# Kinetics of Sodium Borohydride Hydrolysis on Cobalt with Different Structures

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**Abstract-** In the present study cobalt with a fiber and smooth structures were deposited onto the titanium surface. The morphology, structure and composition of the prepared catalysts were examined by means of Field Emission Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy. The catalytic activity of cobalt with a fiber and smooth structures deposited onto the titanium surface was investigated towards the hydrolysis of sodium borohydride. It was found that a fiber structure Co shows higher activity towards the hydrolysis of sodium borohydride as compared with that of Co with a smooth structure.

## I. Introduction

Among chemical hydrides sodium borohydride is an attractive alternative fuel for application in fuel cells as alternative hydrogen sources (indirect borohydride fuel cells (IDBFC)) due to its advantages of high hydrogen storage efficiency (10.8 wt.%), stability in air at high pH values, easily controlled generation of hydrogen and high purity of hydrogen obtained from the catalytic hydrolysis of sodium borohydride solution, non-flammability and side product recyclability[1,2]. The development of low-cost non-noble metal catalysts with high activity with respect to the hydrolysis reaction of borohydride and durability plays an important role in the hydrogen generation for fuel cells.

In the present study cobalt with a fiber and smooth structures were deposited onto the titanium surface (denoted as Cofiber/Ti and Cosmooth/Ti) by means of electrodeposition and electroless metal plating. The morphology, structure and composition of the prepared catalysts were examined by means of Field Emission Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy. The catalytic activity of cobalt with a fiber and smooth structures deposited onto the titanium surface was investigated towards the hydrolysis of sodium borohydride.

## II. Experimental Details

### Chemicals

Titanium sheets (99.7% purity, 0.127 mm thickness), NaBH4 and CoCl2 were purchased from Sigma-Aldrich Supply. H2SO4 (96%) and NaOH (99%) were purchased from Chempur Company. All chemicals were of analytical grade. Deionized water with the resistivity of 18.2 M cm–1 was used to prepare all the solutions.

### Fabrication of Catalysts

Cobalt coatings with a smooth structure were deposited by electroless deposition. Prior to electroless cobalt deposition, the titanium sheets (1 x 1 cm) were degreased with ethanol, rinsed with deionized water and dried in an Ar stream. Then the cobalt coatings were deposited on the titanium surface according to the following procedures: a) activation of the Ti surface in a 0.5 g/l PdCl2 solution for 60 s; b) subsequent rinsing of the activated surface with deionized water; c) followed by immersion of the activated sample into an electroless cobalt bath for 45 min [3]. The bath operated at a temperature of 25 ± 2 oC. The surface-to-volume ratio was 1.3 dm2 l–1.

Cobalt coatings with a fiber structure and the thickness of 3 m were deposited onto the titanium surface (1 x1 cm) via electro deposition [4, 5]. Prior to deposition of the Co coating with a fiber structure, the titanium plates were degreased with acetone and then pretreated in diluted H2SO4 (1:1 vol) at 90 oC for 10s.

Then, Co coatings deposited onto the titanium surface were used for measurements of hydrogen generation from the sodium borohydride solution without any further treatment.

## Characterization of Catalysts

The morphology and composition of the fabricated catalysts were characterized using a SEM/FIB workstation Helios Nanolab 650 with an energy dispersive X-ray (EDX) spectrometer INCA Energy 350 X-Max 20.

## Kinetic Studies of the Catalytic Hydrolysis of NaBH4

The amount of generated hydrogen was measured by using a classic water-displacement method with the aim to characterize the catalytic effectiveness of the Cosmotth/Ti and Cofiber/Ti catalysts. In a typical measurement the reaction solution containing NaBH4 and NaOH was thermostated in an airtight flask fitted with an outlet for collection of evolved H2 gas, and then the Cosmotth/Ti and Cofiber/Ti catalysts were immersed into the designated temperature solution to initiate hydrolysis reaction. As the reaction proceeded, the water displaced from a graduate cylinder connected to the reaction flask was continually monitored. The rate of generation of hydrogen was measured at different solution temperatures (25, 35, 45 and 55 oC) in order to determine the activation energy.

