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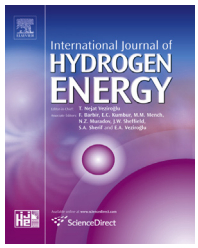

Stacked etched aluminum flow-through membranes for methanol steam reforming

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ABSTRACT

Electrochemical etching has been used to obtain aluminum foil with high surface area for use as electrodes in electrolytic capacitors. In this approach, direct current etching first generates straight penetrating microchannels, and then a second etching step enlarges the microchannel diameter. In the present work, we developed catalyst supports using aluminum etched with microchannels as a microreactor. The metal aluminum foil catalyst support obtained by etching contained microchannels with a diameter of 1.0–3.0 μm (10,000–15,000 microchannels/mm^2). We stacked membrane layers and evaluated their performance in methanol steam reforming. The performance of the reactors containing stacked membranes improved as the layer number increased. The microchannels in this catalytic membrane could be used as reaction channels, were easy to fabricate at low cost, and could be mass-produced continuously. This novel catalytic membrane support opens up new possibilities for practical fabrication of industrial materials.

Introduction

Electrochemical etching with a direct current (DC) has previously been employed to obtain aluminum foil with high surface area for use as electrodes in electrolytic capacitors. Such anisotropic etching provides a rough metal surface with numerous tunnel-shaped etch pits [1–3]. In the manufacture of foil electrodes for use in electrolytic capacitors, the first stage of etching forms the tunnel-shaped pits in the aluminum foil, and the second etching step increases the pit diameter. In the present study, we use this anisotropic etching technique to produce tunnel-shaped penetrating microchannels that act as a catalyst support; that is, a membrane reactor. The characteristic dimensions of such catalytic membrane reactors are smaller than those of general microreactors, which results in excellent heat transfer between the fluid and membrane.

The motivation for the development of a flow-through catalytic etched aluminum membrane reactor is to reach complete conversion in minimum time or space, achieve high catalytic efficiency, or realize maximum selectivity for a given reaction because of the narrow contact time distribution. If a catalyst is placed inside the membrane microchannels and

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the reactants flow convectively through the microchannels, the resulting intensive contact between reactants and catalyst results in high catalytic activity. Several materials and reaction systems using flow-through catalyst membrane reactors have been studied [4]. The mean microchannel size of the membranes in such reactors varies; furthermore, the choice of appropriate microchannel size always represents a trade-off between intensive reactant–catalyst contact and a small pressure drop. For gas-phase reactions in microchannel structures below the micrometer scale, improved understanding of flow processes and microeffects in Knudsen and transition regimes is required. Similar-sized microchannels of flow-through catalyst membrane reactors exist in microporous silicon [5,6], but such examples are limited.

Our research group has developed anodized porous alumina layers as catalyst supports and investigated their application [7–10]. Anodized porous alumina layers can be formed on aluminum plate surfaces by anodic oxidation. These layers have many advantages over conventional catalysts, including high thermal conductivity and ready formation of various shapes and structures.

Steam reforming of methanol (MeOH) was carried out to measure the activity of the stacked membranes. The microreactors fabricated by several methods for steam reforming of MeOH have been studied [11–14]. It is a significant challenge to fabricate materials with microchannels cost-effectively, and catalyst deposition on microchannels remains a major challenge.

Previous research has suggested that an alumina membrane with penetrating microchannels formed by etching can act as an effective catalyst support [15,16]. However, etched aluminum has some limitations as a membrane material. For example, it is difficult to form microchannels more dense than those in present membranes while maintaining the strength of the membrane material. It is also difficult to produce thick aluminum foil suitable for anisotropic etching. These limitations may be overcome by stacking flow-through catalyst membranes. Thus, the purpose of this study is to examine how stacking etched aluminum membranes affects their performance.

Materials and methods

Catalyst preparation

Aluminum foil was treated by electrochemical DC etching to form penetrating microchannels. Conditions for electrochemical etching, anodization, hydration, and calcination were as reported previously [15]. Electrochemical etching was carried out to generate penetrating microchannels. The surface of the microchannels was treated by anodization and hydration. The hydrated alumina filled in the pores of the anodized alumina and covered the surface of the anodized alumina. The membranes contained γ-alumina because the boehmite formed by hydration crystallized to γ-alumina during calcination. The catalyst metals were impregnated into the mesopores in the hydrated alumina membranes. X-ray diffraction results agreed with those reported previously [15]. The catalyst preparation process is summarized in our previous paper [15]. A schematic of the preparation of the catalytic membrane is presented in Fig. 1. The membrane diameter was 11 mm and the diameter of the reaction area determined from the region where the catalyst color changed during reduction was 7.3 mm. The catalytic membrane was about 100 μm thick, and was fixed vertically in a reactor with carbon and metal gaskets. The reaction gas flowed through the penetrating microchannels in the membrane.

The performance of a commercial alumina bead catalyst support (AA300, granular, Nippon Light Metal Co. Ltd., Tokyo, Japan) with a diameter of 1.4–2 mm was compared with that of the membrane catalyst support. AA300 was crushed and sieved to give a particle diameter of 0.212–0.350 mm. We successfully used the crushed granular catalyst with a diameter of 0.5–1.0 mm in our previous research [15] although its size was too large because it led to a long diffusion length in the external boundary film. As a result, the reaction rate

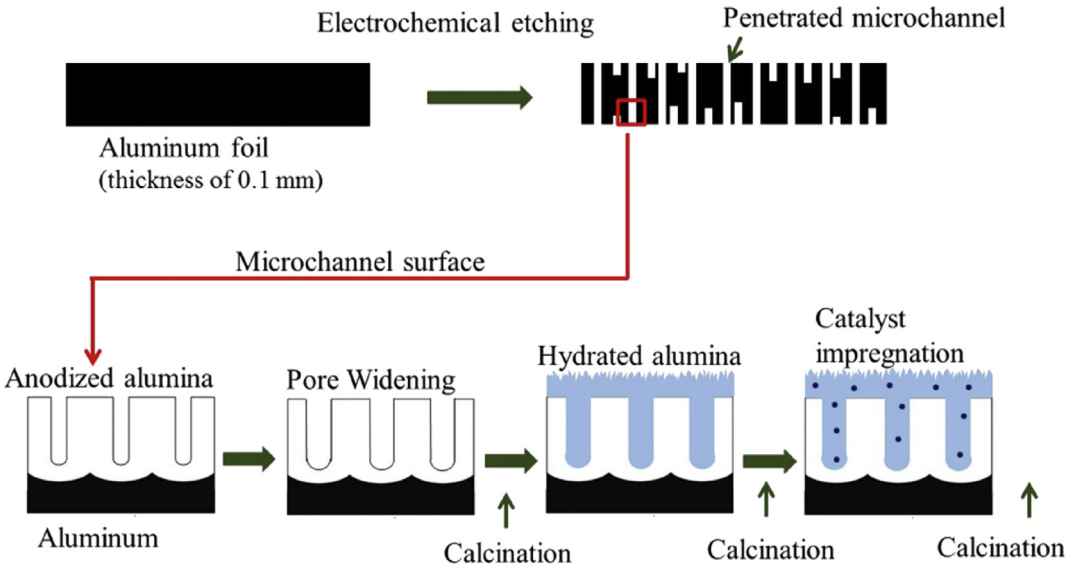

Fig. 1 – Schematic of the structure of the catalytic membrane.

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