Pulse Plated Mn-Cu-ZnO Nanowires/ tubes for Synthesis of Ethanol from CO Hydrogenation

M. Gupta and J. J. Spivey*

Cain Department of Chemical Engineering,
Louisiana State University, Baton Rouge, LA 70803, USA
* jjspivey@lsu.edu

Introduction

CO hydrogenation reaction can be used to produce many valuable products including methanol [1], ethanol and higher alcohols [2, 3]. Methanol synthesis from hydrogenation of CO is an industrial process [4]. However, the yields of ethanol and higher alcohols are generally low. The production of ethanol and higher alcohols has been the area of growing research interest [2, 3] because they can be used as fuel/fuel additive and also as hydrogen carriers [5]. To date, rhodium-based catalysts have been proven be the most promising but their prohibitive cost and limited supply hinder their ability to be used as industrial catalysts [3]. Thus, several researchers have focused their research on less expensive metal oxides such as copper-based catalysts (modified methanol synthesis catalysts) [6].

Generally, these catalysts are prepared by conventional methods such as co-precipitation and impregnation. However, it has become necessary to explore novel preparation methods that can provide some control over the morphology and structure of these catalysts that cannot be achieved with conventional methods.

Here, we report on the use of a novel method for the preparation of these catalysts – specifically pulse plating or pulse electrodeposition of nanowires/ tubes. Pulse electrodeposition of copper-based nanowires/ tubes is a promising catalyst preparation tool because of its ability to tailor the active metal environment in a way that is not possible with conventional techniques.

Materials and Methods

The nanowires/ tubes were fabricated by using a template synthesis technique. A gold sputtered polycarbonate membrane having a pore diameter and thickness of 400 nm and 10 μm, respectively, was used as working electrode. A platinum mesh and a saturated calomel electrode were used as counter and reference electrode, respectively. The electrodeposition was carried out in a one compartment cell at 60±2 ^{0}C. Electrolytes were magnetically stirred during experiments to ensure proper mixing of ions. Electrolytes contained varying amount of nitrates of Mn, Cu, Zn, and NH_3. Different current pulses were applied using a VersaSTAT 3 potentiostat/ galvanostat manufactured by Princeton Applied Research. CO hydrogenation was carried out in a fixed bed reactor at varying ratios of CO and H_2 and pressures of 5-20 bar at 270^0 C.

Results and Discussion

Fig. 1 is an example of Mn-Cu- ZnO nanowires/ tubes that were used as catalysts in CO hydrogenation reaction. The thickness and length of the nanowires were 400 nm and 4 μm, respectively. The metal environment was controlled by applying various current pulse schemes during pulse plating. Short current pulses of a few milliseconds were given in order to obtain uniform composition along the length of the nanowires.

The following table summarizes the results at a flow rate of 30 scc/min, pressure of 10 bar and, H_2:CO ratio of 2 at 290 ^{0}C.

Catalysts (composition (wt %))	Selectivity (%C)			
	Methanol	Ethanol	Methane	CO_2
Zn 33.5, Cu 66.2, Mn 0.45	8.92	5.15	41.8	24.0
Zn 82.0, Cu 17.8, Mn 0.62	10.2	4.60	43.40	23.5

Significance

Pulse plated nanowires of Mn-Cu-ZnO are shown to be promising alcohol synthesizing catalysts. One of the main advantages of these catalysts is that the metal environment can be controlled during their fabrication unlike conventional methods.

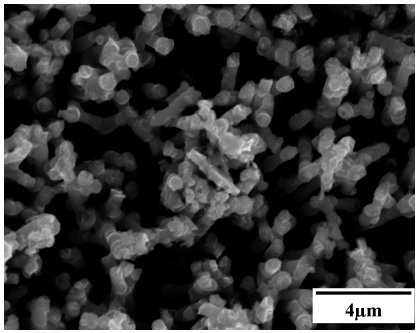

Figure 1. SEM micrograph of Mn-Cu-ZnO nanowire catalyst

References

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