Hydrogenation of Nitrobenzene in Trickle Bed Reactor over Ni/Sio$_2$ Catalyst

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ABSTRACT

Trickle bed reactor was used to study the hydrogenation of nitrobenzene over Ni/SiO$_2$ catalyst. The catalyst was prepared using the Highly Dispersed Catalyst (HDC) technique. Porous silica particles (capped cylinders, 6x5.5 mm) were used as catalyst support. The catalyst was characterized by TPR, BET surface area and pore volume, X-ray diffraction, and Raman Spectra. The trickle bed reactor was packed with catalyst and diluted with fine glass beads in order to decrease the external effects such as mass transfer, heat transfer and wall effect. The catalyst bed dilution was found to double the liquid holdup, which increased the catalyst wetting and hence, the gas-liquid mass transfer rate. The main product of the hydrogenation reaction of nitrobenzene was aniline. Reaction operating conditions, i.e., temperature, liquid flow rate, and initial feed concentration were investigated to find their influences on the conversion and rate of nitrobenzene hydrogenation. Under normal conditions without bed dilution, the system was mass transfer controlled. In the diluted reactor, on the other hand, the resistance of mass transfer was nearly absent and the system became under surface kinetic control. The catalyst showed significant deactivation during the reaction period due to the adsorption of intermediate amine products on the surface of the catalyst. The kinetic study revealed that the reaction is zero order with respect to nitrobenzene concentration for the range of concentration between 0.58 to 1.17 mol/L while it was of positive order for the initial concentration less than 0.58 mol/L.

KEY WORDS: **Hydrogenation, Trickle Bed, Nitrobenzene, Bed Dilution, Highly Dispersed Catalyst**

هدرجة النتروبنزين في مفاعل سيحي باستخدام النيكل/سيليكا كعامل مساعد

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الخلاصة

تم استخدام المفاعل السيحي لدراسة عملية هدرجة النتروبنزين على العامل المساعد نيكل/سيليكا. تم تحضير العامل المساعد باستخدام تكنيك الـ HDC. تم استعمال حبيبات السيليكا المسامية (شكل اسطواني 5.5x6) كمادة حاملة للعامل المساعد. تم ايجاد خواص العامل المساعد المحضر بفحص TPR و طريقة BET للمساحه السطحية و حجوم المسامات و التحليل الطيفي بطريقة انكسار اشعة اكس و كذلك التحليل الطيفي بجهاز رامان. تم شحن المفاعل بالعامل المساعد المخفف بكرات الزجاج الدقيقة و ذلك لخفض التأثيرات الخارجية كانتقال المادة و انتقال الحرارة و تأثير الجدار. و قد وجد ان استخدام الحبيبات الدقيقة مع العامل المساعد في المفاعل قد ادى الى مضاعفة محتوى السائل في المفاعل و الذي أدى بدوره الى زيادة درجة تبلل العامل المساعد و بالتالي زيادة معدل انتقال المادة للسائل و الغاز. كان المنتج الرئيسي من تفاعل هدرجة

النترو بنزين هو الانيلين. تم ايجاد تأثير كل من الحرارة و معدل جريان السائل و التكيز الابتدائي للنتروبنزين على مقدار التحول للنتروبنزين و كذلك على سرعة التفاعل. في الظروف الطبيعية و بدون استخدام التخفيف بحبيبات الزجاج كان النظام تحت تأثير انتقال المادة. من جهه اخرى كانت مقاومة انتقال المادة في المفاعل المخفف بحبيبات الزجاج غائبة تقريبا و النظام تحت سيطرة التفاعل السطحي. كما لوحظ ان العامل المساعد يفقد فعاليته خلال فترة التفاعل بسبب بسبب امدصاص المواد الناتجه على السطح. بينت الدراسة ان تفاعل هدرجة النتروبنزين من الدرجه الصفر نسبة الى تركيز النتروبنزين في مدى التراكيز من 0.58 الى 1.17 مول/لتر بينما تصبح درجة التفاعل موجبة لمدى التراكيز اقل من 0.58 مول/لتر.

- **الكلمات الرئيسية: هدرجة، مفاعل سيحي، نتروبنزين، عمود مخفف، عامل مساعد كثيف التوزيع**

1. INTRODUCTION

The catalytic hydrogenation of substituted aromatic compounds in the liquid phase is important in many processes and industries. Hydrogenation of nitrobenzene is used to produce aniline which is one of the most important chemicals and intermediates in the production of pharmaceuticals, dyes, pigments, and pesticides (Wang, et al., 2010). The majority of the reactors used to carry out this process are batch stirred reactors due to their simplicity and flexibility especially when used for small scale production. For the large scale production of some specific chemicals such as that used in fine chemicals industry, the trickle bed reactor is one of the suitable options due to its better selectivity control of the desired product, with no moving parts, and no need for the catalyst filtration (Hindle, et al, 2008). On the other hand, batch reactors can be effectively used to measure the kinetics with stable catalytic activity which is not affected by heat or mass transfer and axial dispersion. However, when the activity of catalyst gradually changes, the reaction process and the catalyst deactivation cannot be separated in batch-wise experiments. In such a case, trickle bed flow-type reactors are widely used for the kinetic measurements (Hiroshi, et al., 1999).

