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An effective method for increasing the activity of nickel boride catalyst nano-particles in hydrogenation reactions: Low-temperature hydrogen treatment

Firouzeh Taghavi[a,b], Cavus Falamaki[c,d,*], Alimemad Shabanov[a],
Mina Seyyedi[b], Mehdi Zare[b]

[a] *Research Institute of Geotechnical Problems of Oil, Gas and Chemistry, Azerbaijan State Oil Academy, Baku, Azerbaijan*
[b] *Research and Development Department, Chlor Pars Co., P.O. Box 51335-1717, Tabriz, Iran*
[c] *Chemical Engineering Department, Amirkabir University of Technology, P.O. Box 15875-4413, Tehran, Iran*
[d] *Petrochemical Center of Excellence, Amirkabir University of Technology, P.O. Box 15875-4413, Tehran, Iran*

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ABSTRACT

It is shown that low temperature (<100 °C) hydrogen treatment of nano nickel boride catalysts is an efficient process for the enhancement of their activity in the p-nitrophenol (PNP) to p-aminophenol (PAP) hydrogenation reaction. It has been shown that such a process excludes initial borate species present on the surface and within the catalyst nano-particles by promoting their dissolution in the liquid phase. The latter phenomenon is enhanced by increasing the temperature. Treatment in the absence of hydrogen results in no reaction rate enhancement. Instead, the activity falls significantly below that of the as-synthesized catalyst. The effect of hydrogen treatment on the catalyst physical properties was investigated using FTIR, XRD, nitrogen adsorption and FESEM analysis. Mathematical simulation of the PNP hydrogenation reaction rate supports the hypothesis that the rate enhancement is mainly due to the increase of the catalyst specific surface area and partial reduction of surface nickel oxide species. The mechanism by which hydrogen increases the specific surface is discussed.

1. Introduction

Nickel boride nano-catalysts have gained increasing interest as novel catalytic materials in hydrogenation reactions [1]. The high concentration of coordinating unsaturated active sites in these amorphous alloy nano-particles donates them higher activity and selectivity with respect to their crystalline counterparts [2].

The hydrogenation of p-nitrophenol (PNP) to p-aminophenol (PAP) using nickel boride and nickel nano-catalysts has attracted much attention in the last decade [3–6]. The authors of this work recently published a thorough study on the synthesis and characterization of Ni_2B nano-catalysts and their catalytic behavior for the PNP direct hydrogenation reaction to PAP in a batch slurry reactor[7]. As a continuation of the latter research, we were strongly interested in developing a catalyst pre-treatment procedure with the aim of improving its activity. Survey of the related literature shows that many attempts have been performed for the ‘hydrogen treatment’ of nickel boride catalysts at temperatures higher than 250 °C (in the absence of organic liquids like ethanol) [8–11]. Li et al. [8] treated a Ni-B/γ-Al_2O_3 catalyst with hydrogen up to 527 °C. They concluded that such treatments result in the crystallization of the initial amorphous phase and the creation of extra phases such as metallic nickel. They did not study the catalytic behavior of the treated catalyst. Li et al. [9] treated the Ni-B/SiO_2 catalyst under hydrogen atmosphere in the temperature range of 250–700 °C for 4 h. The final catalysts showed very low activity for the glucose hydrogenation reaction in comparison with the original sample. This phenomenon was attributed to particle growth and creation of new phases like metallic Ni and alloys like Ni_3B and Ni_2B. Wang et al. [10] obtained similar results pre-treating Ni-B catalysts under hydrogen at elevated temperatures. Chen et al. [11] treated a Ni-B/SiO_2 catalyst at 400 °C for 2 h with hydrogen and observed a clear reduction of activity for the hydro-dechlorination of chlorobenzene.

Generally, high temperature hydrogen treatment of nickel boride nano-catalysts results in a sharp decrease of activity due to two main reasons: (a) loss of active area due to the high sinter-activity of the parent nano-metal boride particles and (b) crystallization of the highly active amorphous initial alloy and eventual creation of new phases like metallic Ni and Ni_xB_y. We

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[*] Corresponding author at: Chemical Engineering Department, Amirkabir University of Technology, P.O. Box 15875-4413, Tehran, Iran. Tel.: +98 21 64 54 31 60; fax: +98 21 66 4058 47.
E-mail address: c.falamaki@aut.ac.ir (C. Falamaki).

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astonishingly found out that low temperature hydrogen treatment ($T < 100\,^{\circ}C$) of the as-synthesized catalyst in the presence of ethanol may induce a substantial increase in the catalyst activity for the direct hydrogenation of PNP to PAP. Such a phenomenon has not been reported so far in open literature. The present work aims at studying the effect of low temperature hydrogen pre-treatment in detail and elucidating the phenomena leading to activity enhancement. In this regard, the effect of hydrogen treatment temperature (40, 60 and 94 °C) on the catalyst activity has been studied. The effect of hydrogen pressure (2.5–4.0 MPa) for a treatment temperature of 94 °C on the catalytic performance of the nickel boride catalysts has also been investigated. A single site mechanism with atomically absorbed hydrogen and PNP adsorption as the controlling step was applied to predict the experimental data. In addition, the effect of treatment in ethanol medium in the absence of hydrogen has also been investigated. Finally, the effect of treatment on the physico-chemical properties of the catalyst is explained.

