38 *Egypt. J. Chem.* **53**, No. 4 , pp. 565-579 (2010)

Innovative Method for the Reduction of Nitrophenols Using Nickel Nanocatalysts in Zeolite-Y Prepared from Egyptian Kaolin

Haiam H. Ibraheem, Doaa M. El-Mekkawi[*], S. A. Hassan[**] and M. M. Selim[#]
Ministry of Scientific Research, [*]Phys. Chem. Dept., National Research Center and [**]Dept. Chem., Faculty of Science, Ain Shams University, Cairo, Egypt.

THE REDUCTION of ortho and para nitrophenols into the corresponding aminophenols has been proceeded via a new efficient catalytic reduction method. Hydrazine hydrate in the presence of nickel exchanged zeolite was used in the preparation of nickel nanocatalyst in zeolite surfaces. Zeolite-Y prepared from Egyptian kaolin has been used. At low temperature hydrazine hydrate molecules first decompose to give hydrogen atoms. Hydrogen atoms reduce the nickel ions exchanged inside the zeolite cages. This allows the formation of nickel clusters in the nanoscale size. Further decomposition of the hydrazine hydrate on the nickel atom surfaces yields nascent hydrogen atoms that efficiently reduce the nitro groups. Many techniques such as XRD, IR, TEM, UV-Visible absorption spectroscopy, and atomic absorption measurements have been used. XRD analysis confirms that zeolite Y retained its framework after nickel exchange processes. The atomic absorption measurements were used to determine the amount of nickel ions exchanged in zeolite. TEM shows the formation of nano nickel atoms inside the zeolite cages. IR analysis confirms the appearance of the characteristic peaks of only ortho or para aminophenols. UV-Visible absorption measurements have been used to follow up the disappearance of the nitro compounds as well as the estimation of the conversion percentage. 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 indicate that at a given experimental conditions, the conversion percentage reaches 100% within few minutes. Comparing the results to the previously published studies, it can be concluded that this method is more economic, faster and more efficient.

Keywords: Nickel nanocatalyst, Zeolite, Nitrophenols, Aminophenols, Reduction and Egyptian kaolin.

Reduction of aromatic nitro compounds to the corresponding amines is a useful chemical transformation in synthetic organic chemistry, mainly due to the fact that the amino group serves as a site for further derivatization. The amines are also important intermediates in the production of many pharmaceuticals,

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[#]Corresponding author: E-mail: mmaselim@yahoo.com photographic materials, agrochemicals, polymers, dyes and rubber materials. Aminophenol is of great commercial importance as an intermediate for the preparation of analgesic and antipyretic drugs (1–5) . The first use of a catalyst in reductions of nitro compounds using hydrazine has been reported by Busch and Schulz in 1929 (9).

Reduction can be achieved by several reagents in solution phase reactions (6) . Substituted nitro compounds are also reduced efficiently using hydroiodic acid(7). Varma *et al.* (8) have reported recently a solvent-free microwave reduction protocol that leads to a facile preparation of aromatic amines from the corresponding nitro compounds with hydrazine hydrate supported on solid materials such as alumina, silica gel and clays. The interesting potential and versatility of zeolites have prompted a study of the title reduction of nitroarenes by hydrazine in the presence of divalent and trivalent cation-exchanged faujasites as heterogeneous catalysts. The reaction mixture stirred overnight to give the higher yield percentage 94% (8) . In comparison to the reduction process with sulphides (where hydrogen sulfide gas might evolve and endanger the operating personnel), the reduction with hydrazine hydrate produces harmless byproducts such as nitrogen gas and water (6) . Hydrazine hydrate has also been employed as a hydrogen donor in the presence of heterogeneous catalysts such as activated Zn–Cu (10) , Zn–C (11), Fe–C (12), $FeCl_3 \cdot 6H_2O$-activated carbon (13), Fe(III) oxides(14) , Fe(III)–MgO (15) , iron oxide hydroxide (16), graphite (17) and clays (18). In previous works by one of the authors Ni/TiO_2 ,Ni/SiO_2 and Ni/Al_2O_3 were also used for reduction of p-nitrophenol (19 , 20) .

