The effect of NaOH on the kinetics of Hydrogen production from sodium borohydride using Ni-based catalysts doped with Ruthenium

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Abstract

Previous work by the authors has demonstrated a high rate and high yield hydrolysis of sodium borohydride in the presence of a Ni-Ru catalyst synthesized by wet chemistry. The catalyst has been fully characterized and utilized more than 300 times, exhibiting high stability and durability. In this work, the effect of temperature on the reaction rate was studied and the activation energy of the process estimated for temperatures up to 65 ºC. Typical data in the form of an Arrhenius type relationship showed two slope regions suggesting a change of mechanism that lead to a more accentuated role of ruthenium for temperatures higher than 45 ºC. This effect is maintained with increasing Ru doping of the catalyst. The effect of NaOH as a stabilizer was also studied and the role of Ni and Ru in the hydrolysis of sodium borohydride is under study on the basis of data obtained for various Ru concentrations and data for 100% Ni and 100% Ru as catalysts. An increase in the concentration of Ruthenium in the catalyst allowed effective utilization of the catalyst without the need for the stabilizer, minimizing the induction reaction time. Excellent catalytic activity and catalyst minimal deactivation for sodium borohydride hydrolysis are characteristic of the series of Ni-Ru catalyst synthesized by wet chemistry used in this work.

Keywords: *sodium borohydride, Ni-based catalyst, Ni-Ru catalyst, activation energy, alkali free hydrolysis*

1 Introduction

In spite of a no-go recommended by US DOE for $NaBH_4$ for on-board automotive hydrogen storage, interest continues to find solutions for portable applications [1]. Sodium borohydride good stability in alkaline solution, easy control of hydrogen generation rate, moderate operation temperatures and environmentally benign hydrolysis by-products has prompted numerous research works contemplating catalyzed hydrolysis in stabilized solutions (with added alkali) as a means to produce meaningful reaction rates [2-11].

A large number of metal or metal compounds have been reported to be active for catalytic hydrolysis of sodium borohydride in alkaline solutions under near ambient temperature conditions, including Co, Ni, Co and Ni borides, Ru, Pt, Pd, Pt-Ru, Pt-Pd [12].

Several research groups have utilized transition-metal catalysts to control hydrogen generation and have found Ru to yield the highest reaction rates for $NaBH_4$ hydrolysis [12]. The strategy of our research group has been to employ a cheap catalyst based on Ni and use Ru "doping" in order to produce high rates and yields, which has been possible using a reduced amount of the more noble metal. Catalyst minimal deactivation has been demonstrated by the authors after a 300 times utilization [13].

Once a durable and active catalyst has been demonstrated, one of the critical issues in the developing of an efficient hydrogen generator using $NaBH_4$ is the increase of the system energy density, necessary to put it into practical use. The concentration of sodium borohydride in the hydrolysis system is very important to that objective in terms of gravimetric and volumetric density. This brings about constrains related with the amount of water needed for reaction completion given the concentration of borohydride, by-products and stabilizer that can be dissolved in aqueous solutions, at a given temperature. The system looses efficiency of storage because the reaction needs excess water to account for their solubility. To be noticed that the captured water by the reaction products reduces even further the

efficiency of the reaction, equation (1). In practice, four moles of water are necessary for full hydrolysis of 1 mol of borohydride.

$$NaBH_4 + (2+x)\,H_2O \rightarrow NaBO_2.x\,H_2O + 4H_2\uparrow + \text{heat} \quad (1)$$

where *x* represents the excess hydration factor [14].

Various authors have investigated the effects of NaOH concentration on hydrogen generation and very different, even conflicting, results have been found. When using noble metal catalysts, such as Ru, the hydrogen generation rate has been found to decrease with increasing NaOH concentration. According to Amendola et al. [2, 3], this is probably due to lowered solubility of the reaction product and hence reduced availability of water at higher NaOH concentration.

