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Surface area enhancement of nickel foam by low-temperature chemical alloying/dealloying and its application for sodium borohydride hydrolysis

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ABSTRACT

Structured nickel catalysts for sodium borohydride hydrolysis (SBH) were synthesized by surface modification of nickel foam. The fabrication process consisted of i) nickel aluminization, ii) post-annealing, and iii) selective aluminum leaching. Through low-temperature chemical alloying, nickel was aluminized at 400 °C, and a 0.5 μm-thick NiAl₃ alloy outer-layer was formed. While discontinuing the influx of the aluminum source, post-annealing was conducted to transform the NiAl₃ outer-layer into different Ni–Al alloys, such as NiAl₃ on Ni₂Al₃, Ni₂Al₃ on NiAl, and NiAl on Ni₃Al at 400, 500, and 600 °C, respectively. After the selective aluminum leaching, the surface treatment increased the surface area by factors of 2.2–77.1, leading to a significant enhancement of activity in SBH hydrolysis. Additionally, the catalyst undergoing post-annealing at 400 °C achieved superior performance in both initial activity and durability, due to the adhesion layer of Ni₂Al₃ formed between the outermost catalytic layer and the nickel substrate. Finally, continuous SBH-based hydrogen generation using the catalyst with post-annealing at 400 °C was achieved and the as-developed nickel catalyst produced hydrogen at a rate of up to 400 ± 27 sccm/g_{catalyst} while exhibiting excellent durability for 3 h.

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1. Introduction

Surface modification on nickel (Ni) by aluminizing is of great interest in providing chemical and mechanical stability to bulk Ni substrates [1,2] as well as enlarging the Ni surface area [3]. Diffusing aluminum (Al) into Ni substrates followed by selectively removing Al [4–6] has been studied for enhancing catalytic activity through the extension of the Ni surface area. There are several methods for aluminizing Ni structured substrates, such as plasma spraying [7], hot dipping [8], slurry aluminizing [9], and pack cementation [10].

According to pack cementation, the most cost-effective and commercially successful method, Ni-based structures are inserted into a reactor with a mixture of aluminum and alumina powders and then the reactor is heated while filled with a halide gas (e.g., NH₄Cl and AlF₃) [1,2,10]. Notably, utilizing halide gas as an activator simplifies the process of aluminizing nickel substrates with complex 3D structures by forming volatile aluminum-deposit sources. Pack cementation has been applied mostly to achieve Ni-rich Ni–Al alloy-based coating layers (e.g., NiAl and Ni₃Al) for enhancing high-temperature oxidation resistance [11,12]. However, a higher alloying temperature (>950 °C) was required in this method, and the resulting coating layers had a thickness of more than 100 μm [13].

Hence, the conventional pack cementation method should be modified for aluminizing nickel substrates with a thickness of several tenths of a micrometer. For example, when aluminizing commercial nickel foam for fabricating structured catalysts, it is

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