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EFFECT OF COBALT SOURCES ON PROPERTIES OF Co-B CATALYSTS SYNTHESIZED BY SOL-GEL METHOD

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Abstract

In this studying, Co-B catalysts were prepared by sol-gel method via kinds of cobalt source for clarifying the effect of these for characteristic properties of Co-B catalysts. Co sources, cobalt(II)chloride ($CoCl_2.6H_2O$), cobalt(II)sulfate ($CoSO_4.7H_2O$) and cobalt(II)nitrate ($Co(NO_3)_2.6H_2O$), were used as a metal source with boron oxide (B_2O_3) while citric acid ($C_6H_8O_7$) used as organic ligand to forming sol-gel structure. The crystalline structures of Co-B catalysts were determined by X-ray diffraction. The N_2 sorption technique was used for analyzing catalysts surface area. The variety of Co-B catalysts morphological properties were investigated via scanning electron microscope. By the effect of cobalt sources the Co-B catalyst's properties were altered that clarified from analysis results. The amorphous Co-B catalyst produced from $CoCl_2.6H_2O$ as metal source had the largest porous surface area with 122.7 $m^2.g^{-1}$. Investigation of hydrolysis were performed under variety of temperatures (22, 40 and 60 ^oC), NaOH concentrations (1-15 wt. %) and $NaBH_4$/Co-B catalyst ratio (2-40 wt./wt.) ratios in order to investigate the activation of Co-B catalyst. The maximum hydrogen generation rate 0.84L $H_2.min^{-1}.g^{-1}$ was obtained under 40 °C, 10 wt. % NaOH and 9.52wt./wt. $NaBH_4$/Co-B catalyst ratio. Yet the kinetic investigations, the reaction order was found that zero order with 0.9954 coefficient of correlation and 51.83 kJ/mol activation energy.

Key words: *Sol-gel, Co-B Catalyst, Boron*

1 INTRODUCTION

Due to its non-toxic, environmental friendly, availability to easily and low cost production, hydrogen is recognized as competitive alternative energy to fossil fuels (Yang et al. 2011). Hydrogen can be stored as a compressed gas, as a liquid, in a chemical compound (e.g., chemical hydrides or metal hydrides), or physically held within nanoporous structures (Santos & Sequeira 2011). For vehicular applications, the U.S. Department of Energy (DOE) has set storage targets; the gravimetric (volumetric) system targets for near-ambient temperature (from 40 to 85 ^oC) and moderate pressure (less than 100 bar) is 9.0 wt. % (81 g/L) for 2015 (Umegaki et all. 2009). Among various hydrogen storage media, chemical hydrides have been regarded as the most promising materials for hydrogen supply and storage due to their capability in supplying ultra pure H_2 and their larger H_2 storage capacity (Liu et al. 2012).

The $NaBH_4$ is non-flable, non-toxic, selective and environmentally friendly as one of the light weight complex hydride with high hydrogen capacity (10.6 wt.%). The hydrolysis reaction of $NaBH_4$ is efficient and 4 mol H_2 per mol $NaBH_4$ is generated in the reaction. The x (mole of water) is generally

was 2 in the reaction (Amendola et al. 2000). Basically, $NaBH_4$ is self-decomposable in aqueous solution and can be stabilized by alkalization (Retnamma et al. 2011).

$$NaBH_4 + (2+x)H_2O \xrightarrow{catalyst} NaBO_2.xH_2O + 4H_2 \quad (1)$$

The Co-B catalysts are known optimal catalyst as not only with its activeness for hydrolysis reaction of sodium borohydride ($NaBH_4$) but also its economic cost. In literature Co-B catalyst are prepared by chemical reduction method by using $NaBH_4$ as a boron source and also for supports prepared by sol-gel and impregnation methods (Akdim et al. 2009, Delmas et al. 2011, Jeonga et al. 2007, Liu & Li 2008, Lu et al. 2012). The sol–gel method for catalyst preparation has several advantages such as a well-defined pore size distribution, high purity control of reactants, homogeneity, very large and controlled porosity combined with the ability to form large surface area (Tanaka et al. 2002, Lecloux & Pirardi 1998, Ward & Ko 1995).

