

## Development of Anodic Oxidation Process and Boehmite Process in Production Process of Dehydrogenation Catalyst

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Organic hydride is anticipated for use as a future hydrogen carrier because it has both high gravimetric and volumetric hydrogen density for storage and transportation. Improving the performance of the dehydrogenation catalyst is necessary to miniaturize the reactor, which generates H<sub>2</sub> from organic hydride in an endothermic reaction. The porous anodic oxide film on aluminum is widely known for its application to dehydrogenation catalysts. Increasing the specific surface area of a porous anodic oxide film improves the catalytic performance. For this study, we obtained a catalyst with high specific surface area by investigating the anodic oxidation temperature and boehmite process time. The specific surface area of a porous anodic oxide film produced at higher temperature was larger than that at a lower temperature. It increased with boehmite processing time. However, when the specific surface area became too large, the micropores were too small for Pt particles to enter. Consequently, at 50 °C anodic oxidation temperature and at about 5 h boehmite processing time, the catalyst had the most suitable specific surface area to generate H<sub>2</sub> from methylcyclohexane because the smallest Pt particles were supported on the porous anodic oxide film. Furthermore, a microreactor using the proposed catalyst had twice the methylcyclohexane conversion as that using a conventional catalyst.

**Keywords:** Dehydrogenation, Anodic oxide film, Anodic oxidation temperature, Boehmite process time, Pt particles.

### INTRODUCTION

Reduction of CO<sub>2</sub> emissions is an urgent requirement to avoid global warming and ensure the sustainable development of society. In the near future, because it engenders no CO<sub>2</sub> emissions, hydrogen is thought to be an ideal energy carrier as a fuel for engines or fuel cells. Liquid hydrogen and highly compressed hydrogen are major hydrogen media, but hydrogen is difficult to store and transport without loss of energy.

Organic hydrides such as methylcyclohexane (MCH) and cyclohexane are expected to serve as hydrogen carriers in future applications because each has high gravimetric and volumetric hydrogen density for hydrogen storage and transportation [1-5]. Additionally, because organic hydrides are liquid at room temperature and normal atmospheric pressure, the present energy infrastructure, with its oil tankers and gasoline stations, is useful for the storage and transportation of hydrides.

A reactor using dehydrogenation catalyst is necessary to generate H<sub>2</sub> from the organic hydride. Especially, it is important to miniaturize the reactor for use on vehicles. Improving the dehydrogenation catalyst performance is an effective method

to reduce the reactor size. The anodic oxide film on aluminum is widely known for its application as a catalyst support; increasing the anodic oxidation's specific surface area can boost the catalytic performance [6-10]. We are developing a high-performance dehydrogenation catalyst with anodic oxide film on aluminum. In this study, we improved the methods to produce porous anodic oxide films with larger specific surface areas on aluminum. These methods involve development of an anodic oxidation process and a boehmite process in the production process of the dehydrogenation catalyst. Using these methods, the dehydrogenation catalyst performance was improved.

### EXPERIMENTAL

**Preparation of catalyst:** An aluminum plate (purity > 99.5 %) was treated in 4 wt % NaOH aqueous solution for 2 min to remove the natural oxide film on the aluminum surface. After washing with deionized water, the plate was treated in 30 wt % HNO<sub>3</sub> aqueous solution for 2 min to remove impurity metals such as Cu and Fe from the aluminum surface. The pretreated aluminum plate was then anodized in aqueous solutions of 0.3 mol/L oxalic acid at 40 V (constant voltage).

The solution temperatures were 30, 40 and 50 °C, as controlled with a water bath. Consequently, the thickness of the anode-oxidized porous film was about 10–100 μm. Then, to obtain a larger surface area of porous anodic oxide film, the plate was immersed in 5 wt % H<sub>3</sub>PO<sub>4</sub> at 30 °C for 30 min (pore widening) and washed with deionized water. The boehmite process consisted of immersion of the anodized specimens in deionized water at 95 °C for 2, 5 and 10 h and subsequent baking at 550 °C for 1.5 h [9].

