



Co-Mn/TiO₂ catalyst to enhance the NaBH₄ decomposition

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ABSTRACT

Developing catalyst to create a feasible system for NaBH₄ hydrolysis would increase the widespread use of clean energy producing fuel cell system. However, transfer difficulties such as; three phase reaction mechanism and reactant-side product solubility problems limit the promising properties of the hydrolysis systems. In this study Co_{1-x}Mn_x bimetallic catalyst was produced and adhered on TiO₂ support by co-reducing method. Optimum NaOH concentration for the catalyst and reaction conditions was determined before the studies. In the experiments it was proved that only 40 mg of Co_{0.7}Mn_{0.3}/TiO₂ catalyst is highly active to decompose NaBH₄ at 20 °C. SEM-EDX results revealed that the catalyst homogeneity and active sites existence are valid after reaction. Released hydrogen was collected by inverse burette apparatus and maximum hydrogen generation rate was calculated as 43.6 mL_{H₂}·s⁻¹·g_{catalyst}⁻¹ at 20 °C. Investigations resulted that the reaction obeys first order kinetic on the basis of NaBH₄ and the activation energy is 38.7 kJ.mol⁻¹.

1. Introduction

Environmental and waste problems might be stated as the hardest task addressed to scientists for feasible solutions. Waste problems can be mainly divided in to two categories; first waste materials produced due to the production necessities and the second matters (mostly gases) trashed by energy production processes. Concisely, industry and transportation are named as the main sources of pollution. Energy production methods for both of these sectors must not be interrupted however it is believed a revolution is needed to update these methods to more environmentalist and economic form. That would double the low yield of interior combustion engine and makes its waste tens of times less. Fuel cell (FC) technologies are seems to be the best candidate to take the duty, however a few problems retards the widespread use. Continuously hydrogen feeding to FC anode side is one of the technical problems since the current storage alternatives are not able to meet the expectations [1]. At this point metal borohydrides are lifesaving. Especially NaBH₄ is known as the most applicable one with its 10.8 wt% hydrogen capacity.

Catalytic hydrolysis of NaBH₄ in alkaline medium offers advantageous reactant spent fuel composition for recycling process and possibility of wide range of active metal utilization. Noble Pt, Pd, Ir, Rh, Ru [2] and non-noble metals Co, Ni, Fe, Cu, Mn, Mo [3-6] can be utilized solely or in alloy like structures for NaBH₄ dehydrogenation. Rapid catalytic decomposition of NaBH₄ should be suppressed by increasing the reaction medium pH value. For that purpose NaOH is introduced to reaction medium. It has two distinct advantageous apart from other hydroxides, first economic point of view and second no risk to give cation exchange reaction with NaBH₄. In the literature many concentration values are advised for NaOH between 2-30 wt% (%10 [5], %2.5-30 [7], %2 [8]). Effect of NaOH amount differs according to the catalyst and support type [9]. Thus pioneer experiments should be performed to be sure about the optimum NaOH concentration.

Decomposition of NaBH₄ is favorable in the presence of supported catalysts. There are many materials to be used as support material such as: activated carbon, Al₂O₃, TiO₂, diatomite, zeolites, etc. Aim of support material usage may be explained in

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a few captions; (a) Separation of the used catalyst become easy, (b) Support-precursors engagement may increase the catalytic effect, (c) Catalyst may be designed in any 3 dimensional shape (d) Support provides broaden surface area that is necessary to achieve high hydrogen generation rates (HGR). The proper selection of support provides catalyst to retain its specific properties, such as porosity, surface area, dispersion, selectivity, and activity. The morphology and pore size of the selected support materials play an important role in enhancing the catalyst's stability and performance. TiO_2 , due to its nontoxicity, long-term photostability, and high effectiveness, has been widely utilized in mineralizing toxic and nonbiodegradable environmental contaminants. TiO_2 possesses good mechanical resistance and stabilities in acidic and oxidative environments. These properties make TiO_2 a prime candidate for catalyst support.

Dehydrogenation process of NaBH_4 shows quite differences depending on the catalyst materials and reaction conditions. Kinetic studies performed report that the reaction order of the dehydrogenation can differ from negative [10] to positive values. Mostly reactions obey first order [8, 11] while a few are zeroth order [12, 13]. Negative reaction order means decreasing kinetics with NaBH_4 amount. Actually this behavior is valid for all the catalyst type if the NaBH_4 concentration is kept high because of its and NaBO_2 limited solubility. Role of the catalyst is decreasing the activation energy. Decrease in the activation energy would let the reaction yield further even the reaction temperature is unchanged. The activation energy variation of the performed studies is summarized by Rakap et al. between 27-76 kJ/mol [5].

