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Influence of Support on Catalytic Activity of Nano-Ni Catalysts in P-nitrophenol Reduction to P-aminophenol

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THE CATALYTIC activities of $CaCO_3$-, TiO_2-, Al_2O_3 - and SiO_2-supported Ni catalysts in reduction of p-nitrophenol to p-aminophenol were investigated. The catalysts were prepared by impregnation using a solution of appropriate concentrations of $NiCl_2$ in order to obtain catalysts with 2.5, 5 and 10% nickel. The dried solids were treated with hydrazine hydrate to reduce nickel ions to metallic nickel, on which the reduction of p-nitrophenol takes place. The catalysts were characterized by XRD and SEM before and after conducting the reduction reaction of p-nitrophenol .The results showed that all catalysts contain crystalline nano nickel. The catalysts were active in reduction of p-nitrophenol into p-aminophenol. The activity was in the following order: Ni/ TiO_2 > Ni/ $CaCO_3$ > Ni/ SiO_2> Ni/ Al_2O_3, *i.e.* the activity was decreased with increasing the acidity of the supports.

Keywords: p-Nitrophenol, p-Aminophenol, Catalytic reduction, Nano-sized nickel, Hydrazine hydrate and Supports.

P-aminophenol is an important intermediate in the manufacture of pharmaceuticals such as paracetamol, acetanilide, phenacetin …,etc (1-7). P-aminophenol is also used as a photographic developer, corrosion inhibitor and as a dyeing agent(8). Due to the significance of p-aminophenol, there is a demand for direct catalytic reduction of p-nitrophenol. Conventionally, p-aminophenol is produced by iron-acid reduction of p-nitrophenol(9). The major disadvantage of the iron-acid reduction process is the generation of large amount of Fe–FeO sludge (1.2 kg/kg product) which causes a serious pollution problem(2). Now the production of p-aminophenol is mainly via a single step catalytic hydrogenation of nitrobenzene using both noble metal (Pt) and strong mineral acid (H_2SO_4) as co-catalysts(2,3). The disadvantages of this process are that strong corrosive sulphuric acid and high cost noble metal are used and that aniline as a competitive byproduct is largely and unavoidably formed.

Direct reduction of p-nitrophenol catalyzed by Pt, Pd, Ru and Ni is considered as an alternative green process for the production of p-aminophenol(3,4). It is well known that nickel is an active and facile catalyst in reduction reaction. However, commercially available Raney Ni catalyst not only catalyzes the reduction of

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*Corresponding author e-mail: mmasliim@yahoo.com nitro group to amino one but also catalyzes the hydrogenation of aromatic ring, perhaps caused by the micropores of Raney Ni$^{(3)}$. In contrast to Raney Ni catalyst, active metallic nickel present in supported catalysts usually exists in the style of nanosized crystallites, avoiding formation of micropore structure.

However, the nature of support affects the performance of active phase, especially for nickel where metal-support interactions are involved$^{(10–16)}$. The catalytic performance of supported Ni catalyst in reduction of p-nitrophenol to p-aminophenol is seldom investigated. In our previous works we studied the reduction of p-nitrophenol over nano nickel on different supports $^{(12-16)}$.

In our present work, $CaCO_3$-, TiO_2-, Al_2O_3- , and SiO_2-supported Ni catalysts were prepared by incipient wetness impregnation method. The supported Ni catalysts were characterized by Scanning Electron Microscope and X-ray diffraction techniques. The influence of support on the catalytic activity of Ni in reduction of p-nitrophenol to p-aminophenol was investigated.

Experimental

Catalyst preparation

Silica support preparation

Dilute commercial sodium silicate solution was treated with dilute HCl until pH 6.5 at which complete precipitation of silica occurred. The precipitated silica was filtered, washed , dried and calcined at 550 °C for 2 hr.

Al_2O_3 preparation

The Al_2O_3 was prepared from Al-salt by precipitation with ammonia solution with heating and washing the obtained precipitate. The solid was dried and calcined at 550 °C for 2 hr.

Supported catalysts

All catalysts were prepared by impregnation of the supports with appropriate quantity of $NiCl_2$ solutions in order to obtain 2.5, 5 and 10 wt. % Ni on the supports.