This porous anodic oxide film plate was dipped in 4 wt % Pt colloid (Pt particle diameter: 2 nm) and treated at 450 °C in air for 20 min to finish the catalyst plate.

The film thickness was measured using scanning electron microscopy (SEM; JSM-7100F, JEOL) and a film thickness meter (A456FNFSII, Innex Co. Ltd.). The specific surface area, pore size distribution and pore volume were determined by measuring nitrogen gas adsorption isotherm at -196 °C. Pore voidage was evaluated using the pore volume and catalyst volume. The Pt particle diameter was measured using transmission electron microscopy (TEM; JEM-3010, JEOL) and X-ray diffraction (XRD; RU200B, Rikaku). Thermal conductivity of the catalyst plate was measured using temperature wave analysis (TWA Mobile, ai-Phase Co. Ltd.).

**Dehydrogenation reaction:** To measure the catalyst plate performance, it was divided into 1 mm squares and inserted into a reactor (SUS pipe, 0.64 cm diameter) as presented in Fig. 1.

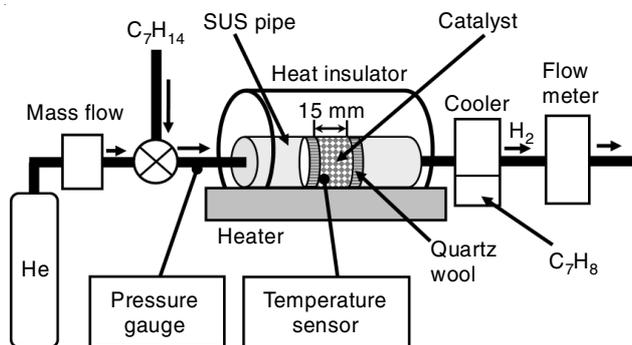


Fig. 1. Experimental apparatus of dehydrogenation reaction

The catalyst volume was about 0.5 mL. Using a helium gas carrier, methylcyclohexane (C<sub>7</sub>H<sub>14</sub>) was flowed into the reactor. The reactor was heated using a heater under the reactor and a heat insulator surrounding the reactor was used to maintain the temperature. Toluene gas and H<sub>2</sub> gas from the reactor outlet were separated using a cooler and the volume of flowing H<sub>2</sub> was measured using a soap film flow meter. The pressure and temperature of the reactor were evaluated, respectively, with a pressure gauge and temperature sensor. The methylcyclohexane flow rates were controlled in 30, 50, 100 and 200 μL/min and the reaction temperatures were controlled in 230, 250, 280 and 300 °C. The methylcyclohexane conversion was evaluated using eqn. 1. Measurement results were confirmed using gas chromatography-mass spectroscopy.

$$\text{Methylcyclohexane conversion} = \frac{H_2(\text{mol})}{3 \times C_7H_{14}(\text{mol})} \quad (1)$$

C<sub>7</sub>H<sub>14</sub> = Methylcyclohexane.

Because of its both higher heat conduction and higher space diffusion, the catalyst is suitable for an onboard microreactor for vehicle to generate H<sub>2</sub> from organic hydride. To confirm the catalyst plate performance, one catalyst plate (6 cm square) was welded with an aluminum plate to form a microreactor, spaced 50 μm deep for micro-passage. The dehydrogenation performance of the microreactor was measured using the experimental apparatus (Fig. 1) using the method described above.

## RESULTS AND DISCUSSION

**Improved anodic oxidation process:** Fig. 2 depicts the relation between anodizing time and anodic oxide film thickness at solution temperatures of 30, 40 and 50 °C. The anodic oxide film can be formed more quickly in a higher solution temperature. However, a low temperature is effective for forming a thick anodic oxide film. The thickness of the anodic oxidation film decreased with an increase in solution temperature. This is explainable by the fact that the film's growth is slower than the film's dissolution at higher temperature over some anodizing time. The anodic oxide film thickness can therefore be controlled with the processing time and solution temperature.