In this study Co-Mn bimetallic catalyst is produced by impregnation technique on TiO_2 support. Hydrolysis condition, behavior and kinetic data of the produced catalyst are reported for different reactant ratios and temperatures.

2. Materials and methods

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ were provided by Sigma-Aldrich with 98% and 99% purity, respectively. Hexadecyltrimethylammonium bromide (CTAB, $\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{Br})(\text{CH}_3)_3$) was provided by Sigma Aldrich with 98% purity and utilized as surfactant.

2.1. Catalyst preparation

The $\text{Co}_{1-x}\text{Mn}_x$ bimetallic catalysts were synthesized at four different mole ratios ($x=0, 0.1, 0.3$ and 0.5) in the presence of surfactant (CTAB). Amounts of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ were calculated and dissolved in 5 mL of distilled water. Then solution trickled on 200 mg TiO_2 support in a way that results 20wt% $\text{Co}_{1-x}\text{Mn}_x$ on support. 75 mg of CTAB was added to the precursors and solution was stirred for 10 min. Then,

3 mL of aqueous solution of the reducing agent NaBH_4 (1.632 mmol) was added drop wise to the solution. The solution was then strongly shaken and stirred for 5 more min to uniformly form the black particles suspension. Reactor content was centrifuged at 6000 rpm for 5 min to put aside the particles, subsequently solid residue was washed with deionized water. Centrifugal and washing processes were repeated for 3 times. Catalyst particles were dried in vacuum-oven which, operates at 50°C and under 150 mmHg pressure.

2.2. Catalyst testing

100 mg of NaBH_4 and 70 mg of NaOH are weighed and dissolved in 5 mL of distilled water. 40 mg of $\text{Co}_x\text{Mn}_{1-x}/\text{TiO}_2$ catalyst was put in the dehydrogenation reactor whose two outlets are designed to feed the alkaline NaBH_4 solution and to transfer produced hydrogen to the inverse burette. Reactor temperature was set to 20°C with 0.1°C accuracy for all experiments. Before introducing the alkaline NaBH_4 solution, reactor and its content is rested for 15 minute to provide thermal equilibrium and check for the risk of leakage. Dissolved NaBH_4 and NaOH were introduced in reactor and hydrogen product was collected in the measured burette and volume versus time data were reported. Temperature increase of the reactor due to the exothermic reaction of hydrolysis was neglected since the reactor contents are very dilute and the decomposition reaction is slightly exothermic.

2.3. Kinetics of the catalyst

In order to determine the kinetic data of the catalysts, similar method explained for catalyst testing was applied. Reactor temperature was arranged between $20\text{-}60^\circ\text{C}$ by 10°C increasing steps to calculate the activation energy by Arrhenius equation. A temperature controlled oil bath was utilized to provide reaction condition with 0.1°C accuracy. Reaction rate order was investigated on the NaBH_4 basis. For this purpose, 0.263, 0.526, 1.053 and 1.579 M, 5 mL of NaBH_4 was decomposed at 20°C . In each of the experiments 40 mg 20wt% $\text{Co}_{0.5}\text{Mn}_{0.5}/\text{TiO}_2$ catalyst was used and the amount of hydrogen released was continuously recorded.

3. Results and discussion

3.1. Effect of NaOH concentration

Alkaline reaction medium is always used to suppress and control the sudden hydrolysis kinetics. Competition between OH^- and the BH_4^- ions slows down the hydrolysis. However the mechanism is not clear all the time. Concentration of the NaOH can make radical changes on the reaction. Thus a series of hydrolysis test were performed to decide the optimum NaOH amount. 100 mg of NaBH_4 is decomposed in the presence of 40 mg $\text{Co}_{0.5}\text{Mn}_{0.5}/\text{TiO}_2$ catalyst in each of the

trial. Results, are drawn in Figure 1, depicts on its logarithmic scale that the optimum NaOH concentration is around 0,35 M (1,4 wt%) NaOH if the hydrogen generation rates are considered. Similarly, Yuan and coworkers are also reported the optimum NaOH concentration for Co-Mn-B catalyst as 1-5 (wt)% [4].

