

Comparative Study on the Effect of Support for Nanonickel Catalyst in Reduction of Nitrophenols

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THE CATALYTIC reduction of para- and ortho- nitrophenols to the corresponding aminophenols was investigated over Ni/TiO₂ catalysts prepared by reduction method. Hydrazine hydrate in the presence of nickel ions supported on TiO₂ was used in the preparation of nanonickel catalyst over rutile and anatase. Further decomposition of the hydrazine hydrate on the nickel atoms surfaces yields nascent hydrogen atoms that efficiently reduce the nitro groups. Many techniques such as XRD, IR, TEM and UV-Visible absorption spectroscopy have been used. TEM shows the formation of nanonickel clusters on TiO₂. IR analysis confirms the appearance of the characteristic peaks of only ortho or para aminophenols. The kinetics of reduction reaction was studied. Catalyst recovery and factors affecting the reduction reaction such as phenol concentration, pH, catalyst loading and temperature have been studied. The obtained data and kinetic results show that the conversion percentage reaches 100% within few minutes. The results indicate that the nanonickel loaded over rutile or anatase TiO₂ exhibit nearly the same catalytic activity in reduction of nitrophenols but more active than nanonickel in zeolite catalyst.

Keywords: Nickel nanocatalyst, Rutile, Anatase, Nitrophenols, Aminophenols and Reduction.

Nitrophenols are among the most common organic pollutants in industrial and agricultural wastewaters. Many processes have been developed for their removal such as adsorption⁽¹⁾, microbial degradation⁽²⁾, photocatalytic degradation⁽³⁾, microwave-assisted catalytic oxidation⁽⁴⁾, electro-Fenton method⁽⁵⁾, electro-coagulation⁽⁶⁾, electrochemical treatment⁽⁷⁾ and so on. On the other hand, 4-aminophenol (4-AP) is an important intermediate for the manufacture of analgesic and antipyretic drugs. They can be synthesized by the catalytic hydrogenation of 4-nitrophenol (4-NP) in ethanol at relatively high temperature and high hydrogen pressure⁽⁸⁻¹⁰⁾.

Raney nickel⁽¹¹⁾, nano-sized nickel⁽¹²⁾ and several noble metal catalysts such as Pd/C⁽¹³⁾ have been used as catalysts for reduction reaction of nitrophenols. Due to cheaper price and higher catalytic activity, supported nickel catalysts are

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widely used in various reactions⁽¹⁴⁻²⁰⁾. Moreover, compared to unsupported nano-sized nickel catalysts, supported nickel catalysts are easy to recover in a slurry reactor. There are few reports on the catalytic reduction of p-nitrophenol over supported nickel catalysts.

Titania has attracted much interest as a support material for metals or metal oxides due to its ability to modify the catalytic properties of the supported phase⁽²¹⁻²²⁾. It is known that titania exists in three main structures: anatase, rutile, and brookite, and each structure shows different physical properties. It is inferred that metal supported on titania with different structures might exhibit different physio-chemical properties and catalytic properties. However, little on such difference has been reported^(23, 24).

The reduction of aromatic nitro compounds with hydrazine or hydrazine hydrate represents a special variation of the catalytic reduction, where hydrazine is the source of the hydrogen. The hydrogen can be generated by a variety of H-transfer catalysts. Especially with the use of noble metal catalysts, such as Pd, Pt or Ru, but also with the application of Ni or Cu, the catalytic hydrazine reduction gives high yields comparable to or better than the catalytic hydrogenation⁽²⁵⁾. In a previous work, the catalytic activity of nanonickel supported zeolite on the reduction of nitrophenols was studied⁽²⁶⁾. Moreover, the use of TiO₂ (anatase) as a support for nanonickel catalyst was investigated, and it was found that the catalyst exhibited activity more than Raney nickel⁽²⁷⁾. In this work, the effects of titania structure (rutile and anatase) on the rate of reduction reaction of o- and p-nitrophenols to o- and p-aminophenols have been investigated. The catalytic reduction over Ni/TiO₂ catalysts in presence of hydrazine hydrate as a reducing agent in mild conditions has been performed. The conversion percentage as well as catalyst recovery using Ni/TiO₂ catalysts are conducted. Factors affecting the reduction processes such as (concentration, pH, temperature and catalyst loading) are also studied and discussed in details.