In this study, Co-B catalyst was prepared by sol-gel method for hydrogen production by hydrolysis of $NaBH_4$. Different Co sources ($CoCI_2.6H_2O$, $CoSO_4.7H_2O$, $Co(NO_3)_2.6H_2O$) and B_2O_3 are used as metal preciouses and boron source, respectively in order to syntheses of Co-B catalyst. The structural property of the Co-B catalyst is characterized by XRD, BET, SEM and ICP-OES analysis methods. The hydrolysis reactions were performed under variety of temperatures, % (wt.) NaOH concentrations and $NaBH_4$/Co-B catalyst ratio in order to investigate the activation of prepared Co-B catalyst that has improved properties.

2 EXPERIMENTAL

2.1 MATERIALS

All reagents used in this research were of analytical grade. Cobalt(II)chloride ($CoCl_2.6H_2O$), cobalt(II)sulfate ($CoSO_4.7H_2O$) and cobalt(II)nitrate ($Co(NO_3)_2.6H_2O$), from Merck, citric acid ($C_6H_8O_7$) from Carlo Erba, boron oxide (B_2O_3) from Eti Mine Works General Management-Turkey, sodium hydroxide (NaOH) from Labor Technic and sodium borohydride ($NaBH_4$) from Fluka were used as received.

2.2 PREPARATION OF Co-B CATALYST

The Co-B catalyst was prepared by the sol-gel method. Hence 0.5 M B_2O_3 solution was prepared and then mixed with $C_6H_8O_7$ and Co sources as $CoCI_2.6H_2O$, $CoSO_4.7H_2O$, $Co(NO_3)_2.6H_2O$ ($C_6H_8O_7$: Co source= 1: 0.2) as an oligomer and a metal precursor. Then an aqueous solution was mixed with magnetic stirring for 2 hours and then gel structure was maintained. Soon after, the obtained gel was dried at approximately 100 °C under the vacuum condition for overnight to eliminate the remaining water molecules. Moreover removing organic components from the structure, dried gel was calcined at 500 °C for 4 hour. The catalysts code were given as Cat-1, Cat-2 and, Cat-3 for Co sources $CoCI_2.6H_2O$, $CoSO_4.7H_2O$ and, $Co(NO_3)_2.6H_2O$, respectively.

2.3 CHARACTERIZATION

To characterized obtained Co-B catalyst, crystalline structures were determined by XRD technique (Philips PanalyticalX'Pert-Pro diffractometer) with CuKα radiation (λ = 0.15418 nm) at an ambient temperature by using a at operating parameters of 40 mA and 45 kV with step size 0.02° and speed of 1°/min. Phase identification of solids were performed by inorganic crystal structure database (ICSD). By N_2 adsorption at 77.35 K, the Brunauer-Emmett-Teller (BET) surface area (S_{BET}) of the catalyst was measured. The surface morphology was observed by scanning electron microscope (SEM,

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CamScan) and the chemical composition was investigated by inductively coupled plasma optical emission spectrometry (ICP-OES; Perkin Elmer Optical Emission Spectrometer Optima 2100 DV).

2.4 HYDROGEN GENERATION TEST

For catalytic activity measurements, system shown Fig.1 was used. Hydrogen generation volume was measured, as a function of time, during the hydrolysis of alkaline $NaBH_4$ (0.12 M) solution in the presence of Co-B catalyst ($NaBH_4$/catalyst: 2.38, 4.76, 9.52, 19.04 and 39.66 wt./wt.) at variety temperatures (22, 40 and 60°C). As an alkaline stabilizer, NaOH was used with 1, 5, 10 and 15 wt.%.ratio in $NaBH_4$ solutions. The generated hydrogen quantity was measured though a water displacement method. Datas were received by time for calculating kinetic results as specific hydrogen generation rate, activation energy and reaction order.

