73.3	187	1.1	98.8
14	8	4	12.4	0.12	61.3	213	1.3	98.6

[a]Reaction temperature 250 °C, time 1 h, Ar 30 mL/min, Steam/Carbon 1.0. [b]Total weight of CuO and ZnO. [c]W/F catlyst weight (g)/feed methanol (mol/h). [d]Reaction temperature 300 °C. [e]Reaction temperature 200 °C.
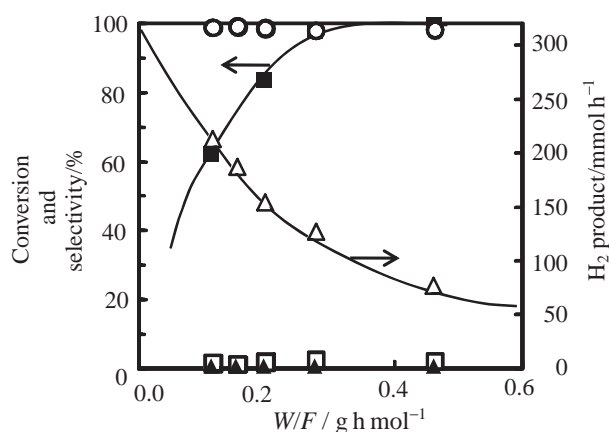

Figure 3. Effect of W/F on steam reforming of methanol. Temperature 250 °C, Reaction time 1 h, Steam/Carbon ■, conversion; △, H$_2$ yield. Product selectivity: ○, CO$_2$; □, CO; ▲, DME.

sion of 45.5 and 98.8% at 200 and 250 °C, respectively, with a very low CO selectivity at 200 °C (Runs 9 and 10).

The effect of the contact time (W/F) of the methanol was examined at a constant CuO + ZnO loading, by varying methanol feed rate. As shown in Figure 3, at a W/F of 0.46 g h/mol (feed rate: 26.8 mmol/h), methanol conversion of 98.8% and H$_2$ yield of 75.8 mmol/h were obtained, while a

decrease in the W/F to 0.12 g·cat/mol (feed rate: 107 mmol/h) decreased in the methanol conversion to 61.3%. Owing to an open tubular reactor, at a high space velocity, a part of fed methanol might have passed through without contacting on active catalyst. At 250 °C, space time yield of this tube was estimated as ca. 50 mmol H$_2$/h cm^3 from the result of Run 11. This value is much higher than reported results,[6] although the catalyst and conditions are different.

All these results clearly indicate that SRM using a wall tube reactor afforded high CH$_3$OH conversion to give high H$_2$ yield with a low CO selectivity.

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