2. Experimental

2.1. Materials

High purity hydrogen (99.999 wt %) was purchased from Chlor Pars Co. (Iran). Reagent grade caustic soda, sodium borohydride and nickel chloride was provided by Merck. Ethanol (96 wt. %) was purchased from Nasr Co. (Iran). PNP (99.5 wt. %) was purchased from Anhui Bayi (China).

The catalyst synthesis procedure was as follows: 25 mL of a 1.8 M $NaBH_4$ aqueous solution containing 0.05 M NaOH was added drop wise to 25 mL of a 0.3 M aqueous solution of $NiCl_2$ under vigorous stirring. Excess amount of $NaBH_4$ was used to ensure complete reduction of nickel. The black precipitate was thoroughly washed with a large amount of distilled water, soaked in distilled water to remove soluble boron species and Na^+ cations which are considered poisons of the nickel boride catalyst. Finally, the product was washed with ethanol and stored under ethanol prior to any further treatment.

2.2. Catalyst treatment

The catalyst hydrogen treatment was performed as follows: the as-synthesized catalyst and 25 mL ethanol were charged into the reactor system. The reactor temperature was raised to the desired temperature (40, 60 and 94 °C) and afterwards the pressure of the system was set to the predetermined value (2.5–4.0 MPa) by introducing pressurized H_2. Hydrogen treatment was continued for 35 min.

Some treatments were performed in the absence of hydrogen but in the presence of ethanol medium at 60 and 94 °C for comparative means. The treatments period has been 35 min in each case.

2.3. Hydrogenation tests

The hydrogenation reaction was carried out in a 400 mL stainless steel autoclave charged with 1 g catalyst, 3.5 g PNP and 25 mL ethanol as solvent. The autoclave was shacked with a special external system (no internal mixer) connected to an electric motor with variable speed. An optimum agitation speed of 46 rpm was used for the catalytic tests according to our previous work to ascertain absence of any gas–liquid phase mass transfer resistance [7]. The temperature of the reactor was controlled in the range of RT-94 °C by means of an external jacket and water as heating fluid. The hydrogenation reaction was carried out as following: the reactor was heated to 60 °C and then hydrogen was charged to the reactor. The pressure of hydrogen was adjusted to 2.5 MPa and stirring was commenced and fixed at 46 rpm. The H_2 consumption was monitored by a pressure gauge installed on the hydrogen inlet line. It should be mentioned that according to Taghavi et al. [7], the kinetic results obtained are independent of the amount of catalyst and the agitation rate is high enough to eliminate any diffusional resistances in the liquid phase.

Analysis of the hydrogenation product was performed using a GC instrument (Agilent 7890 Series, USA) equipped with a FID detector. Analysis of the gas phase after hydrogen treatment was performed using a GC/MS apparatus (Agilent 6890 Series, USA). The FTIR spectrum of the liquid phase after hydrogen treatment was performed using a Brucker Tensor 27 apparatus. The melting point of the solid product was measured using an Electrothermal 9100 apparatus (Digital Melting Point Co.). More details may be found elsewhere [7].

2.4. Catalyst characterization

X-ray diffraction patterns of the catalysts were taken using a Siemens D5000 powder diffractometer using Cu-K_{α} radiation. FTIR transmission spectra were recorded on a Brucker Tensor 27 apparatus. The samples were occasionally treated (heated in vacuum at 60 °C for 24 h or the same followed by heating in ambient air at 100 °C for 2 h) before the latter analysis.

The chemical composition of the as-synthesized and hydrogen treated nickel boride catalysts was determined by ICP analysis using a ICP-OES instrument equipped with an Integra XL (GBC) spectrometer. For this analysis, 0.1 g catalyst was dissolved in 100 cm^3 aqua regia and further diluted 100 times. The morphology of the samples was studied using a field emission scanning electron microscope using a S-4160 Hitachi instrument. Specific surface area of the as-synthesized and hydrogen treated samples was evaluated using an Autosorb-1 (Quanta Chrome) apparatus through nitrogen adsorption.

3. Results and discussion

The XRD patterns of un-treated (as-synthesized) and hydrogen treated samples at 60 and 94 °C with an initial H_2 pressure of 2.5 MPa are shown in Fig. 1. The patterns are essentially similar

