

UDC 547. 572

EFFECT OF HYDROGEN TREATMENT OF NANO-NICKEL BORIDE ON DIRECT HYDROGENATION OF P-NITROPHENOL**Firouzeh Taghavi^{a,b}, B.T. Usubaliyeva, Z.O. Gahramanova^a, M.M. Hasanova^a**

^a Research institute of Geo-technological problems of oil, gas and chemistry, Azerbaijan State Oil Academy, Baku, Azerbaijan E-mail: a.shabanov_36@mail.ru

^b Research and Development Department, Chlor Pars Co., P.O. Box 51335-1717, Tabriz, Iran

The amorphous alloy nanoparticles have gained increasing attention as novel catalytic materials with the unique isotropic structure and high concentration of respectively unsaturated sites leading to catalytic activity and selectivity superior to their crystalline counterparts. In this study, hydrogen treated nickel boride was developed to accelerate the direct hydrogenation reaction of p-nitrophenol. It was found that p-nitrophenol could reduce in the presence of nanonickel boride catalyst. The characteristics and properties of Ni-B catalysts proved to be very sensitive to their treatment conditions. The catalytic activity of nickel boride was strongly dependent on the temperature and pressure during its treatment with hydrogen and effect rate of hydrogenation of p-nitrophenol; the temperature affected the characteristic of nano-nickel boride. Complete conversion of the nitro compound to amino compound was achieved and approved by Gas Chromatograph.

Keywords: hydrogenation, borohydride, amino phenol, catalyst, hydrogen treatment, nitrophenol, nickel boride.

1. INTRODUCTION

Nickel boride nanocatalysts have gained increasing interest as novel catalytic materials in hydrogenation reactions. The high concentration of coordinating unsaturated active sites in these amorphous alloy nanoparticles donates them higher activity and selectivity with respect to their crystalline counterparts.

The hydrogenation of p-nitrophenol (PNP) to p-aminophenol (PAP) using nickel boride nano-catalysts has caused much attention in the last years [1-5]. Taghavi et al. [6] recently published a thorough study on the synthesis and characterization of Ni₂B nano-catalyst and their catalytic behavior for the PNP direct hydrogenation to PAP in a batch slurry reactor. The aim of the latter work was to present an optimal synthesis procedure and operational conditions for obtaining a catalyst with maximum activity. As a continuation of this research, we were strongly interested in developing a catalyst 'pretreatment' procedure with the aim of increasing the further catalyst activity. Survey of the related literature shows that many attempts had been performed in the

'hydrogen pretreatment' of nickel boride catalysts, however at temperature higher than 250 °C and in absence of an organic liquid like ethanol [7-11]. Li et al. [7] treated the Ni-B/ γ -Al₂O₃ with hydrogen in the temperatures ranging between 300- 800 K. It revealed that such a treatment results in the crystallization of the initial amorphous phase and the creation of extra phases such as metallic nickel. No catalytic behavior of the treated catalyst has been studied.

Li et al. [8] treated the Ni-B/SiO₂ under nitrogen atmosphere in the temperature range of 523-973 K for 4 h. The final catalysts showed very low activity in glucose hydrogenation when compared with the original sample due to particle growth and creation of new phases like Ni, Ni₃B and Ni₂B.

Wang et al. [9] obtained similar results pretreating Ni-B catalyst under hydrogen at elevated temperatures.

Chen et al. [10] treated a Ni-B/SiO₂ catalyst at 673 K for 2 hour and observed a clear reduction of activity for the hydro-dechlorination of chlorobenzene.

Wen et al. [11] annealed a Ni-B/SiO₂ catalyst under H₂ atmosphere in the temperatures ranging between 250-300 °C. All the treated catalysts had a lower activity in comparison with the original amorphous sample.

All these pre-treatment resulted in the sharp decrease of activity due to two main reasons: a) Loss of specific surface area due to the high sinter-activity of the original nanometal boride and b) crystallization of the highly active 'amorphous' initial alloy and eventually production of extra phases like Ni

and Ni_xB_y. We were astonished to reveal that low temperature (T<100 °C) hydrogen treatment of the as-synthesized catalyst in the presence of ethanol (the solvent used for the PNP direct hydrogenation to PAP) may induce a substantial increase of its activity. Such a phenomenon is new for this class of metal boride catalysts and has not been reported so far in open literature. The present work aims at studying the effect of low temperature hydrogen treatment in detail and elucidation of the activity enhancement mechanism behind.

2. EXPERIMENTAL DETAILS

High purity hydrogen (99.999 % w/w) was from Chlor Pars Company. Caustic soda and main starting materials such as sodium borohydride and nickel chloride was prepared from Merck. Ethanol was purchased from Nasr Company.