The problem with using trickle bed reactor for investigating the kinetics of reaction is that the superficial velocities in the lab-scale trickle bed reactor (TBR) are considerably lower than that of the industrial scale TBR, although the space velocities are in the same order which results in reduced catalyst wetting. Furthermore, the lab-scale TBR suffered of wall effect due to the small value of the bed to catalyst pellets ratio which gives rise to incorrect kinetic data. This problem can be resolved by diluting the catalyst bed with fine inert particles. The dilution reduces axial dispersion substantially to the extent where plug flow can be established and much higher liquid hold-up improves the wetting contact efficiency at lower velocities of gas and liquid.

In the present work, the hydrogenation of nitrobenzene was carried out over Ni/SiO_2 catalyst in a trickle bed reactor. In this process, the aromatic nitro-group is reacted with three mole equivalents of hydrogen gas, in the presence of the catalyst, to produce the amine and water. This hydrogenation is usually carried out under relatively mild conditions and produces a low level of by-products and impurities (Qing, et al., 1997). The hydrogenation of nitrobenzene occurs rapidly over most metals and is often employed as a reference reaction to compare the activity of other hydrogenation catalysts and of new reactor systems (Hatziantoniou, et al., 1986).

Thermodynamically, the nitro group is one of the most easily performed of all functional group hydrogenations (Augustine, et al., 1976). The following thermodynamic data were evaluated for the hydrogenation of the nitrobenzene; the apparent activation energy is in the range of 12-104 kJ/mol, the estimated value of the equilibrium constant is about 1600 at standard temperature and pressure and indicates that reaction may be considered totally irreversible for all practical purposes. The reaction is exothermic with heat of reaction of 500 kJ/mol (Gelder, 2005). This means that dissipation of the exothermic heat of the reaction is very important in controlling the temperature during the hydrogenation reaction.

There have been many studies on the kinetics of the hydrogenation of nitrobenzene (Gelder, 2005, Holler, 2000), the majority of which were in the liquid phase carried out in batch-type reactors with a variety of kinetic proposals have been put forward. As expected from a hydrogenation reaction, a first order dependence on hydrogen concentration was widely reported. On the other hand, wide variations in the reaction order with respect to the nitrobenzene concentration have been reported in literature (Hatziantoniou, et al., 1986, Li, et al., 1994, Collins, et al., 1982). Like the hydrogen order, the value for nitrobenzene appears to be influenced by a high number of factors. Zero order reactions with respect to nitrobenzene, at different initial concentrations of nitrobenzene have been reported. (mostly greater than 0.1 mol/L). Holler, et al., 2000 stated a zero order reaction dependence at high nitrobenzene concentrations (greater than 0.1 mol/L), whereas, a first order reaction dependence when the nitrobenzene concentration was low. Conversly, Metcalfe and Rowden found that at concentrations below 0.15 mol/L the reaction proceeded with a zero oder dependence on the nitrobenzene concentration (Metcalfe, et al., 1971). As with hydrogen, the order of reaction with respect to nitrobenzene is variable and appears to be sensitive to the specfic reaction conditions.

In the present work, it was aimed to study the performance of the trickle bed reactor when used for hydrogenation of nitrobenzene. The reactor bed dilution with fine inert particles was studied as a technique that can increase the liquid hold up in the bed which will has a useful effect in increasing the wetting efficiency of the catalyst particles in this type of reactors which are normally working at low liquid velocities. Nickel catalyst supported on silica particles were synthesised using HDC (Highly Dispersed Catalyst) preparation technique (Nele, et al, 1999, Martin Lok, et al., 2004). In the HDC method, the metals are precipitated from solution (precursor) onto the support in a similar way to the deposition-precipitation methods. The conversion of nitrobenzene, the effect of mass transfer, and kinetics of the hydrogenation reaction were studied.

2. EXPERIMENTAL WORK

2.1 Preparation of nickel catalyst by HDC technique

The first step in preparation Ni/SiO$_2$ catalyst was the preparation of nickel hexamine solution. All materials, the ammonium carbonate chip, nickel hydroxy carbonate were purchased from Aldrich. The demineralised water was obtained from an internal supply. Calculated amounts of ammonia solution, water, ammonium carbonate chips and nickel hydroxycarbonate were used to prepare 2.5% of the hexamine solution. 25% ammonia solution (Sigma-Aldrich) was added to demineralised water in a 5 L conical flask with constant stirring by a magnetic stirrer. Ammonium carbonate chips were added to the solution with stirring. The solution was left until all the ammonium carbonate chips were dissolved. A certain amount of nickel hydroxyl carbonate (BDH) were divided into small portions, each portion was added to the above solution with constant mixing. After each addition, the solution was left for 45 minutes at constant stirring. The reaction was considered to complete when the solution colour changed from green to blue. When all carbonate dissolved, the solution was left overnight under constant stirring, and then filtered. The reaction of HDC catalyst preparation is:

$$NiCO_3 + 6NH_3(aq) \rightarrow [Ni(NH_3)_6]^{+2} + CO_3^{-2}$$

Green Blue

Calculated amount of the prepared hexamine solution was used with AEROSIL-200 silica pellets (capped cylinders of 6 x 5.5 mm dimensions) manufactured by Degussa, to prepare Ni catalyst of approximately 20% loading of nickel. The preparation was carried out in a 5 L rotating flask device (BÜCHI Rotavapor R-114) equipped with water condenser and connected to vacuum device (BÜCHI Vac V-511). The solution and support were put together in the flask. The flask with its content was allowed to rotate inside a controlled-temperature water bath (BÜCHI Water bath B-480) at a rate of 250 rpm. The temperature was set at 30 ^{o}C to let slow evaporation under vacuum. The reaction mixture was refluxed until all ammonia had been distilled off and metal deposition on silica was complete. This was visible by the change in the colour of the solution from blue to green. The pH of the reaction mixture was monitored throughout the course of the reaction and following full deposition using a pH meter (Hanna Instrument-USA). The pH value decreased from 10.5 at the beginning of the process to 7.8 at the end. Reflux was continued for 15 minutes to age the reaction mixture. The product solution with coloured silica pellets was filtered via Buckner flask and washed with demineralised water many times, left for 30 minutes in air and then put in an oven with 110 ^{o}C temperature overnight to dry the catalyst pellets.

2.2 Characterisation of the catalyst

Temperature programmed reduction (TPR) of the newly synthesised HDC catalyst was performed to find the most efficient reduction conditions. This was measured using 0.1 g of catalyst in a Quantachrome Corporation TPR/TPD with 5% H_2 in N_2 as a reducing gas mixture and a linear heating rate of 5 deg/min over a temperature range of 293 to 1373 K.

The BET surface area and the pore volume of the prepared catalyst were measured in a Micromeritics ASAP 2400 gas adsorption analyser. The catalyst was outgased at 413 K in flowing nitrogen for one hour prior to the nitrogen absorption experiment at 77 K. Nitrogen adsorption and desorption isotherms were collected and used to derive the BET surface area, which quantifies the entire surface area of the catalyst, including the metal and the porous support material. The pore volume of each catalyst was also measured using a relative pressure of 0.98 on the desorption branch. The average pore diameter was also calculated using this method. **Table 1** shows the measurement results.

The UV-Vis Spectra analysis of the silica-supported catalyst was performed using a Varian Cary 500 scan UV-Vis-NIR spectrophotometer. Samples were run over a 200-1000 nm range with a scan rate of 200 nm/min and a resolution of 2 nm. Catalyst sample were ground for the suitability of the analysis.

Raman spectra analysis was performed on a LABRAM HR Raman spectrophotometer (HORIBA JOBIN YVON) using a green laser (532 nm, solid state, 10 mW). A range of 0-4000 cm^{-1} was taken for the sample.

To investigate the crystallographic properties of the catalyst, X-ray diffraction (XRD) spectra of the catalyst were performed in a SIEMENS D 5000 X-ray diffractometer. Diffraction data were recorded using a continuous scanning starting at 5^{o} and ending at 85^{o} at a rate of 0.02°/s and a step of 0.02°.

2.3 Trickle bed reactor

The trickle bed reactor was a glass tube of 2.2 cm inner diameter and 35 cm height. The liquid was pumped to the reactor where a shower head distributor (6 tubes,1 mm inner diameter each) was employed at the exit of the fluid stream allowing a more dispersed fluid distribution over the catalyst. The liquid flow rate was controlled by HPLC pump (Gilson-307, flow rate 0-10 cm^3/min). The gas flow rate was controlled by a mass flow controller (Brooks, Model 5850, maximum pressure 100 bar, flow rate 0-100 cm^3/min) connected to a gas flow monitor (BROSE, Model 5878). Hydrogen and nitrogen were both available as gas feed when required. The bed temperature was controlled using a hollow cylindrical furnace (WATLOW 425 W) fitted around the reactor wall and connected to a temperature controller (WEST 4400), accuracy ±1 K. Two thermocouples were used; the first was fitted inside the catalytic bed through a specially designed capillary glass tube, while the other thermocouple was fitted at the outside of the reactor wall at half length of the catalyst bed. **Fig. 1** shows the experimental rig of the hydrogenation experiments.

2.4 Experimental procedure

Hydrodynamic experiments were carried out at first to investigate the effect of diluting the catalytic bed on the liquid holdup in the bed. Glass beads (0.5-1.0 mm diameter) were used as fine particles. The void fractions were found by a measuring cylinder. The value of void fraction was 0.45 for the packed bed with coarse silica particles and 0.23 for the packed bed diluted with fines. Therefore, the void fraction in the diluted bed was nearly half of that in the undiluted bed. The packing technique of Al-Dahhan et al., 1995, was adopted for diluting the catalytic bed. 10 g of silica particles (catalyst support) were divided into 5 portions. The first portion of the coarse particles was loaded to the reactor with vibration. Then, fine glass bead particles were loaded gently with vibrating until the fine particles covered the top layer of coarse particles. This procedure was repeated for all portions. Liquid hold up was measured by quick closing of valves. Decalin solvent and nitrogen gas were used as liquid and gas, respectively. The gas and liquid were let to flow to the reactor and after the steady state conditions were achieved, the inlet and outlet valves were quickly closed. Then, the volume of liquid drained from the reactor was measured. Experiments were carried at room temperature and atmospheric pressure and for different values of liquid flow rate.