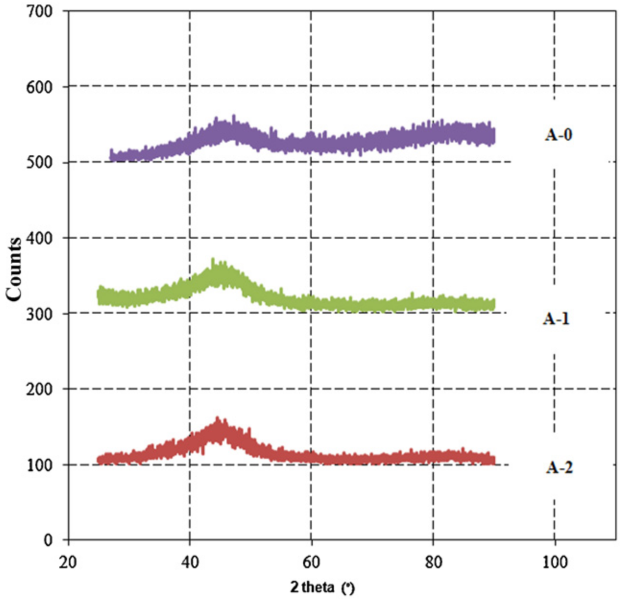

Figure 1. XRD patterns of the un-treated catalyst (A-0) and hydrogen treated catalysts at 60 °C (A-1) and 94 °C (A-2).

revealing no observable change in the original amorphous structure upon hydrogen treatment. Thus the treatment doesn't change considerably the amorphous structure of the Ni-B material.

Based on ICP analysis as shown in Table 1, the general chemical formula of the un-treated (A), hydrogen treated at 60 °C (A-1) and hydrogen treated at 94 °C (A-2) samples were determined as $Ni_{1.84}B$, $Ni_{2.33}B$ and $Ni_{2.40}B$, respectively. It is observed that hydrogen treatment decreases the boron content of the original sample. The higher the hydrogen treatment temperature, the higher is the loss of boron.

Fig. 2 (spectra a to f) shows a series of FTIR spectra for elucidating the effect of hydrogen treatment on the characteristics of the catalyst. Fig.s 2a and 2b show the FTIR spectra of the fresh (A-0) and hydrogen treated catalyst at 94 °C (A-2), respectively. Fig. 2c shows the FTIR spectrum of the hydrogen treated catalyst at 94 °C (A-2) after heating it at 60 °C for 24 h under vacuum. Fig. 2d shows the same catalyst (A-2) after being heated at 60 °C for 24 h and further heated at 100 °C for 2 h in ambient conditions. For a better interpretation of the FTIR spectra we resume some characteristic peaks according to the recent work of Taghavi et al. [7]. BO_3 units exhibit peaks in the range of 1411–1454 and 1266–1285 cm^{-1} (asymmetric stretching vibrations) and around 580 cm^{-1} (bending vibrations), BO_2 units exhibit peaks in the range of 1081–1100 cm^{-1}(symmetrical stretching vibrations), BO_4 units exhibit peaks at around 970 cm^{-1} (symmetrical stretching vibrations), and in the range of 631–670 cm^{-1} (bending vibrations). It is clear that the FTIR spectrum of the fresh catalyst A-0 shows the presence of all the above mentioned boron oxide groups. However, it is difficult to attribute the observed peaks of the FTIR spectrum of the hydrogen treated catalyst A-2 to any boron oxide species or other species from Fig. 2b due to the evident presence of peaks belonging to adsorbed ethanol. The FTIR spectrum of ethanol has been shown in Fig. 2e. It is essential to recall that the sample A-0 was synthesized in an aqueous solution but maintained in ethanol media prior to any analysis or catalytic activity assessment to avoid any surface oxidation. This is while for catalyst A-2, hydrogen treatment has been performed using ethanol as solvent. Taking into consideration the exposure of both samples to ethanol, it is surprising to observe that the sample A-0 does not show any appreciable adsorption of ethanol while the hydrogen treated sample (A-2) shows strong peaks belonging to ethanol (2925, 2856, 2360 cm^{-1}) (Fig. 2, spectrum b). It was necessary to exclude any 'adsorbed' ethanol to obtain the FTIR pattern of the 'pure' hydrogen treated nickel boride catalyst A-2. For this means, the hydrogen treated sample was heated at 60 °C under vacuum for 24 h (Fig. 2, spectrum c). A substantial reduction of the major peaks of ethanol is observed that shows the near complete exclusion of alcohol from the sample. The preservation of the double peaks centered ca. at 2358 cm^{-1} and triple peaks centered ca. at 2891 cm^{-1} are mainly attributed to the adsorption of impurity hydrocarbons from air prior to the FTIR measurement. The same impurity peaks are observed in the FTIR pattern of the same sample treated for 2 h at 100 °C under atmospheric condition, after being treated at 60 °C for 24 h under vacuum (Fig. 2, spectrum d).

