JOTCS B
JOURNAL of THE TURKISH CHEMICAL SOCIETY
SECTION: B
CHEMICAL ENGINEERING
TURKISH CHEMICAL SOCIETY

DEVELOPMENT OF Co - B / MAGNESITE CATALYST FOR HYDROGEN GENERATION BY HYDROLYSIS OF SODIUM BOROHYDRIDE

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(This article was presented first to the PPM2017, then submitted to JOTCSB as a non-peer-reviewed article)

Abstract: The Co-B supported on magnesite catalyst was developed by impregnation-reduction method. The catalyst was characterized by XRD, SEM, EDS and XRF. The effects of catalyst amount, $NaBH_4$ concentration and reaction temperature on the hydrogen generation rate were investigated. The hydrogen generation rate was obtained as 29000 mL/ min g_{Co} at 50 ºC. The activation energy of hydrolysis reaction was estimated be 68.56 kJ/mol. The Co-B/magnesite is a promising catalyst for the hydrolysis of sodium borohydride.

Cite this: Erol S, Özdemir M. DEVELOPMENT OF Co - B / MAGNESITE CATALYST FOR HYDROGEN GENERATION BY HYDROLYSIS OF SODIUM BOROHYDRIDE. Journal of the Turkish Chemical Society, Section B: Chemical Engineering. 2017;5(sp. is. 1):69–76.

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INTRODUCTION

Nowadays, the increasing of energy demand has become a serious issue with the fast worldwide economic development. Hydrogen is considered to be an efficient energy carrier for the future due to the increasing demand of energy along with the depletion of conventional fossil fuel reserves. There are many processes for producing hydrogen. Among them, the most notable is the production of hydrogen by the hydrolysis of alkaline metal hydrides. Sodium borohydride ($NaBH_4$) is a suitable hydrogen source due to its advantages of high hydrogen density (10.8 %) and stability in alkaline solution. Hydrogen can be generated by sodium borohydride hydrolysis using a suitable catalyst as follows [Amendola et al., 2000]:

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 \quad \Delta H=-217\ \text{kJ/mol} \tag{1}$$

Metal boride catalysts received considerable attention due to their high efficiency, low cost and simple preparation methods. However, unsupported metal boride catalysts have low surface area and also tend to agglomerate during hydrolysis reaction. The supported metal boride catalysts are more useful for practical application. The supported metal boride catalysts such as alumina, titanium oxide, cerium oxide [Ye *et al*. 2007; Li *et al*. 2014; Lu *et al*. 2012], silica [Yang *et al*. 2011; Patel *et al*. 2013], activated carbon [Xu *et al*. 2008], glassy carbon, graphite [Özdemir, 2015] and attapulgite [Tian *et al*., 2010] were used in the hydrolysis of sodium borohydride.

Magnesite ($MgCO_3$) is one of the most important magnesium minerals. It is the basic source for production of magnesium and magnesium compounds. These products are extensively used in the manufacture of basic refractory bricks, heat-insulating compositions, paper, plastics, rubber, ink, glass, ceramics, paints, and pharmaceuticals [Othmer, 1978]

In this study, magnesite-supported Co-B was prepared by impregnation-reduction method. The catalyst was characterized by using the XRD, SEM, EDS and XRF methods. The effects of reaction parameters on the hydrogen generation rate were investigated in detail.

EXPERIMENTAL

Materials

All chemicals were analytical grade. The magnesite sample was obtained from the KUMAŞ Plant in Turkey. It was crushed, ground, and sieved through a 200 mesh sieve.

Catalyst Synthesis

Magnesite supported catalyst was prepared by impregnation-reduction method. Magnesite was mixed with an excess quantity of precursor solution containing an appropriate amount of cobalt chloride in distilled water (Co / (Magnesite + Co) ~ 15 wt. %) by vigorous stirring at 75 °C for 1 h. Then, the cobalt-impregnated magnesite catalyst was placed in an ice-water bath and reduced by adding sodium borohydride aqueous solution (mole ratio = 3 mole $NaBH_4$ / 1 mole $CoCl_2$) under 400 rpm stirring. The produced catalyst was filtered, washed with distilled water and dried at 100 °C for 24 h in an oven.

Catalyst Characterization

The catalyst sample was characterized by X-ray diffraction (XRD) with a PANalytical Empyrean X-ray diffractometer using Cu Kα radiation. The morphology of the catalyst was examined using scanning electron microscopy (SEM) (JEOL JSM-5600LV). The elemental composition in the catalyst was analyzed with an energy dispersive X-ray spectroscopy (EDS). The chemical analyse of the catalyst was carried out using X-ray fluorescence analyzer (XRF Panalytical Zetium).