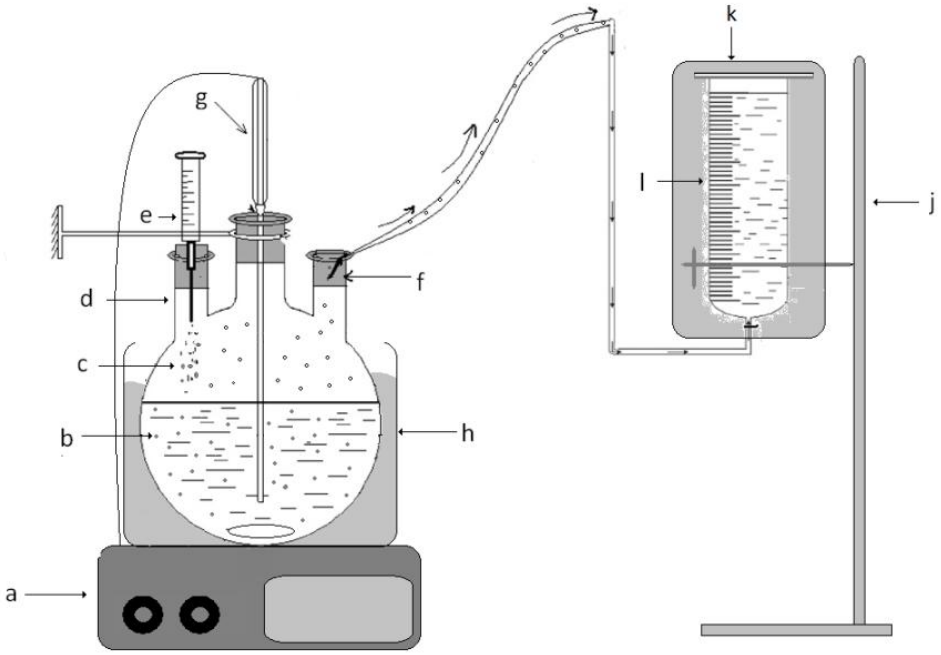


Figure.1 Hydrogen generation system: a-Temperature controlled magnetic stirrer, b-Three necked reactor, c-Co-B catalyst, d-Alkaline $NaBH_4$ solution, e-Injector, f-Silicon pipe for H_2 gas exit, g-Thermocouple, h-Beaker with full of water, l- Generating H_2 gas volume, j-Laboratory stand, k-Jacket

3 RESULTS AND DISCUSSION

3.1 Co-B CATALYST CHARACTERIZATION

In the present study, Co-B catalyst were prepared trough sol-gel method that boron oxide was used as a boron sources for the first time. Pink-to purple gel obtained after the drying at 100 °C and dark brown-black solids were formed after the heat treatment at 500 °C.

The XRD pattern of Co-B catalysts prepared by sol-gel technique is shown in Fig. 2. Co-B catalysts show a specific single broad peak at around $2\theta = 45^{\circ}$ attributed to the amorphous phase of Co-B structure as Co-B catalyst powders produced (Patel at al. 2010, Feng et al. 2007). This formation

indicated that in the Cat-1, besides Cat-2 included Co sources that did not convert into the Co-B structure. Cat-3 had amorphous structure.