Nano-sized Ni-B metal catalysts were prepared by a chemical reaction method using sodium borohydride. Nickel chloride was used as the precursor. An aqueous solution of nickel chloride (25 ml, 0.3 M) was prepared. A NaBH₄ solution was used as a reducing agent. Briefly, 25 ml of 1.8 M NaBH₄ solution containing 0.05 M NaOH was added drop wise into 25 ml of aqueous solution of NiCl₂ under vigorous stirring, and the black precipitate was

formed. To ensure full reduction of nickel, excess amount of NaBH₄ in a molecular ratio of 3:1 was used. The black precipitate was washed thoroughly with a large amount of distilled water, and soaked in distilled water to remove the soluble boron species and Na⁺ ions which may act as a poison for nickel then washed with ethanol and finally it was stored in EtOH until use.

The synthesized catalyst and 25 ml ethanol was charged into the 400 ml stainless steel autoclave, hydrogenated under hydrogen at pressure (2.5-4 MPa) and temperature (40-60 °C). The pressure of hydrogen was decreased to 24 bars during 35 min.

3. ACTIVITY TEST

The hydrogen treated catalysts were tested for the liquid-phase hydrogenation of p-nitrophenol to p-aminophenol. A newly prepared catalyst was used in each reaction run. The hydrogenation reaction was carried out in a 600 ml stainless steel autoclave containing catalyst, 3.5 g of P-nitro phenol and 25 ml of ethanol as the solvent. A special shaker was placed for effective agitation, and the agitator was connected to an electric motor

with variable speed up to 55 rpm. A pressure gage and an automatic temperature controller were also provided. The gases were supplied from cylinders and introduced to the reactor. When the desired reaction temperature, 60°C, was achieved, the H₂ pressure was adjusted to 2.5MPa and the stirring was commenced and fixed at 46 rpm. The H₂ uptake was monitored by a pressure gage installed on the hydrogen inlet line.

4. RESULTS AND DISCUSSIONS

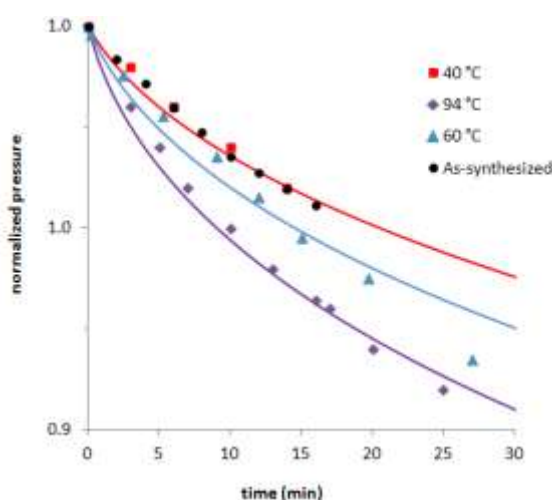
Based on the p-nitrophenol hydrogenation reaction mechanism as suggested in our previous work [Taghavi et. al], the reaction rate involves a single site

mechanism with automatically adsorbed hydrogen and p-nitrophenol adsorption as the controlling step. Accordingly, the reaction rate may be derived as:

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

Based on the constants obtained by Tagahavi et al. [6], we tried to fit the kinetic data pertaining to the hydrogen temperature 40, 60, 94 °C (2.5 MPa initial pressure). The simulated data have been shown as bold units in figure. A reasonable agreement between experimental and simulated data exists. It is observed that the kinetic data could be fitted simply by changing properly the reaction rate constant of the hydrogenation reaction, the

other factors remaining the same. This is theoretically explainable as hydrogen treatment actually increases the 'specific surface area' of the catalyst. This phenomenon, by itself, cannot change the thermodynamic constant K_{H_2} , K_{PAP} and K_W , which depend only on the nature of the moieties and their concentration. Instead, the reaction rate k_1 depends directly on the reciprocal of the surface area and should increase with the increase of the available surface.



Pressure variation as a function of reaction time and hydrogen treatment temperature.
Bold lines represent the simulated data.

5. CONCLUSION

Low temperature ($T < 100$ °C) hydrogen treatment of nano-nickel boride catalysts is an efficient process for the enhancement of the PNP hydrogenation reaction rate. The higher the treatment temperature, the more the hydrogenation reaction rate is enhanced. This treatment may be performed at temperature 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.

The treatment has been shown to increase the hydrophobicity of the catalyst surface. The rate enhancement has been shown mathematically through the simulation of the pressure/time diagram during the p-nitrophenol hydrogenation reaction to be the result of 'specific surface area' increase due to hydrogen treatment.

In all probability, there is an optimum pressure for treatment temperature of 94 °C.

Acknowledgements

The authors would like to thank Chlor Pars Co. for financially supporting this research.