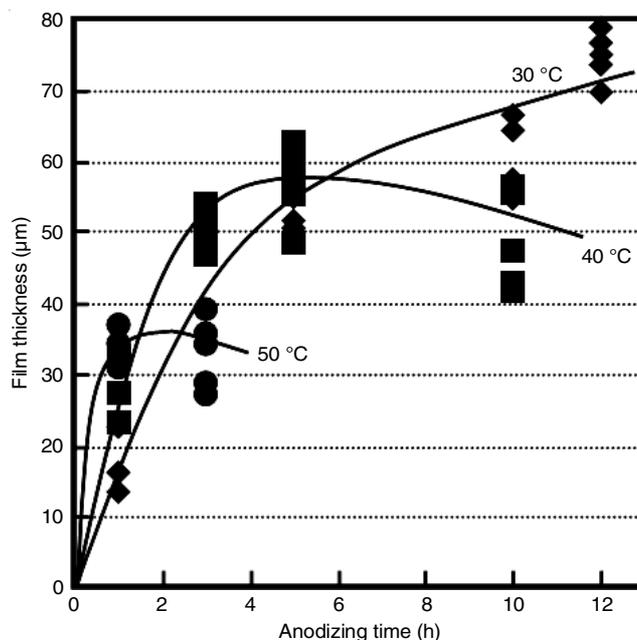


Fig. 2. Relation between anodizing time and anodic oxide film thickness and the solution temperature

Fig. 3 depicts the change in specific surface area and average pore diameter of porous anodic oxides after anodic oxidation, pore widening, boehmite process and baking process. The average pore diameter of the porous film decreases, but the specific surface area of porous film increases with these production processes. The surface area after the boehmite and baking processes is about 12 times that after the anodic oxidation and pore widening processes. The specific surface area of porous anodic oxide film produced at the anodic oxidation temperature of 50 °C is 1.5 times that of a porous anodic oxide film produced at 30 °C after boehmite processing.

Fig. 4 depicts the relation between pore voidage and methylcyclohexane conversion and Pt particle diameter. Platinum particle diameter is inversely proportional to methylcyclohexane

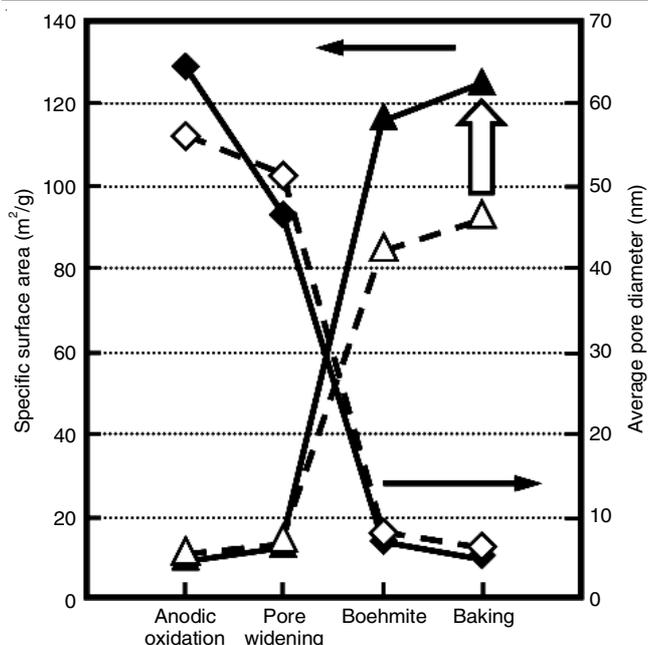


Fig. 3. Influence of fabrication process on the surface area and average pore size of porous anodic alumina. The anodic oxidation temperatures were 30 °C (broken line) and 50 °C (solid line). In both cases, the boehmite processing time was 2 h