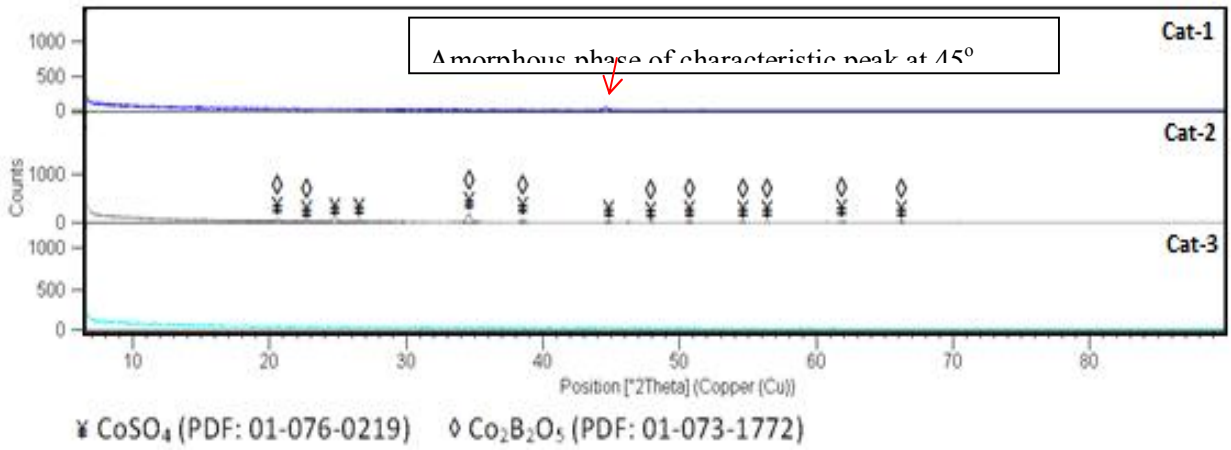


Figure.2 XRD pattern of Co-B catalysts powder

Table.1 BET and SEM analysis results of Co-B catalysts

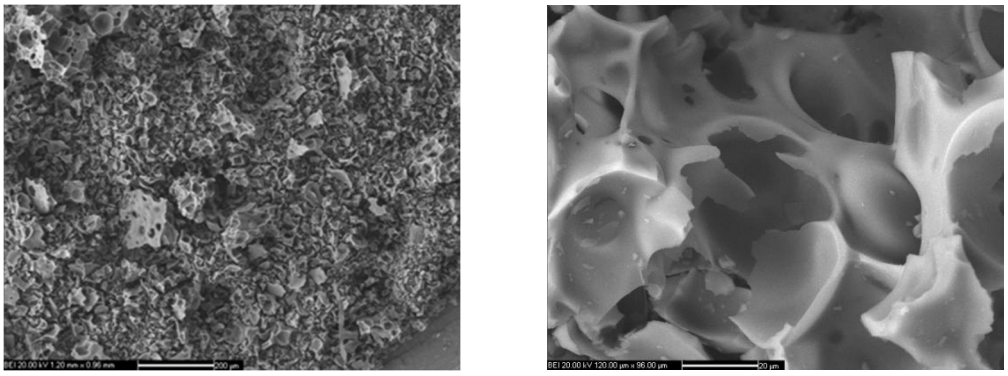
Catalyts Code	BET Surface Area, $m^2.g^{-1}$	Average Particle Size, µm
Cat-1	122.70	20
Cat-2	0.48	107
Cat-3	8.40	17

The specific surface area estimated from BET measurement as given in Table.1. These results shows that Cat-1 was prepared from $CoCl_2.6H_2O$ has advanced surface area compared with Cat-2 and Cat-3 moreover this result support Cat-1was proper catalyst with the amorphous structure observed by XRD. Moreover the prepared Co-B catalyst has one of the largest surface area reported in the literature without support. In addition to this, the elemental analysis of the Cat-1 performed by ICP-OES spectroscopy gives a content of 21.62 wt.% in Co and 13.57 wt.% in B.

In Fig. 3 illustrated a SEM image of the Cat-1 catalysts prepared in this study. The SEM image of amorphous Cat-1 powder show porous like morphology with a size of average 20 µm and also particles dimension were between 5 and 28 µm.

During catalyst preparation, firstly the use of alkoxide as citric acid provide polymerization and polycondensation reactions. These reactions were to allow branching to occur before particle growth. Hence the product gives large surface area and pore volume upon calcination. After formation of gel, its ageing, removal of water and heat treatment. With this processes the condensation slows down to form a weakly branched network. The collapse of this network during calcination leads to a decrease in the surface area and pore volume (Perego & Villa 1997, Campanati et al. 2003, Schmidt 2001,

Ward & Ko 1996). Despite spherical shaped Co-B catalysts were prepared by chemical reduction method in literature, we obtain Co-B catalyst has a vugular structure by the sol-gel method (Fernandes et al. 2009, Liu &Li 2008).