In this work nickel nanoclusters in zeolite Y prepared from Egyptian kaolin, has been used as a catalyst to reduce p-nitrophenol and o-nitrophenol in the presence of hydrazine hydrate as a reducing agent in mild conditions. The conversion percentage as well as catalyst recovery have been investigated. Factors affecting the reduction processes such as (concentration, pH, temperature and catalyst loading) have been studied and discussed in details.

Experimental

Materials

Zeolite Y powder prepared from Egyptian kaolin was used as a starting material for ion exchange process (21). The transition metal salt solution was prepared using $Ni(NO_3)_2.6H_2O$ (purity 98%, lab Rasayan), p-NO_2 phenol (purity 98%, oxford lab Rasayan, Mombay- India), o-NO_2 phenol (purity 99%, BDH, England), p-NH_2 phenol (purity 96%, pract), o-NH_2 phenol (purity 96%, pract), hydrazine hydrated (H_6N_2O) (purity 99-100%, Laboratory Rasayan rankem), sodium hydroxide (purity 97% min, spectrum chemical mfg. corp.), ethyl alcohol (purity 99.8% analar, alpha chemika) were used in this investigation.

XRD analysis

X-Ray diffraction patterns were obtained using a Bruker D8 advance instrument with CuKα1 target with secondary monochromator 40 KV, 40 mA.

TEM measurements

The tested samples of zeolite by 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 1mg of the fine sample powder was of the nitro and/or amino phenol mixed with ~200 mg KBr. The mixture was then pressed to form a more or less transparent disk and then scanned in the range of 4000 to 400 cm^{-1}.

UV–visible measurements

UV–visible measurements were obtained using a UV 2401PC record spectrometer, Shimadzu.

Preparation of zeolite

Na-Y zeolite was prepared by hydrothermal treatment of Egyptian kaolin with alkali solution and sodium silicate at 100-120°C according to the Egyptian patent (21) .

Preparation of ion-exchanged zeolites

The ion exchange of transition metal nickel in zeolite was carried out using the batch method. Batch experiments were conducted using 10g of zeolite Y with 100ml of nickel nitrate solution of concentration 0.01M at constant temperatures (25°C) in 250-ml bottles. The bottles were shaken for 30 min. After each ion exchange the solid material was filtered, washed with deionized water and dried at 100°C in air. The exact concentration of metal ions and filterable metal concentrations were determined by AAS (thermoelemental, solar S4, England atomic absorption spectrophotometer). The ion exchange percentage (%) was calculated using the following equation

$$\%\ \text{ion exchange} = (C_i - C_f)/\ C_f \times 100$$

where C_i and C_f are the concentrations of the metal ion in initial and final solutions, respectively.

Reduction of nitrophenols

0.1 g of Ni-Y zeolite mixed with 15 ml of hydrazine hydrate and 5 ml of NaOH (10%) was heated at 70°C. Within few minutes, black color appears indicating the reduction of nickel ions into atoms. To the formed Ni-zeolite catalyst 0.5 g of nitrophenol in ethanol was added. Again 15 ml of hydrazine hydrate along with aliquots 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 of nitrophenol at a given wavelength (nm) at 0 time and definite time, respectively.

Results and Discussion

Characterization of zeolite

XRD

XRD measurement was used for comparing the crystallinity of zeolite before and after the ion exchange process, as well as after the reduction of Ni^{2+} ions into Ni atoms, the patterns are shown in Fig. 1. From this figure it can be observed that the structure of zeolite was not affected neither by nickel ion exchange after five times exchange nor the reduction process.