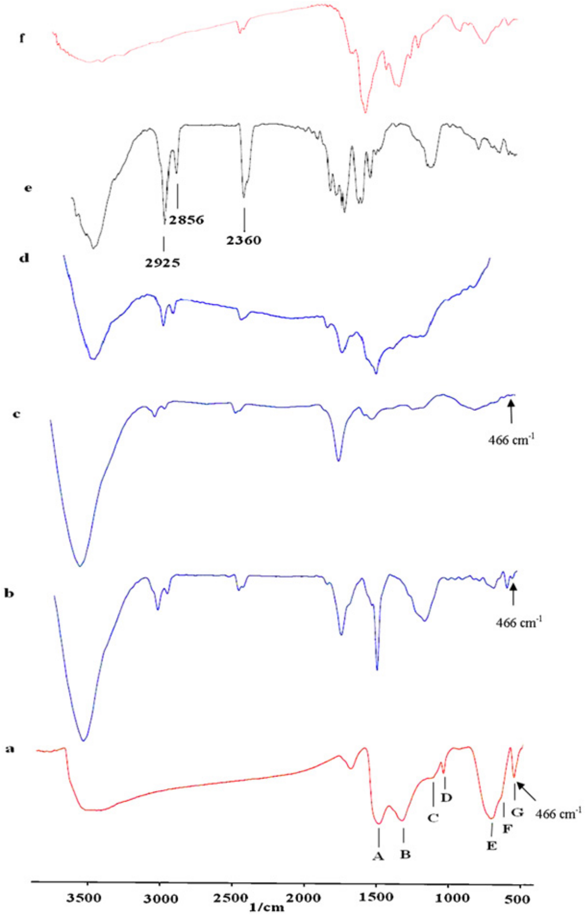

Figure 2. FTIR patterns of (a) un-treated catalyst (A-0) which has been maintained in ethanol prior to the catalytic experiments to avoid oxidation; (b) hydrogen treated catalyst at 94 °C (A-2); (c) hydrogen treated catalyst at 94 °C and heat treated at 60 °C under vacuum for 24 h; (d) case (c) further heat treated at 100 °C under ambient air; (e) fresh ethanol (f) as-synthesized catalyst treated at 94° in ethanol in the absence of hydrogen (A-3) (A and B: asymmetrical stretching vibration (BO_3 units); C: symmetrical stretching vibration (BO_2 units); D: symmetrical stretching vibration (BO_3 units); E: bending vibration (BO_4 units); F: bending vibration (BO_3 units); G: bending vibration (BO_4 units)).

Based on what has been said, we may now compare the FTIR pattern of the fresh catalyst A-0 (Fig. 2, spectrum a) with the pattern of the hydrogen treated catalyst, A-2, after having applied the due thermal treatment in vacuum to exclude adsorbed ethanol (Fig. 2, spectrum c) (further heat treatment at 60 °C under

Table 1
Characteristics of the un-treated and heat-treated catalyst.

Description	Un-treated	Hydrogen treated at 60 °C	Hydrogen treated at 94 °C	Ethanol treated at 94 °C	Used catalyst
Symbol	A-0	A-1	A-2	A-3	A-0-U
Ni wt. % in solid	50.0	77.1	72.9	83	50
B wt. % in solid	5.0	6.1	5.6	6.8	4
Corresponding chemical formula of the solid phase	$Ni_{1.84}B$	$Ni_{2.33}B$	$Ni_{2.40}B$	$Ni_{2.248}B$	$Ni_{2.279}B$
Specific surface area($m^2 g^{-1}$)	50	–	130	38	–
Selectivity (%)	98.5	98.5	98.5	98.5	–
Conversion (%)	100	100	100	100	–
Reaction time for ca. 100% conversion of PNP (min)	60	40	30	70	–
Qualitative catalytic activity with respect to the un-treated catalyst	–	Slightly increased	Significantly increased	Significantly decreased	–

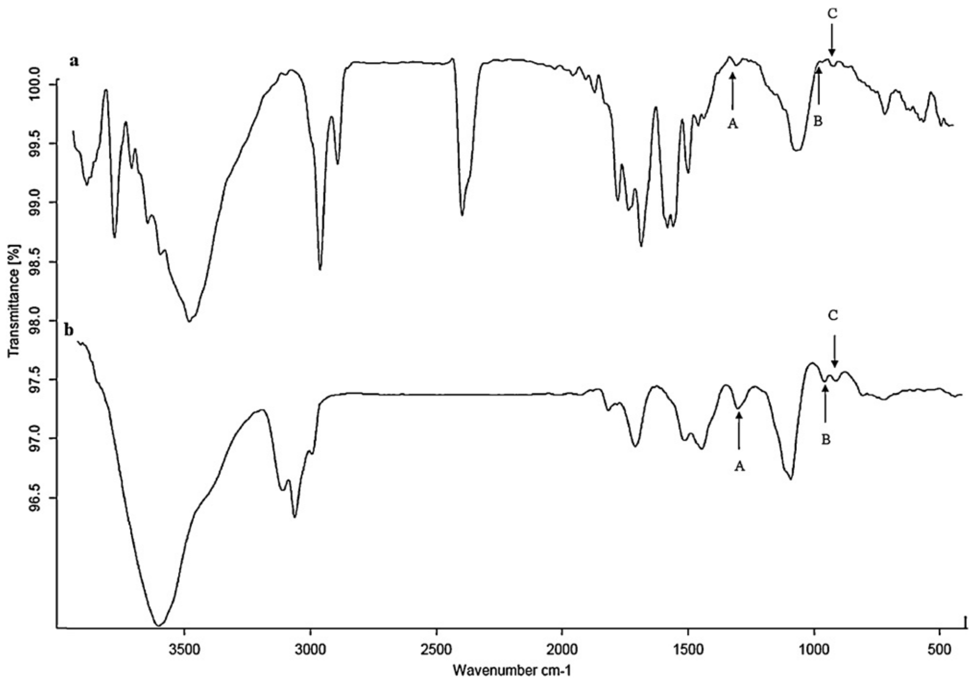

Figure 3. (a) FTIR pattern of raw ethanol (before use) (b) FTIR of the ethanol medium used for the catalyst hydrogen treatment at 60 °C after the treatment (A and B: asymmetrical stretching vibration (BO_3 units); C: symmetrical stretching vibration (BO_2 units)).