Catalyst Testing

The sodium borohydride hydrolysis reaction was carried out in a 150 mL jacketed-heated batch reactor. The reactor was kept at the desired temperatures by circulating water from a constant – temperature bath with ± 0.1 °C sensitivity. A magnetic stirrer was used for constant stirring. An alkaline stabilized solution of sodium borohydride was prepared by addition of NaOH. In the experiments, 20 mL of freshly prepared alkaline sodium borohydride solution was added to the reactor which was heated to the reaction temperature. Then a definite amount of catalyst was fed into the reactor. The reactor content was stirred at 400 rpm. The volume of hydrogen released during the experiment was measured by a water displacement method and converted to the standard temperature and pressure.

RESULTS AND DISCUSSION

Characterization of the Catalyst

The XRD pattern of the Co-B / magnesite catalyst is shown in Figure 1. The XRD pattern of the catalyst indicated essentially magnesite ($MgCO_3$), quartz (SiO_2) and dolomite ($CaMg(CO_3)_2$). The peaks at 20.88 and 45.78 indicated the presences of CoO and Co_2B, respectively. Figure 2 shows the surface morphology of the Co-B / magnesite catalyst (a) before and (b) after hydrolysis reaction. The cottony balls were observed in catalyst. After the hydrolysis reaction, these balls merged, becoming larger. Figure 3 indicates the EDS patterns of the Co-B/magnesite catalyst (a) before and (b) after the hydrolysis reaction. The cobalt in the catalyst was confirmed by EDS and XRF.

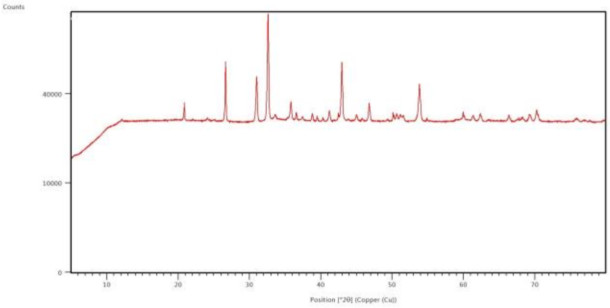
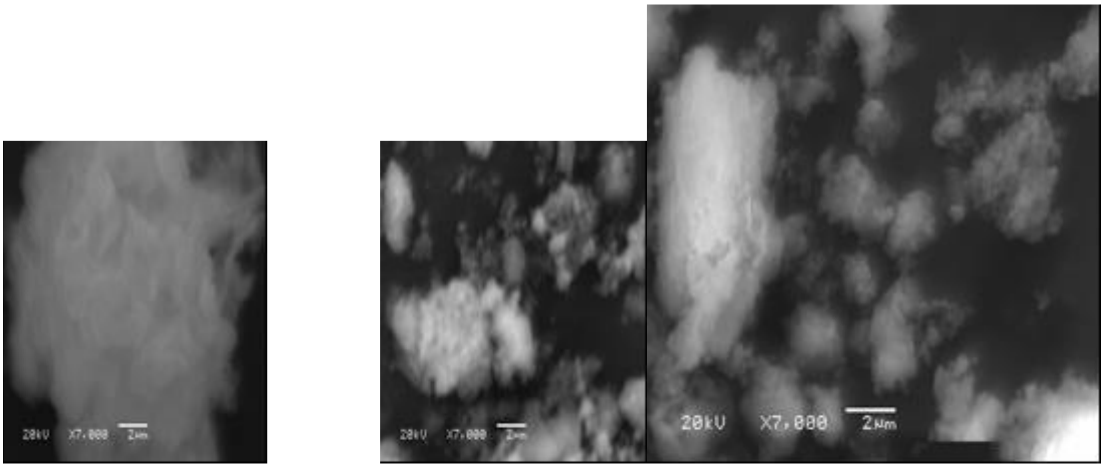
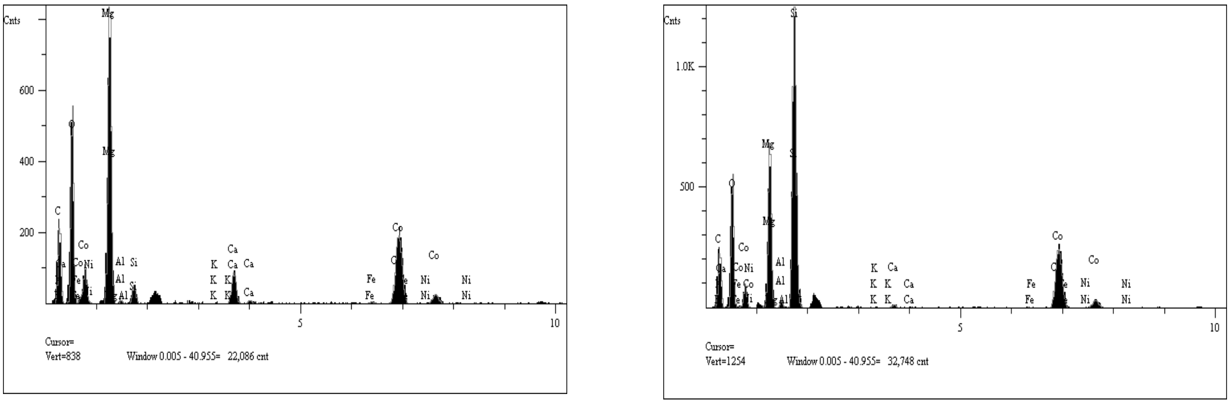