Experimental

Materials

The following materials were used in the investigation: Ni(NO₃)₂.6H₂O (purity 98%, Lab Rasayan), p-NO₂ phenol (purity 98%, Oxford Lab Rasayan, Bombay- India), o-NO₂ phenol (purity 99%, BDH, England), p-NH₂ phenol (purity 96%, pract), o-NH₂ phenol (purity 96%, pract), hydrazine hydrated (H₆N₂O) (purity 99-100%, Laboratory Rasayan rankem), sodium hydroxide (purity 97% min, spectrum chemical mfg. corp.), ethyl alcohol (purity 99.8% analar, alpha chemika).

Impregnation method

The present work describes a simple procedure for the preparation of Ni/TiO₂ (rutile or anatase) using the wet impregnation method. 5% Ni/TiO₂ was prepared by the impregnation method. As 5 g of TiO₂ in rutile or anatase form was

impregnated with a solution composed of a definite weight of Ni (NO₃)₂.6H₂O dissolved in the least amount of distilled water.

Reduction of nitrophenols

0.1 g of Ni/TiO₂ was mixed with 15 ml of hydrazine hydrate and 5 ml of NaOH (10%) and heated at 70°C. Within few minutes, a black color appeared indicating the reduction of nickel ions into atoms.

To the formed Ni/TiO₂ catalyst 0.5 g of nitrophenol in ethanol was added. Again 10 ml of hydrazine hydrate along with a quantity of NaOH solution were added to help the reduction of nitrophenols into the corresponding aminophenols. The initial reaction volume was kept constant at 100 ml using ethanol.

The total conversion of nitrophenols was calculated using the following equation:

$$\% \text{ Conversion} = (A_0 - A) / A_0 \times 100$$

where A_0 and A are the absorbance values of nitrophenol at a given wavelength (nm) at 0 time and definite time, respectively.

TEM measurements

The tested samples of Ni/TiO₂ by means of the transmission electron microscope (TEM) were prepared by dispersing these samples in distilled water followed by ultrasonic vibration for half an hour. A drop of the dispersed sample was placed onto a copper grid coated with a layer of amorphous carbon. A Jeol Transmission Electron Microscope, jel 1230, RV 120 KV was used to study the shape and size of the sample.

Infrared spectral analysis

IR spectra were collected on Perkin Elmer 1000 with a resolution of 4. This technique was used to investigate quantized molecular resonance that absorbs electromagnetic energy selectively from a broad band infrared source, where 1 mg of the fine sample powder was of the nitro and / or amino phenol mixed with ~ 200mg KBr. The mixture was then pressed to form a more or less transparent disk and then scanned in the range of 2000 to 400 cm⁻¹.

UV-Visible measurements

UV-Visible absorption measurements were obtained using a UV 2401PC record spectrometer, Shimadzu.

Results and Discussion

Characterization of the catalyst

Hydrazine hydrate in the presence of nickel ions supported on TiO₂ was used in the preparation of nanonickel catalyst over rutile and anatase. Ni ions supported on TiO₂ are transferred into metallic nickel after reduction with

hydrazine hydrate in presence of NaOH at pH 9. TEM micrograph of Ni/TiO₂(R) in Fig. 1 indicates that the nickel clusters (dark field) are uniformly dispersed on the surface of rutile titania support and the average size of Ni cluster is about 25 nm.