The final catalysts preparations are:

TABLE 1. Final catalyst preparations.

Support	Catalysts		
Unsupported Ni			
TiO_2	2.5% Ni/ TiO_2	5% Ni/ TiO_2	10% Ni/ TiO_2
$CaCO_3$	2.5%Ni/ $CaCO_3$	5%Ni/ $CaCO_3$	10%Ni/ $CaCO_3$
SiO_2	2.5%Ni/ SiO_2	5%Ni/ SiO_2	10%Ni/ SiO_2
Al_2O_3	2.5%Ni/ Al_2O_3	5%Ni/ Al_2O_3	10%Ni/ Al_2O_3

Reduction of the catalysts

All the prepared solids were reduced by the addition of hydrazine hydrate and few drops of concentrated sodium hydroxide and heating the mixture at 80°C until the color of the mixture turned black or grayish black, indicating complete reduction of nickel ions into nano nickel metals.

Characterization of the prepared and reduced catalysts

XRD: X-Ray diffraction patterns were done using Bruker D8 advance instrument with CuKα target with secondly monochromator 40 kV, 40 mA.

Scanning Electron Microscopy: The scanning electron microscope (SEM) photographs were carried out using SEM Model Philips XL 30 attached with EDX unite, with accelerating voltage 30 k. magnification 10 x up to 400.000x and resolution for W.(3.5nm) . The samples were coated with gold.

Catalytic activity procedure: The process of reduction of p-nitrophenol into p-aminophenol was carried out as follows:

1g of the reduced catalyst was taken with 10 ml of hydrazine hydrate and few drops of sodium hydroxide. To this mixture a solution of 0.5 g p-nitrophenol in 5ml methanol was added. The mixture was heated at 80°C with stirring until the color is turned from yellow to colorless, indicating complete reduction of p-nitrophenol. This time was taken as a measure for the activity of the catalyst, *i.e* the small time indicating the high activity.

Results and Discussion

In this work the effect of the support on the catalytic activity of nickel catalysts in reduction of p-nitrophenol into p-aminophenol was conducted. The catalysts were characterized using X-ray analysis and scanning electron microscopy.

XRD analysis

(2.5wt% Ni/TiO_2 gave no detectable XRD patterns for crystalline nickel due to the small amount of nickel.)

Figures 1-4 illustrate the obtained results of X-ray data.

Figure 1a shows the XRD of 5% Ni/TiO_2 which gave the XRD patterns of nanonickel crystallites. This figure shows also the crystalline TiO_2 phase. Figure 1b shows the catalyst after reaction in which the degree of crystallinity of nano nickel decreased.

Figure 2(a) shows the XRD of the reduced 5% 5% Ni/SiO_2; from this figure , it can be shown that no patterns for SiO_2 were detected, *i.e.* it is an amorphous phase, but only a crystalline nanonickel metal was obtained. The participation of the catalyst in the reduction of p-nitrophenol led to sharp decrease in the crystallinity of nickel metal Fig. 2 (b). This confirms the idea about the formation of unstable intermediate complex of nickel with the reacting compound leading to a considerable change in the crystallinity of the crystalline nano nickel.

Figure 3(a) shows the patterns of the catalyst prepared with 5% Ni/Al_2O_3. The inspection of the X-ray data of this catalyst, nanonickel crystalline metallic phase was detected with amorphous Al_2O_3 phase. Figure 3(b) shows the x-ray data of nickel on aluminium oxide which illustrates the existence of crystalline nickel with somewhat less degree of crystallinity on the amorphous alumina.

Figure 4(a) shows the patterns of the catalyst with 5% $Ni/CaCO_3$. From this figure, it can be observed that nanonickel crystalline metallic phase was obtained with well crystalline $CaCO_3$ phase. Figure 4 (b) showed a considerable decrease in the degree of crystallinity of nickel while a somewhat retaining the crystallinity of calcium carbonate. This is also a confirmation for the participation of the active nickel in the process of reaction as an intermediate complex and converting into less crystalline phase .

