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**MODELING AND SIMULATION OF AMORPHOUS NANO-NICKEL BORIDE BEHAVIOR IN THE REACTION OF HYDROGENATION OF P-NITROPHENOL****F.Taghavi<sup>a,b</sup>, C. Falamaki<sup>c</sup>, E.N.Aliyev<sup>a</sup>, M.M.Hasanova<sup>a</sup>, M.Bahrami<sup>b</sup>**

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*Hydrogenation of nitrophenol is an industrially important process for the manufacture of aminophenol. In this study, nickel borides were developed to accelerate the hydrogenation reaction of p-nitrophenol (PNP) a batch slurry reactor using ethanol as solvent. The synthesized catalyst has been characterized by FESEM, BET, XRD, ICP and FTIR techniques. The research revealed that it consists of aggregates of nano-Ni<sub>2</sub>B particles. The synthesized catalyst shows a better activity with respect to Raney nickel. The effect of reaction temperature (40-90 °C), PNP initial concentration (0.07-0.28 g mL<sup>-1</sup>) and hydrogen initial pressure (10-35 bar) on the kinetics of the hydrogenation reaction has been investigated. The activation energy of the hydrogenation reaction was calculated to be 42 kJ mol<sup>-1</sup>. A mathematical model (Hougen-Watson-type) based on a surface reaction controlling single-site mechanism has been developed that predicts reasonably the kinetic behavior of the catalyst. The new catalyst is a potential candidate for use in the industrial hydrogenation of PNP to PAP.*

**Keywords:** simulation, modeling, nickel boride, hydrogenation, aminophenol, nitrophenol, catalyst

**1. Introduction**

Recently, particular attention has been given to non-noble hydrogenation catalysts produced via metal salt reduction such as cobalt, cobalt boride, nickel boride and nickel cobalt boride [1-3]. Nickel and cobalt borides are among the most investigated catalysts. These compounds are gaining interest in the industrial production of H<sub>2</sub> from NaBH<sub>4</sub>. The present work aims to examine the performance of a nickel boride catalyst for the direct hydrogenation of PNP to PAP in a batch slurry reactor using ethanol as solvent. The synthesized catalyst has been characterized by FESEM, BET, XRD, ICP and FTIR techniques. The catalytic activity of the synthesized catalyst has been compared with a Raney nickel catalyst. The effect of reaction temperature, PNP initial concentration, hydrogen initial pressure on the kinetics of the hydrogenation reaction has been investigated. It is shown that an optimum reaction temperature exists. A mathematical model (Hougen-Watson-type) based on a surface reaction controlling single-site mechanism has

been developed that reasonably predicts the kinetic behavior of the catalyst.

To synthesize the nickel boride catalyst, 1.71 g NaBH<sub>4</sub> was dissolved in 25 mL 0.05 M aqueous NaOH solution. Then, solution of sodium borohydride in caustic soda was added drop-wise to 25 mL of an aqueous solution of NiCl<sub>2</sub> (0.3 M) at RT under adequate agitation. The formation of the black precipitate was accompanied with the release of hydrogen gas. The latter precipitate was first washed with de-ionized water and afterwards with ethanol. The final product was kept under ethanol prior to use in the catalytic experiments. For comparative means, a Raney nickel catalyst was also produced by methods reported in literatures [4]. The amounts of raw materials were chosen appropriately to obtain the same weight of final catalyst as in the case of nickel boride catalyst synthesis.

The catalytic hydrogenation of p-nitrophenol to p-aminophenol was carried out in a stainless steel autoclave equipped with a special shaker. The particles used for the

kinetic studies had been smaller than 50  $\mu\text{m}$ . Size comminuting was accomplished through wet milling of the product in ethanol media. The reactor was equipped with an external heating jacket (hot water circulation). A definite amount of catalyst was introduced to the reactor. Then, dry PNP (3.5 g) and ethanol as solvent (12.5 -50 ml) were added to the reactor. Afterwards, the reactor was purged

