Short communication

Preparation and catalytic behavior of second metal Ni supported on a novel conductive structured Cu/γ-Al₂O₃/Al catalysts through electrolysis on steam reforming of dimethyl ether

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ABSTRACT

Electrochemical treatment was employed to improve the electric conductivity of γ-Al₂O₃/Al. Optimal conditions were found to be 0.5 M KCl solution along with potential of 4 V for 7.5 min. The modified γ-Al₂O₃/Al support showed higher catalytic activity at low temperature because of its bigger specific surface area and more acid amount than γ-Al₂O₃/Al. Moreover, Ni was easily loaded on the modified Cu/γ-Al₂O₃/Al catalyst through electrolysis because of the high electric conductivity. The novel Ni/Cu/γ-Al₂O₃/Al catalyst also exhibited excellent stability for 40 h at 623 K with 100% conversion and 70% H₂ yield in steam reforming of dimethyl ether.

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1. Introduction

Recently, a novel structured porous anodic alumina catalyst forming on the surface layer of alumina substrate has been attracting considerable attention from scientific and commercial fields. Compared with the conventional granular catalysts, such as zeolites and γ-Al₂O₃ [1–3], structured anodic alumina is very promising for the application of micro-channel reformers because of its high transport rate and good shape flexibility [4]. Many studies have demonstrated that the anodic alumina had been well applied in the field of VOC's combustion, NOx reduction, CH₄ steam reforming, and dimethyl ether steam reforming [5–8] (DME SR).

Developing an efficient method to support catalytic components on anodic alumina is therefore important. This study aims to achieve high deposition of catalytic component and fully utilize the outstanding conductivity of Al plate. Conventional methods, such as wash coat method [9], impregnation method [7,10], immersion method [11], and electroless deposition [12] for many plate-type supports have been reported. However, these methods also encountered with some disadvantages, such as toxicity and environmental safety of the reaction solution, long load cycle, and low load efficiency of the target chemical component. Therefore, developing a new environmentally friendly and timesaving method is essential and urgent.

From this perspective, a novel direct current (DC) electrolysis technique with the prepared anodic alumina catalyst as the cathode and a stainless steel as the anode was proposed to efficiently prepare a low-loading amount of bi-component catalysts. However, a non-conductive compact alumina between the porous layer and the Al substrate prevented the direct electric and chemical contacts and finally induced small currents. Some techniques were developed to decrease or remove the compact alumina, including chemical etching, voltage drop [13], and current-limited anodization [14]. However, there are many challenges: application is on ultrathin and extremely brittle porous alumina membranes and removal of the barrier layer is non-uniform. Some researchers [15,16] further developed an electrochemical treatment for open-through porous anodic alumina membrane used in the synthesis of the nanowire arrays or carbon nanotube [17,18]. However, the details on investigated conditions of electrochemical treatment on plate-type anodic alumina and the application of as-treated Al₂O₃/Al have been rarely reported.

In this study, various conditions of electrochemical treatment were investigated to develop a novel electric anodic alumina, and the simplified mechanism of electrochemical treatment was also proposed. The DC electrolysis method was used to support Ni on

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Cu-based anodic alumina catalyst for improving its thermal stability. The activity and durability of those prepared catalysts were then targeted for DME SR in a tubular reactor.

2. Experiments

2.1. Catalyst preparation

The structured Al_2O_3/Al support was prepared through anodization [19]. The pretreated Al plate was anodized in a 0.4 M oxalic acid solution for 12 h under a current density of 50 A/m^2 at 293 K, followed by calcine at 623 K for 1 h. Electrochemical treatment was performed under different conditions with Al_2O_3/Al support as the cathode and a stainless steel as the anode. Subsequently, the as-treated supports named EC-Al_2O_3/Al and Al_2O_3/Al supports were subjected to hydration treatment in deionized water at 353 K for 1 h. Finally, the two hydration-treated monoliths were dried and calcined at 773 K for 4 h and defined as EC-γ-Al_2O_3/Al and γ-Al_2O_3/Al, respectively.

Cu-based catalysts (Cu/γ-Al_2O_3/Al and Cu/EC-γ-Al_2O_3/Al) were prepared through impregnation for requisition of the amounts and crystal size of Cu [20]. First, γ-Al_2O_3/Al and EC-γ-Al_2O_3/Al supports were impregnated in a 1.5 M Cu $(NO_3)_2$ solution for 12 h under ambient conditions. The resulting catalysts were then calcined in air at 773 K for 4 h. The electrodeposition process was conducted in the 1 M Ni $(NO_3)_2$ solution for 2 min with Cu/γ-Al_2O_3/Al or Cu/EC-γ-Al_2O_3/Al as the cathode and a stainless steel as the anode. Finally, the obtained plates were calcined again in air at 773 K for 4 h.