vacuum for 24 h) in more detail. The bands due to trigonal BO_3 and tetrahedral BO_4 units show themselves in the wave number range of 426–1500 cm^{-1} [7]. It is observed that the relative integrated intensity of these peaks is substantially reduced after hydrogen treatment. In other words, FTIR results show the significant reduction of 'surface' borate entities as a function of exposure to hydrogen at 94 °C for 35 min. This deduction readily explains the enhanced 'hydrophobicity' obtained after hydrogen treatment due to increased affinity for ethanol adsorption. Surface borate entities give a 'hydrophilic' character to the outer surface of the nano-particles. Their 'exclusion' may increase the surface 'hydrophobicity.' At this point, it seems useful to consider the effect of catalyst treatment at 94 °C in ethanol medium but in the absence of hydrogen (Fig. 2, spectrum f). Compared with the FTIR spectrum of the fresh catalyst A-0 (Fig. 2, spectrum a), an increase in the peak intensity due to borate species in the range of 1100–1500 cm^{-1} is observed. In other words, treatment in ethanol but in the absence of hydrogen results in an increased oxidation of boron atoms of the parent NiB catalyst.

There exists another peculiarity in the spectra of Fig. 2 that is worth mentioning. It is known that absorption bands around 460 cm^{-1} belong to NiO stretching vibrations [12–14]. Accordingly, the presence of a peak centered around 466 cm^{-1} in the FTIR spectrum of the fresh catalyst A-0 (Fig. 2, spectrum a) may be attributed to the presence of surface nickel oxide species. This peak vanishes upon hydrogen treatment (catalyst A-2, Fig. 2, spectrum c). In other words, surface nickel oxide species are reduced upon hydrogen treatment.

Fig. 3 (spectra a and b) shows the change in the FTIR spectrum of the liquid phase (ethanol) before and after the hydrogen treatment at 60 °C. Recall that the hydrogen treatment has performed in ethanol medium and we aimed at analyzing the ethanol liquid used before after the treatment. The relative intensities of the peaks A, B and C (due to borate species) increase significantly after the treatment. This is an evidence for the dissolution of borate species in the liquid phase (ethanol). Accordingly it may be stated that the reduction of the number of the surface borate entities is partly due to their dissolution in the liquid phase(ethanol). Higher treatment temperatures result in more dissolution and this is in accordance with the FTIR results.

The specific surface area of the original sample is 50 m^2 g^{-1} [7]. After hydrogen treatment at 94 °C for 35 min, the specific surface area of hydrogen treated sample (A-3) as shown in table 2 undergoes a substantial 2.6 fold increase to 130 m^2 g^{-1}. Comparison of the SEM pictures of the samples A and A-3 confirms the latter finding (Fig. 4-a and 4-b). A substantial increase of external surface area after hydrogen treatment is observed and it looks like as if the particles have been corroded by hydrogen. This may be related to the exclusion of surface and intra-particle borate groups as schematically shown in Fig. 5-a and 5-b. We suppose that the original nano-particles are agglomerates of Ni_xB nano-entities (like Ni_2B as shown in Fig. 5-a) that are glued to each other through boron oxide species. Upon hydrogen treatment, most of the boron oxide molecules residing on the surface and between the nickel boride particles are excluded, thus providing extra porosity in accordance with the nitrogen adsorption and SEM analysis.

At this stage it would be informative to consider the specific surface area of the catalyst treated in ethanol but in the absence of hydrogen (A-3). The specific surface area in this case has been measured to be 40 m^2 g^{-1} and this is 20% smaller than the as-synthesized catalyst. This shows that mere treatment in ethanol media is not accompanied by specific surface area increase due to the exclusion of borate species through significant dissolution in ethanol medium. It goes without saying that some dissolution of borate species takes place by contacting them with ethanol.

The exclusion of surface borate species has a pronounced effect on the catalytic performance of the sample. This is shown in Fig. 6. It is observed that the rate of hydrogen consumption is significantly increased when compared to the sample A. It should be emphasized that treatment of the catalyst at 40 °C did not result in any observable enhancement of the reaction rate. In addition, the rate enhancement increases with the increase of the hydrogen treatment temperature. This last finding is in accordance with the favored exclusion of surface borate species at higher treatment temperatures. The TOFs of the un-treated (A), hydrogen treated at 40 °C, hydrogen treated at 60 °C (A-1) and hydrogen treated at