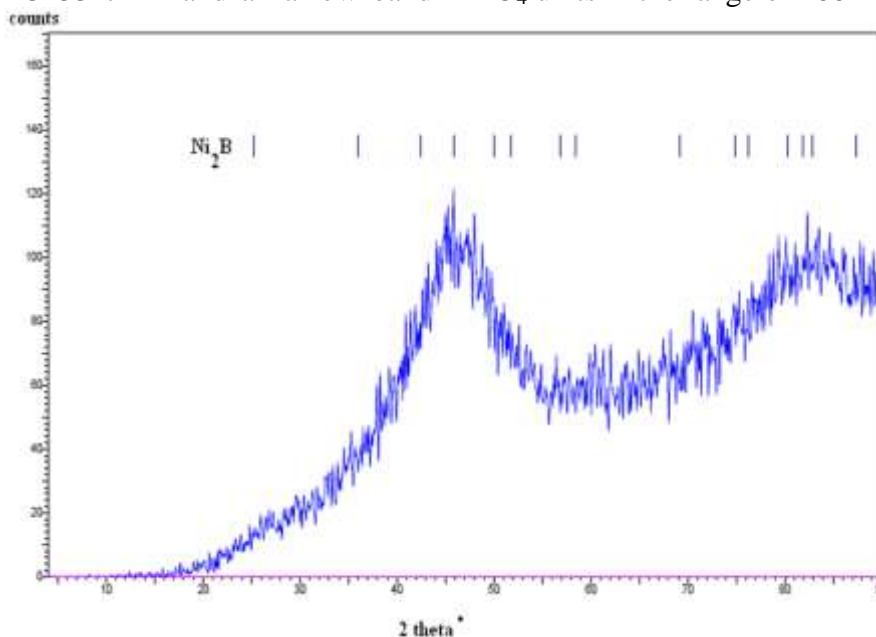
with a stream of nitrogen to remove air. The reactor was then heated to the reaction temperature (40-90  $^{\circ}\text{C}$ ). Shaking (14-55  $\text{turn min}^{-1}$ ) was commenced after reaching the reaction temperature. Immediately after hydrogen was fed to the reactor (10-35 bar). The pressure of the reactor was monitored throughout the reaction. There action time varied between 20 min to 3 h.

## 2. Results

The two weak main peaks as shown in XRD pictures (figure 1) may be identified as the strongest peaks of  $\text{Ni}_2\text{B}$ . It is observed that the particles are mostly amorphous. This finding is based on the chemical composition of the solid product obtained by ICP analysis. Chemical analysis showed that the stoichiometric composition may be written approximately as  $\text{Ni}_{1.85}\text{B}$ .

The FtIR spectra of the as synthesized catalyst are shown in figure 2. The catalysts show a broad absorption band centered in the range of 3421-3453  $\text{cm}^{-1}$  and a narrow band

centered around 1631-1634  $\text{cm}^{-1}$  corresponding to the hydrogen bonded O-H stretching and H-O-H bending vibrations, respectively in FTIR spectrum. Asymmetrical stretching vibration of  $\text{BO}_3$  units appear in the range 1411-1454  $\text{cm}^{-1}$  and 1266-1285  $\text{cm}^{-1}$ , symmetrical stretching vibration of  $\text{BO}_2$  units in the range of 1081-1100  $\text{cm}^{-1}$ , symmetrical stretching vibration of  $\text{BO}_3$  units at ca. 970  $\text{cm}^{-1}$ , bending vibration of  $\text{BO}_4$  units in the range of 631-670  $\text{cm}^{-1}$ , bending vibration of  $\text{BO}_3$  units at ca. 580  $\text{cm}^{-1}$  and bending vibrations of  $\text{BO}_4$  units in the range of 466-487  $\text{cm}^{-1}$ [5].



**Figure 1.** XRD picture of the of the as-synthesized catalyst particle.

System pressure variation versus reaction time as a function of temperature ( $\text{H}_2$  initial pressure = 25 bar, agitation speed = 46  $\text{turn min}^{-1}$ ) are shown in figure 3. For each of the initial PNP concentrations investigated, it is observed that the rate of hydrogen consumption increases in the temperature span of 40 to 80

$^{\circ}\text{C}$ . In the case of an initial concentration of 0.28  $\text{g mL}^{-1}$ , a reaction temperature of 90  $^{\circ}\text{C}$  was also investigated. It is observed that the reaction rate at 90 $^{\circ}\text{C}$  is substantially smaller than at 80  $^{\circ}\text{C}$ . This phenomenon may be attributed to a change of the reaction mechanism in the temperature range of 80 to

90 °C. In other words, it seems that an optimum reaction temperature may exist for a determined initial PNP concentration.