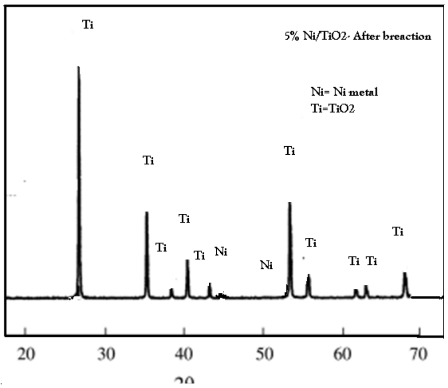

Fig. 1. (a)The representative XRD patterns of 5% TiO_2- supported Ni catalyst before reaction .

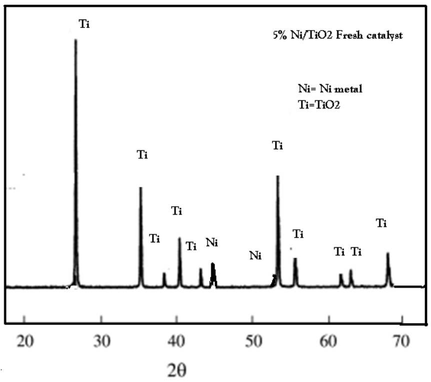

Fig. 1.(b)The representative XRD patterns of 5% TiO_2- supported Ni catalyst after reaction .

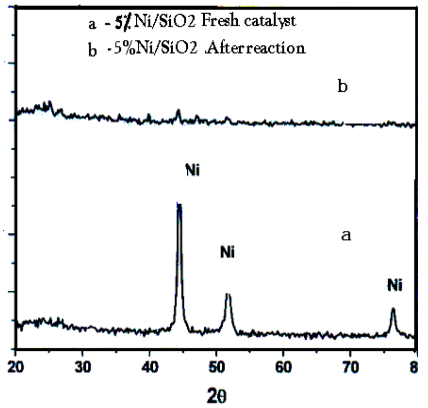

Fig. 2.The representative XRD patterns of 5% SiO_2- Al_2O_3- supported Ni catalyst before and after reaction .

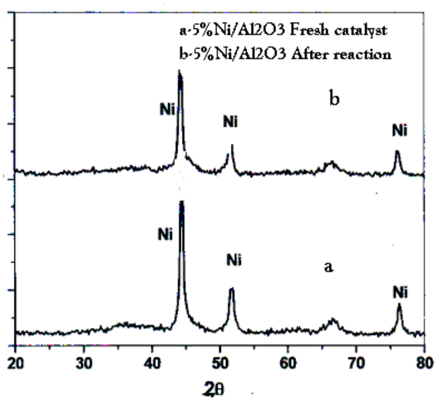

Fig. 3. The representative XRD patterns of 5% supported Ni catalyst before and after reaction .

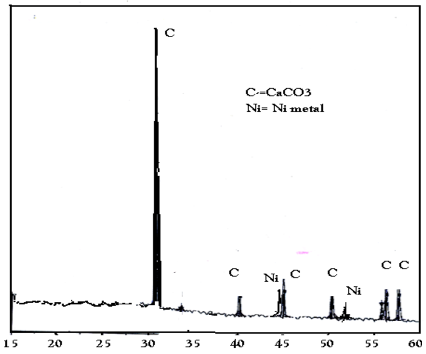

Fig. 4.(a)The representative XRD patterns of 5% $CaCO_3$- supported Ni catalyst before reaction .

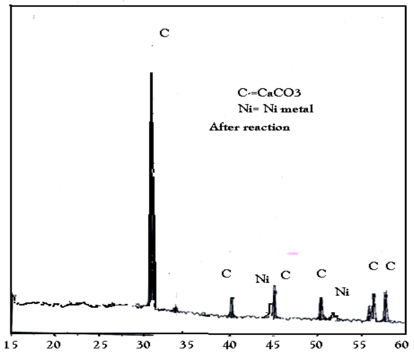

Fig. 4.(b)The representative XRD patterns of 5% $CaCO_3$- supported Ni catalyst after reaction .

Scanning electron microscopy

The SEM data are illustrated in Fig. 5-12.