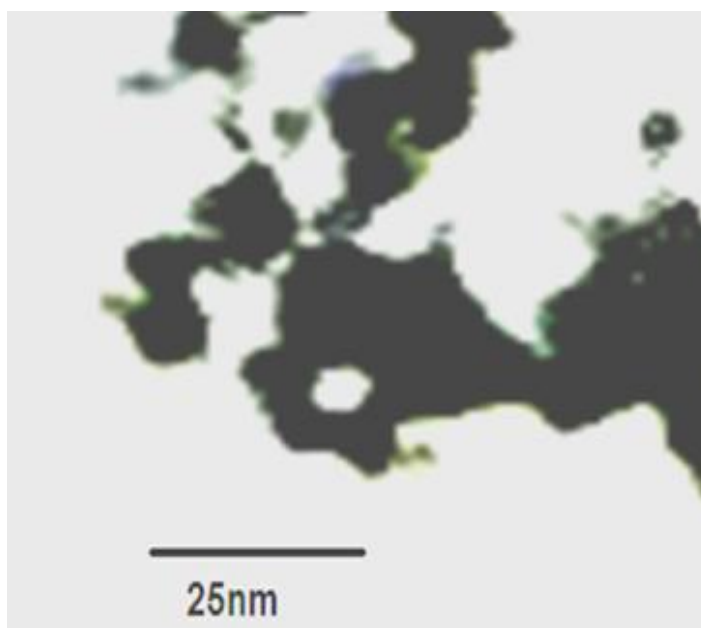


Fig. 1. TEM image of Ni/TiO₂ (R).

Reduction of nitrophenols (preliminary studies)

UV-Visible measurements

UV-Vis technique was used in studying the reduction reaction of nitrophenols into the corresponding aminophenols. P-nitrophenol shows maximum absorbance in the visible region at wavelength 400 nm, whereas the maximum absorbance of pure p-aminophenol is in the UV region at 300 nm. The absorbance values at these wavelengths are quite suitable to follow up the reduction of p-nitrophenol to the corresponding aminophenol. Since no interference is observed between both compounds (Fig. 3). The same was found for o-nitrophenol and o-aminophenol where the absorbance at wavelengths 415 nm and 286 nm were taken to follow up the reduction of o-nitrophenol into o-aminophenol, respectively. Starting the reduction reaction, the characteristic peaks of nitrophenols at longer wavelengths decrease and at complete reduction they completely disappear while the characteristic peaks for aminophenols at shorter wavelength increase, which is considered as an evidence for the reduction of nitro group into amino group (Fig. 2 and 3).

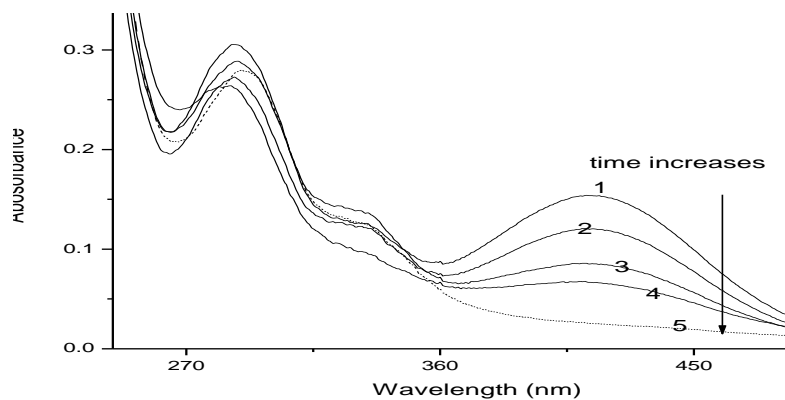


Fig. 2. UV-Visible absorption spectra of o-nitrophenol and different intervals of reduction reaction (pure o-nitrophenol: (1) and pure o-aminophenol: (5)).

