



Synthesis of cobalt-doped bead type catalyst for hydrogen production via hydrolysis reaction of NaBH₄

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Cite this study: Akti, F. (2023). Synthesis of cobalt-doped bead type catalyst for hydrogen production via hydrolysis reaction of NaBH₄. *Advanced Engineering Days*, 6, 58-60

Keywords

Cobalt
Bead
NaBH₄
Hydrogen

Abstract

Cobalt-doped bead type catalyst was synthesized for hydrogen generation from sodium borohydride hydrolysis reaction by using sodium hydroxide. Synthesized catalyst was characterized using XRD (X-ray diffraction), nitrogen adsorption/desorption isotherm and FTIR (Fourier transforms infrared) analyses techniques. XRD pattern showed presence of chitosan in the structure, while cobalt species were not observed. Nitrogen adsorption/desorption isotherm was exhibited a behavior indicating of micro-mesoporous structure. The surface area, total pore volume and pore diameter values of catalyst were determined as 35.0 m²/g, 0.03 cm³/g and 3.4 nm, respectively. FTIR spectra showed existence of peaks related to chitosan. The catalyst was test in sodium borohydride hydrolysis reaction and hydrogen production rate was determined as 28 mL. min⁻¹. g⁻¹.

Introduction

Nowadays, the search for new and renewable clean energy sources continues due to the decrease in fossil fuels and their harmful effects on the environment. Hydrogen still attracts attention as an environmentally friendly clean energy source. Sodium borohydride (NaBH₄) is the most widely used metal hydride source due to its high hydrogen storage capacity (10.8 by wt%), stability in alkaline solution, pure hydrogen generation and easy reproduction from by-products. The catalytic hydrolysis reaction of NaBH₄ is an exothermic reaction and it produces two times as much hydrogen than its content at the end of the reaction [1,2]. The self-hydrolysis reaction of NaBH₄ without a catalyst is quite slow. Although noble metals such as platinum, palladium, rhodium and ruthenium have been widely used due to their excellent catalytic activity, their rarities and the resulting high cost have caused to the development of alternative catalysts. However, the direct use of these metals causes agglomeration problem and low surface area. This situation can reduce the catalytic activity by affecting the catalytic active centers. In addition, the problem of separating the catalysts from the reaction medium reduces the reusability of the catalyst and increases the cost at this rate. Therefore, synthesized catalysts using support structure largely eliminates these disadvantages. In general, zeolite, metal oxides, clay, activated carbon, graphene, carbon nitride, silica, alumina, aerogel and hydrogel materials were used as catalyst support materials [3-5].

In this study, cobalt which is cheap and having high catalytic activity were preferred catalyst active metal. Aforementioned problems were tried to be eliminated by synthesizing the catalyst active components in the form of bead using chitosan.

Material and Method

Synthesis of catalyst

CoCl₂.6H₂O was chosen as catalyst active component. Chitosan was used to obtain the bead structure. First, 0.2 g CoCl₂.6H₂O was dissolved in 50 mL acetic acid (1% v/v) and then chitosan (2% w/v) was added and mixture was stirred for 3 hours at room temperature until a clear homogeneous viscous solution was obtained. The resulting

gel was kept for one night to elimination of bubbles and then it was dropped into the 1 M NaOH solution using a syringe and stirred for 2 hours to form a stable bead structure. The resulting beads were filtered using filter paper, washed several times with distilled water and dried at room conditions. The catalyst was coded as Co@C. The all chemicals were of analytical purity and supplied from Sigma-Aldrich.

Characterization of catalyst

X-ray diffraction (XRD) pattern of catalyst was recorded by a Philips PW 3040 diffractometer equipped with CuK α radiation ($\lambda=0.15406$ nm) in the 2θ range of $10\text{--}90^\circ$ with 0.02° step size and $1^\circ/\text{min}$ scan speed.

Nitrogen adsorption/desorption isotherm was obtained with a Quantachrome®ASiQwin™ instrument at -196°C after degassing the catalyst for 3 h at 120°C . Before analysis catalyst was waited in an oven for overnight at 110°C . Multi point BET (Brunauer Emmet Teller) surface area was calculated using adsorption data in the range of $0.05 < P/P_0 < 0.30$. Total pore volume was determined at relative pressure of $P/P_0=0.99$. Pore diameter was estimated by Barrett-Joyner-Halenda (BJH) method [6].

The FTIR (Fourier transforms infrared) spectra of the catalyst was recorded on a Thermo Scientific/Nicolet IS50 device with ATR (attenuated total reflectance) in the wavelength range of $600\text{--}4000\text{ cm}^{-1}$.

Catalytic activity test

The performance of catalyst was tested in the NaBH_4 hydrolysis reaction for hydrogen generation. In the reaction experiments, firstly a mixture containing 5 mL water, 1.0 wt% NaOH and 1.0 wt% NaBH_4 were prepared after that the 30 mg of catalyst was added. Generated hydrogen volume was measured using a classical water displacement method. The hydrogen generation rate was calculated from the slope of the volume-time plot in the linear region using formula $\text{HGR} = V / (t \cdot m)$. Where HGR is hydrogen generation rate ($\text{mL} \cdot \text{min}^{-1} \cdot \text{g}_{\text{cat}}^{-1}$), V is generated hydrogen volume (mL), t is time (min) and m is weight of the catalyst (g).