The hydrogenation of nitrobenzene experiments were carried out at different temperatures, liquid flow rates, and nitrobenzene feed concentrations. **Table 2** shows the values of the experimental variables used in hydrogenation experiments. 10 g of catalyst was packed with glass beads in the bed. The catalyst was reduced in a flow of 15 cm^3/min of hydrogen gas according to the appropriate heating program pre-determined TPR data. The temperature ramped from 303 K to 723 K at a rate of 2K/min, holding at this temperature for 8 h, and then decreased to the required reaction temperature. The catalyst was then treated in hydrogen at a flow rate of 20 cm^3/min at room temperature for 30 minutes. The hydrogen flow was then set to the required value and a flow of methanol solvent (2 cm^3/min) was introduced for 10 minutes to wet the catalyst bed before the flow was switched to the feed solution of nitrobenzene in methanol at the required flow rate. After the steady state condition was achieved, samples (2.5 cm^3) were collected and analysed.

The analysis of samples were performed using gas chromatography (FOCUS GC-Thermo Finnigan) fitted with a VF-5ms, 25 m capillary column. Throughout all sample analysis, the GC operating conditions were held constant. The injector temperature was set at 513 K. The column oven was initially kept at 353 K and was ramped to 493 K at a rate of 15 K/min and then held at 493 K for 10 minutes. Calibrations were carried out for nitrobenzene, aniline, and nitrozobenzene. Standard solutions for each of the components were made-up and a series of dilutions performed to obtain a series of solutions of known concentration.

3. RESULTS AND DISCUSSION

3.1 Change of pH during HDC catalyst preparation

The pH of the metal solutions was monitored throughout preparation of the HDC catalyst. The depositions were carried out under high pH conditions to facilitate a strong interaction between the positive nickel metal ions and the negatively charged alumina support material. **Figure 2** shows how the pH altered during preparation of the catalyst. The pH decreased fairly rapidly over the first 0-30 minutes of the deposition process as the ammonia was distilled off and then levelled off during the rest of the procedure after complete removal of the ammonia had occurred.

Although the HDC method of catalyst preparation has been used extensively in industry to prepare a range of commercial products, the majority of research into the technique and resultant catalysts has focused upon the precipitation of one metal ion from solution. The pH profile measured during synthesis of the catalyst (**Fig. 2**) showed a decrease in pH throughout reaction and was found to stabilize between at 8.5-7.7 indicating that ammonia was being totally removed from solution by the distillation process and was not retained by the metal used.

3.2 Catalyst characterization

The Temperature Programmed Reduction profile of the catalyst was measured. The results showed that the initial and final temperatures were 360 ^{o}C and 880 ^{o}C respectively. The profile displayed one main reduction peak at 530 ^{o}C. This has been attributed to the reduction of the metal +2 ion down to the zero valent state, which is consistent with previous findings on similar catalyst systems published in the literature (Hoffer, et al., 2000).

Elemental weight analysis of the HDC catalyst was employed to confirm that the preparation had been performed successfully and that the precipitated metals were present in the intended quantities. The estimated nickel loaded on the silica support was 18.2%.

XRD tests showed that all the unreduced catalyst is amorphous and the reduced catalysts gave poorly crystalline nickel-containing phase on catalysts. The XRD patterns of reduced samples are displayed in **Fig. 3** which shows the XRD patterns for both silica and nickel-silica combination. The nearer matching of the catalyst structure is crystalline phase of Ni_2SiO_4 (Liebenbergite).

Raman spectrum was collected for Ni/SiO_2 catalyst and compared with reference spectrum. The spectrum of silica support displayed a strong, sharp signal at around 500 cm-1 that was also clearly visible in the Raman spectra of the prepared catalyst. The Raman spectrum of the 20 % Ni catalyst was compared to the spectra of its metal oxides. **Fig. 4** shows the Raman Spectra for silica particles and Ni/SiO_2 catalyst particles. The spectra of the silica support displayed a strong, signal at around 450 cm^{-1} that was clearly visible in the Raman spectrum of the catalyst.

3.2 Liquid holdup

Figure 5 shows the effect of liquid velocity on the liquid holdup for three kinds of beds; the undiluted, diluted, and fine beds. The liquid holdup for the diluted bed packed with glass beads was higher than the holdup of the undiluted one and less than the holdup of beds packed with fine particles only. It is clear that diluting the coarse catalyst particles with inert fine glass beads will increase the liquid holdup by a factor two.