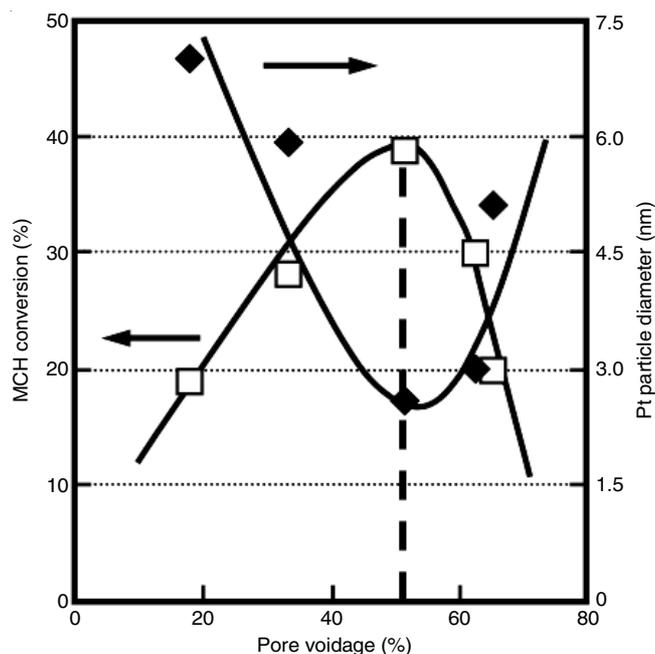


Fig. 4. Influence of pore voidage of catalysts on methylcyclohexane conversion at the reaction temperature of 280 °C and methylcyclohexane flow rate of 100 µL/min and Pt particle diameter. The boehmite processing time was 2 h

conversion. The catalyst has the highest methylcyclohexane conversion at about 50 % pore voidage. Fig. 5 shows that the thermal conductivity of the catalyst plate is highest at about 50 % pore voidage.

**Boehmite process improvement:** The boehmite process was the most effective to increase the specific surface area of porous anodic oxide film (Fig. 3). Here, we investigated the effects of boehmite processing time on methylcyclohexane conversion. The specific surface area of porous anodic oxide

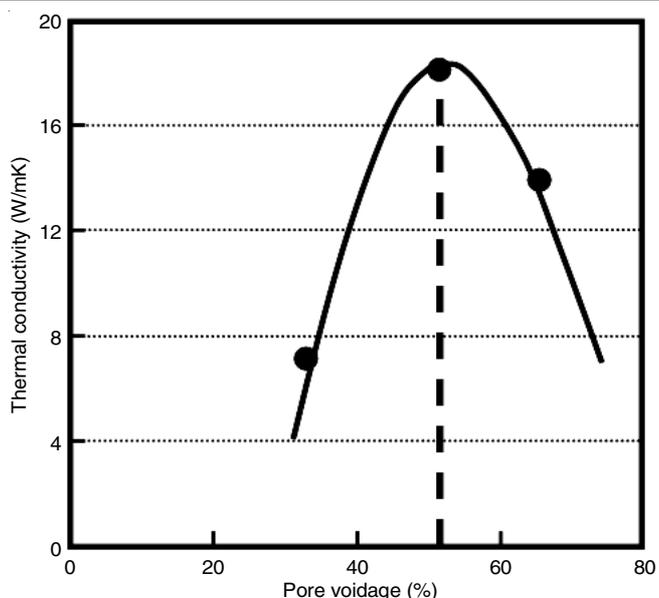


Fig. 5. Relation between pore voidage and thermal conductivity of catalyst plate, after supporting platinum

film increases with the boehmite processing time, as depicted in Fig. 6. The specific surface area can be increased from 125 m<sup>2</sup>/g in the original process treated for 2 h to 170 m<sup>2</sup>/g treated for 5 h. Platinum catalyst particle has the smallest diameter in a specific surface area of about 170 m<sup>2</sup>/g (boehmite processing time: 5 h), as shown in the figure.