## III. Results and Discussion

Figure 1a shows FESEM image of as-prepared Cosmooth/Ti, from which evident that the layer of polycrystalline Co with the average size of crystallites ca. 400-900 nm was deposited onto the titanium surface. The thickness of the electroless Co layer was from ca. 500 nm up to 1 m. As seen from Figure 1b, a fiber structure Co was electrodeposited onto the titanium surface with the fibers in the order of tens of nanometers in thickness and hundreds of nanometers in length [4, 5]. Cobalt coatings with the thickness of 3 m were deposited on the titanium surface.

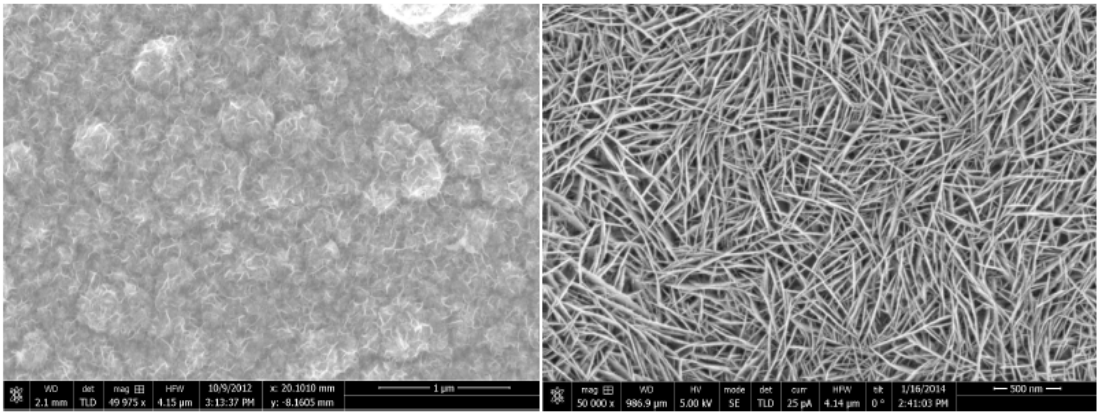

Figure 1. FESEM images of Co layers with a smooth (a) and fiber (b) structure deposited onto the titanium surface.

The activity of the Cosmooth/Ti and Cofiber/Ti catalysts was investigated towards the catalytic hydrolysis of NaBH4. Figure 2 presents the volume of generated hydrogen with respect to reaction time with the Cosmooth/Ti and Cofiber/Ti catalysts in a 0.05 M NaBH4 + 1 M NaOH solution at the temperature of 35 oC.

A higher rate of generation of hydrogen is obtained at the Cofiber/Ti catalyst as compared to that at Cosmooth/Ti, indicating better catalytic properties of fiber structure Co towards to the catalytic hydrolysis of NaBH4.

The kinetics of reaction of hydrolysis of NaBH4 was further investigated at various temperatures at the Co fiber structure deposited onto the titanium surface. Fig. 3a and Table I show the rate of hydrogen generation measured during the hydrolysis of alkaline NaBH4 solution (0.05 M NaBH4 + 1 M NaOH) using the Cofiber/Ti catalyst as function of reaction temperature (25-55 oC).

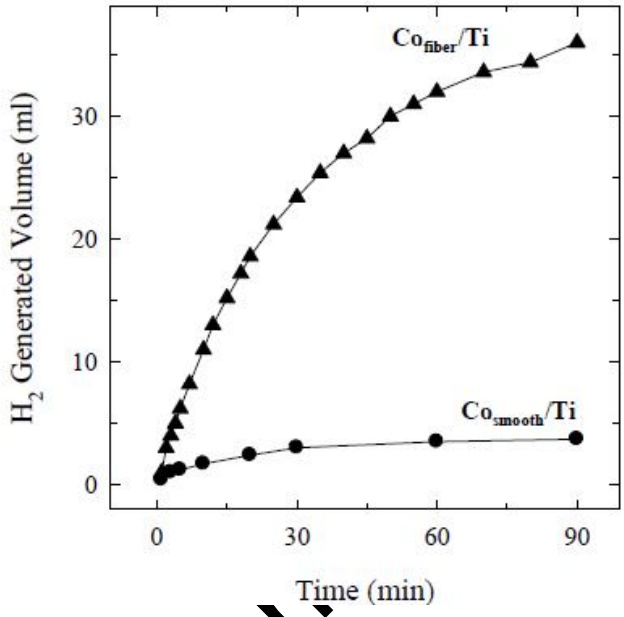


Figure 2. H2 generation from 15 ml 0.05 M NaBH4 + 1 M NaOH at a 35 oC temperature catalyzed by Cofiber/Ti and Cosmooth/Ti.