(a) (b)

Figure. 3 SEM images of Cat-1: (a) x 100, (b) x 1000

3.2 Co-B CATALYST HYDROGEN GENERATION KINETICS

Fig.4 shows the function of reaction time obtained by the hydrolysis of sodium borohydride by Cat-1. The hydrogen production starts immediately without any induction time and reaches the 100% of the theoretical H_2 yield. The effect of NaOH concentration (1, 5, 10 and 15wt.%) on the hydrogen generation rate was studied by performing series experiments using several concentrations of NaOH while keeping catalyst and $NaBH_4$ quantities constant at various solution temperatures (22, 40 and 60^oC). The concentration of $NaBH_4$ is 0.12 M and $NaBH_4$/Co-B catalyst wt./wt. is 9.52:1 during the hydrolysis of $NaBH_4$ for determined optimum reaction conditions.

$NaBH_4$ hydrolyzes to generate hydrogen without catalysts unless it is base-stablized. Therefore, to control the hydrogen generation rate, NaOH was added to $NaBH_4$ solution to make the solution basic [28]. By increasing the NaOH content from 1 to 15 wt.%, there is no functional increasing is observed in the hydrogen generation rate. At 22^oC reaction temperature, $NaBH_4$ solutions with 5 and 20 wt.% NaOH concentration hydrolysis reactions much more faster completed. In addition to this, solution having 1wt. % NaOH content hydrolysis reaction last about 180 min. Increasing in the reaction medium temperature results the hydrolysis reaction's completion period is shriking. At 40^oC, solution with 10 wt. % NaOH concentration gives the shortest period for hydrolyses reaction. Also reaction time varying from 25 to 50 min. At 60 ^oC, the hydrolysis reaction complete about 40 min. with 15 wt. % NaOH in the longest period in various NaOH concentrations. When analysed the reaction results, the most fast conditions were determined as 40 ^oC and 10 wt. % NaOH concentration.

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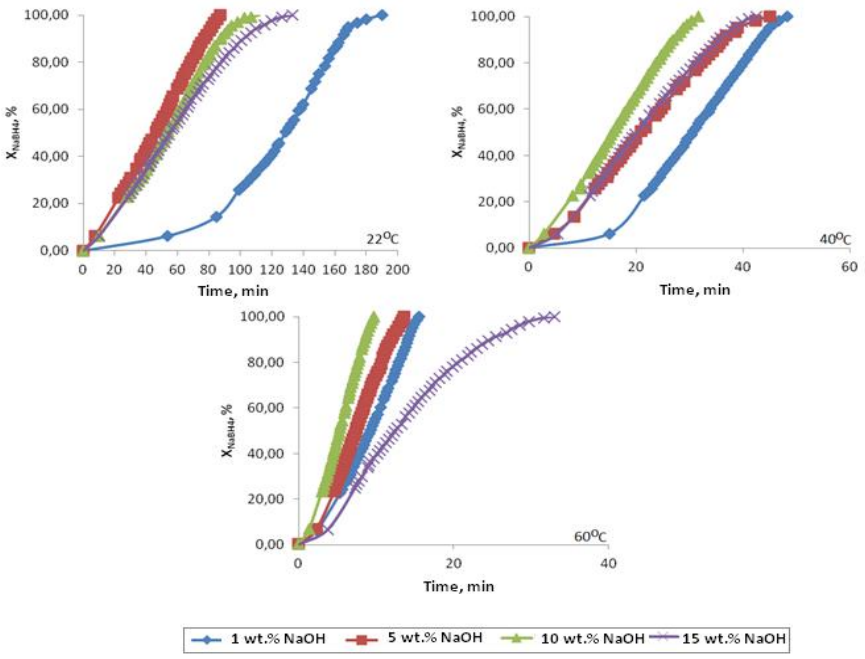


