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The Hydrolysis of Tert-Butylamine Borane By Using Ni-Zr-B-O Catalyst For Hydrogen Production

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This study focuses on the catalytic hydrolysis of tert-butylamine borane (TBAB, $C_4H_9NH_2BH_3$) with Ni-Zr-B-O. For this aim, catalyst mixture was prepared by co-precipitation method using $NaBH_4$. The effect of temperature and catalyst amount on the hydrolysis of TBAB was examined. It has been observed that for each catalyst amounts, an increase at the temperature significantly increases the hydrogen production yield and reduces the reaction time as well. Similar results were also observed in each catalyst amounts when the temperature was kept constant. The maximum yield of the hydrogen production was found as 2.94 mol H_2/mol TBAB (98%) at 55ºC temperature, having 0.05 g catalysis in 656 seconds. Reaction enthalpy (ΔH^{++}) and entropy (ΔS^{++}) and turnover frequency value were calculated as 46.06 kJ.mol^{-1} -189.05 J.mol^{-1}.K^{-1} and 789 mol H_2.mol Ni^{-1}.min^{-1} respectively. Finally, catalyst characterization was done by XRD and XPS and Ni average crystalline size was found as 29.8 nm from Scherrer equation.

Keywords: tert-Butylamine Borane, Hydrogen Storage, Hydrolysis, Dehydrogenation

Introduction

A significant portion of the energy needed today is provided from carbon-based fossil fuels which are limited and non-environmental. Renewable energy sources such as solar energy, and wind energy provide small portion of energy supply where the batteries and super capacitors are used as storage for sustainability. Recently, one of the other approaches' is using hydrogen as an energy carrier[1-5].

Hydrogen is a well-known green energy and plays an important role in sustainable energy. Several types of studies are focused on hydrogen production, storage, safety, utilization and economy. Physicals like carbon based nanotubes, metal organic frameworks or chemicals like ammonia, methanol, borohydrides, amine boranes are well-known for storing hydrogen. In boron based chemicals researchers mostly use borohydrides. Amine boranes are also used as an alternative of borohydrides for hydrogen storage material. The most studied material is ammonia borane (basic of amine boranes) a widely known H_2 storage material. Owing to ammonia boranes theoretically high H_2 content, being stable and non-toxic structure, it can be used as hydrogen storage material for fuel cell applications[2, 6-10]. The dehydrogenation of the amine boranes is generally carried out by catalytic or non-catalytic hydrolysis, thermolysis or methanolysis[11-13]. $RuCl_3$, $RhCl_3$, $PdCl_2$, $CoCl_2$, $NiCl_2$, Pd/C, and Raney-Ni were the first catalyst types that were reported for catalytic hydrolysis of amine boranes at low temperatures[14]. Various support materials such as graphene oxide, TiO_2, activated carbon, and

alumina are used on the catalyst. Ru, Rh, Pd are used as the coating of support materials by impregnation method. In addition, cheaper materials such as Co, Cu and Ni are used[15-21]. Similar to catalytic hydrolysis, catalytic methanolysis is carried out at low temperatures. Thermolysis of ammonia borane releases 3 moles of H_2 in different temperature ranges (110-500ºC). During dehydrogenation of ammonia borane, trace amounts of byproducts such as ammonia (NH_3), and diborane (B_2H_6) may cause catalyst poisoning. One of the approaches used to avoid poisoning was using alkyl or aryl amine boranes. Low carbon alkyl amine boranes like methylamine borane and dimetyhlamine borane were hydrolyzed for hydrogen generation[22-24]. At the end of hydrolysis, these low carbon alkyl amines are formed into gases which affect the impurity of hydrogen. However, tert-butylamine is suitable because at the end of hydrolysis this material stays as liquid which does not change the purity of hydrogen. Moreover, having an alkyl group in the structure accelerates the release of hydrogen compared to ammonia borane. In many studies, hydrolysis reaction of amine boranes was used for in-situ catalyst preparation. Due to their Lewis structure, these compounds are suitable for hydrogen production by catalytic dehydrogenation. Tert-butylamine borane (TBAB, 16wt% H_2) like any other amine boranes is already well known as a reduction agent for various substances. Thermolysis of tert-butylamine borane conducted close to the melting point (90-95ºC), releases hydrogen, polyimidoboranes ($(BNH)_n$ and $(CBNH)_n$) according to MAS-NMR and thermo gravimetric analyses. These by-products could be used as a good regeneration path[25-27].