Figure 1: XRD pattern of Co-B / magnesite catalyst.



(a) **(b)**

Figure 2: SEM images of Co-B/magnesite catalyst (a) before (b) after hydrolysis reaction.



(a) **(b)**

Figure 3: EDS images of Co-B/magnesite catalyst (a) before (b) after hydrolysis reaction.

Effect of the Amount of Catalyst

The effect of the catalyst amount on the hydrogen generation rate was studied using four different catalyst amounts (20 mg, 30 mg, 40 mg and 50 mg) at a $NaBH_4$ concentration of 0.7 M and a reaction temperature of 50 °C (Figure 4). As the amount of the catalyst increased, the hydrogen generation rate increased with increasing hydrogen volume and shortened the reaction time. In the presence of 20 mg catalyst, the hydrogen volume was 1420 mL in 20.2 min. When the catalyst amount increased to 50 mg, the reaction ended in 6.67 min with a hydrogen volume of 1450 mL. The increase may be attributed to the increase in active sites with more catalyst.

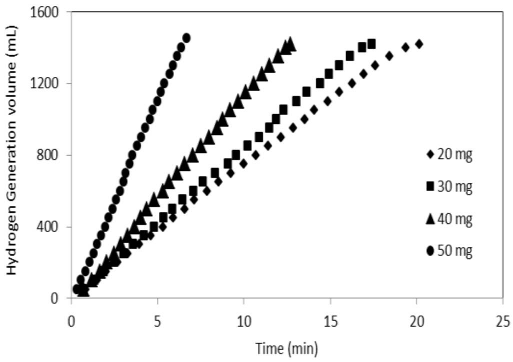


Figure 4: Effect of catalyst amount on hydrogen generation rate of $NaBH_4$.

Effect of the Concentration of $NaBH_4$

The effect of $NaBH_4$ concentration on the hydrogen generation rate was studied using four different $NaBH_4$ concentrations (0.27 M, 0.41 M, 0.55 M and 0.70 M) at a catalyst amount of 50 mg and a reaction temperature of 50 °C (Figure 5). The hydrogen generation volume increased from 600 mL to 1450 mL and the reaction time increased from about 5 min to 7 min with the increase in $NaBH_4$ concentration. Finally, the hydrogen generation rate increased since the hydrogen generation volume was as high as the capacity.

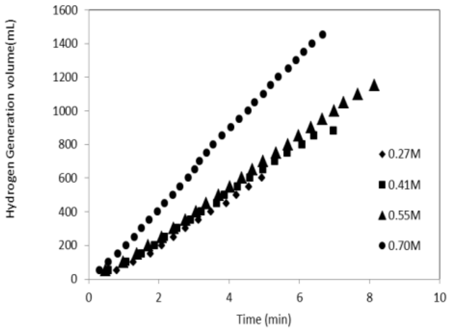


Figure 5: Effect of $NaBH_4$ concentration on hydrogen generation rate of $NaBH_4$.

Effect of Reaction Temperature

Figure 6 shows the effect of reaction temperature on the hydrogen generation rate at a catalyst amount of 50 mg and a $NaBH_4$ concentration of 0.7 M. The hydrogen generation rate increased exponentially with increasing reaction temperature from 20 ºC to 50 ºC. The hydrogen generation rate varied between 2120 and 29000 mL/min g_{Co} depending on the temperature. The volumes of the generated hydrogen increased linearly with reaction time. This case suggested zeroth-order reaction with respect to $NaBH_4$ concentration. The zeroth-order equation can be given as follows [Levenspiel, 1999]:

$$-r_{NaBH4} = -dC_{NaBH4} / dt = k \qquad \textbf{(2)}$$

If the above equation is separated and integrated, then the following is obtained.