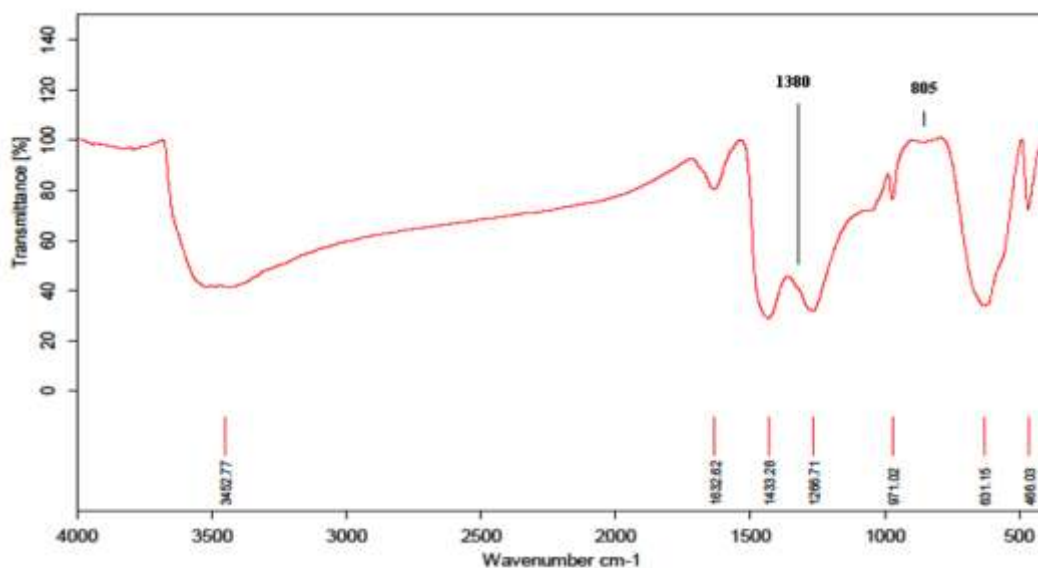


Figure 2. FTIR pattern of the as-synthesized catalyst particle.

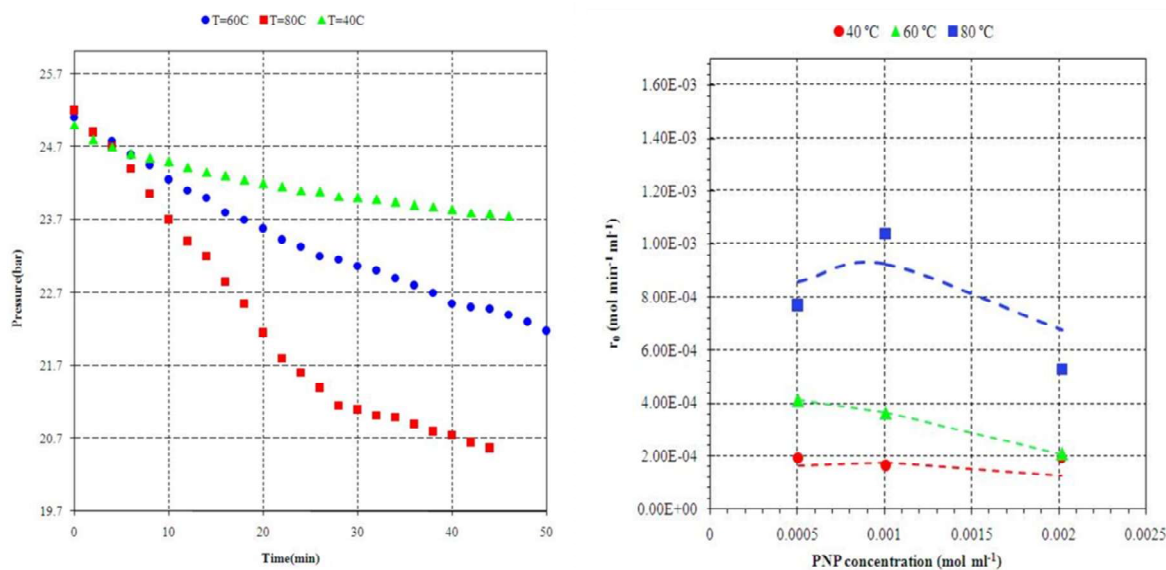


Figure 3. System pressure variation versus reaction time as a function of temperature ( $H_2$  initial pressure = 25 bar, agitation speed = 46 turn  $min^{-1}$ ). Dashed lines represent simulated data

As a final step, two experiments were performed to compare the activity of the nickel boride catalyst with respect to conventional Raney nickel. As mentioned in the experimental section, the same weight of catalyst was used for each experiment. The experiments were run at a temperature of 80 °C, PNP initial concentration of 0.14  $g mL^{-1}$  and initial hydrogen pressure of 40 bar. The time duration for complete conversion ( $> 99$