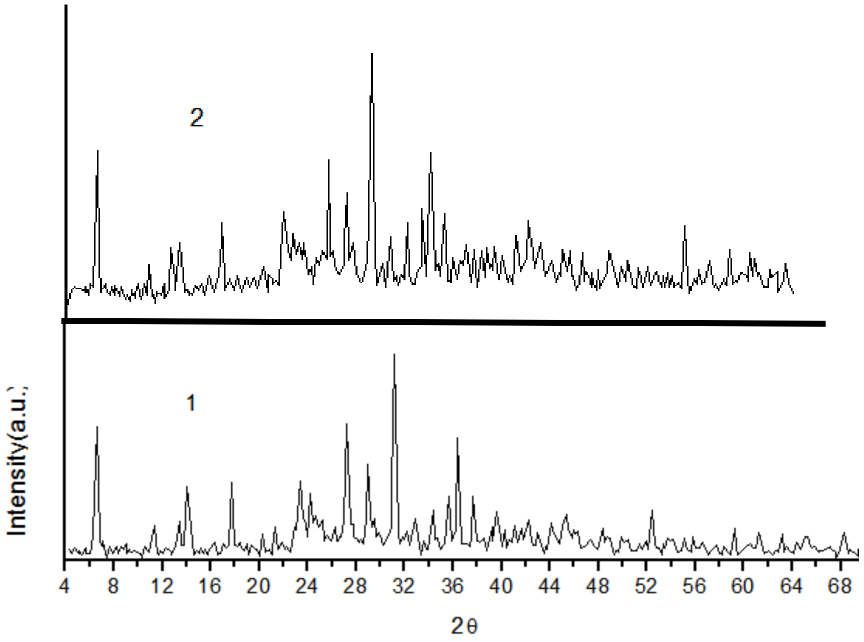

Fig. 1. XRD pattern of Ni-zeolit Y (1) after Ni ion exchange for 5 times and (2) after reduction.

Ion exchange process

The process of nickel ion exchange was performed several times. Five cycles of ion exchange were found to be the most favorable, since further exchanges lead to a decrease in zeolite crystallinity (this was conformed by XRD analysis). The effect of the number of ion exchange repetition on the amount of nickel ions exchanged per 1 g of zeolite is illustrated in Table 1.

TABLE 1. The amount of exchanged Ni^{2+} per 1 g zeolite after different number of exchange cycles.

No of ion exchange*	**Amount of exchanged Ni^{2+} ($mg.g^{-1}$)**
1	5
2	9
3	14
4	19
5	24

* Initial concentration of Ni^{2+} solution = 500 $mg.l^{-1}$.

TEM

Ni ions in zeolite Y transferred into metallic nickel after reduction with hydrazine hydrate in presence of NaOH at pH 9. Transmission Electron Microscope (TEM) examination revealed that the Ni atoms are located inside the cages of zeolite in shape of nano clusters. The data are illustrated in Fig. 2 where the dark spots represent the nickel particles distributed among the zeolite bulk.

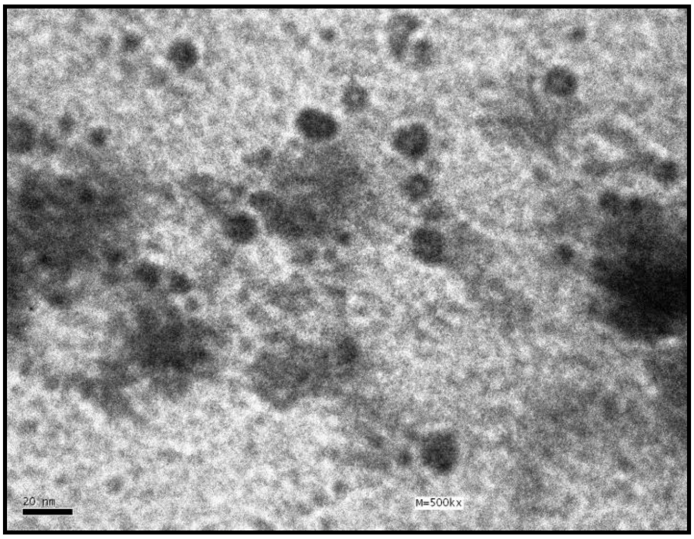

Fig. 2.TEM images of reduced Ni-Y zeolite, magnification 500000x.

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. 4). The same was found for o-nitrophenol and o-aminophenol where the absorbance values 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 wavelengths increase, which is considered as an evidence for the reduction of nitro group into amino group (Fig. 3& 4).