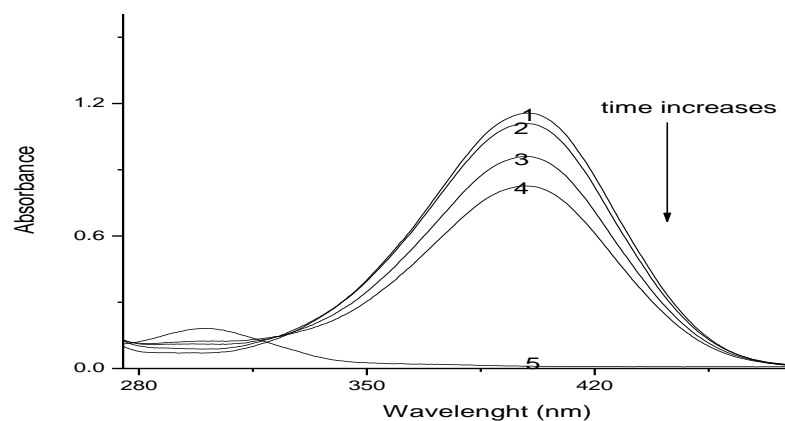


Fig. 3. UV-Visible absorption spectra of p-nitrophenol and different intervals of reduction reaction (pure p-nitrophenol: (1) and pure p-aminophenol: (5)).

pH Effect

The effect of pH on the reduction reaction of o- and p- nitrophenols has been studied. It was found that the pH 9 is the most suitable one because the absorption spectra for nitrophenols did not interfere with that of o- and p-aminophenol. These results can be seen in Fig. 4 and 5. Besides, preliminary studies on the effect of pH on the reduction of nitrophenols into the corresponding aminophenols were done. At low pH's less than 9 no reduction was observed, these observations lead us to adjust the medium at pH 9 during the reduction processes.

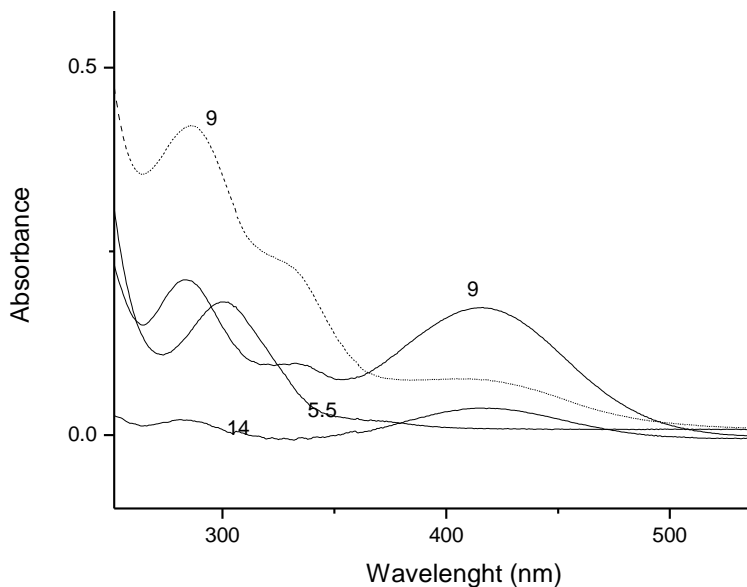


Fig. 4. UV/Visible absorption spectra of *o*-nitrophenol (solid lines) and *o*-aminophenol (dot line) at different pH (5.5, 9 and 14).

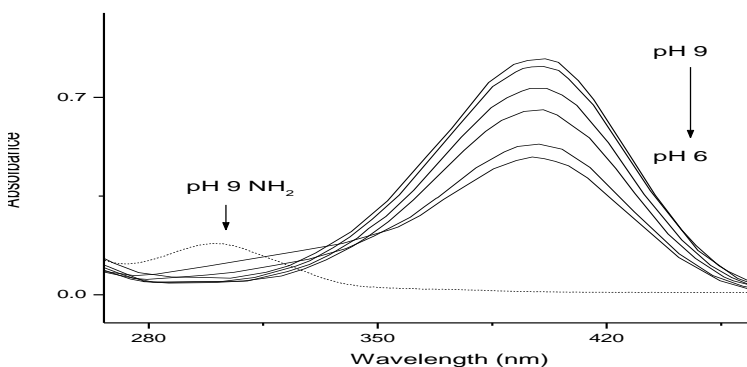


Fig. 5. UV/Visible absorption spectra of *p*-nitrophenol (solid lines) and *p*-aminophenol (dot line) at different pH (6-12).