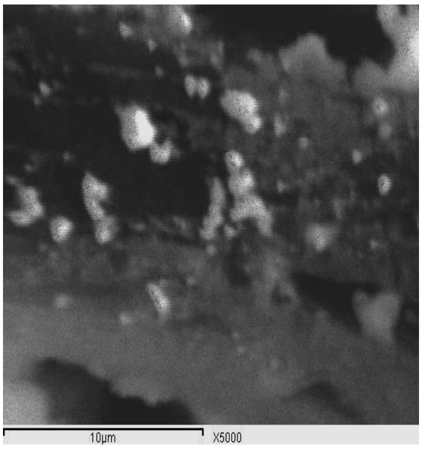

Fig. 5. Scanning electron micrograph of 5% Ni/ $CaCO_3$ before addition of p-nitropheno .

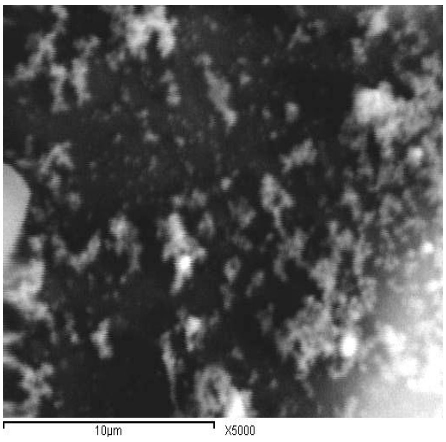

Fig. 6. Scanning electron micrograph of 5% Ni / $CaCO_3$ after addition of p-nitrophenol.

Reduction of p-nitrophenol

In this series of experiments one gram of the catalyst was firstly reduced using hydrazine hydrate as hydrogen donor with drops of sodium hydroxide. The reduction of nickel ions in solution was completed when the color of the solution becomes black or grayish black.

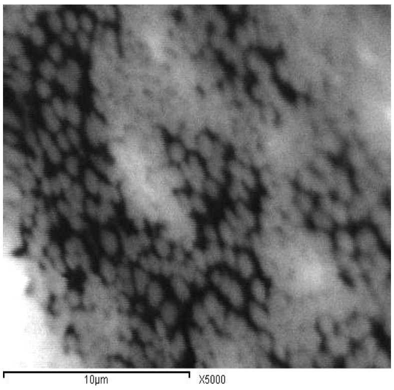

Fig. 7. Scanning electron micrograph of 5% Ni / Al_2O_3 before addition of p-nitrophenol.

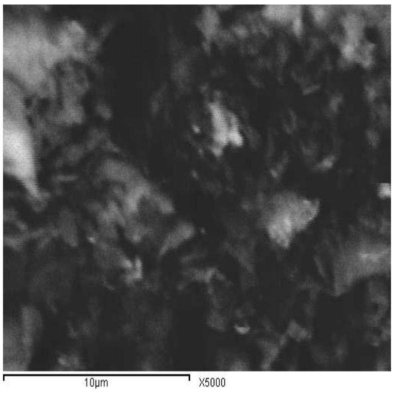

Fig. 8. Scanning electron micrograph of 5% Ni / Al_2O_3 after addition of p-nitrophenol.

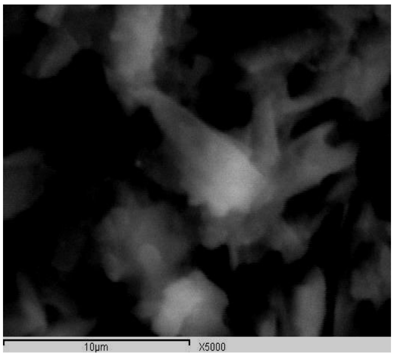

Fig. 9. Scanning electron micrograph of 5% Ni / TiO_2 before addition of p-nitrophen

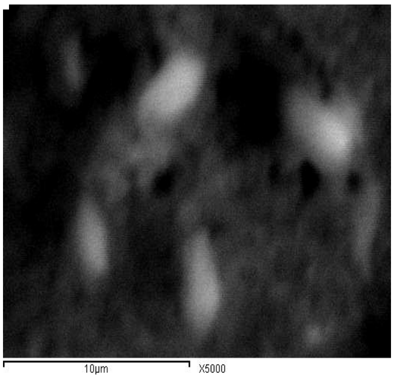

Fig. 10. Scanning electron micrograph of 5% Ni / TiO_2 after addition of p-nitrophenol