Figure. 4 Hydrogen generation yield with respect to time at temperatures of 22, 40, 60 °C and with the concentrations of NaOH 1, 5, 10 and 15 wt. % with 0.12 M $NaBH_4$

For kinetic analysis, it is preferable to convert the hydrogen generation rate into the reactant (sodium borohydride) concentration- both as function of time. If the rate of consumption of $NaBH_4$ (C_{NaBH4}) with respect to time is equal to a reaction rate constant, the reaction has zero order kinetics (independent of any concentration).

$$\frac{dC_{NaBH4}}{dt} = -r_{NaBH4} = k(T) \quad (2)$$

where C is the concentration, r is the rate of reaction, k is the reaction rate constant base on the solution volume. Integrating the differential Eq. (2) it then becomes:

$$C_{NaBH40} - C_{NaBH4} = k(T) \,.\, (t - t_o) \quad (3)$$

A plot of ($C_{NaBH4,0}$- C_{NaBH4}) should be a linear function of time, where the slope is simply the reaction rate constant. If the Arrhenius law is used Eq. (3) then comes:

$$C_{NaBH40} - C_{NaBH4} = k_0 \,.\, e^{-E_a/RT} . (t - t_o) \quad (4)$$

A plot of Arrhenius law's slope is activation energy of $NaBH_4$ catalytic hydrolyses and also its intercept is Arrhenius constant (Fogler 1999, Levenspiel 1999, Hung et al. 2008).

As can be Fig.4 the datas collected from the hydrolysis system as shown in Fig. 1 were analysis by least-square method for investigate the reaction order. While all reaction kinetics were investigated depended on the % (wt.) NaOH concentration, the zero order kinetic was found most proper one for hydrolysis of $NaBH_4$ in the presence of Cat-1 (Fig.5).

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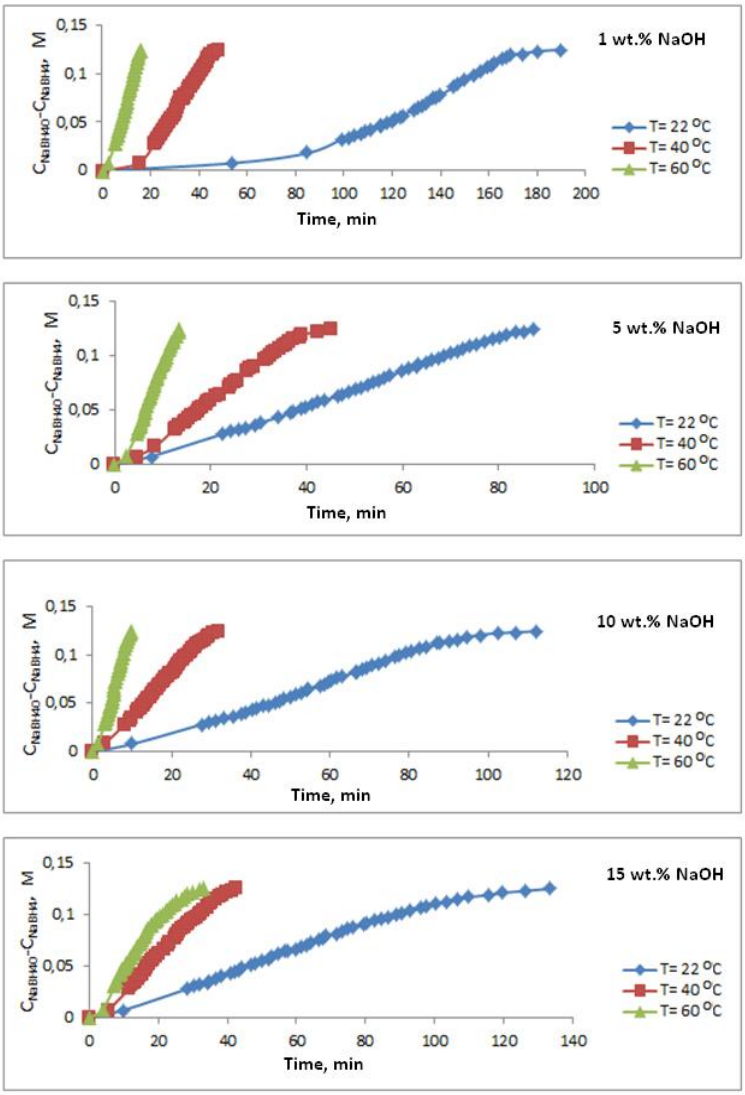