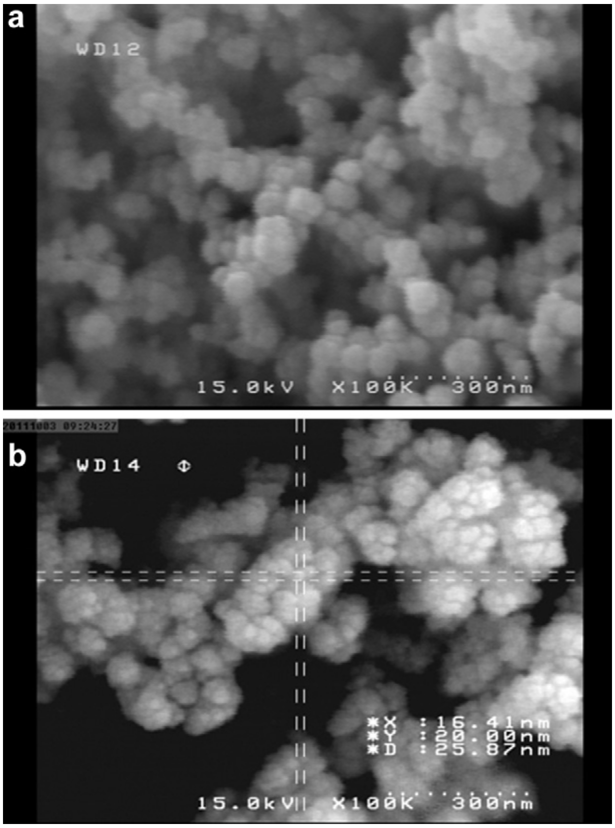

Figure 4. FESEM pictures of the (a) un-treated (A-0) and (b) hydrogen treated at 94 °C (A-2).

94 °C (A-2) have been calculated as 375.8, 309.8, 449.3 and 616.9 g PAP h^{-1} (kg catalyst)$^{-1}$. It is reminded that these values have been obtained for 1 g catalyst, 3.5 g PNP and 25 mL ethanol as solvent for an initial pressure of 25 bar.

Considering the catalysts treated in ethanol medium (A-3) (Fig. 7), it is clearly observed that the resultant catalysts have a lower activity with respect to the catalyst A. It comes out that the treatment is effective only if performed under hydrogen atmosphere.

Based on the p-nitrophenol hydrogenation reaction mechanism proposed in our previous work [7], the reaction rate involves a single site mechanism with automatically adsorbed hydrogen and p-nitrophenol adsorption as the controlling step. The expression for the reaction rate may be derived as follows:

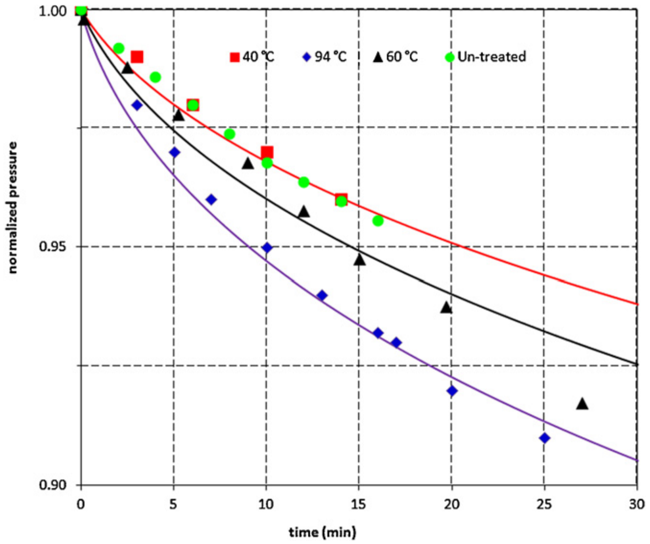

Figure 6. Pressure variation as a function of reaction time and hydrogen treatment temperature (40, 60 or 94 °C). Bold lines represent the simulated data. The experimental data due to the un-treated catalyst (A-0) have been added for comparison (experimental conditions: $T = 60$ °C; initial pressure = 25 bar; PNP initial concentration = 0.14 g/Ml; mixing speed = 46 rpm).

$$r = \frac{k_1 C_{PNP}}{(1 + K_{PAP}C_{PAP} + K_W C_W + \sqrt{K_{H_2} C_{H_2}})} \tag{1}$$

where r is the reaction rate (mol PAP min^{-1} mL^{-1}), k_1 the PNP adsorption rate constant, C_{PNP} the concentration of PNP in the liquid phase (mol mL^{-1}), C_{PAP} the concentration of PAP in the liquid phase (mol mL^{-1}), C_W the concentration of water in the liquid phase (mol mL^{-1}), C_{H_2} the concentration of H_2 in the liquid phase (mol mL^{-1}), K_{PAP} the adsorption coefficient of PAP (mL mol^{-1}), K_W the adsorption coefficient of water (mL mol^{-1}) and K_{H_2} the adsorption coefficient of H_2 (mL mol^{-1}). Fig. 6 shows the predicted total pressure as a function of reaction time for the catalysts treated at 40, 60 and 94 °C (2.5 MPa initial pressure). A reasonable agreement between experimental and simulated data exists. The values used for K_{H_2}, K_{PAP} and K_W had been 5.873×10^6, 1.08×10^5 and 1.17×10^5 cm^3 mol^{-1}, respectively and independent of