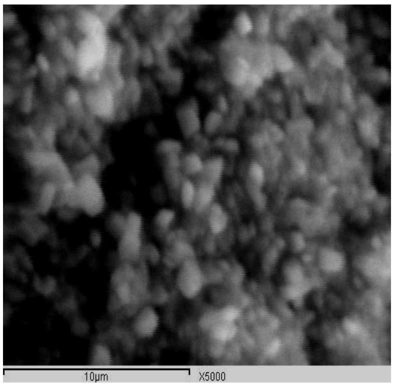

Fig. 11. Scanning electron micrograph of 5% Ni / SiO_2 before addition of p-nitrophenol.

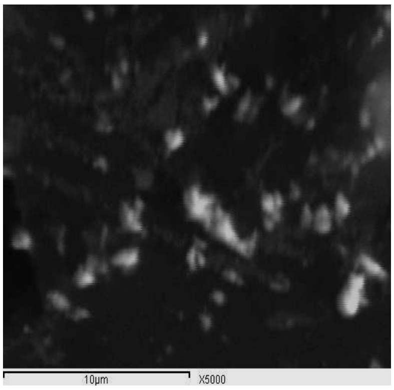

Fig. 12. Scanning electron micrograph of 5% Ni / SiO_2 after addition of p-nitrophenol.

To the reduced nickel, 0.5 g p-nitrophenol in 5 ml methanol was added. 10 ml of hydrazine hydrate and few drops of conc. NaOH were introduced to the mixture with heating at 80 °C. The mixture was stirred until the color of the solution converted from yellow to colorless, indicating complete conversion of p-nitrophenol into p-aminophenol. The time for complete conversion was taken as a measure of the catalytic activity of the catalyst used.

Reduction of p-nitrophenol on 2.5% Ni

The reaction of reduction of p-nitrophenol to p-aminophenol was conducted on all catalysts containing 2.5% Ni on different supports. The data are included in the following table:

TABLE 2. The time taken for complete reduction to p-aminophenol with 0.5 g p-nitrophenol in each experiment .

Support	**No.of repetitions**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
Titania		17	23	23	24	25	27	29	29	30	30	39	54	63	64
Silica		60	65	70	75	75	80	85	85	88					
Alumina		43	97	146	170	200	215	230	240						
Calcium carbonate		14	15	20	27	39	53	58	80						
Unsupported Ni		85	300	360	440	632									

From this table, it can be noted that, the nickel catalyst takes 85 sec. in the first experiment. This time increases to 300 sec for the second experiment while the 5th experiment takes more than 600 sec. On the other hand, 2.5% Ni/ TiO_2 completed the reduction in the first experiment within 23 sec. The time for complete reduction on this catalyst was found to increase gradually up to 25 sec. for the 5th experiment. Further performing catalysis on this catalyst high stability and durability even up to the 14th experiment which needs 64 sec.

2.5% Ni/ $CaCO_3$ showed also high catalytic activity with respect to reduction of p-nitrophenol to p-aminophenol but less than 2.5% Ni/ TiO_2, *i.e* , the 8*th* experiment in case of Ni/ $CaCO_3$ needs 80 sec., while for Ni/ TiO_2 it needs about 30 sec.

The activity and durability of 2.5% Ni/ SiO_2 was found to be stable at about 75 sec. from the first up to the 8th experiment.

Dealing with the conversion of p-nitrophenol to p-aminophenol on 2.5% Ni/Al_2O_3, the conversion takes 43 sec. for the first experiment but for the 8*th* experiment , it takes 200 sec.

This means that, the most active and durable catalyst is 2.5% Ni/ TiO_2, and the most inactive one is the unsupported one (Fig 13).