Products characterization

After complete reduction reaction of the sample of nitrophenol, the products were extracted many times with methyl ethyl ketone in case of *p*-aminophenol and petroleum ether in case of *o*-aminophenol. The extracted solids after vaporization under vacuum were used for IR investigation. The results confirm the formation of the corresponding aminophenols. The obtained solids were weighed to ensure that the conversion is about 100%. Moreover, the melting

point of these samples were performed and we found that the melting point was 190°C after complete reduction of p-nitrophenol (m.p. 114°C) as the yellow colour of the sample disappeared and the reaction solution colour became colourless. The disappearance of orange colour of o-nitrophenol was an evidence of complete reduction ensured by measuring the melting point 170°C characterized to o-aminophenol (m.p. 45°C).

Kinetics of the reduction reaction

The kinetics of reduction reaction using 5% Ni-TiO₂ on anatase, rutile forms and Ni-Y zeolite catalyst was studied. The reduction reactions follow the first order kinetic analysis. Plotting $\ln A$ versus time gives a linear relationship of a slope equals to the rate constant of the given reaction (Fig. 6 and 7). The rate constant values for the reduction reaction of p- and o-nitro phenols at different amounts of the catalyst are given in Table 1. The data are compared to that obtained in a previous work using Ni supported zeolite keeping the amount of supported Ni constant in all experiments⁽²⁶⁾. Inspection of Table 1 shows the following: (i) Nanonickel supported on TiO₂ is more catalytically active than the nanonickel in zeolite. (ii) The rate constant of the reduction of p-nitrophenol is slightly higher than that of the o-nitrophenol in case of Ni-Y zeolite. (iii) The rate constant of the reduction of o-nitrophenol is slightly higher than that of the p-nitrophenol in case of Ni-TiO₂. (iv) Both rutile and anatase show comparable rate constant values for the reduction of p- and o-nitrophenols.

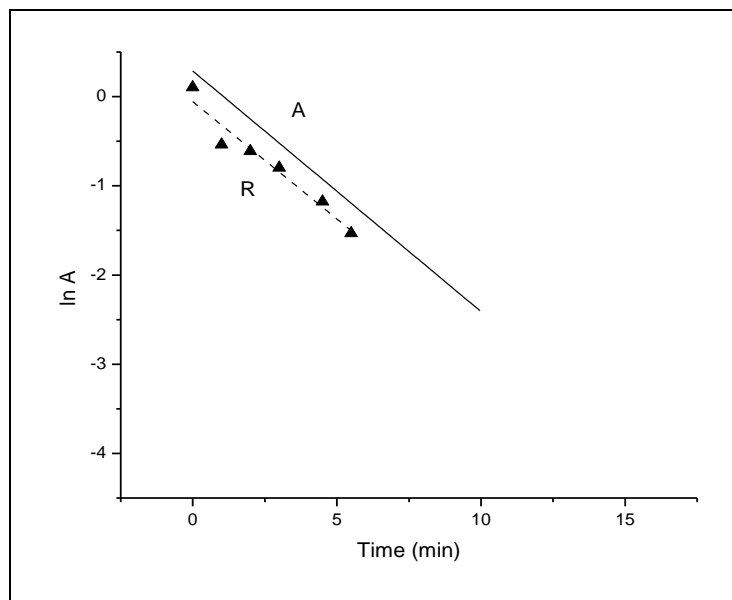


Fig. 6. First order kinetic analysis of the catalytic reduction of (0.4 gm) of p-nitrophenol using 0.1 gm Ni/TiO₂ (anatase and rutile) .