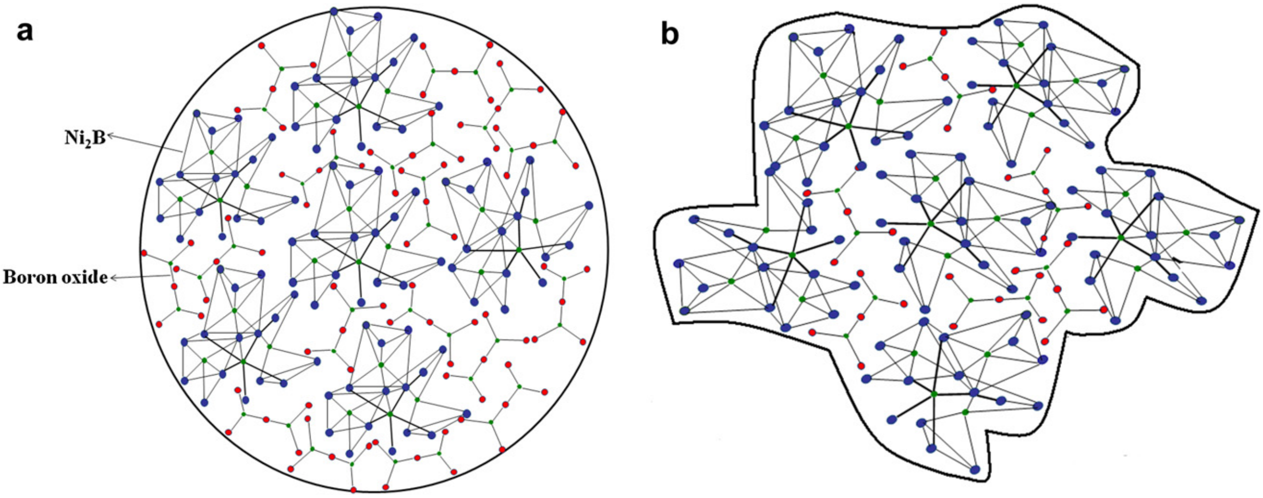

Figure 5. Schematic representation of the effect of hydrogen treatment on the particle surface morphology (a) un-treated catalyst (A-0) and (b) after hydrogen treatment.

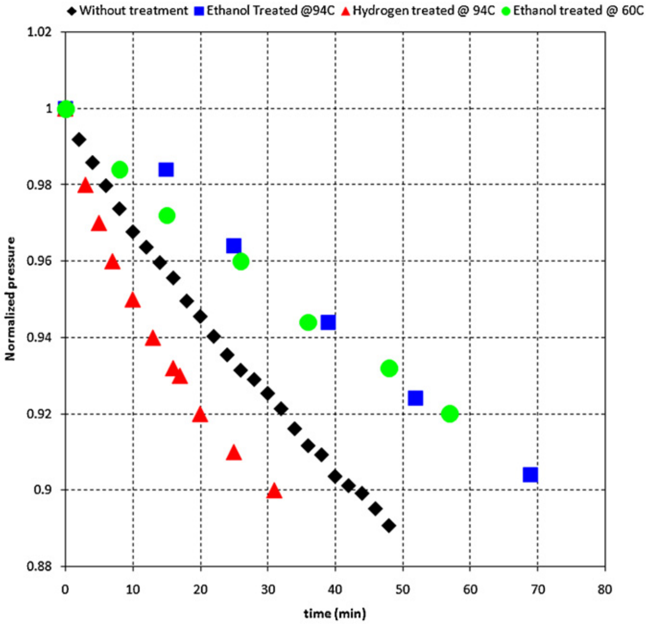

Figure 7. Pressure variation as a function of reaction time for the un-treated and heat treated catalyst: catalyst treated with hydrogen at 94 °C; catalyst treated in ethanol medium at 94 °C in the absence of hydrogen; and the catalyst treated in ethanol medium at 60 °C in the absence of hydrogen (Experimental conditions: $T = 60\,^{\circ}C$, $P = 25$ bar, PNP initial concentration = 0.14 g/mL, mixing speed = 46 rpm).