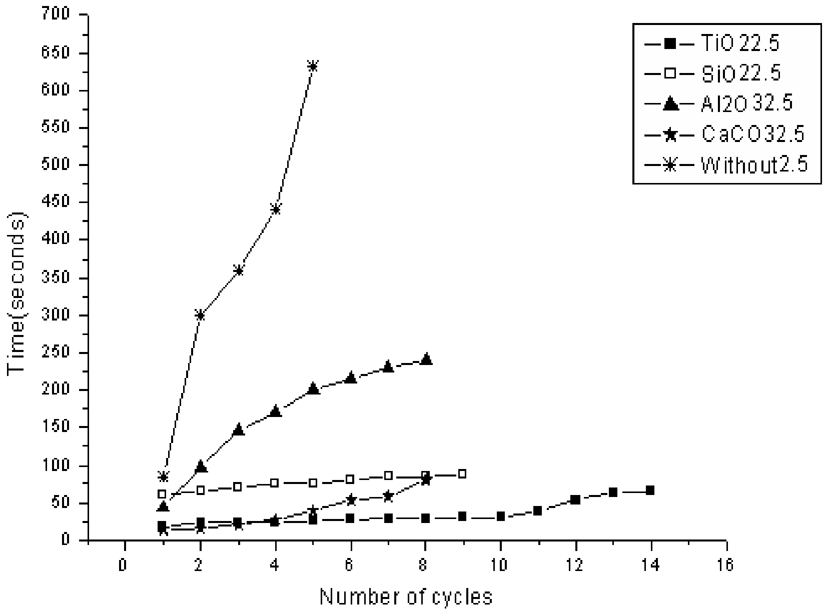

Fig. 13. 2.5% Supported catalyst.

Reduction of p-nitrophenol with 5% Ni/support

This series was done with 5% Ni on all supports. The time for complete conversion of p-nitrophenol into p-aminophenol was taken for all catalysts and included in the following table;

TABLE 3. The time taken for complete reduction of p-nitrophenol to p-aminophenol for 5% Ni/different supports.

Support	**No. of repetitions**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
Titania		35	35	37	38	39	40	42	45	47	50	50	52	54	;
Silica		55	60	60	70	80	85	90	90						
Alumina		60	90	110	140	150	160	165	165						
Calcium carbonate		11	12	15	24	36	43	48	64	80					
Unsupported Ni		120	130	136	140										

From the above table it can be observed that for 5% Ni/TiO_2, the time taken for the first experiment 35 sec. and the 14^{th} experiment took about 40 sec.. This indicates that this catalyst is durable, *i.e.* a very small change in its activity was monitored.

The lowest activity in reduction of p-nitrophenol into p-aminophenol was measured for Ni-catalyst without support, *i.e.* , the first experiment takes 120 sec. and the 4^{th} experiment takes 140 sec.

Inspecting the obtained results for the catalysts containing 5% Ni , it can be concluded that the Ni/TiO_2 was the most activeand durable one among all catalysts. On the other hand, unsupported Ni catalyst showed the lowest activity in the reduction of p-nitrophenol into p-aminophenol.

In case of 5% Ni/SiO_2 this catalyst showed less activity than 5% Ni/TiO_2 with moderate durability.

5%Ni/$CaCO_3$ started with high catalytic activity, *i.e*., the complete conversion of p-nitrophenol takes about 11 sec. but at the 4^{th} experiment it takes 24 sec. while further conductivity experiments up to the 9^{th} one it takes 80 sec., *i.e.* a considerable drop in the activity .

5% Ni/Al_2O_3 showed the least activity and durability for p-nitrophenol reduction.

This indicates that the highly active catalyst is the more basic one and the less active catalyst is the more acidic one (Fig. 14).