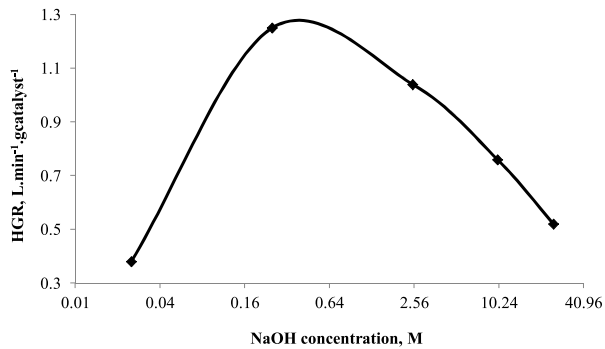


Figure 1. Effect of alkalinity (on logarithmic scale) on hydrogen generation rate (20 °C, 100 mg NaBH₄, 40 mg Co_{0.5}Mn_{0.5}/TiO₂)

3.2. Hydrolysis tests

100 mg NaBH₄ is hydrolyzed each time in the presence of 40 mg Co_{0.5}Mn_{0.5}/TiO₂ supported bimetallic catalyst. SEM-EDX analysis given in Figure 2 shows that even after hydrolysis process catalyst is still keeping its chemical and physical properties. EDX mapping indicates the active sites which are the composition of Co and Mn are homogenously adhered on the surface. Co and Mn catalyst alloy is close to the outer surface (in the range of EDX electron gun) and ready for another hydrolysis experiment. The elements of side product NaBO₂ are also strongly visible on the surface as seen in oxygen and sodium mapping. Accumulation of these elements eventually ends the activity of the catalyst. Low solubility of the side product NaBO₂ is the main reason of that harmful deposition. In order to avoid coverage of side product excess

amount of water usage may be a temporary solution for small scale devices. NaBH₄ decomposition product hydrogen was collected by inverse burette. Hydrogen levels in the burette were recorded versus time at 20 °C. Temperature rise of the reaction exponentially increases the rate therefore temperature should be arranged to able to follow gas release properly. HGR for the catalyst with different Co:Mn content are depicted in Figure 3. Inactivity of sole Mn catalyst is the most interesting part of the graph. In the periodic table, Mn is on the left of iron and it is at the edge of non-noble catalytic elements. However Co-Mn alloy perform better HGR than that of Co catalyst could do solely. The addition of small amounts of Mn to a Co/TiO₂ catalyst affects the catalytic performance by increasing the activity and suppressing the byproducts. These variations in the catalyst selectivity are due to Mn promotion effects that influence the final catalyst active site distribution, playing a role under reaction conditions. In Table 1, HGR values which were calculated between a certain time intervals are given. Initial 30 seconds and time required to release 85% of total hydrogen are selected as the first and last points for HGR calculation. In Figure 3 it is clear that the Co_{0.7}Mn_{0.3}/TiO₂ catalyst result in the maximum performance. Co is the most active non-noble element for NaBH₄ decomposition and its activity can be increased further by alloying with suitable elements. Alike elements can be alloyed according to Hume-Rothery rules in metallurgy science. It is interesting to see the same elemental behavior and validity of these rules in catalyst synthesis.

Table 1. HGR for produced catalyst (Same conditions of Fig. 3.)

Catalyst	HGR, mL _{H₂} ·s ⁻¹ ·g _{catalyst} ⁻¹
Co _{1.0} Mn ₀ /TiO ₂	11
Co _{0.9} Mn _{0.1} /TiO ₂	21.1
Co _{0.7} Mn _{0.3} /TiO ₂	43.6
Co _{0.5} Mn _{0.5} /TiO ₂	35
Co ₀ Mn _{1.0} /TiO ₂	0.2

The life cycle of the Co_{0.7}Mn_{0.3}/TiO₂ catalyst was tested in 5 distinct tests. HGR and cumulative hydrogen