REFERENCE

1. Y.Du, H. Chen, R. Chen, N. Xu. Synthesis of p-aminophenol from p-nitrophenol over nano-sized nickel catalysts. // Appl. Catal. A: General. 277(2004). 259-264.
2. H.Wen, K.Yao, Y.Zhang, Z.Zhou, A.Kirschning. Catalytic transfer hydrogenation of aromatic nitro compounds in presence of polymer-supported nano-amorphous Ni-B catalyst. // Catal. Comm 10(2009). 1207-1211.
3. A.Rahman, S.B.Jonnalagadda. Swift and Selective Reduction of Nitroaromatics to Aromatic Amines with Ni-Boride-Silica Catalysts System at Low Temperature. // Catal. Lett., 123(2008). 264-268.
4. H.Liu, J.Deng, W.Li. Synthesis of Nickel Nanoparticles Supported on Boehmite for Selective Hydrogenation of p-Nitrophenol and p-Chloronitrobenzene. // Catal. Lett., 137(2010). 261-266.
5. V.R.Choudhary, M.G.Sane, S.S.Tambe. Kinetics of Hydrogenation of o-Nitrophenol to o-Aminophenol on Pd/Carbon Catalysts in a Stirred Three-Phase Slurry Reactor. // Ind. & Eng. Chem. Res., 37 (1998). 3879-3887.
6. F.Taghavi, C.Falamaki, A.Shabanov et al. Kinetic study of the hydrogenation of p-nitrophenol to p-aminophenol over micro-aggregates of nano-Ni₂B catalyst particles. // Applied catalysis A: General. 407 (2011). 173-180.
7. J.Li, M.Qiao, J.Deng. Amorphous Ni-B/ γ -Al₂O₃ catalyst prepared in a modified drying approach and its excellent activity in benzene hydrogenation. // Journal of Molecular Catalysis A: Chemical. 169(2001). 295-301.
8. H.Li, H.Li, J.-F. Deng. Glucose hydrogenation over Ni-B/SiO₂ amorphous alloy catalyst and the promoting effect of metal dopants. // Catalysis Today 74(2002). 53-63.
9. M.Wang, H.Li, Y.Wu, J. Zhang. Comparative studies on the catalytic behaviors between the Ni-B amorphous alloy and other Ni-based catalysts during liquid phase hydrogenation of acetonitrile to ethylamine. // Materials Letters. 57(2003). 2954-2964.
10. X.Y.Chen, S.Wang, J.H.Zhuang, M.H.Qiao et al. Mesoporous silica-supported NiB amorphous alloy catalysts for selective hydrogenation of 2-ethylanthraquinone. // J. Catal, 227(2004). 419-427.

***p*-NİTROFENOLUN BİRBAŞA HİDROGENLƏŞMƏSİNDƏ NANO-NİKELBORİDİN
HİDROGENLƏ İŞLƏNMƏSİNİN SƏMƏRƏLİLİYİ**

Firuzeh Taghavi, B.T.Usubəliyev, Z.O.Qəhrəmanova, M.M.Həsənova

Amorf xəlitəli nanohissəciklər özlərinin unikal izotrop quruluşları ilə yeni katalitik materiallar kimi böyük maraq doğurur. Bu tədqiqat işində nikelboridin hidrogenləşlənməsi p-nitrofenolun birbaşa hidrogenləşməsini sürətləndirmək məqsədilə aparılmışdır. Öyrənilmişdir ki, p-nitrofenol nanonikelborid katalizatoru iştirakında reduksiya olunna bilər, iş şəraitində nikelborid katalizatorunun xassələri yüksək həssaslıq göstərirlər. Nikelborid katalizatorunun aktivliyi bütün hidridləşmə prosesi müddətində temperatur və təzyiqdən ciddi şəkildə asılı olur. Nitrobirləşmənin tam konversiyası qaz xromatoqrafiyası metodu ilə də təsdiqlənmişdir. Açar sözlər: hidrogenləşmə, borhidrid, aminofenol, kataliz, nitrofenolun hidrogenləşlənməsi, nitrofenol, nikel borid.

ЭФФЕКТ ВОДОРОДНОЙ ОБРАБОТКИ НАНО-НИКЕЛЬБОРИДА ПРИ ПРЯМОМ ГИДРИРОВАНИИ П-НИТРОФЕНОЛА

Фирузех Тагхави, Б.Т.Усубалиев, З.О.Гахраманова, М.М.Гасанова

Наночастицы аморфного сплава представляют большой интерес как новый каталитический материал с уникальной изотропной структурой. В этом исследовании проводилась водородная обработка никельборида для ускорения прямого гидрирования п-нитрофенола. Было найдено, что п-нитрофенол может восстанавливаться в присутствии нано-никельборидного катализатора, характеристики и свойства никельборидного катализатора были чувствительны к условиям их обработки. Каталитическая активность никельборида находилась в строгой зависимости от температуры и давления в течение всего процесса гидрирования. Полная конверсия нитросоединений была доказана методом газовой хроматографии.

Ключевые слова: гидрирование, боргидрид, аминофенол, катализ, водородная обработка нитрофенола, никельборид.

Redaksiyaya daxil olub 13.04.2012