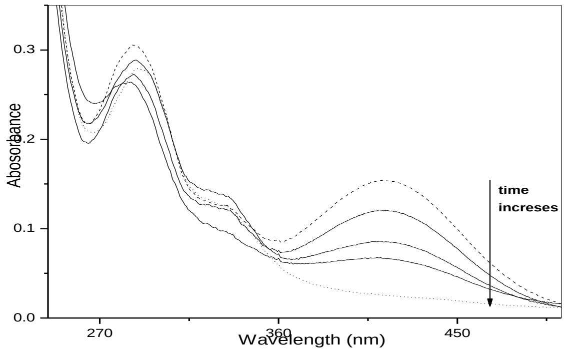

Fig. 3. UV-visible absorption spectra of o-nitrophenol at different intervals of reduction reaction (dashed line: pure o-nitrophenol, dot line: pure o-aminophenol).

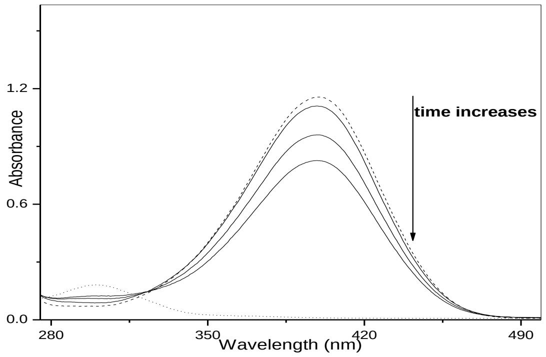

Fig. 4. UV-visible absorption spectra of p-nitrophenol at different intervals of reduction reaction (dashed line: pure p-nitrophenol, dot line: pure p-aminophenol).

pH effect

It was found that the pH 9 is suitable because the absorption spectra for nitrophenol show no interference with that of o- and p-aminophenols. These can be clearly seen in Fig. 5 & 6. On the other hand, 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.

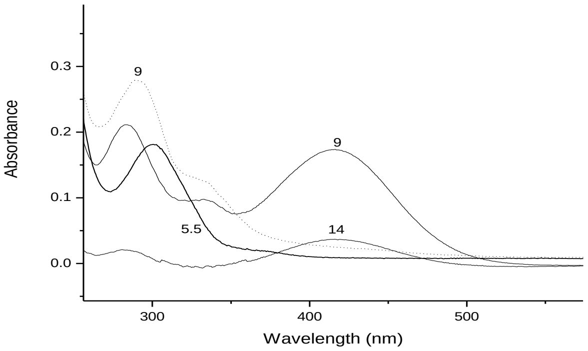

Fig. 5. UV-visible absorption spectra of o-nitrophenol and o-aminophenol at different pH (5.5, 9 and 14). Solid lines: o-nitrophenol and dot line: o-aminophenol.

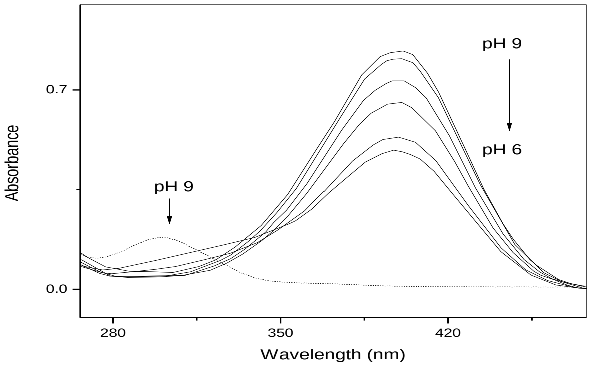

Fig. 6. UV-visible absorption spectra of p-nitrophenol and p-aminophenolat different pH (6-12). Solid lines: p-nitrophenol and dot line: p-aminophenol.

Products characterizations

During the reaction, the yellow colour of p-nitrophenol and the orange colour of o-nitrophenol samples was disappearing till the colour of the reaction solution became colourless. These visual observations can be considered as evidences of complete reduction. After complete reduction 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 examined by IR-spectrophotometer. The results of the IR spectroscopy are illustrated in Fig. 7 & 8. The obtained solids were weighed. The yield was calculated and it was 100%. In addition, the melting points of the samples were performed and it was found that the melting point was 190°C for the obtained p-aminophenol after complete reduction of p-nitrophenol (m.p. of p-nitrophenol= 114°C). While the melting point of o-aminophenol was 170°C which characterized to o-aminophenol (m.p.of o-nitrophenol= m.p. 45°C).