In this study, catalytic hydrolysis of TBAB was examined. Ni-Zr-B-O catalyst was prepared by co-precipitation method with $NaBH_4$ containing 40% Ni and 60% Zr by mass and analyzed by X-Ray Diffraction (XRD) and X-Ray Photoelectron Spectroscopy (XPS). Catalyst amount (0.0025g and 0.05g) and temperature (30ºC, 40ºC and 55ºC) effect on hydrolysis were investigated. Kinetic studies were applied. E_a, ΔH^{++} and ΔS^{++} were calculated.

Experimental

(A) Materials

Tert-butylamine borane ($C_4H_9NH_2BH_3$, Sigma), nickel (II) chloride hexahydrate ($NiCl_2.6H_2O$, Aldrich), zirconium (IV) chloride ($ZrCl_4$, Aldrich), sodium borohydride ($NaBH_4$, Fluka) and deionized water were used.

(B) Preparation of Ni-Zr-B-O Catalyst

The mixture of 0.059M nickel chloride hexahydrate and 0.065M zirconium chloride, 0.18 M sodium borohydride was added in droplets and homogeneously dispersed by magnetic stirrer in ice-water bath. The precipitate was separated by centrifuge, washed 4 times using deionized hot water to separate from impurities and finally left to dry at 105ºC.

(C) Characterization of Catalyst

Phase structures of the catalyst were analyzed by XRD analysis (the PANalytical brand Empyrean), using copper (Cu) tube between 5-90º, operating at 45 mA and 40 kV. The electronic states of the catalyst surface were examined XPS (Thermo Scientific / K-Alpha Brand XPS Device).

(D) Catalytic Hydrolysis of TBAB

Hydrolysis of 0.2% by weight aqueous solution of tert-butylamine borane was performed at 30ºC, 40ºC and 55ºC having two different catalyst amounts (0.0025g and

0.05g). Batch reaction system is given in Fig. 1. System contains 50 ml volume 2 neck glass reactor, 50 ml volume pressure stabilizing liquid feeding apparatus and washing bottle having 0.1M H_2SO_4 solution. The produced hydrogen was measured as function of time in a 250 ml gas burette system.

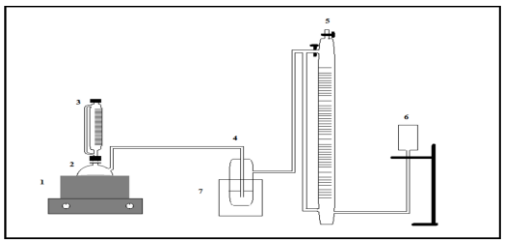

Fig. 1. Batch reaction system experimental setup, ((1) heater-magnetic stir plate, (2) batch reactor, (3) TBAB-water solution, (4) wash bottle, (5) gas burette system (6) drip funnel (7) cold water bath)

Results and discussion

(A) Catalyst characterization

XRD analysis of Ni-Zr-B-O catalyst is given in Fig.2. The non used catalyst is found to be crystalline (Isometric - Hexoctahedral) Ni at angles of 44.72º; 51.99º; 76.49º. Ni average crystalline size was calculated by using Scherrer equation (Eq. 1):

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

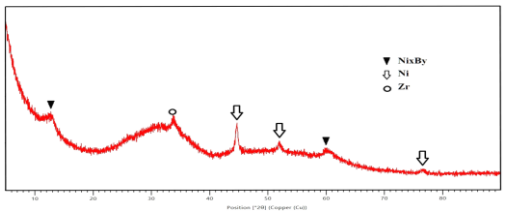

Fig. 2. XRD result of Ni-Zr-B-O

where, D is grain/crystallite size, k is shape factor (0.9), λ is X-ray wavelength, β is the line broadening at half the maximum intensity in radians (FWHM) and the θ is the Bragg angle. Ni average crystallite size was calculated as 29.8nm. The structure contains Ni_xB_y observed at 12.67º and 60.03º. Also semi-amorphous form of Zr is observed between 23-40º. Broad peaks around the 30º is found to be amorphous $Zr(OH)_4$ which is good agreement in previous studies[28,29].

Fig. 3 shows the B, Ni, O and Zr XPS spectra of the catalyst. Peak of B1s having an electron binding energy at 191.78 eV shows oxidized boron. At 874.88 eV region of Ni $2p_{1/2}$ peak was observed which represents Ni(0). From peaks of Ni2p and O1s having an electron binding energy at 855.51 eV and 531.19 eV belong oxidized Ni. On the Zr 3d spectra of the sample, the peaks at 181.3 eV and 184.58 eV can be assigned to the Zr $3d_{5/2}$ and Zr $3d_{3/2}$ binding energy levels.