In this work the effects of NaOH on the hydrogen generation rate in the catalyzed hydrolysis of sodium borohydride was evaluated for a series of Ni-Ru catalyst. Having established the concentration for maximum generation rate, the activation energy was estimated for the various catalyst.

The role of Ni and Ru in the hydrolysis of sodium borohydride is under study on the basis of catalyst produced with various Ru concentrations and data for catalyst with 100% Ni and 100% Ru. Selected results are herein summarized.

2 Experimental

A series of nickel-ruthenium based catalysts, with different concentrations of ruthenium were synthesized by reduction of nickel and ruthenium salts, using sodium borohydride as a reducing agent, followed by a heat-treatment (see Table 1). The final catalysts consisted in finely divided black catalytically active powders.

Table 1. Amount (%) of Ru used in the working solution for the synthesis of various Ni-based catalyst for the hydrolysis of sodium borohydride.

Catalyst	A	B	C	D	E
Ru	0	15	30	50	100

Work is in progress in order to determine the actual amount of Ru in the catalyst and fully characterize the catalysts.

The typical experimental setup used in the kinetics study consisted in a tubular glass reactor chamber immersed in a thermostatically-controlled water bath. The temperature of the bath was controlled by a Memmert heater and the temperature inside of reactor was measured by a thermocouple. Hydrogen generation measurements were obtained by the water displacement method.

In each experiment 50 mg of catalyst were placed into the reaction chamber and the sodium borohydride (ROHM and HAAS) stabilized solution with NaOH (PRONALAB), previously heated at required temperature, was added. Hydrogen generated volume, reaction site temperature and induction time were measured as a function of time.

3 Results and Discussion

In order to investigate the catalytic activity of the various prepared catalysts, a set of experiments were made measuring the hydrogen generation in a 10 wt % $NaBH_4$ solution, stabilized with various amounts of NaOH varying from 1 wt% to 20wt%. A maximum rate was found at 10wt%, which for catalyst B (lower concentration in Ru) was of ~ 7 $Lmin^{-1}g^{-1}$ at 45 ºC.

Taking the above experimental conditions in $NaBH_4$ and NaOH concentration and temperature the hydrogen generation rate was measured for the various catalyst. As expected, the obtained results show faster kinetics for the catalyst with apparent higher ruthenium loading, the increase being more pronounced for catalysts C, D and E. Rates from ~7 $Lmin^{-1}g^{-1}$ to ~ 54 $Lmin^{-1}g^{-1}$ were observed at 45 ºC, see figure 1.

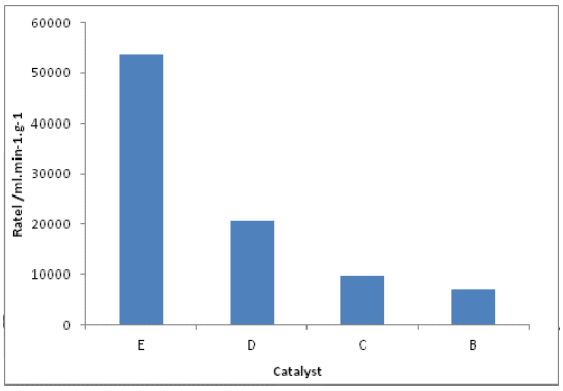

Fig. 1. Hydrogen production rates at 45 ºC for the various Ni-Ru catalyst in 10 wt % $NaBH_4$ solution stabilized with 10wt% NaOH.

The activation energy for Ni-Ru catalysts was estimated, performing a set of experiments, in the same experimental conditions, in the temperature range from 25 to 65ºC, for a fixed concentration of 10 wt % NaBH4, stabilized with 10 wt % NaOH.

The values of the rate constants, k, were determined and plotted (lnk) vs 1/T. The activation energies, Ea, were estimated for the slopes of those graphs and their values are given in Table 2. Comparison is made with values found for pure Ni and pure Ru as catalyst for the hydrolysis of sodium borohydride in the same conditions.