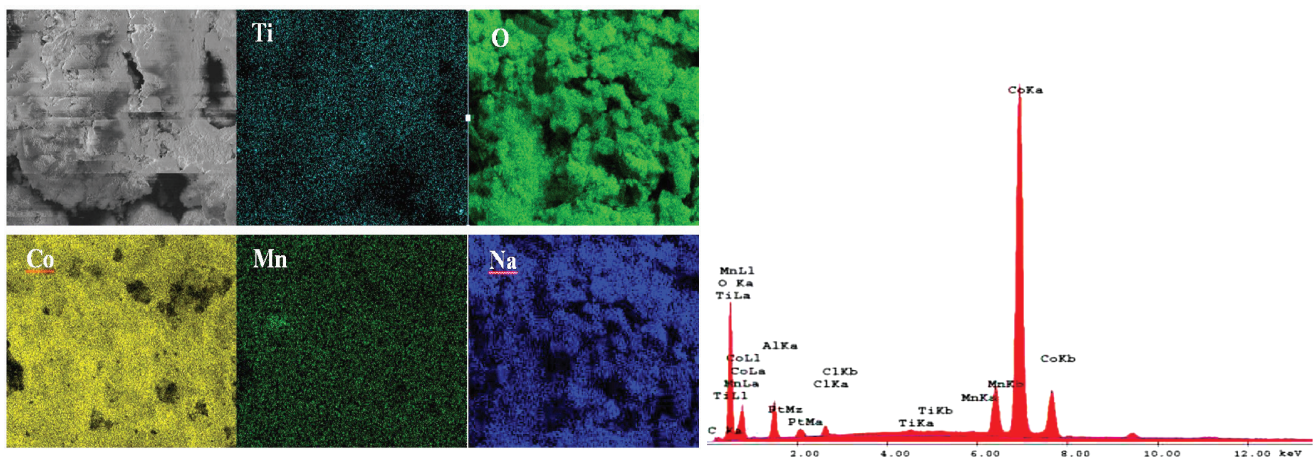


Figure 2. Elemental distribution over catalyst surface (20 wt% Co_{0.5}Mn_{0.5}/TiO₂)

amount obtained are compared. Results are indicating that no detectable activity change occurs on the surface after 5 runs. That encourages using the catalyst for long term periods. However, reactant concentration and catalyst washing-rinsing procedures mainly affect the results and detailed investigations considering these parameters should be performed.

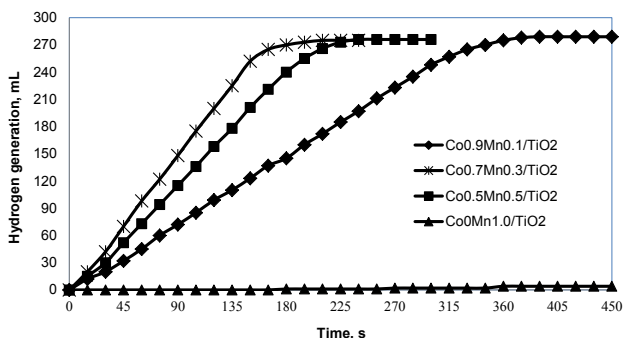


Figure 3. Hydrogen generation rate dependence on catalyst composition (100 mg NaBH₄, 40 mg catalyst, 20 °C, 1.5 wt% NaOH)

Kinetic calculation of the catalysts was done according to the rate equation given below. Firstly NaBH₄ concentration effect on the rate equation was determined. In 5 mL alkaline solution four different molar concentration of NaBH₄ were decomposed in the presence of constant amount of Co_{0.5}Mn_{0.5}/TiO₂ catalyst. Initial values of decomposition were recorded as shown in Figure 4. Increasing the reactant molarity results higher initial rates. If the reaction rate is assumed as first order on the basis of NaBH₄, logarithmic drawing of the initial rates and NaBH₄ concentration gives a straight line and the slope is close to one. Thus the reaction can be accepted to happen according to the first order rate law. First order reactions depended on reactants concentration. If the reactant concentration has effect on the rate, it can be concluded that the catalyst surface reactant concentration is also depend on the bulk concentration. If the bulk is dilute, amount of reactant on the (inner and outer) surface decrease because of the poor adsorption mechanism. In other word, in such condition, adsorption process is the rate limiting due to Langmuir-Hinshelwood approach.

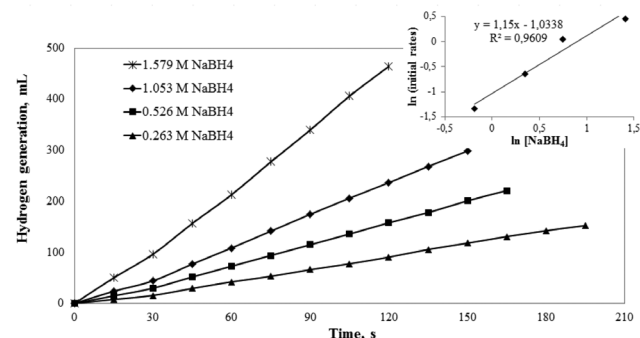


Figure 4. Initial rates of NaBH₄ decomposition against time. The inset depicts the logarithmic initial rates versus logarithmic NaBH₄ concentration (5 mL solution, 40 mg Co_{0.5}Mn_{0.5}/TiO₂, 1.5 wt% NaOH)