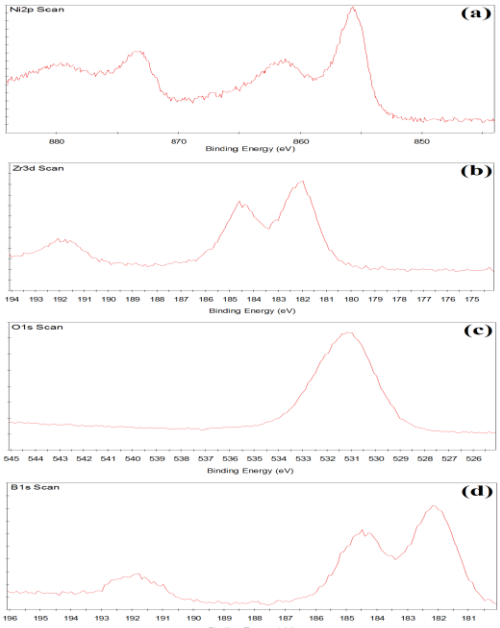

Fig. 3. XPS results of Ni-Zr-B-O (a) Ni 2p (b) Zr 3d (c)O1s and (d) B1 scans

The standard value of the Zr$3d_{5/2}$ peak is at 182.2 eV and the binding state level represents amorphous/hydrous zirconia (ZrO_2nH_2O) according to previous studies[29-33]. However, when compared with this study, zirconium is in the oxide state similar to the nickel. This is due to the preparation conditions where the

catalysts were produced in aqueous dilute solution. Ni^{2+} was reduced to Ni(0) by $NaBH_4$, and nickel boride and $Ni(OH)_2$ were also formed. Zr was not reduced but oxidized where the catalyst was not exposed to any heat above 105ºC in preparation steps. In order to form Zr oxide, product must be heated above 700ºC[28]. So mostly Zr was in the form of $Zr(OH)_4$.

(B) Catalytic Hydrolysis Results of TBAB

Catalytic hydrolysis of TBAB was studied with Ni-Zr-B-O catalyst. Temperature (30ºC, 40ºC and 55ºC) and the amount of catalyst effect (0.0025g, and 0.05g) were studied. At the end of TBAB hydrolysis 3 mol of hydrogen was released from borane part (Eq. 2).

$$(CH_3)_3CNH_2BH_3 + 2H_2O \rightarrow 3H_2 + (CH_3)_3CNH_3^+ + BO_2^- \quad (2)$$

In Fig. 4, when the catalyst amount was 0.0025g and the temperature was between 30ºC and 55ºC, reaction time shortened (3000s to 720s) and hydrogen production increased (2.2 to 2.72 mol H_2/mol $TBAB_0$) respectively. When the amount of catalyst was increased to 0.05g, mol ratios of $nH_2/nTBAB_0$ were achieved 2.77 at 3130s, 2.94 at 656s for temperatures 30ºC and 55ºC respectively. Clearly for both catalyst amounts, an increase in temperature significantly increased the hydrogen production yield and reduced the reaction time. The same effect was also observed for the catalyst amount. Ruthenium is one of the best active side on hydrolysis reaction of amine boranes given in literature[14]. However, using nickel is less expensive and can be well effective according to these results. Akbayrak et. al. used Ni (95wt.%) activated carbon catalyst for the hydrolysis of ammonia borane at room temperature in 30min and achieved a result that was close to 100% yield H_2 production[34]. In this study, 98% efficiency was obtained with Ni-Zr-B-O catalyst in 50min reaction time at 30ºC. When compared with the literature, using Ni-Zr-B-O catalyst provided high efficiency (98%), however reaction time can be reduced by either variables; increasing the amount of nickel or increasing the temperature.

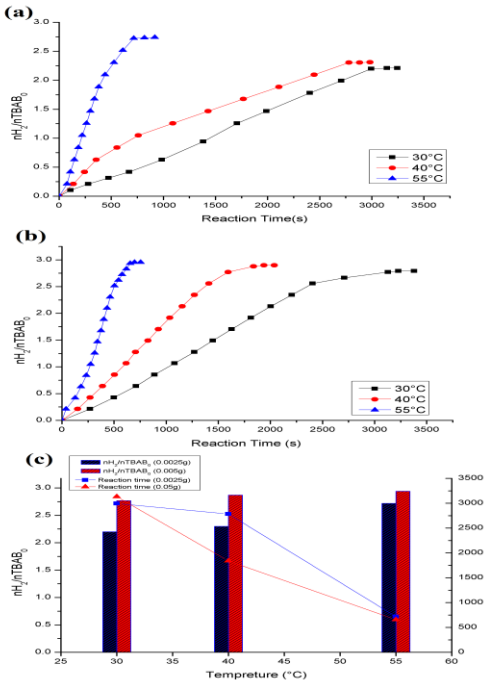

Fig. 4. Hydrolysis of 0.2% TBAB in the presence of Ni-Zr-B-O catalyst; (a) 0.0025g cat., (b) 0.05g cat., (c)nH_2/ $nTBAB_0$-Temperature-Reaction Time graph