Results and Discussion

XRD pattern of catalyst is given in Fig.1a. The catalyst exhibited amorphous structure, it was determined that the broad peaks obtained at Bragg angle values of $\sim 20^\circ$ and 40° belong to chitosan [7]. The peaks corresponding to cobalt was not observed, this situation suggested that the metals might be embedded in the chitosan structure.

The nitrogen adsorption/desorption isotherm is given in Fig. 1b and the structural properties determined from the isotherms are inset in Figure 1b. The catalyst exhibited Type IV isotherm behavior, representing porous materials containing micro and mesopores, according to the IUPAC classification [6]. Amount of adsorbed gas volume increased with relative pressure for catalyst. Total adsorbed gas volume for Co@C was approximately $19\text{ cm}^3/\text{g}$. The surface area, total pore volume and pore diameter values of catalyst were determined as $35.0\text{ m}^2/\text{g}$, $0.03\text{ cm}^3/\text{g}$ and 3.4 nm , respectively.

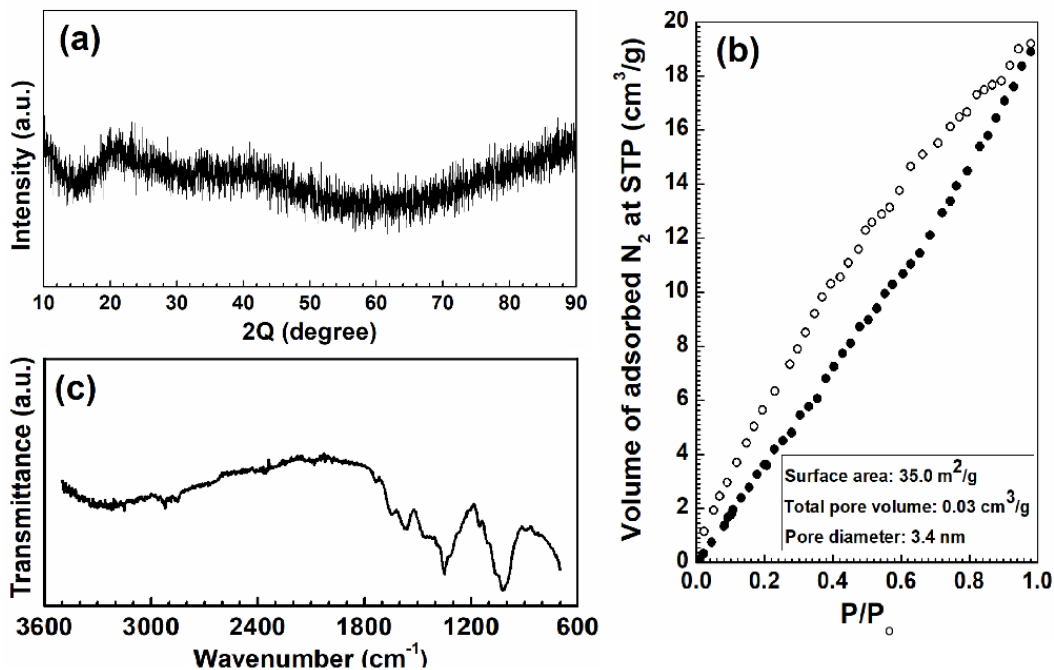


Figure 1. (a) XRD patterns (b) Nitrogen adsorption/desorption isotherms (STP: Standard temperature and pressure) (c) FTIR spectra of Co@C catalyst

The FTIR spectra of the catalyst is shown in Figure 1c. Functional groups related with chitosan were clearly observed in catalyst. The peak observed around 1030 cm^{-1} indicates C-O vibration, the peaks obtained at 1350 and 1460 cm^{-1} show C-H vibration originating from the CH_2/CH_3 groups. In addition, the peak at 1644 cm^{-1} was assigned to C=O bond in the chitosan structure, and the peaks at 1557 and 3270 cm^{-1} to N-H group [7, 8].

Catalytic activity test of catalyst is given in Figure 2. Hydrogen generation was not observed in the first 60 min over Co@C catalyst. It was thought that the reason for this might be due to the contact time of the catalyst surface with reactants or the pore diffusion resistance [9]. During the NaBH_4 hydrolysis reaction, BH_4^- ions, which are first separated from NaBH_4 , are adsorbed on the catalyst surface, and H^- ions transfer to metal ions, and hydrogen is released at the end of a series of reactions [10]. Hydrogen production volume with cobalt catalyst was measured as 124 mL within 210 min. The hydrogen production rate was determined as $28\text{ mL}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$.

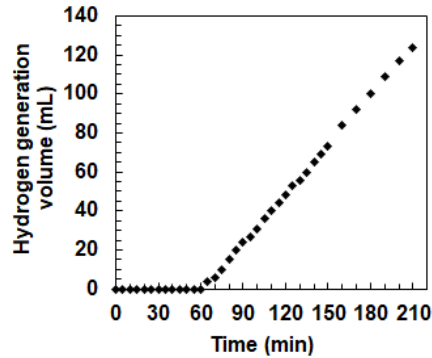


Figure 2. Catalytic activities of Co@C catalyst

Conclusion

Cobalt-doped bead type catalyst was synthesized using chitosan. Characterization results showed that catalyst was prepared successfully. Hydrogen generation rate was $28\text{ mL}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$. In present study, the development of cobalt-doped bead type catalysts for hydrogen production might be initiative for next studies.

Acknowledgements

This study was supported by Hitit University Scientific Research Projects Department (Project number: MUH19001.21.004).

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