Figure.5 Zero-order kinetic of 1.2 M $NaBH_4$ hydrolysis reaction with respect to time at temperatures of 22, 40, 60 °C and with the concentrations of NaOH 1, 5, 10 and 15 wt. %

$NaBH_4$ hydrolysis via Co-B catalyst shown in all temperatures and varying wt.% NaOH concentrations zero-order reaction kinetic model is given more fitting results than first and second order reaction kinetic model. For all wt.% NaOH concetrations reaction kinetic parameters as activation energy and reactions rate constant were calculated from Arhennius graphic in Fig. 6.

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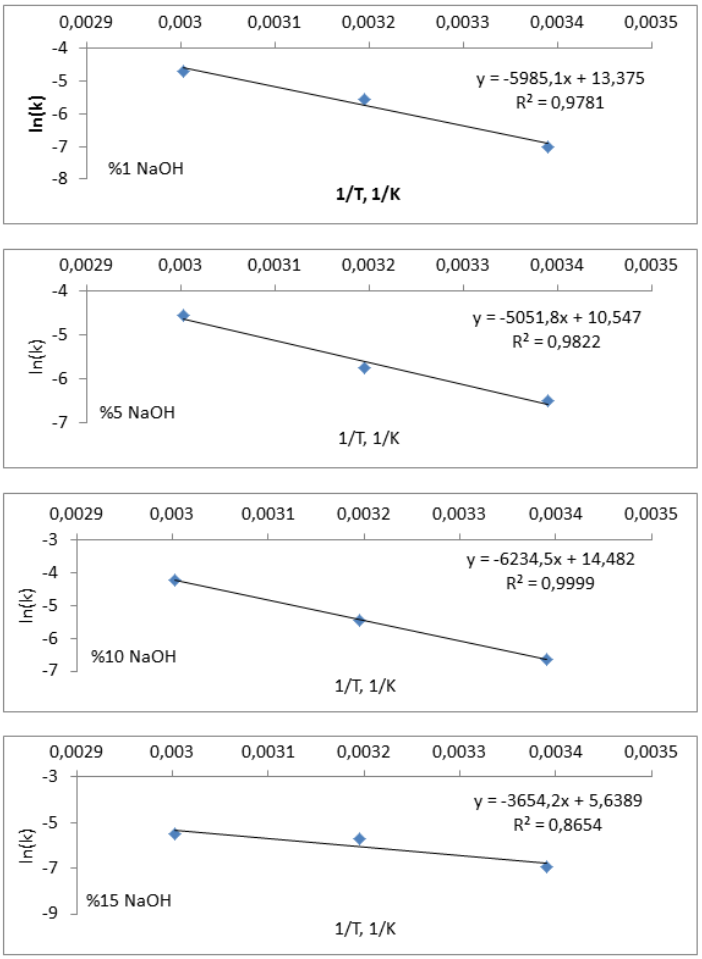


Figure. 6 Arrhenius plot for 0.12 M $NaBH_4$ with the concentrations of NaOH of 1, 5, 10 and 15 wt.%

Table.2 Zero- order reaction kinetics results of $NaBH_4$ hydrolysis by Co-B catalyst

NaOH Concentration, wt.%	Activation Energy, kJ/mol	Arrhenius Constant, min^{-1}	H_2generation rate (40°C), L $H_2.g^{-1}$catalyst.min^{-1}
1	49.76	13.38	0.66
5	42.00	10.55	0.62
10	51.83	14.48	0.84
15	30.38	5.64	0.63