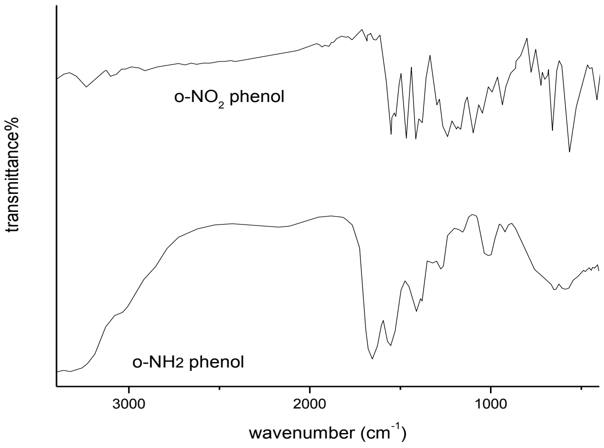

Fig. 7. IR spectra of o- nitrophenol and o- aminophenol.

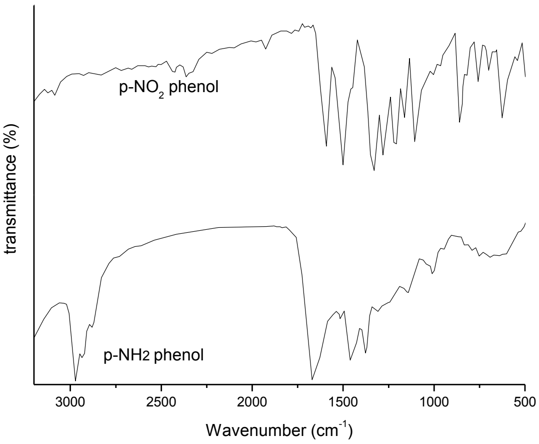

Fig. 8. IR spectra of p- nitrophenol and p- aminophenol.

Optimization

Effect of temperature

The reduction of o- and p-nitrophenols was conducted at different temperatures (60-80°C). It was found that the optimum temperature for complete reduction was higher than 70°C. The results of this series of experiments are given in Table 2 and illustrated in Fig. 9.

TABLE 2. The effect of reaction temperature on the conversion of p-NO_2 phenol (reaction period = 10 min, weight of catalyst = 0.5 g, weight of nitrophenol= 0.4 g, volume of the solution = 100 ml and pH = 9).

Temperature	Conversion %
60	14.9
65	18.3
70	26.2
75	98.9
80	100

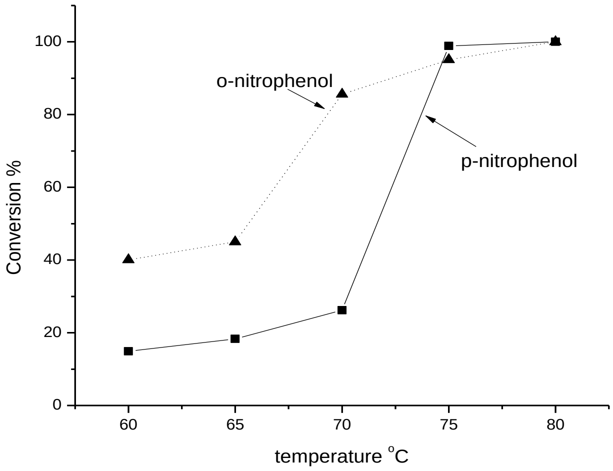

Fig. 9. The relation between conversion % against temperature for o-,p-nirtophenols (reaction period = 10 min, weight of catalyst = 0.5 g, weight of nitrophenol = 0.4 g, volume of the solution = 100 ml and pH = 9).