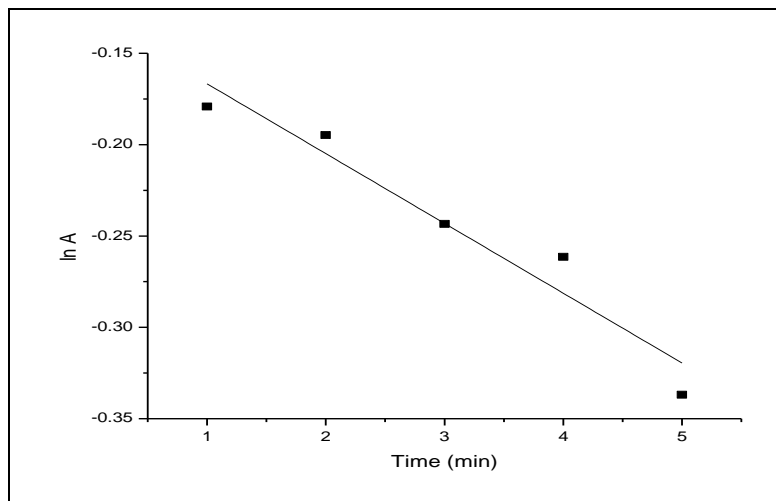


Fig. 7. First order kinetic analysis of the catalytic reduction of (0.4 gm) of p-nitrophenol using 0.1 gm Ni-Y zeolite.

TABLE 1. The kinetics of the reduction reaction of p- and o-nitrophenol using Ni-TiO₂ in anatase form, rutile form and Ni-Y zeolite. (weight of nitrophenol 0.4 g, temperature = 70 °C, volume of the solution 100 ml, and pH = 9).

Catalyst	Wt. of catalyst (g)	Rate constant (min ⁻¹)	
		p-nitrophenol	o-nitrophenol
5% Ni-TiO ₂ (R)	0.15	0.20	0.29
5% Ni-TiO ₂ (A)	0.15	0.20	0.28
2.5% Ni/Y* zeolite	0.30	0.10	0.08

*2.5% Ni in zeolite is the maximum amount of exchanged nickel ions after which the structure of zeolite collapses (confirmed by XRD)⁽²⁶⁾.

The above results can be explained on the light of the following: (i) The lower rate of the reduction reaction of nitrophenols using Ni-Y zeolite than that of Ni-TiO₂ may be attributed to the open surface of Ni-TiO₂ that may facilitate the interaction between nickel atoms with both hydrazine and nitrophenols during the reduction reaction. (ii) The rate constant of the reduction of p-nitrophenol is slightly higher than that of the o-nitrophenol in case of Ni-Y zeolite. This can be due to the steric hindrance arising from the o-nitrophenol structure – in contrary to p-nitrophenol structure- which may cause difficulty for their entrance into zeolite cages. (iii) The rate constant of the reduction of o-nitrophenol is slightly higher than that of the p-nitrophenol in case of Ni-TiO₂. This may be explained in terms of the adsorption of o-nitrophenol on TiO₂ surfaces through formation of surface complex between Ti(IV) and the adjacent hydroxyl and nitro groups. (iv) Both rutile and anatase show comparable rate

constant values for the reduction of p- and o- nitrophenols. This leads us to use the lower cost rutile TiO₂ in the following experimental work.

Optimization

Several experiments were performed for studying the reduction reaction of o-nitrophenol and p-nitrophenol at different conditions to reach the optimum results.

Temperature

The reduction of o- and p-nitrophenols using 5% Ni-TiO₂ (R) was conducted at different temperatures (60-80°C).