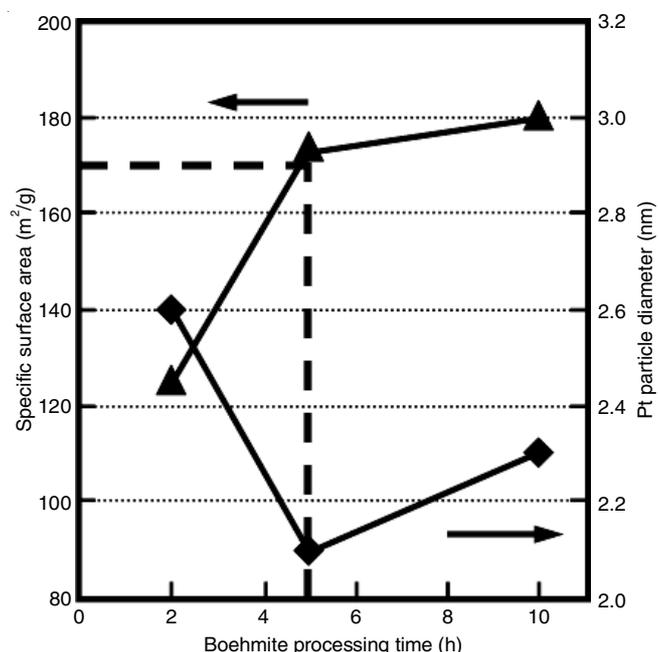


Fig. 6. Influence of boehmite processing time on specific surface area and Pt particle size of the catalysts. The anodic oxidation temperature was 30 °C

Fig. 7 depicts the relation between boehmite processing time and methylcyclohexane conversion. The methylcyclohexane conversion increases with boehmite processing time and is saturated over 5 h. The methylcyclohexane conversion can be improved from 40 % in the original process treated for 2 h to 50 % treated for 5 h.

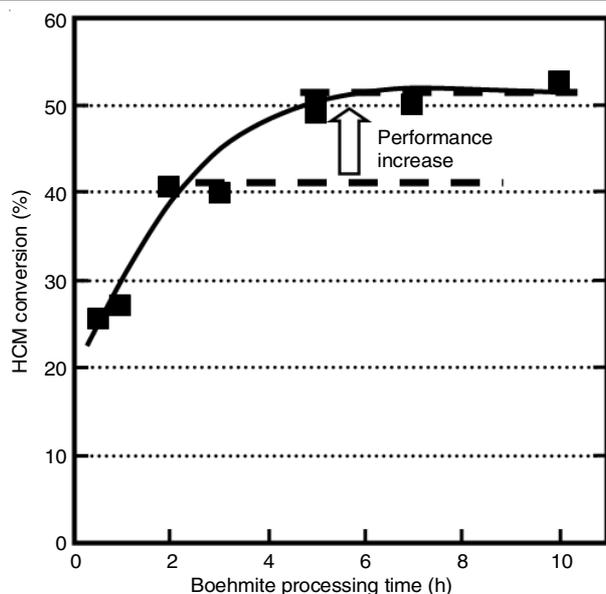


Fig. 7. Relation between boehmite processing time and methylcyclohexane conversion: solution temperature of anodic oxidation is 50 °C; reaction temperature, 280 °C; methylcyclohexane flow rate, 100  $\mu\text{L}/\text{min}$

**Dehydrogenation reaction of the microreactor:** Fig. 8 depicts the methylcyclohexane conversion of the microreactor composed of the catalyst plates. In the figure, the original process denotes the anodic oxidation temperature of 30 °C and the boehmite process time of 2 h. At the reaction temperature of 280 °C, the methylcyclohexane conversion was 20 % on the catalyst produced at the original process. The improvement of anodic oxidation process, *i.e.*, the increase in the anodic oxidation temperature to 50 °C, increased the methylcyclohexane conversion to 30 %. Further improvement of the boehmite process by increasing the process time to 5 h enhanced the methylcyclohexane conversion to 40 %.

The conversion of the methylcyclohexane microreactor was increased at every reaction temperature after catalyst improvement. Improving the anodic oxidation and boehmite

