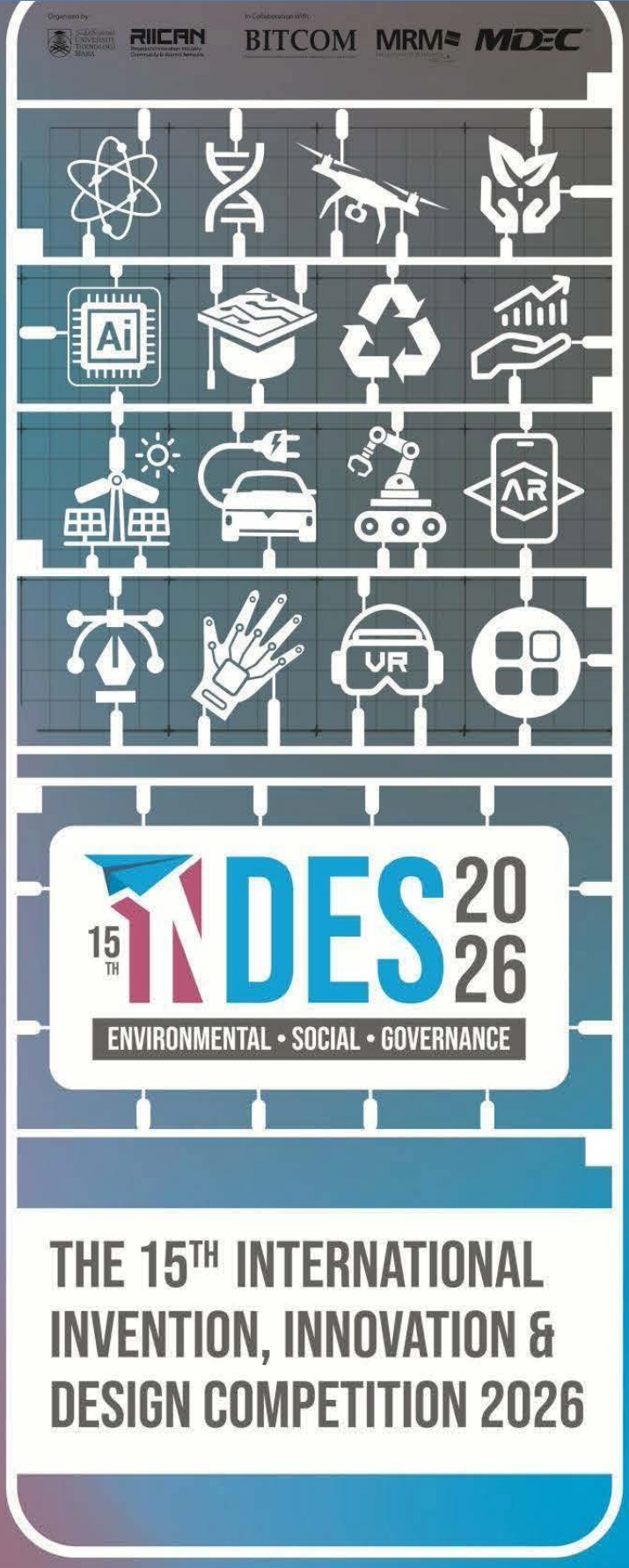

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THE 15th INTERNATIONAL
INVENTION, INNOVATION &
DESIGN COMPETITION 2026

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Office of Research, Industry,
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FABRICATION AND PERFORMANCE OF NANOPOROUS ANODIC ALUMINA OXIDE (AAO) SUPPORT FOR DRY METHANE REFORMING

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ABSTRACT

Nanoporous anodic alumina oxide (AAO) hollow-tube supports were successfully fabricated via a two-step anodization method and subsequently coated with Ni-based catalysts using a sol-gel technique for application in dry methane reforming (DMR). The catalytic performance of monometallic, bimetallic, and trimetallic systems was systematically evaluated to investigate the effect of catalyst composition on activity and stability. Field emission scanning electron microscopy (FESEM) confirmed the formation of a well-ordered nanoporous structure on both the outer and inner of the hollow-tube surface, providing high surface area and enhanced dispersion of active metal species. Catalytic performance was assessed using gas chromatography with a thermal conductivity detector (GC-TCD), focusing on conversion of the reactant gases (CH4 and CO2), syngas yield, and H2/CO ratio. The results demonstrated that all tested catalysts exhibited a stable performance after exposed to DMR condition up to 5 hours of reaction. Trimetallic catalyst, consist of Ni, Co and WC metal exhibited superior performance compared to mono- and bimetallic counterparts, delivering the most high and stable CH4 and CO2 conversions over prolonged reaction time. Additionally, the trimetallic system achieved higher H2 yield and a H2/CO ratio close to unity. This enhanced performance is attributed to the synergistic interaction between metal components, which promotes reactant activation, improves oxygen mobility, and suppresses carbon deposition. The integration of nanoporous AAO hollow-tube supports coated with catalysts presents a promising strategy for enhancing catalytic efficiency and stability in DMR applications.