$$C_{NaBH40} - C_{NaBH4} = kt \qquad \textbf{(3)}$$

where $-r_{NaBH4}$ is the rate of disappearance of $NaBH_4$ (mol / volume min), $-dC_{NaBH4} / dt$ is the rate of change in the $NaBH_4$ concentration (mol / L min) and k is rate constant (mol / L min). The activation energy (E_a) is determined by the following Arrhenius equation:

$$\mathrm{lnk = InA} - \mathrm{E_a / RT} \qquad \textbf{(4)}$$

where *A* is the pre-exponential factor, E_a is the activation energy (J / mol), R is the gas constant (J / mol K) and *T* is the absolute temperature (K). The value of E_a was calculated from the slope of the straight line of *lnk* versus *1/T*. The activation energy of the hydrolysis reaction was found to be 68.56 kJ / mol. For other supported Co-B catalysts, the activation energies were reported in the range of 45 - 57 kJ/mol [Ye *et al*. 2007; Tian *et al.,* 2010; Lu *et al*., 2012; Li *et al.,* 2014; Özdemir, 2015]. The higher activation energy was obtained in the present.

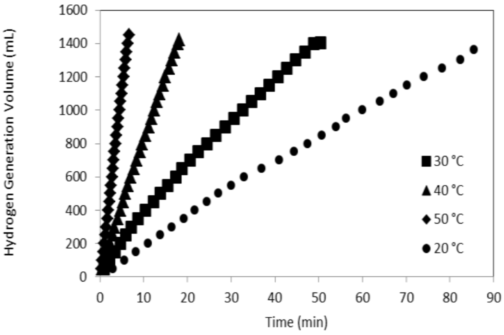


Figure 6: Effect of reaction temperature on hydrogen generation rate of $NaBH_4$.

CONCLUSIONS

The Co-B supported on magnesite catalyst was synthesized by impregnation-reduction method. The most effective parameter was reaction temperature followed by sodium borohydride concentration and catalyst amount for the ranges of studied parameters. The highest hydrogen generation rate of 29000 mL/min g_{Co} was achieved at a catalyst amount of 50 mg, a $NaBH_4$ concentration of 0.7 M and a reaction temperature of 50 ^{o}C. The Co-B / magnesite catalyst is a promising catalyst for the hydrolysis of sodium borohydride. Because magnesite is available at low cost and locally abundant, it can be used as a support material for the catalyst required in the hydrolysis reaction.

REFERENCES

Amendola, S. C. Sharp-Goldman, S. L. Janjua, M. S. Spencer, N. C. Kelly, M. T. and Petillo P. J. et al., 2000. A safe, portable, hydrogen gas generator using aqueous borohydride solution and Ru catalyst, International Journal of Hydrogen Energy, Volume(25), 969.

Levenspiel, O., 1999. Chemical reaction engineering, John-Wiley,

Li, Z. Li, H. Wang, L. Liu, T. Zhang, T. Wang G.and Xie, G., 2014. Hydrogen generation from catalytic hydrolysis of sodium borohydride solution using supported amorphous alloy catalysts (Ni-Co-P/Ɣ-Al_2O_3), International Journal of Hydrogen Energy, Volume (39), 14935.

Lu, Y. C. Chen M. S.and Chen, Y., 2012. Hydrogen generation by sodium borohydride hydrolysis on nanosized CoB catalysts supported on TiO_2, Al_2O_3 and CeO_2, International Journal of Hydrogen Energy, Volume (37),4254.

Othmer, K., 1978. Encyclopedia of Chemical Technology, John-Wiley,

Özdemir, E., 2015. Enhanced catalytic activity of Co-B/glassy carbon and Co-B/graphite catalysts for hydrolysis of sodium borohydride, International Journal of Hydrogen Energy, Volume (40), 14045.

Patel, N. Fernandes, R. Gupta, S. Edla, R. Kothari, D.C. Miotello, A., 2013. Co-B catalyst supported over mesoporous silica for hydrogen production by catalytic hydrolysis of ammonia borane: a study on influence of pore structure. Applied Catalyst B, Volume (140), 125,

Tian, H. Guo Q.and Xu, D., 2010. Hydrogen generation from catalytic hydrolysis of alkaline sodium borohydride solution using attapulgite clay-supported Co-B catalyst, Journal of Power Sources, Volume (195), 2136.

Xu, D. Dai, P. Guo Q.and Yue, X., 2008. Improved hydrogen generation from alkaline NaBH4solution using cobalt catalysts supported on modified activated carbon, International Journal of Hydrogen Energy, Volume (33), 7371.

Yang, C. C. Chen M. S. and. Chen, Y. W.,2011. Hydrogen generation by hydrolysis of sodium borohydride on CoB/SiO2 catalyst, International Journal of Hydrogen Energy, Volume 36.

Ye, W. Zhang, H. Xu, D. Ma L.and Yi, B., 2007. Hydrogen generation utilizing alkaline sodium borohydride solution and supported cobalt catalyst, Journal of Power Sources, Volume (164), 544.