%) of PNP was measured to be 20 and 60 min for the nickel boride and Raney nickel catalysts, respectively. The  $Ni_2B$  catalyst showed a significant better performance. Such an enhancement in catalytic activity may be attributed to an increased electron density of the nickel atom due to boron electron donation [6] leading to a higher intrinsic activity [7]. We considered a single-site mechanisms with PNP adsorption (1),  $H_2$  adsorption (2) and

surface reaction (3) as controlling steps for the PNP hydrogenation to PAP reaction as follows:

$$r_0 = \frac{k_3 K_{PNP} K_{H_2}^3 C_{PNP} C_{H_2}^3}{(1 + K_{PNP} C_{PNP} + K_{H_2} C_{H_2})^4}$$

### 3. Conclusions

Micro-aggregates (< 50 μm) of nano-Ni<sub>2</sub>B particles have been successfully used for the hydrogenation of PNP to PAP in a batch slurry reactor. The catalyst exhibits an increasing activity in the temperature range of 40-80 °C. At a temperature of 90 °C, the activity is subject to substantial decrease, presumably due to a change in reaction mechanism. In addition, it has been observed that for an initial pressure of 25 bar and reaction temperature of 80 °C, an optimum PNP concentration exists. The activation

This model gave the best match between the data and simulated curves as shown above.

energy in the temperature range of 40-80 °C had been calculated to be 42 kJ mol<sup>-1</sup>.

The reaction kinetics could be reasonably predicted using a Hougen-Watson model based on a surface reaction controlling step. The model covers the following range of operating parameters: reaction temperature of 40-80 °C, initial H<sub>2</sub> pressure of 10-35 bar and initial PNP concentration of 0.07-0.28 g mL<sup>-1</sup>. The nickel boride catalyst synthesized in this work shows a better performance in comparison with Raney nickel.

### Acknowledgements

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### **МОДЕЛИРОВАНИЕ И ВОСПРОИЗВЕДЕНИЕ ПОВЕДЕНИЯ АМОРФНОГО НАНО-НИКЕЛЬ-БОРИДА В РЕАКЦИИ ГИДРИРОВАНИЯ П-НИТРОФЕНОЛА**

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Гидрогенизация *p*-нитрофенола (ПНФ) является важным промышленным процессом при производстве *p*-аминофенола (ПАФ). В рамках настоящего исследования был получен никель-борид, предназначенный для ускорения реакции гидрогенизации *p*-нитрофенола. Синтезированный катализатор был исследован с помощью физико-химических методов анализа – ИКС, БЭТ, FESEM, BET, XRD, ICP и FTIR. Показано, что он состоит из совокупности наночастиц  $Ni_2B$ . Испытания проводили в суспензионном реакторе периодического действия, используя этанол в качестве растворителя. Синтезированный катализатор продемонстрировал более высокую активность по сравнению с никелем Ренея. Было исследовано влияние температуры реакции (40-90 °C), начальной концентрации ПНФ (0.07-0.28 г мл<sup>-1</sup>), а также начального давления водорода (10-35 бар) на кинетику реакции гидрогенизации. Расчеты показали, что энергия активации реакции гидрогенизации составила 42 кДж моль<sup>-1</sup>. Разработана математическая модель (типа Хюгенса-Ватсона), с помощью которой представляется возможным прогнозировать кинетическое поведение катализатора. Новый катализатор потенциально может быть применен в промышленной гидрогенизации ПНФ в ПАФ.

**Ключевые слова:** воспроизведение, моделирование, никель-борид, гидрогенизация, аминофенол, нитрофенол, катализатор.

### **P-NİTROFENOLUN HİDROGENLƏŞMƏ REAKSİYASINDA AMORF NANO-NİKELBORİDİN DAVRANIŞININ MODELƏŞDİRİLMƏSİ**

**Firuzeh Taghavi, Kavus Falamaki, E.N. Əliyev, M.M. Həsənova, Mohammad Bahrami**

İşdə *p*-nitrofenolun birbaşa hidrogenləşərək *p*-aminofenola çevrilməsi prosesində nikelborid katalizatorundan istifadə olunmasından bəhs olunur. Temperaturun (40-90°C), *p*-nitrofenolun başlanğıc qatılığının (0.07-0.28 q/ ml<sup>-1</sup>), hidrogenin başlanğıc təzyiqinin (10-35 bar) hidrogenləşmə reaksiyasının kinetikasına təsiri öyrənilmişdir. Reaksiyanın riyazi modeli işlənilib hazırlanmışdır.

**Açar sözlər:** modelləşdirmə, nikel borid, hidrogenləşmə, aminofenol, nitrofenol, katalizator.

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