Table. 2 indicate that activation energy and H_2 generation rate of $NaBH_4$ hydrolysis by the Cat-1 wais varifying by hydrolyses medium NaOH concentrations. For example; reaction medium having 5 and 15 wt.% NaOH content hydrolysis reaction rate are roughly same. Also with 30.38 kj/mol activation

energy 15 wt.% NaOH medium has the minimum H_2 generation rate. As result of kinetic investigation, hydrolyses conditions that 40 ^oC and 10 wt.% NaOH concentration were found optimum for the Cat-1 with 0.84 L $H_2.g^{-1}$catalyst.min$^{-1}H_2$ generation rate, 51.83 kJ.mol^{-1} activation energy and 14.48 min^{-1} Arrhenius constant.

Fig. 7 shows the H_2 generation rate measured using the prepared Co-B catalyst and 0.12 M $NaBH_4$ with wt. 10 % NaOH at 40 ^oC. To examine the effects of catalyst loading on the hydrogen generation rate, 2.38, 4.76, 9.52, 19.04 and 39.66 $NaBH_4$/Co-B catalyst ratios of the catalyst were employed. Obviously, there is no functional relationship between increasing in Co-B catalyst amount and H_2generation rate as seen Fig. 7. For $NaBH_4$ hydrolysis reaction via Cat-1, 19.04 as $NaBH_4$/Cat-1 ratio gave maximum hydrogen generation rate with 1.1 L $H_2.g^{-1}$catalyst.min^{-1}.

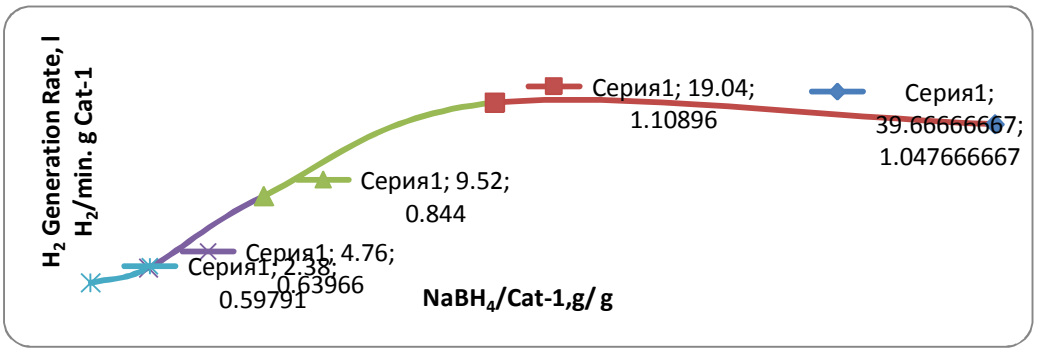


Figure. 7 Effect of $NaBH_4$/Cat-1 ratio on hydrogen generation rate

4 CONCLUSION

In this study, to develop a low-cost high performance catalyst for hydrogen generation from alkali $NaBH_4$ solution prepared by sol-gel method from boron oxide as a boron source for the first time. The characterization of the prepared Co-B catalysts were carried out by XRD, BET, SEM, and ICP-OES analysis. The characterization results show that the catalyst with amorf crystalline, porous structure and high surface area was produced from $CoCl_2.6H_2O$. Then, the activity of Co-B catalyst to the hydrogen generation reaction was measured by varifying temperature and wt. % NaOH concentration. With increasing reaction temperature hydrolyses reaction rate increased and yet there was no functional alteration in it with increasing in NaOH concentration. All the hydrolysis reaction were completed with 100% conversion fitting with zero-order kinetic model and optimum hydrolyses reaction conditions were determined as 40 ^oC and 10 wt. % NaOH with 9.52 $NaBH_4$/catalyst. For this conditions Co-B catalyst results in a 0.84 L $H_2.g^{-1}$catalyst.min$^{-1}H_2$ generation rate, 51.83 kJ/mol activation energy and 14.48 min^{-1} Arrhenius constant for hydrogen production.

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