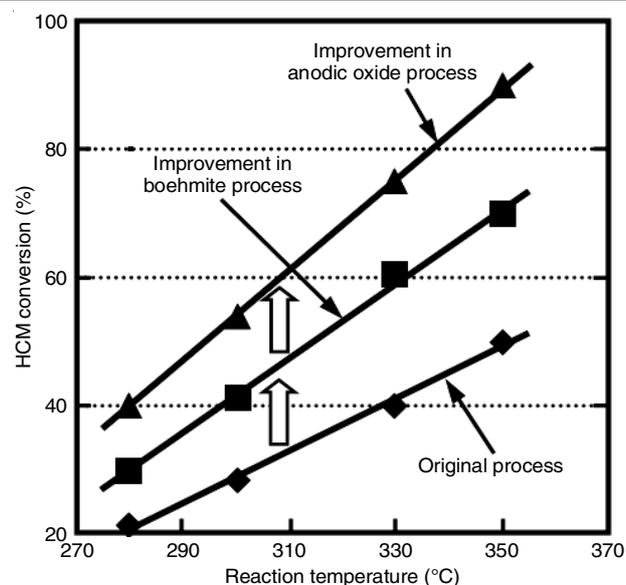


Fig. 8. Temperature dependence of the methylcyclohexane conversion on the catalysts. The anodic oxidation temperature and boehmite processing time are 30 °C and 2 h for the original process, 50 °C and 2 h for the improvement in anodic oxide process and 50 °C and 5 h for the improvement in boehmite process, respectively. The reactor volume is 0.1 L

processes is effective to improve the dehydrogenation catalyst performance.

Fig. 3 shows that the higher solution temperature of the anodic oxidation process was effective in stimulating the boehmite process to increase the specific surface area of porous anodic oxide film. Therefore, the supported Pt particle on porous film can become smaller, which can increase the reaction site to promote a reaction (Fig. 4). The thermal conductivity of the catalyst plate was highest at about 50 % pore voidage, (Fig. 5), because smaller metallic Pt particles are dispersed into the porous anodic oxide film to improve the catalyst plate conductivity.

The increase in the boehmite processing time was effective in increasing the specific surface area of porous anodic oxide

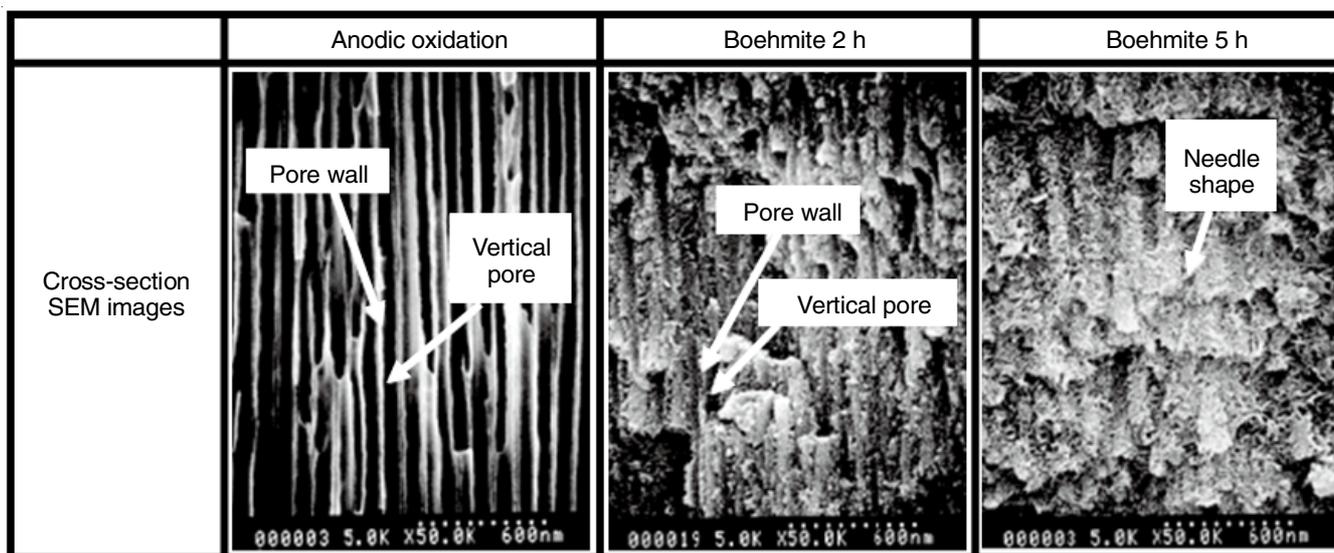


Fig. 9. Cross-sectional SEM images of porous anodic oxide films produced at the solution temperature of 50 °C before and after boehmite process for 2 h and 5 h