From Tables 2, 3 and Fig. 9, it can be observed that after fixed time (10 min) at temperatures lower than 70°C, the conversion for both nitrophenols was less than 90%. At 75°C, conversion was more than 95% and further reaction time was required for both case to achieve complete conversion. However, 100% conversion was achieved at 80°C for both nitrophenols. Tables 2 & 3 include the data obtained from the conversion of p-NO_2 phenol and o-NO_2 phenol in presence of the same quantities of catalyst, hydrazine hydrate and pH=9, at constant time at different temperatures (60, 65, 70, 75 and 80°C):

TABLE 3. The effect of reaction temperature on the conversion of o-NO_2 phenol (reaction period = 10 min, weight of catalyst = 0.5 g, weight of nitrophenol= 0.4 g, volume of the solution = 100 ml and pH = 9).

Temperature (°C)	Conversion %
60	40.1
65	45
70	85.6
75	95.1
80	100

The effect of Ni content in zeolite

The data of the dependence of nitrophenol conversion percentage on the degree of Ni ion exchange is given in Tables 4 and 5. It was noticed that at 5 times ion exchange for Ni ions in zeolite Y decreases the time required for the reduction of o- and p-nitrophenol with 100% conversion at constant temperature, pH and the volume.

TABLE 4. The effect of the degree of Ni-ion exchange on the conversion of p-NO_2 phenol. (reaction period = 10 min, weight of catalyst = 0.5 g, weight of nitrophenol = 0.4 g, volume of the solution = 100 ml and pH = 9).

Number of ion exchange	Conversion %
1	25.6
2	38.5
3	72.6
4	78.6
5	99.15

TABLE 5. The effect of the degree of Ni-ion exchange on the conversion of o-NO_2 phenol (reaction period = 10 min, weight of catalyst = 0.5 g, weight of nitrophenol = 0.4 g, volume of the solution = 100 ml and pH = 9).

Number of ion exchange	Conversion %
1	50
2	72
3	82
4	83.3
5	92

The obtained results suggest that the increase of the nano nickel in zeolite leads to a noticeable increase in the percentage conversion of nitrophenols into aminophenols. Further increase in the loading of nickel leads to collapse in the structure of zeolite and consequently to the decrease in the nitrophenol conversion.

The effect of the amount 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 was 0.1 g at 70°C in the presence of 0.5 g catalyst. At these conditions, 2 and 2.5 min were enough for complete reduction of p- and o-nitrophenols, respectively. However, 0.7 g of nitrophenols need about 30 min for complete reduction at the same conditions.

The dependence of conversion on the amount of nitrophenols was illustrated in Table 6.

TABLE 6. The effect of nitrophenols concentration on the time required for complete conversion (weight of catalyst = 0.5 g, volume of the solution = 100 ml 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	2	2.5
0.4	6	8
0.7	25	30

The effect the amount of 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 in Tables 7,8. It can be seen increasing the quantity of the catalyst leads to remarkable decrease of the time required for complete conversion of nitrophenols to the corresponding aminophenols.

TABLE 7. The effect of the amount of catalyst on the time required for complete conversion of p-NO_2 phenol (weight of nitrophenol = 0.4 g, volume of the solution = 100 ml and pH = 9).

Weight (g) of catalyst	Time (min) for complete conversion
0.3	10
0.5	5
0.7	2
0.8	2

TABLE 8. The effect of the amount of catalyst on the time required for complete conversion of o-NO_2 phenol on the weight of catalyst (weight of nitrophenol = 0.4 g, volume of the solution = 100 ml and pH = 9).

Weight (g) of catalyst	Time (min) for complete conversion
0.3	12
0.5	6
0.7	3
0.8	2

Catalyst recovery

Viability of catalyst recycling was tested after the reduction reaction of both p- and o-nitrophenols. A five cycles experiment was performed with Ni-zeolite catalyst and nitrophenols. The initial weight of phenols and catalyst was 0.4 g and 0.3 g, respectively. The catalyst was filtered after each cycle and reused to the next cycle. The time required for complete conversion for each cycle was recorded and given in Table 9. From this table, it can be observed that Ni-zeolite showed high catalytic activity for 5 times of conversion, yielding 100% conversion for each case.

