



Halloysite nanotube-based cobalt mesocatalysts for hydrogen production from sodium borohydride



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ARTICLE INFO

Keywords:

Nanotubes
Surface-modification
Cobalt nanoparticles
Mesoporous catalysis
Sodium borohydride
Halloysite

ABSTRACT

We report the novel hybrid metal-clay mesocatalysts with halloysite nanotubes as carriers and cobalt as catalytic metal for hydrogen production from sodium borohydride. The ligand assisted metal adsorption on the surface of halloysite and intercalation into nanotubes was achieved using azines or silane. The catalyst with pre-formed cobalt oxide nanoparticles adsorption on the pristine halloysite surface showed low catalytic efficiency. The most active cobalt-containing system was formed using ketazine as the ligand. The chelating agent selection strongly affected the hydrogen evolution process and was optimized. The best halloysite based core-shell mesocatalyst contained 16 wt% of cobalt with maximum hydrogen evolution rate of 3 L/min×g(cat).

1. Introduction

Hydrolysis of sodium borohydride is a promising and thoroughly studied reaction with possible practical implementation as a source of hydrogen fuel. Sodium borohydride has significant advantages such as high energy density, relatively low cost and high stability [1,2]. The reaction takes place at room temperature without additional conditions and can also be efficiently held with water mixtures like water-methanol, where activation energy and freezing point of the solution could be decreased [3,4].

The catalytic hydrolysis of sodium borohydride is a complex electrochemical process where decomposition of adsorbed borohydride ion on the catalyst surface proceeds via electrochemical oxidation of BH₄[−] accompanied by water reduction together with side reactions. In the process, activation of water is the limiting step irrespective of its excess in the reaction medium [5].

This reaction is catalyzed well by noble metals: among the VIII group metals, the highest activity is expected for rhodium and ruthenium, and the lowest activity – for palladium. But because of their high cost, many investigations were made to improve the economic feasibility of this process. One of the possible solutions is to use less expensive cobalt-based systems, made by a wide range of methods from simple precipitation to electrodeposition [6–9]. It is a well-known fact that a synergistic effect within the triple “non-metal-other metal-cobalt borides” systems occurs, as in the CoB-Mo-P, Co-P-Pd and Co-Ru-Pt due to the redistribution of electron density in cobalt-

borides [8]. Larger atoms of precious metals also participate in reaction catalysis and establish steric constraints restricting further aggregation of particles. Calcination is widely used to change the borates crystalline structure to increase the electric conductivity and contact area [10]. Different additives influence the electronic interaction between Co and B during the formation of CoB_x nanoparticles, which have a number of unique features like the transition state of cobalt within them.

Another way to increase the activity of cobalt and noble metal-based systems is to find the appropriate carrier for metal nanoparticles. Various sustainable supports were widely used to stabilize metal particles on catalysts like carbon [10], graphene [11,12], carbon nanotubes [13], clays [14,15]. In [15] modified clay nanotubes called halloysite were used as catalysts for methanolysis of sodium borohydride but loss of active metals lead to low efficiency of the produced catalyst. In here we present cobalt based mesoporous catalysts for hydrogen evolution from sodium borohydride solution with enhanced activity. Halloysite has been reported as a carrier for noble metal nanoparticles [16–20] and used as a catalyst for various redox reactions like hydrogenation [21,22]. We propose to use cobalt instead of platinum metals due to its low cost and high activity. In this work we compare three different halloysite-cobalt catalysts preparation methods using the surface modification of halloysite with silane or azines and as a comparison using pristine halloysite for metal salt wet impregnation.

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