3.3 Hydrogenation of Nitrobenzene

The prepared Ni/SiO_2 was used for the hydrogenation of nitrobenzene in the diluted trickle bed reactor. Nitrobenzene (NB) was used as the inlet feed using methanol as solvent. Nitrobenzene and aniline were the only components visible on the GC chromatograms along with low levels of azobenzene (less than 1 % of the sample composition) were also detected in most of the reaction samples. Samples were collected from the reactor outlet at selected time intervals and analyzed. Each sample was analyzed using GC to identify and quantify each component. In all reactions performed, over the range of experimental conditions, a constant decrease in the nitrobenzene conversion was observed throughout the reaction which indicates a catalyst deactivation due to the adsorption of the intermediates and/or product aniline on the catalyst surface. During the early stages of hydrogenation, delays in the time the feed took to pass over the catalyst bed were sometimes experienced; leading to varying volumes of sample collected each interval, often much lower than expected. Towards the end of each catalytic run, the volume of sample obtained began to increase towards that expected from inlet rate and become more stable suggesting a more consistent performance could have been achieved if the reactions were left for a longer period of time. However, the catalyst displayed a loss in catalytic activity throughout the duration of the experiment and sampling was required in the early stages to ensure the reaction was monitored when the catalysts were most active. The reaction profile for typical initial concentration of nitrobenzene (0.5836 mol/L) and temperature of 323 K for different liquid feed flow rates is shown in **Fig. 6**. It can be shown a maximum of 19 % conversion of nitrobenzene to aniline in the exit samples after

1 hour reaction time. The activity then dropped off as the reaction progressed until about 13 % of the feed steam was composed of aniline after 10 hours.

When comparing with the previous works conducted on the same reaction using nickel catalyst prepared by wet impregnation method (Nele, et al, 1999), it is evident from the experimental results that the prepared HDC catalyst displayed less activity compared to catalysts prepared by wet impregnation method. The catalyst prepared appeared to be unsuitable for use as hydrogenation catalysts, with low percentages of aniline present in the exit streams. However, it should be noted that the large quantities of unreacted nitrobenzene exiting the reactor made detection of the products more difficult and exaggerated the poor activity of the catalysts. Examination of the reaction rates determined from these data shows that the levels of activity, although not approaching the precious metal catalysts, are not of an unreasonable level.

Three nitrobenzene initial concentrations (0.2926, 0.5853, and 1.1706 mol/L) were used to examine the dependence of the reaction rate on the nitrobenzene concentration at a temperature of 323 K. Experimental determination of the reaction order with respect to nitrobenzene, (**Fig. 7**), has revealed that at nitrobenzene concentration of 0.5853 and 1.1706 mol/L, the reaction appeared to be zero order with respect to nitrobenzene. Below this value (0.2926 mol/L), the reaction shifted to a ppositive order as the aniline amount decreased with the decrease in nitrobenzene concentration. If the adsorption of hydrogen is assumed to be the rate determining step in the nitrobenzene hydrogenation reaction (Gelder, 2005, Yao, et al., 1962), the shifting order can be explained with respect to the surface coverage of the catalyst. At low concentration of nitrobenzene, adsorption sites across the silica support become available for both hydrogen and nitrobenzene. This could affect an increase in the reaction rate by holding more nitrobenzene molecules adsorption on the catalyst. However, at high concentrations, nitrobenzene would be expected to saturate the surface of the metal and support and inhibiting the further hydrogen adsorption.

To generate a rate of reaction, the following equation was used to determine the rate of reaction depending on the assumption of differential reactor (Gelder, et al., 2002).

$$Rate\ of\ aniline\ formation = \frac{F_{NB}x}{W} \qquad (1)$$

Where,
F_{NB}: Molar flow rate of nitrobenzene (mol/L)
W: Weight of catalyst bed (g)
x: Fractional conversion

The actual number of moles of aniline produced was used taking into account the volume of each sample. This gave a clear indication of the absolute quantity of aniline produced throughout hydrogenation. As the behavior at each experimental condition was slightly different, the maximum rate was selected as a comparison. These values are shown in **Table 3** and a plot of maximum rate with respect to the hourly space velocity is presented in **Fig. 8**.

The rate of reaction data at different temperatures were used to calculate the activation energy of the hydrogenation reaction using Arrhenius law. The average activation energy of the reaction is calculated as 31.78 kJ/mol which agrees with the values found in literature (Gelder, 2005). **Figure 9** shows the Arrhenius plot for the reaction carried out at WHSV of 9.75 h^{-1}.

3.4 Mass Transfer Resistance

Experiments were carried out to check the resistance to mass transfer during the hydrogenation reaction for undiluted and diluted beds. The reaction was performed with two different liquid flow rates (1 and 2 ml/min) at constant weight hourly space velocity, WHSV of 9.75 hr^{-1}. Different conversions of nitrobenzene were noticed for the undiluted reactor indicating external mass transfer control. The diluted bed showed nearly the same conversions for both liquid flow rates which can be interpreted as that the dilution of the bed already increased the mass transfer coefficient inside the reactor. Figure 10 shows the mass transfer effect on the conversion of nitrobenzene for the two beds.

Pore diffusion was checked by the application of the method used by Weisz-Prater, 1954. Weisz-Prater relation correlates wp to the observed rate of the reaction and many other parameters as:

$$wp = \frac{r_{obs}\rho(d/6)^2}{D_e C_s} \qquad (2)$$

Where r_{obs} is the observed rate of the reaction, ρ is the catalyst density, d is the average catalyst support diameter, D_e is the effective diffusivity, and C_s is the concentration of solute in solution. Weisz-Prater criterion states that the factor wp should be << 1 for the internal resistance to be negligible.