film (Fig. 6). Cross-sectional SEM images of porous anodic oxide film are shown in Fig. 9. The needle shapes extracted from the pore walls increase with the boehmite processing time. This phenomenon is explainable according to Fig. 10. The vertical pores are formed by anodic oxidation (Fig. 10a). The needle shapes are extracted on the pore walls to form micropores during the boehmite process (Fig. 10b) and the specific surface area of porous anodic oxide film increases as the boehmite processing time increases (Fig. 10c) [9]. However, the supported Pt particle size increased when the boehmite process was longer than 5 h (Fig. 6) because the micropores are too small for the Pt particles to enter and larger Pt particles are supported on a porous anodic oxide film surface for a boehmite processing time of 10 h (Fig. 6). Consequently, the catalyst performance is expected to decrease. Results also suggest that the base site on the catalyst support surface formed by boehmite processing can promote its dehydrogenation performance. We will investigate the effect of the base site on a catalyst support in the future by adding a solid base oxide to the proposed dehydrogenation catalyst.

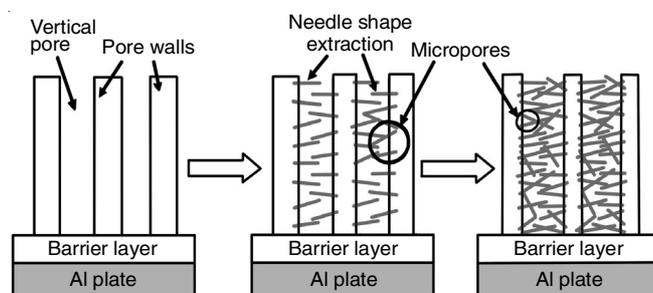


Fig. 10. Images depicting boehmite effects

## Conclusion

For this study, we have developed a high-performance dehydrogenation catalyst with an anodic oxide film on aluminum. The thickness and specific surface area of porous

anodic oxide film can be controlled by the anodic oxidation temperature and boehmite processes time. Consequently, the highest performance is obtained at the anodic oxidation temperature of 50 °C and boehmite processing time of 5 h. Its pore voidage and specific surface area were 50 % and 170 m<sup>2</sup>/g, respectively. The thermal conductivity of the catalyst plate was highest at about 50 % pore voidage, which can better promote endothermic dehydrogenation reactions.

The microreactor composed of the improved catalyst exhibited twice the methylcyclohexane conversion as that composed of the original catalyst. Based on the result, the reactor volume using this improved catalyst could be reduced to half that of the original reactor while generating the same volume of H<sub>2</sub>.

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## REFERENCES

1. A. Shukla, S. Karmakar and R.B. Biniwale, *Int. J. Hydrogen Energy*, **37**, 3719 (2012).
2. N. Kariya, A. Fukuoka and M. Ichikawa, *Phys. Chem. Chem. Phys.*, **8**, 1724 (2006).
3. S. Yolcular and O. Olgun, *Catal. Today*, **138**, 198 (2008).
4. H. Hondo, Y. Moriizumi and T. Usui, *J. Jpn. Inst. Energy*, **87**, 753 (2008).
5. N. Kariya, A. Fukuoka, T. Utagawa, M. Sakuramoto, Y. Goto and M. Ichikawa, *Appl. Catal. A*, **247**, 247 (2003).
6. T. Hashioka, S. Kosedo, M. Itoh, K. Yamamoto, H. Kameyama and T. Kabe, *Chem. Lett.*, **16**, 1067 (1987).
7. Z. Lu, F. Zhang, X. Lei, L. Yang, S. Xu and X. Duan, *Chem. Eng. Sci.*, **63**, 4055 (2008).
8. C. Jiang, J. Tu, S. Guo, M. Fu and X. Zhao, *Mater. Heat Treat.*, **25**, 1253 (2004).
9. S. Inoue, *Mater. Integration*, **20**, 34 (2007).
10. Y. Okada, M. Saito and T. Makabe, *Hydrogen Energy Syst.*, **31**, 8 (2006).