Keyword: AAO, curve surface, two-step anodization, dry methane reforming

1. INTRODUCTION

The fabrication of anodic alumina oxide (AAO) has evolved significantly from its early reliance on conventional flat aluminum foil to more complex geometries such as aluminum wire, and more recently, to three-dimensional (3D) substrates including aluminum hollow tubes (Belwalkar et al., 2008; Jani et al., 2013). This progression has been driven by the increasing demand for high surface-area nanostructures in advanced technological applications. AAO is well known for its highly ordered nanoporous architecture, chemical stability, tuneable pore dimensions, and excellent thermal and mechanical properties, making it an ideal material for applications in nanotechnology, electronics, biosensing, and energy storage. In fixed-bed dry methane reforming (DMR) systems, powder catalysts are among the most commonly used forms. However, their use often leads to several operational challenges, including unstable reactant gas flow, increased pressure drop, and inefficient heat and mass transfer, which ultimately reduce catalytic performance and stability (Abasaeed et al., 2023). These limitations can result in poor reactant distribution, the formation of localized hot spots, and accelerated catalyst deactivation. To overcome these issues, the integration of catalysts onto structured supports such as AAO hollow tubes presents a promising approach. The nanoporous architecture of AAO provides a high surface area for improved dispersion of active species, while its structured geometry enhances gas flow uniformity and promotes more efficient heat and mass transfer. Consequently, transforming unsupported catalysts into supported systems on AAO not only increases the availability of active sites but also significantly improves catalytic stability and overall reactor performance in DMR applications.

2. METHODOLOGY

2.1 Fabrication of AAO layers

AAO was fabricated on an Al hollow tube using a two-step anodization process in a custom-designed cell. The Al substrate was first cleaned by sonication in acetone to remove impurities. The first anodization was carried out by immersing the tube in an acidic electrolyte under controlled temperature and voltage for 1 hour. The formed oxide layer was then removed using an etching solution for 2 hours, creating a textured surface. A second anodization was subsequently performed under the same conditions but for a longer duration to produce the final porous AAO layer.

2.2 Synthesis of Ni-based catalysts

Ni-based catalysts with varying weight ratios of NiO, Co3O4, and WO3 were prepared using the sol-gel method to study their synergistic effects in DMR (Abd Ghani et al., 2018). The catalysts were deposited onto the AAO hollow tube via spin coating. After cleaning, a measured amount of sol was applied to both the inner and outer surfaces of the support, followed by spin coating at 700 rpm for 15 s to ensure uniform distribution. The coating process was repeated to achieve the desired thickness. The coated samples were then dried at room temperature and calcined at 600 °C for 4 hours to activate the catalyst and improve adhesion.

2.3 DMR reactions for catalyst supported on AAO hollow-tube

The coated AAO hollow tube was placed in a vertical furnace for DMR testing. The catalyst was first reduced in H2 at 450 °C (80 mL/min) for 2 hours. The reaction was then carried out by feeding a CH4/CO2 mixture (45:55) continuously for 5 hours. Product gases were analyzed in situ using GC-TCD to monitor reactant conversion and product yield.

3. FINDINGS

The top-view FESEM images of the AAO at 50,000× and cross-section at 180× magnification is shown in Figure 1(a), (b), and (c), respectively. Figure 1(c) shows the cross-section Al hollow tube with well attached layers of AAO between the Al substrate. The outer surfaces exhibit an average pore sizes 80nm while the inner surfaces reported a slightly lower pore sizes, around 70nm due to their in-direct exposure to the electrolyte compared to outer surfaces. A similar pattern is observed for the interpore distance, where the outer AAO layer consistently exhibits larger spacing than the inner AAO layer.