The rate of reaction was obtained at temperature 323 K, liquid flow rate of 2 ml/min, gas flow rate of 135 ml/min and catalyst weight of 10 g. The diffusion coefficient was calculated by using Wilke equation (Wilke, et al., 1955), the solubility of hydrogen in methanol was taken from the data given by Young, 1981as 0.0494 mol/L. For diluted beds, wp was calculated as 0.0102 for nitrobenzene as limiting species indicating the absence of internal mass transfer limitation.

The reaction rates at the steady state for the diluted bed are much higher than those for the undiluted bed. **Figure 10** shows the effects of liquid velocity on the reaction rate. In the case of the diluted bed, the reaction rate is independent of the liquid velocity. On the other hand, in the case of undiluted trickle bed, the reaction rates for lower liquid velocities are unstable and smaller than the rate without external effects. It was revealed from observations that some pellets of catalyst were completely dried. Therefore, they might make no contributions to the reaction.

CONCLUSIONS

1. Trickle bed reactor can be used in the synthesis of fine chemicals. The catalyst efficiency can be improved by dilution of the catalyst particles with fine inert particles to overcome the external mass transfer resistance.
2. Although the HDC method was successful in producing catalyst with a homogeneously distributed, well-dispersed monolayer of metals, the method was not gave advantages over alternative catalyst preparation routes for the synthesis of supported metal catalysts.
3. The diluted trickle bed reactor is suitable to obtain the reaction rate without external effects even if the liquid velocity is low.
4. The prepared catalyst was shown to deactivate over time due to the adsorption of the product aniline.
5. The reaction order of nitrobenzene hydrogenation reaction was zero with respect to nitrobenzene concentration for the values of nitrobenzene initial concentrations of 0.58 mol/L and more, while it is of positive order for the initial concentration less than 0.58 mol/L.

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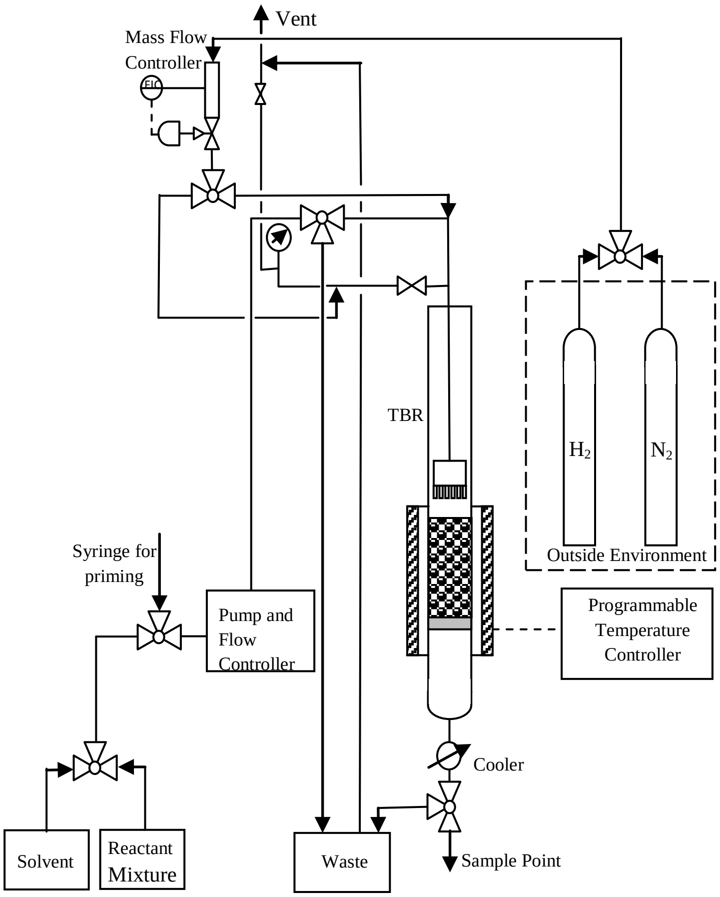