Kinetic results of TBAB hydrolysis with Ni-Zr-B-O catalyst were given in Fig. 5. Reaction rate was found as a zero order which was suitable for exponential kinetics. Most of amine borane catalytic solvolysis reactions are zero or first order[10]. Activation energy was calculated by Arhenius equation (Eq. 3):

$$Ink = Ink_0 - (Ea/RT) \quad (3)$$

where the k_0 is frequency constant, Ea is activation energy, R is gas constant and T is temperature. From the plot of Arhenius (Fig 5b), activation energy was determined as 48.68 kJ.mol^{-1}. Table 1 shows the comparison of Ea of different catalysts. Reaction enthalpy and entropy were calculated according to Erying equation (Eq 4):

$$In\left(\frac{k}{T}\right) = In\left(\frac{k_B}{h}\right) + \left(\frac{\Delta S^{\#}}{R}\right) - \left(\frac{\Delta H^{\#}}{R}\right)\left(\frac{1}{T}\right) \quad (4)$$

where h is Planck's constant and k_B is Boltzman constant. From plot of Erying (Fig. 5c), reaction entalpy and entropy were calculated as 46.06 kJ.mol^{-1} and -189.05 J.mol^{-1}.K^{-1} respectively. Turnover frequency value was found as 789 mol H_2.mol Ni^{-1}.min^{-1} at 55ºC.

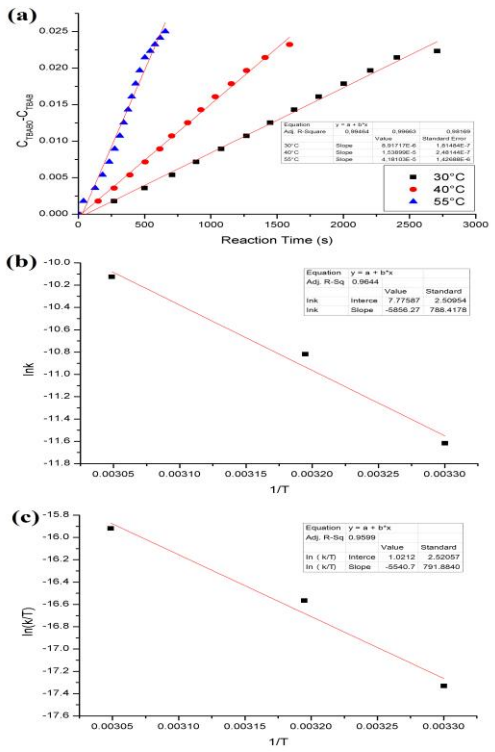

Fig. 5. Kinetic results for Ni-Zr- B-O catalyst (a) C_{TBAB0}-C_{TBAB} versus time graphs (b) ln (k) versus 1/ T plot, (c) ln(k/T) versus 1/T plot

Table 1. Dehydrogenation of amine boranes with different catalyst activation energies

Catalyst	Amine Borane	Ea (kJ/mol)	Ref.
Ru/graphene NPs	AB*	11	35
Ru/Al_2O_3	AB	23	36
$Ni_{0.75}B_{0.25}$	AB	44.16	37
Ni_2P NPs	AB	44.6	38
Ru/Al2O3	AB	48	39
Ni-Zr-B-O	TBAB	48.68	this work
$Cu_{0.75}B_{0.25}$	AB	50.77	37
Pd-PVB-TiO_2	AB	56	40

*AB means ammonia borane

Conclusions

Catalytic hydrolysis of TBAB with Ni-Zr-B-O was carried out. The effect of temperature and catalyst amount was examined. Hydrogen production yield was increased by increasing the temperature or catalyst amount. Moreover, the reaction time was also reduced. Highest hydrogen yield was observed as 98% at 656s where the temperature and catalyst amount were 55ºC and 0.05g respectively. Activation energy was calculated as 48.68 kJ.mol^{-1}. ΔH^{++} and ΔS^{++} were determined as 46.06 kJ.mol^{-1} and -189.05 J.mol^{-1}.K^{-1}. Turnover frequency value was computed as 789 mol H_2.mol Ni^{-1}.min^{-1} at 55ºC.

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