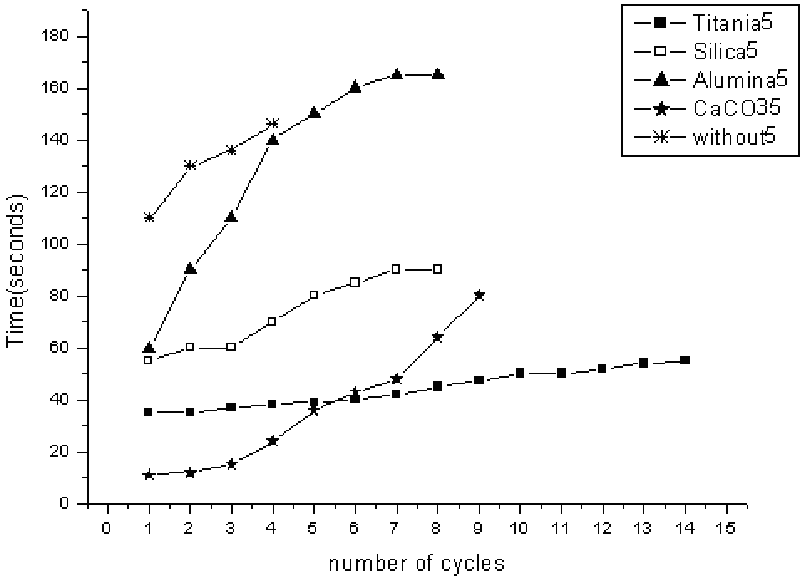

Fig. 14. 5% Supported catalyst .

Catalytic activity of 10% Ni/supports

This series was done with 10% Ni on all supports. The time for complete conversion of p-nitrophenol into p-aminophenol was taken for all catalysts and included in the following table:

TABLE 4. The time taken for complete reduction of p-nitrophenol to p-aminophenol for 5% Ni/different supports.

Support	No. of repetitions	1	2	3	4	5	6	7	8	9	10
Titania		19	20	25	30	30	35	37	37	40	40
Silica		40	42	42	44	46	53	55	55	67	
Alumina		30	74	104	113	116	120	124	125		
Calcium carbonate		13	16	20	36	53	61	71	76	95	
Without support		78	110	130	140	162	180	210			

From Table 4, it can be observed that 10% Ni/TiO_2 is the most active and durable one, while 10% Ni/Al_2O_3 is the lowest active and durable one. On the other hand, unsupported Ni-catalyst has very small activity in comparison with all catalysts containing supports (Fig-15).

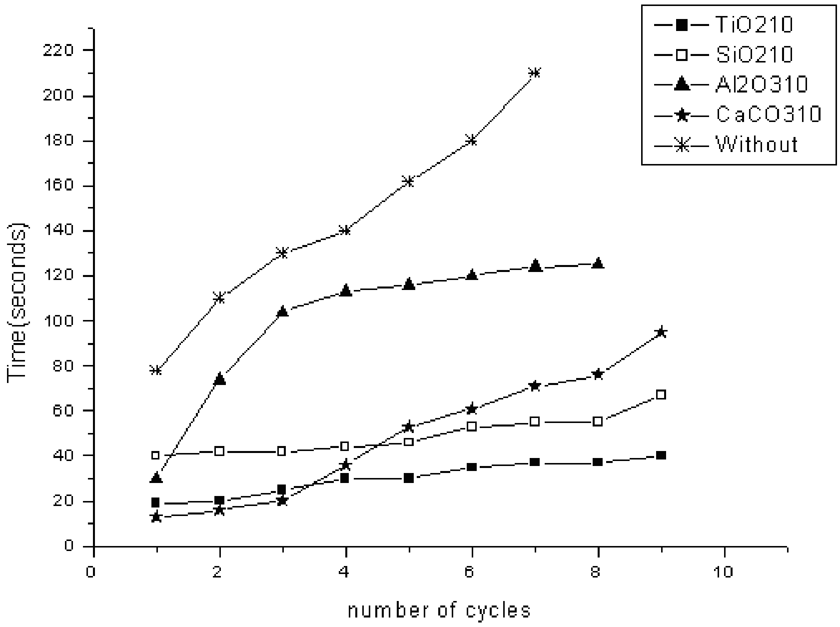

Fig. 15. 10% Supported catalyst.

One step reaction with 4 g p-nitrophenol

a- Reduction of p-nitrophenol with 2.5 % Ni/support

TABLE 5. The results of reduction of 4g p-nitrophenol with Ni/ supports.