$$-r_{NaBH_4} = \frac{-4d[NaBH_4]}{dt} = \frac{d[H_2]}{dt} = k(Co - Mn - B)[NaBH_4]^n$$

$$\ln(-r_{NaBH_4}) = \ln k + n \ln[NaBH_4]$$

Temperature dependence of HGR is studied between 20-50 °C as given in Figure 5. Gas volume of captured hydrogen is used to compute the decomposed NaBH₄ mole numbers and they graphed versus time to create the inset of Figure 5. Increasing HGR values, as the temperature raises, is not a surprise according to the Arrhenius equation given below. Where k is the reaction rate constant, k₀ is the frequency constant, T is the absolute temperature, R the ideal gas constant and E_A is the activation energy of the decomposition. Arrhenius equation in which logarithm of reaction rate constant (slopes of inset in Figure 5) against reciprocal of absolute temperature is plotted in Figure 6 and the activation energy was found as 38.7 kJ/mol.

$$\ln(k) = \ln(k_0) - \frac{E_A}{RT}$$

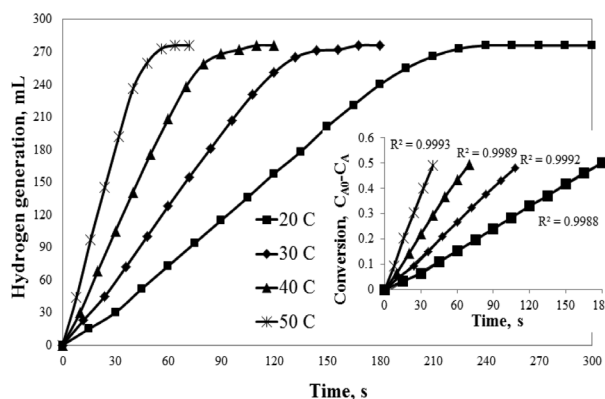


Figure 5. Hydrogen generation rate dependence at various temperatures. The inset shows the Plot of the conversion of NaBH₄ versus time at various temperatures (100 mg NaBH₄, 40 mg Co_{0.5}Mn_{0.5}/TiO₂, 1.5 wt% NaOH)

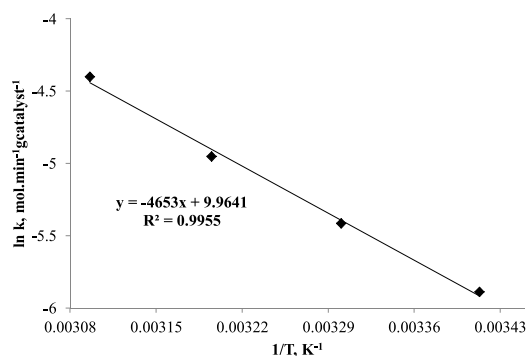


Figure 6. Arrhenius graph for NaBH₄ decomposition (100 mg NaBH₄, 40 mg Co_{0.5}Mn_{0.5}/TiO₂, 1.5 wt% NaOH)

4. Concluding remarks

In this study it was found that the TiO₂ supported Co-Mn bimetallic catalyst is beneficial to develop the NaBH₄ hydrolysis systems. Experimental studies revealed that, 5 mL, 0.526 M NaBH₄ and Co_{0.7}Mn_{0.3}/TiO₂ catalyst is able to reach up to 43.6 mL_{H₂}·s⁻¹·g_{catalyst}⁻¹ hydrogen generation rate at 20 °C. SEM-EDX analysis depicted that the catalyst surface keeps its activity and proper active site distribution even after hydrolysis process. Kinetic data were collected at different temperatures and NaBH₄ concentrations. Results indicate that the Co_{0.5}Mn_{0.5}/TiO₂ catalyst activation energy is 38.7 kJ.mol⁻¹ and the reaction fits to first order rate on the basis of NaBH₄. Mass transfers of the reactant-product are thought to be the limiting step of the process. These findings would be beneficial to develop the hydrogen generating systems to feed devices like fuel cells. However water management (which decrease the system energy density) and scale-up problems still need further investigations.

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