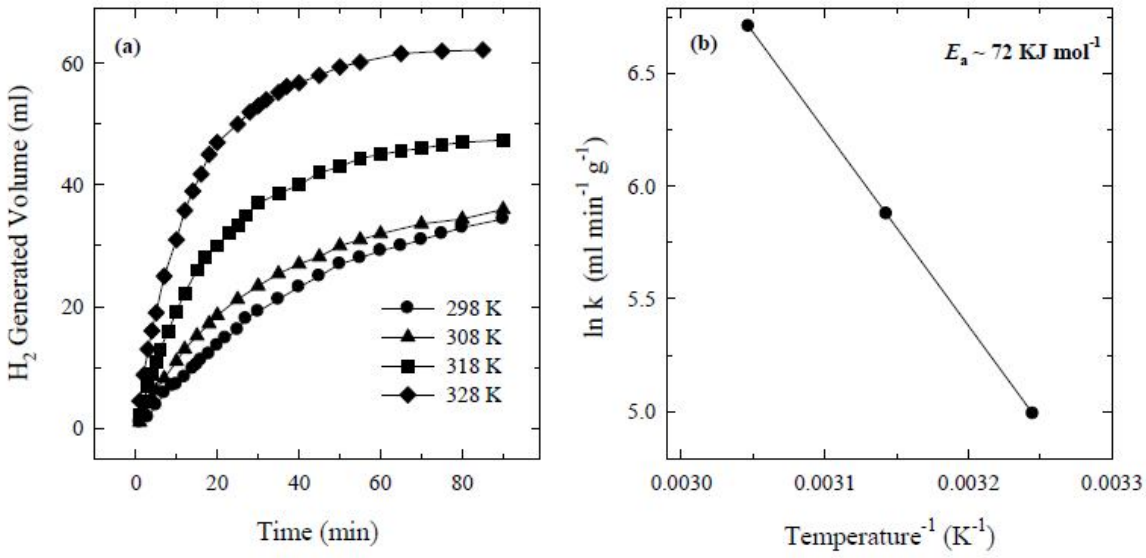


Figure 3. (a) H2 generation from 15 ml 0.05 M NaBH4 + 1 M NaOH at a different solution temperature catalyzed by Cofiber/Ti. (b) The Arrhenius plots calculated from the rates of NaBH4 hydrolysis in a same solution for Cofiber/Ti.

As seen from the data given in Table I, the rate of catalytic hydrolysis of NaBH4 in alkaline solutions increases exponentially with increase in reaction temperature, and a maximum value of 821 ml min–1 g–1 is obtained at 55 oC. Temperature dependence of the rate of generation of hydrogen is expressed by the Arrhenius equation:

$$k = Ae^{-Ea/RT}, \quad (1)$$

where *E*a is the activation energy (J), A - the frequency factor, R - the general gas constant (8.314 J mol–1 K-1). In order to find activation energy and frequency factor, the Arrhenius plot of ln(*k*) vs 1/*T* was constructed from the data presented in Fig. 3a and is given in Fig. 3b. The Arrhenius plot gives activation energy of 72 kJ mol–1. The obtained data confirm that the fiber structure Co layer deposited onto titanium catalyzes efficiently the hydrolysis reaction of NaBH4 in alkaline solutions.

Table I. Dependence of hydrogen generation rate on temperature obtained at Cofiber/Ti in a 0.05 M NaBH4

| Temperature (K) | $H_2$ generation rate (ml $min^{-1}$ $g^{-1}$) |
|---|---|
| 298 | 105.2 |
| 308 | 146.8 |
| 318 | 356.7 |
| 328 | 821.0 |

## IV. Conclusions

A fiber structure Co was electrodeposited onto the titanium surface with the fibers in the order of tens of nanometers in thickness and hundreds of nanometers in length via electrodeposition. The Co with a smooth structure was deposited by electroless deposition of Co. The layer of polycrystalline Co with the average size of crystallites ca. 400-900 nm was deposited onto the titanium surface. It was found that a fiber structure Co shows higher activity towards the hydrolysis of sodium borohydride as compared with that of Co with a smooth structure.

## References


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