Fig. 1 Experimental apparatus

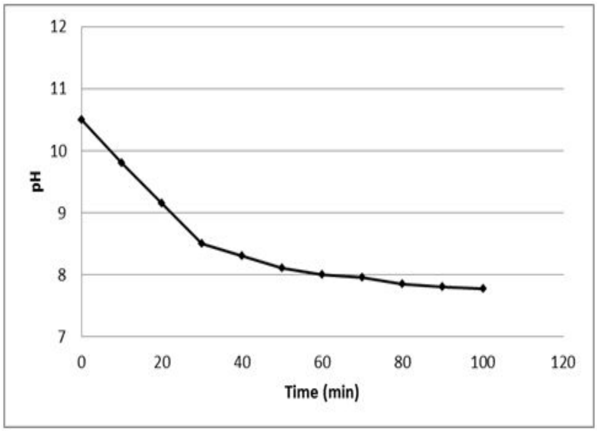

Fig. 2 Change in pH during synthesis of the nickel HDC catalyst

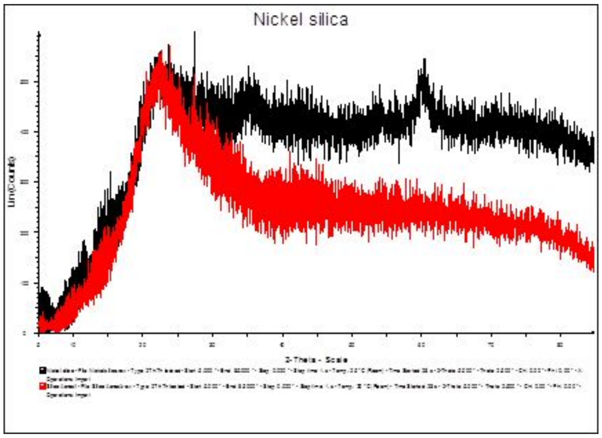

Fig. 3 XRD Patterns of Nickel/Silica Catalyst

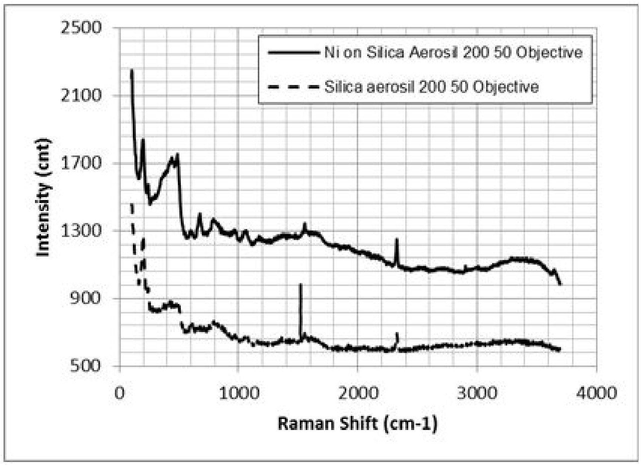

Fig.4 Raman Spectra for Silica particles and Nickel/Silica Catalyst

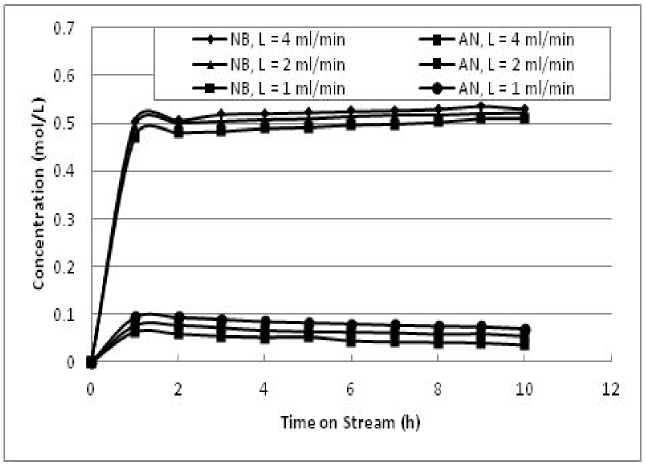

Fig 6. Typical reaction profile at different liquid flow rate, T=323 K, U_g =135 ml/min, Catalyst wt=10 g

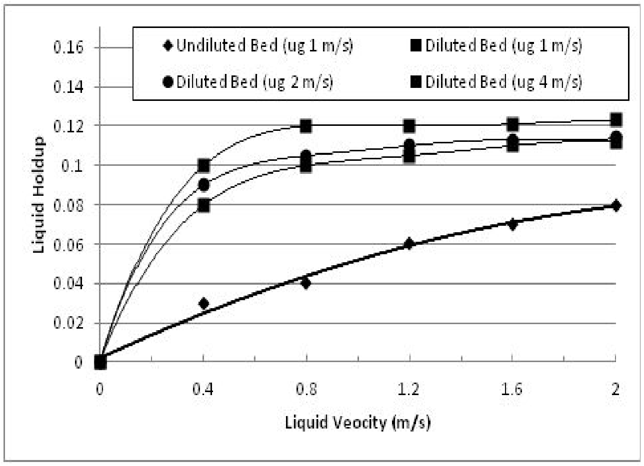

Fig 5. Liquid holdup for diluted and undiluted beds

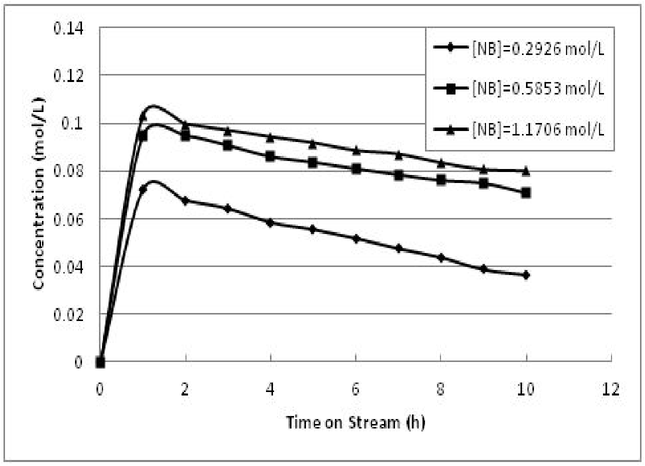

Figure 7 Outlet concentration of aniline vs. time on stream at WHSV = 4.87 h^{-1}, T=323 K, U_g = 135 ml/min and different initial feed concentrations