TABLE 9. Durability of the catalyst for complete conversion of nitrophenols.

No. of experiment	Time for complete conversion of p-nitrophenol	Time for complete conversion of o-nitrophenol
1	2	2.5
2	3	4
3	5	7
4	10	12
5	15	20

Conclusion

Ni-Y zeolite was prepared by ion exchange using Na-Y zeolite synthesized from Egyptian kaolin. TEM showed that the Ni after reduction with hydrazine hydrate existed as nanoclusters in zeolite. Catalytic conversion of nitrophenols into aminophenols was conducted in the presence of the prepared nano-nickel zeolite.

Optimization was followed by studying the effect of many factors on the conversion of nitrophenols. The increase of the temperature increases the percentage of conversion. Optimum conditions to convert nitrophenols were pH=9 and reaction temperature between 70-80°C by using a 5 cycle Ni-exchanged zeolite. The increase of weight of catalyst decreases the time consuming for complete conversion.

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(*Received* 8 / 9 / 2010;
accepted 12/ 10/ 2010)

طريقة مبتكرة لاختزال المواد العضوية (النيتروفينولات) باستخدام حفازات النيكل فى احجام متناهية الصغر في الزيوليت المحضر من الكاولين المصري

هيام حلمى ابراهيم ، دعاء محمد المكاوى[*]، صلاح الدين عبده حسن[**] ومحمد محمد سليم[*]
وزارة البحث العلمى ، [*]المركز القومى للبحوث و[***]كلية العلوم – جامعة عين شمس – القاهرة - مصر .

تم اختزال النيترو فينولات (٢ ، ٤ نيتروفينول) الى الأمينوفينولات المقابلة عبر طريقة جديدة فعالة بالاختزال فى وجود حفاز النيكل. و تم تحضير حفاز النيكل فى الأحجام متناهية الصغر المحضر على الزيوليت باستخدام هيدرات الهيدرازين للنيكل المستبدل فى الزيوليت. واستخدم الزيوليت المحضر من خام الكاولين المصري. تتحلل جزيئات الهيدرازين في درجة الحرارة المنخفضة معطية ذرات الهيدروجين النشطة. ثم تختزل ذرات الهيدروجين هذه أيونات النيكل المستبدلة فى الزيوليت. وهذا يتيح تشكيل عنقوديات النيكل في حجم النانو. وبمزيد من التحلل لهيدرات الهيدرازين على سطح ذرات النيكل ينتج ذرات الهيدروجين الوليدة التي تختزل مجموعات النيترو. وقد تم استخدام العديد من التقنيات مثل حيود الأشعة السينية ، الأشعة تحت الحمراء ، الميكرسكوب الالكترونى ، طيف الامتصاص الأشعة فوق البنفسجية المرئية ، وقياسات الامتصاص الذري. وقد اكد التحليل باستخدام حيود الأشعة السينية أن الزيوليت يحتفظ بشكله البلورى بعد عمليات تبادل النيكل ثم بالاختزال. واستخدم قياس الامتصاص الذري لتحديد كمية أيونات النيكل المتبادلة فى الزيوليت. وقد بين استخدام الميكرسكوب الالكترونى تشكيل ذرات النيكل النانو فى الزيوليت. وقد اظهر تحليل الأشعة تحت الحمراء ظهور مجموعات الأمينو التى تم تحضيرها من اختزال مجموعات النيترو فى النيتروفينولات. ولمتابعة اختفاء مركبات النيترو و تقدير نسبة الاختزال استخدم قياس امتصاص الأشعة فوق البنفسجية المرئية. وتم دراسة اعادة استخدام الحفاز والعوامل المؤثرة على عملية الاختزال مثل تركيز الفينول وتركيز الأس الهيدروجينى وتركيز الحفاز ودرجة الحرارة. و أظهرت النتائج ودراسة معدل التفاعل أن نسبة الاختزال تصل الى ١٠٠ ٪ خلال دقائق قليلة. ومقارنة بالنتائج والدراسات المنشورة سابقا ، يمكن الاستنتاج أن هذه الطريقة تعتبر أكثر اقتصاديا ، وأسرع وأكثر كفاءة.