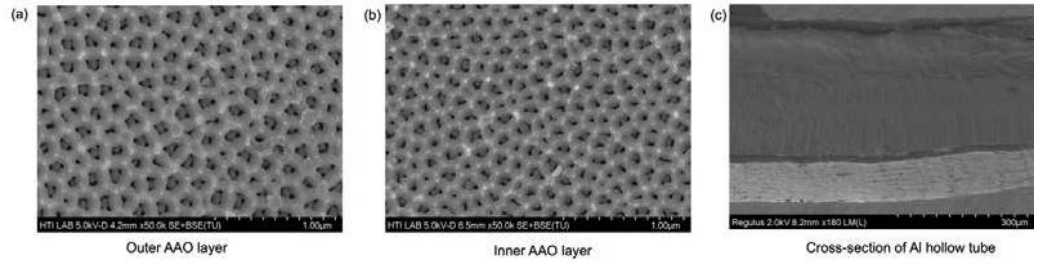

Figure 1 FESEM images of (a) outer layer, (b) inner layer, and (c) cross-section of the AAO support.

The catalytic performance trends in Figure 2(a-d) demonstrate the influence of catalyst composition on activity and stability during DMR. For CH4 conversion, all catalysts show a gradual decline with time, indicating deactivation; however, the trimetallic 46NiO–24Co3O4-30WO3 maintains the highest and most stable conversion (~27–30%) compared to the monometallic NiO and bimetallic systems, which exhibit more pronounced decreases. A similar trend is observed for CO2 conversion, where the trimetallic catalyst consistently delivers superior and more stable performance, suggesting enhanced CO2 activation. In terms of H2 yield, the trimetallic catalyst again shows the best stability with minimal decline over 300 minutes, while NiO and especially the bimetallic catalysts experience significant reductions, indicating faster deactivation. The H2/CO ratio further confirms this behavior, where the trimetallic system maintains a value close to unity with minimal fluctuation, reflecting more balanced syngas production.

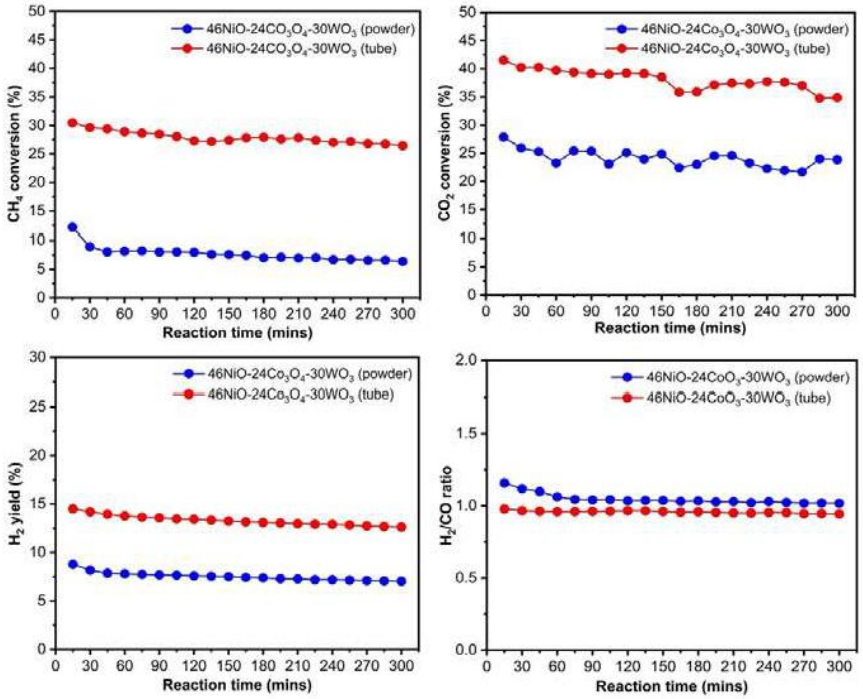

Figure 2 (a) CH4 conversion, (b) CO2 conversion, (c) syngas yield, and (d) H2/CO ratio of Ni-based catalyst supported on nanoporous AAO in DMR.

4. CONCLUSION

The dual-layer AAO was successfully fabricated on the Al hollow tube, and the findings demonstrate its potential for diverse applications, including gas separation, sensing, energy storage, and as a template for nanostructure synthesis. The DMR results are consistent with earlier observations using unsupported powder catalysts, which exhibited unstable performance, rapid deactivation, and fluctuating product distribution due to poor gas flow distribution, increased pressure, and inefficient heat and mass transfer within the packed bed. In contrast, the present system shows improved catalytic stability and performance, indicating that integrating catalysts onto a structured support effectively mitigates these limitations.

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