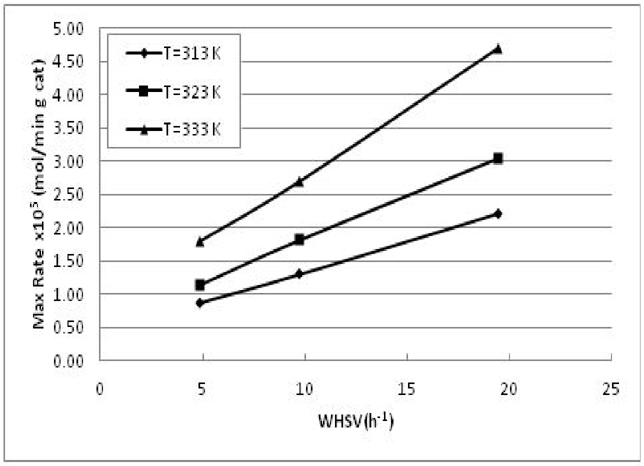

Fig. 8 Maximum rate of nitrobenzene hydrogenation vs. weight hourly space velocity at different temperatures at T=323 K, U$_g$ = 135 ml/min

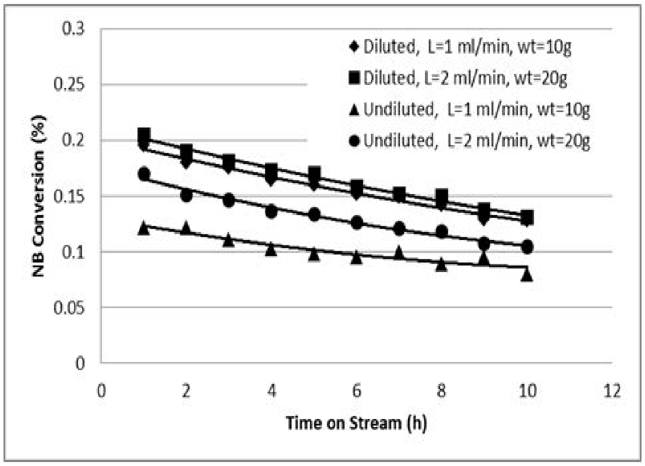

Fig. 10 Conversion of nitrobenzene vs. time on stream at WHSV = 9.75 hr^{-1}. T=323, and U$_g$ = 135 ml/min for undiluted and diluted beds

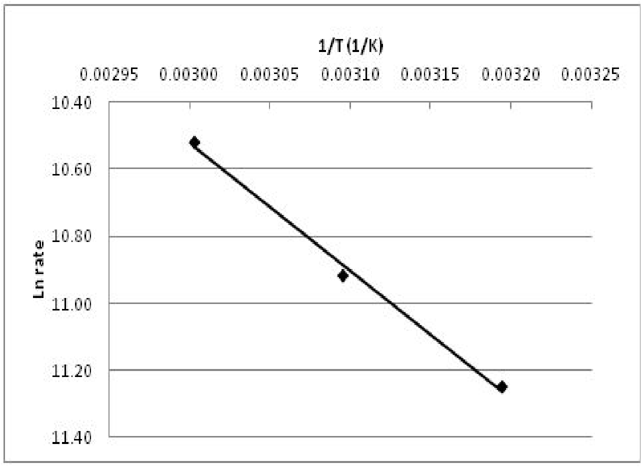

Fig. 9 Arrhenius plot for the reaction carried out at WHSV 9.75 h^{-1}, U$_g$= 135 ml/min, catalyst wt=10g

Table 1: Values of the surface area and pore volume for the prepared Ni/SiO_2 catalyst

Area	
Single point surface area at P/Po = 0.285	238.782 m^2/g
BET surface area	243.387 m^2/g
BDH desorption cumulative surface area of pores between 17 and 3000 °A diameter	261.920 m^2/g
Volume	
Single point total pore volume of pores less than 1070.5 °A diameter at P/Po = 0.981	0.589 cm^3/g
BDH desorption cumulative pore volume of pores between 17 and 3000 °A diameter	0.594 cm^3/g
Pore Size	
Average pore diameter (4V/A by BET)	96.944 °A
BDH desorption average pore diameter (4V/A)	90.764 °A

Table 2 Experimental variables used in hydrogenation experiments

Experimental Variable	Range
Feed concentration (mol/L)	0.2926 - 1.1706
Liquid feed flow rate (ml/min)	1 - 4
Temperature (K)	313 - 333

Table 3 Maximum rate of aniline formation with weight hourly space velocity and reaction temperature

WHSV (hr^{-1})	Maximum Rate x 10^5 (mol/min g cat)		
	T = 313 K	T = 323 K	T = 333 K
4.87	0.88	1.14	1.80
9.75	1.30	1.81	2.70
19.49	2.2	3.04	4.70