From Table 2 it can be observed that fixed time (10 min) at temperature lower than 70°C the conversion for both nitrophenols was very low and increasing the reaction time did not affect the conversion percentage. At 75°C the conversion of o-NO₂ phenol was more than 84% while, 100% conversion was achieved at 80°C for both nitrophenols.

TABLE 2. The effect of temperature on the conversion of p- and o-NO₂ phenol (weight of nitrophenol 0.4 g, weight of catalyst 0.1 g, volume of the solution 100 ml , 10 min and pH 9) .

Temperature	Conversion % of p-NO ₂ phenol	Conversion % of o-NO ₂ phenol
60	19.8	47
65	22.4	63.6
70	31.3	75.2
75	40	84
80	100	100

Ni- loading in TiO₂

The data for the dependency of p- and o-nitrophenol conversion percentage on the amount of Ni loaded on TiO₂ (R) surfaces is given in Table 3. It was noticed that 5 % Ni on TiO₂(R) support is the most favorable loading percentage for the reduction process for o- and p- nitrophenol at constant temperature, pH and volume.

TABLE 3. The effect of loading of Ni ions on the support (R) on the conversion of p- and o-NO₂ phenol (weight of nitrophenol 0.4 g, weight of catalyst 0.1g volume of the solution 100 ml , 75°C and pH 9) .

% Ni/TiO ₂ (R)	Conversion % of p-NO ₂ phenol	Conversion % of o-NO ₂ phenol
3	25	60
5	85	90
7	80	85

Weight of the catalyst

In this series of experiments, different quantities of the catalyst were used for the reduction of 0.4 g of nitrophenol at pH 9 and temperature of 70°C. The time required for complete reduction for each experiment is given, Table (4). Under the previous conditions, the reduction reaction does not start using less than 0.05 g of 5 % Ni on TiO₂(R). Increasing the quantity of the catalyst leads to remarkable decrease of the time required for complete conversion of nitrophenols to the corresponding aminophenols.

TABLE 4. The effect of the amount of catalyst on the time required for complete conversion of p- and o-NO₂ phenol (weight of catalyst 0.1 g, volume of the solution 100 ml , 70°C and pH 9).

Weight (g) of catalyst	Time (min) for complete conversion of p-nitrophenol	Time (min) for complete conversion of o-nitrophenol
0.05	15	17
0.08	10	15
0.1	7	6
0.12	5.5	5
0.15	5	3.5

Concentration of nitrophenols

The effect of the amount of nitrophenols was examined at constant catalyst concentration, temperature, pH and the volume of reaction mixture. It was found that the time required for complete reduction increases with increasing nitrophenol concentration.

The shortest time required for complete conversion was achieved when the amount of nitrophenols were 0.1 g at 75°C in the presence of 0.1 g of 5% TiO₂ (R). At these conditions, 2 and 3 min were enough for complete reduction of p- and o-nitrophenols, respectively. The dependence of conversion on the amount of nitrophenols was illustrated in Table 5.

TABLE 5. The effect of the amount of nitrophenols on the time required for complete conversion of p- and o-NO₂ phenol (weight of catalyst 0.1 g, volume of the solution 100 ml , 70°C and pH 9) .

Weights (g) of nitrophenols	Time for complete conversion of p-nitrophenol (min)	Time for complete conversion of o-nitrophenol (min)
0.1	3	2
0.4	7	6
0.7	15	12

Catalyst recovery

For carrying this series of experiments a quantity of the catalyst was employed in conversion of nitrophenols into aminophenols. After complete
Egypt. J. Chem. **54**, No.1 (2011)

conversion, the catalyst was filtered out and another quantity of nitrophenol in ethanol was added to the catalyst and the reaction is preceded till complete conversion. The process was repeated several times with the same catalyst. In each experiment the time for complete conversion was recorded. The results of this series of experiments are listed in Table 6. From this table, it can be observed that Ni/TiO₂ showed high catalytic activity for 5 times of conversion, yielding 100% conversion in each time.