Table 2. Activation energies for sodium borohydride hydrolysis for Ni-based catalyst doped with Ru. Values for pure Ni (A) and pure Ru (B) catalyst are included.

Catalyst	A	B	C	D	E
Ea T>45ºC (kJmol-1)	67[15]	31	30	25	28[16]
T<45ºC ($kJmol^{-1}$)		98	92	64	

While the plots for the pure catalysts show only one linear region, the Ni-based catalyst doped with Ru showed the existence of two linear regions with slope changing at ~45ºC. This is adjudicated to a change in reaction mechanism [17].

Most studies report only one slope but activation energies are generally estimated for temperatures up to 40ºC. In other cases, studies including temperatures over 45 ºC, the observed tendency is similar to that found in this work, even though the authors do not acknowledge the existence of two slopes. It is only recently that the possibility of two slopes has been recognized, for example for the case of cobalt catalyst [18].

From table 2 it is evident that for temperatures higher than 45ºC the activation energy is closer to that obtained for pure Ru, for all Ni-Ru catalyst studied. The obtained values suggest a change of mechanism, where for higher temperatures, ruthenium seems to have a more pronounced role in the hydrolysis reaction.

Since the maximum concentration of sodium borohydride in the hydrolysis system is determined by the amount of water available a decrease in the amount of stabilizer will allow an increase in the concentration of $NaBH_4$, as will an increase in temperature.

In this work, preliminary results indicate that alkali free hydrolysis is more favored, in terms of rate, for catalysts which are richer in Ru.

When the nickel fraction in the catalyst is increased, the larger production rate is associated to the stabilized solution.

The induction reaction time was found to be temperature dependent and lower in the absence of NaOH than in its presence for catalyst with high Ru (catalyst D) for T< 45ºC, see figure 2.

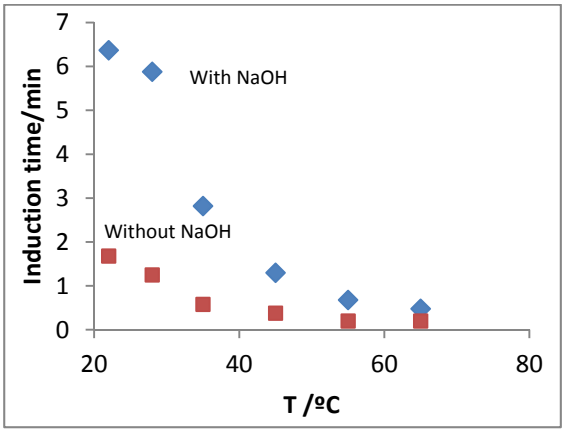

Fig. 2 The induction time as a function of temperature for catalyst D in the presence and absence of stabilizer.

Conclusions

Excellent catalytic activity and catalyst minimal deactivation for sodium borohydride hydrolysis was registered for all the Ni-Ru catalyst synthesized in this work.

An increase in the catalytic activity was observed with the increase of ruthenium incorporated in the catalyst. This point is under investigation in order to determine accurately the % of Ru in the catalyst.

Increasing the amount of ruthenium leads to a decrease on Ea, more pronounced for the Ea obtain at lower temperature. The obtained values suggest a change of mechanism, where for higher temperatures, ruthenium seems to have a more pronounced role in the hydrolysis reaction.

Higher concentration of ruthenium allowed effective utilization of the catalyst without the need for the stabilizer.

An increase in the concentration of Ruthenium in the catalyst allowed effective utilization of the catalyst without the need for the stabilizer, minimizing the induction reaction time.

It is considered that the strength of catalyst lies in the activity of both of the chosen materials: nickel by its activity towards hydrogen evolution and ruthenium by its activity in water dehydrogenation reactions, which in this case play a complimentary role for an effective hydrogen delivery from borohydride.

Research is in progress in order to advance more on the role of both materials and a kinetic model for the Ni-Ru catalyst.

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