2.2. Catalyst characterization

The surface morphology of catalysts was examined under a scanning electron microscope (SEM, JSM-6360LV, JEOL). The specific surface area was measured using the N_2 adsorption method by a physisorption analyzer (ASAP 2020-M, Micromeritics). Temperature-programmed desorption of NH_3 (NH_3-TPD) was performed on a Micromeritics ChemiSorb 2720 apparatus. The Cu/Ni loading of catalysts was determined by an inductively coupled plasma-atomic emission spectrometry (710ES, Varian). The dispersion of Cu and the exposed Cu surface area were determined by N_2O chemical adsorption on a Micromeritics ChemiSorb 2720 instrument using the procedure described by Van Der Grift (provided in supplementary material) [21]. The crystal structure of catalysts was characterized using X-ray diffraction (D/max 2500 V, Rigaku). The PH values at the cathode of different solutions were measured using a pH meter (PHB-4, Leici). Different alumina films were gauged using a coating thickness meter (CM-8822, Landtek).

2.3. Catalytic activity and durability evaluation

The catalytic tests were performed in a fixed-bed reactor (I.D. 12 mm) under atmospheric pressure. Those plate-type catalysts were cut into small pieces and packed into the reactor on each test. The prepared catalysts were reduced at 573 K for 3 h in a 10 vol.% H_2/N_2 stream before the reaction. The mixture of DME, vaporized water, and N_2 was fed into the reactor at a maintained ratio of 1:4:3, whereas the total flow rate was about 76 mL/min (i.e., GHSV = 4000 mL/(h·g), the quality is based on alumina layer).

The compositions of influent and effluent gases were analyzed using an on-line gas chromatograph. DME conversion (X_{DME}), H_2 yield (Y_{H2}), and C_i (CO, CO_2, CH_4) selectivity (S_{Ci}) are defined as follows:

$$X_{DME} = \left(\frac{F_{DME,in} - F_{DME,out}}{F_{DME,in}} \right) \times 100\% \qquad (1)$$

$$Y_{H_2} = \frac{F_{H_2}}{F_{DME}} \times \frac{1}{6} \times 100\% \qquad (2)$$

$$S_{C_i} = \frac{F_{C_i}}{F_{CO} + F_{CO_2} + F_{CH_4}} \times 100\%. \qquad (3)$$

3. Results and discussion

3.1. Optimization of electrochemical treatment for the structured EC-Al_2O_3/Al support

The changes in systemic currents and PH values under different solutions are shown in Fig. 1. In KCl and NaCl solutions, the systemic currents rapidly increased in 3 min; then gradually increased from 3 to 7.5 min; finally tended to stabilize after 7.5 min, whereas the curves of KNO_3 solution nearly remained unchanged during the whole process. Further, the tendency of pH values detected near the cathode showed that the pH curves in KCl and NaCl solution dramatically increased with reaction time, which indicated the enrichment of OH^- ions. The PH values were even close to 14 over 7.5 min, which meant as the treating time increase, the corrosion on Al_2O_3 caused by OH^- ions would be strongly intensified. As shown in Fig. S1 (b) ~ (d), the phenomenon of connected pores and fractures was quite serious above 7.5 min. However, the curve slightly changed during the electrochemical treatment in KNO_3 solution. Based on the consideration above, KCl solution was selected as the treating solution and 7.5 min was applied as the treating time.

The electrochemical phenomena could be explained by the electrochemical reaction mechanism illustrated in Fig. 2. First, H^+ and OH^- ions were decomposed from H_2O, whereas K^+ and Cl^- ions were ionized from KCl. Given that the oxidizing order of the cations was $H^+ > Na^+ > K^+$, the H^+ ions located at the pore bottom preferentially captured the electrons and were reduced to H_2 at the cathode
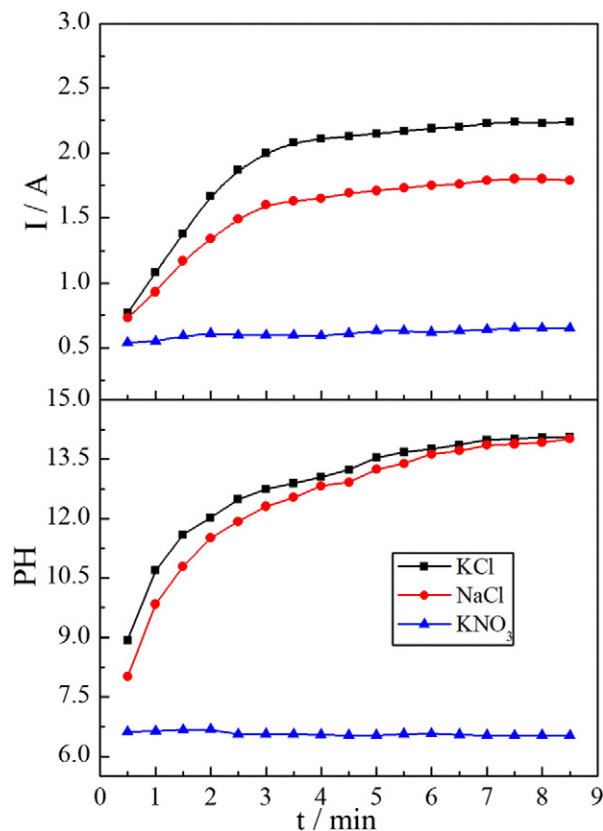

Fig. 1. Curves of systemic currents and PH values under different solutions; Treatment conditions: 0.5 M pretreated solution, potential of 4 V, 8.5 min.

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