TABLE 6. The relation between the numbers of repetition of catalyst against the time required for complete conversion of p- and o-NO₂ phenol (weight of catalyst 0.3 g, weight of nitrophenol 0.4 g, volume of the solution 100 ml, 70°C and pH 9).

No. of experiments	Time for complete recovery of Ni/TiO ₂ (rutile) p-nitrophenol	Time for complete recovery of Ni/TiO ₂ (rutile) o-nitrophenol
1	2	1.5
2	3	3
3	5	4
4	10	7
5	15	12

Conclusion

Ni ions supported on TiO₂ are transferred into metallic nickel after reduction with hydrazine hydrate. The nickel clusters are uniformly dispersed on the surface of titania support and the average size is about 25 nm. Catalytic conversion of nitrophenols into aminophenols was conducted in the presence of the prepared nano-nickel TiO₂. The kinetics of reduction reaction using TiO₂ in rutile and anatase forms against Ni-Y zeolite catalyst was studied. The results indicate that nanonickel supported on TiO₂ was more active than the nanonickel in zeolite. The rate constant of the reduction of p-nitrophenol is slightly higher than that of the o-nitrophenol in case of Ni-Y zeolite. The rate constant of the reduction of o-nitrophenol is slightly higher than that of the p-nitrophenol in case of Ni- TiO₂. Both rutile and anatase show comparable rate constant values for the reduction of p- and o- nitrophenols. Optimization was proceeded by studying the effect of many factors on the conversion of nitrophenols. Increase of the temperature of the reduction reaction raises the percentage of conversion. Optimum conditions to convert nitrophenols are pH= 9 and reaction temperature between 70-80°C by using a 5% Ni- TiO₂. The increase of weight of catalyst decreases the time consuming for complete conversion.

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دراسة مقارنة في تأثير الحامل على حفاز النيكل النانومتري في اختزال النيتروفينولات

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النامومتري في هذا البحث تم عمل اختزال حفزي للبارا و الأرتو نيتروفينولات إلى الأمينو فينولات المقابلة باستخدام حفازات النيكل المحملة على سطح ثاني أكسيد التيتانيوم و المحضرة بطريقة الاختزال ، و قد تم استخدام الهيدرازين المائي في اختزال أيونات النيكل المحملة على سطح ثاني أكسيد التيتانيوم بنوعية الرتابل و الأنتايز إلى حفاز النيكل ذو الأبعاد النانومترية ، و بتحليل المزيد من جزيئات الهيدرازين المائي على سطح ذرات النتيكل تتولد ذرات الهيدروجين التي تختزل بفاعلية مجموعات النيترو ، و قد تم استخدام العديد من التقنيات مثل حيود الأشعة السينية و الأشعة تحت الحمراء و الميكروسكوب الإلكتروني الانتقالي، و جهاز طيف الأمتصاص المرئي والأشعة فوق البنفسجية. و قد أوضح الميكروسكوب الإلكتروني النافذ تكون تجمعات بلورية ذات أبعاد نانومترية للنيكل على سطح ثاني أكسيد التيتانيوم. و أثبتت نتائج تحاليل الأشعة تحت الحمراء ظهور الخطوط المميزة للأرتو أو البارا نيتروفينولات. و قد تم دراسة كيناتيكيات تفاعلات الاختزال. و كذلك تم دراسة اعادة استخدام الحفاز و العوامل المؤثرة على تفاعلات الاختزال مثل تركيز الفينول، الأس الهيدروجيني، كمية الحفاز و درجة الحرارة. و أوضحت النتائج وصول النسبة المئوية للتحويل إلى ١٠٠٪ خلال دقائق قليلة. و تشير النتائج إلى أن النيكل النانومتري المحمل على سطح ثاني أكسيد التيتانيوم الروتابل و الأنتايز لهم تقريبا نفس النشاطية الحفزية في اختزال النيتروفينولات و لكن أكثر كفاءة من النيكل المحمل داخل حفاز الزيوليت.