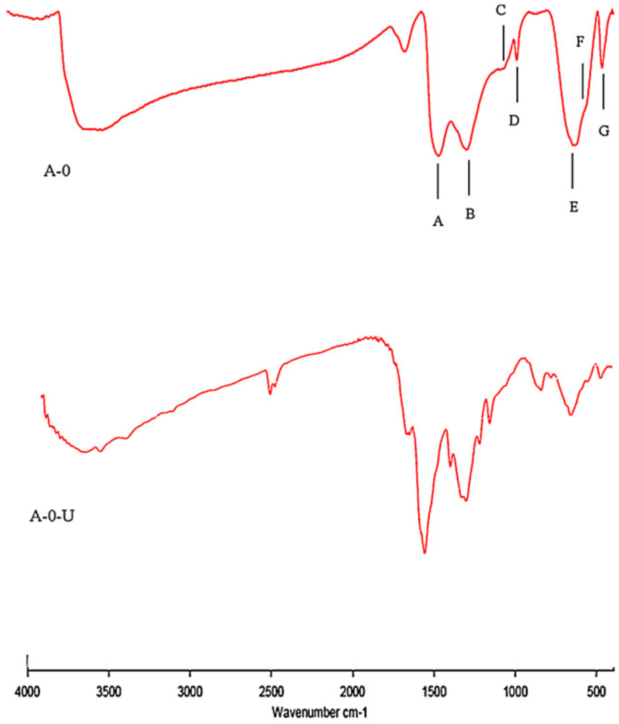

Figure 8. FTIR spectrum of A-0-U catalyst (experimental conditions: $T = 60\,^{\circ}C$, $P = 25$ bar, PNP initial concentration = 0.14 g/mL, mixing speed = 46 rpm).

treatment temperature. The optimum values of k_1 had been 0.56, 0.79 and 1.29 min^{-1} for the treatment temperatures 40, 60 and 94 °C, respectively. This is theoretically explainable as hydrogen treatment actually increases the 'specific surface area' of the catalyst. This phenomenon, by itself, cannot change the thermodynamic constants K_{H_2}, K_{PAP} and K_W, which depend only on the nature of the adsorption sites. Instead, the rate constant k_1 depends directly on the reciprocal of the surface area and should increase with the increase of the available surface. Theoretically, k_1 should increase by a factor of 2.6 when increasing the treatment temperature from 40 to 94 °C. The actual increase is 2.3, in fair agreement with theory. Summing up, it may be claimed that the main effect of hydrogen treatment is the increase of specific surface area, which sequentially increases proportionally the PNP hydrogenation reaction rate.

Based on the experimental evidence on the significant enhancing effect of the presence of hydrogen during the treatment in ethanol medium, we propose the following explanations:

1. During the hydrogen treatment process, dissolved hydrogen in the liquid state adsorbs selectively on the nickel boride particles and undergoes dissociation. Before hydrogen adsorption, the Ni atom of Ni_2B forms a weak electrostatic bond with the adjacent oxygen belonging to boron oxide groups and the boron atom of the nickel boride also forms a weak bond with the adjacent boron belonging to a boron oxide group ($BO^{\delta-} \cdots Ni^{\delta+} - B^{\delta-} \cdots B^{\delta+}O_3$). Nickel is known for its high affinity versus hydrogen molecules. It is most probable that upon dissociation, one hydrogen atom comes close to Ni and the other to the adjacent B atom of Ni_2B. The adsorption of the hydrogen atoms decreases the net positive charge on Ni and the negative charge on B of the primary $\cdots Ni^{\delta+} - B^{\delta-} \cdots$ entity. Accordingly, the primary bonds between the boron oxide groups and nickel boride weaken. Simultaneously, the presence of ethanol molecules that bear a relatively high dipole promote the excavation of the boron oxide groups from the vicinity of the primary $\cdots Ni^{\delta+} - B^{\delta-} \cdots$ entity. As a result of the presence of dissolved hydrogen (in the form of adsorbed hydrogen atoms) and the electrostatic contribution of the ethanol medium, boron oxide species are prone to leave the nickel boride particles and enter into the liquid phase.
2. Surface nickel oxide species in the fresh catalyst are reduced during the hydrogen treatment process. This phenomenon enhances the hydrogenation activity of the catalyst.

We make a brief note at the end of this work regarding the change of the characteristics of the catalyst after being used in the PNP hydrogenation reaction at 60 °C and 25 atm initial pressure. Table 1 shows the composition of the catalyst A-0 and A-0-U (catalyst A-0 after being used once for the reaction). It is observed that the catalyst undergoes a reduction in boron content upon the hydrogenation reaction. Fig. 8 shows the FTIR pattern of the catalyst A-0 and A-0-U. It is observed that the content of the boron oxide entities undergoes a substantial increase upon reaction. Presumably, the catalyst undergoes a reduction in activity after being used once. The authors of this work have studied the effect of reaction on supported NiB catalysts in a separate work. Preliminary studies show that the catalysts undergo reduction in activity after several runs.

4. Conclusions

Low temperature ($T < 100\,^{\circ}C$) hydrogen treatment of nano-nickel boride catalysts is an efficient process for the enhancement of the PNP hydrogenation reaction rate. Based on FTIR analysis, it has been shown that hydrogen treatment enhances the dissolution of surface borate species into the ethanol medium and reduces partly the surface nickel oxide species.

It has been shown that mere treatment of the catalyst at $T < 100^{\circ}C$ in ethanol media not only does not enhance the catalyst activity, but also results in its deterioration (reduction of specific surface area and reactivity).

Mathematical simulation of the PNP reaction rate supports the hypothesis that the rate enhancement due to hydrogen treatment is mainly due to the increase of catalyst specific surface area.

This treatment may be performed at temperatures higher than 100 °C, but caution has to be taken to avoid loss of specific surface area due to the high sinter-ability of the nano-nickel boride catalyst.

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