Support	**Time taken for complete reduction of 4 g p-nitrophenol**
TiO_2	150 seconds
SiO_2	340 seconds
Al_2O_3	365 seconds
$CaCO_3$	125 seconds
without	510 seconds

Comparing these results with the obtained above when the reaction proceeded stepwise with 0.5 g p-nitrophenol in each experiment (Table 6). From these two series, it can be concluded that the one-step reduction is more favorable than stepwise process. The results for all catalysts with 2.5% Ni are included in the following table:

TABLE 6. The results of stepwise and one-step processes reduction of 4g p-nitrophenol with 2.5%Ni/ supports.

Catalyst	Stepwise reduction of 4 g p-nitrophenol	One-step reduction
2.5% Ni/ TiO_2	197 seconds	150 seconds
2.5% Ni/ SiO_2	683 seconds	340 seconds
2.5% Ni/ Al_2O_3	1341 seconds	365 seconds
2.5% Ni/ $CaCO_3$	306 seconds	125 seconds
Ni without support	1817 seconds	510 seconds

From this table it can be observed that all catalysts showed higher catalytic activity for the one-step process than the stepwise reduction, *i.e*. the last process for reduction of 5 g p-nitrophenol needs more time for complete reduction.

The results obtained for catalysts containing 5% and 10% Ni/supports for one-step and stepwise are included in Tables 7 and 8, respectively.

TABLE 7. The results of stepwise and one-step processes reduction of 4g p-nitrophenol with 5%Ni/ supports.

Catalyst	Stepwise reduction of 4 g p-nitrophenol	One- step reduction
5% Ni/ TiO_2	311 seconds	100 seconds
5% Ni/ SiO_2	590 seconds	220 seconds
5% Ni/ Al_2O_3	1040 seconds	160 seconds
5% Ni/ $CaCO_3$	333 seconds	110 seconds
Ni without support	1200 seconds	470 seconds

TABLE 8. The results of stepwise and one-step processes reduction of 4g p-nitrophenol with 10 %Ni/ supports.

Catalyst	Stepwise reduction of 4 g p-nitrophenol	One-step reduction
10% Ni/ TiO_2	160 seconds	33 seconds
10% Ni/ SiO_2	180 seconds	435 seconds
10% Ni/ Al_2O_3	630 seconds	106 seconds
10% Ni/ $CaCO_3$	105 seconds	40 seconds
Ni without support	650 seconds	300 seconds

It can be seen from Tables 7, 8 and 9 that the one-step reduction of a certain amount of p-nitrophenol is more efficient than the stepwise reduction process.

Conclusions

The supported Ni nanoparticle catalyst was prepared by the impregnation method using hydrazine hydrate as a reductant. For the supported Ni catalysts, support property has an important impact on the catalytic activity in p-nitrophenol reduction to p-aminophenol. The catalytic activity increased with the increase of the reduced metallic Ni amount and followed the order of Ni/ TiO_2 > Ni/ $CaCO_3$ >> Ni/ SiO_2 > Ni/ Al_2O_3 >> Unsupported nickel. XRD patterns showed that 5% Ni/SiO_2 catalyst has a well crystalline Ni metal phase while after using the catalyst nearly no crystalline Ni could be observed. In contrast to SiO_2–supported catalyst, the crystallinity of Ni/Al_2O_3, Ni/TiO_2 and Ni/$CaCO_3$ showed very small change after using the catalyst under the same conditions (Fig. 1-4) which can be attributed to the strong metal support interaction between Ni metal and Al_2O_3, TiO_2 and $CaCO_3$ supports, respectively compared to weak metal support interaction between Ni and SiO_2 support. XRD patterns of 2.5wt % Ni/SiO_2, Ni/TiO_2, Ni/$CaCO_3$ and Ni/Al_2O_3 catalysts showed no crystalline Ni metal at all which is attributed to the very small amount of Ni loaded. One-step reduction of p-nitrophenol is better than stepwise process for the same quantity of p-nitrophenol.

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تأثير المادة الحاملة على الكفاءة الحفزية لحفازات النيكل في اختزال البارا نيتروفينول إلى بارا أمينوفينول

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تم تحضير البارامينوفينول باختزال البارانيتروفينول على حفاز النيكل النانو المحمل على أربعة أنواع من المواد الحاملة هي السيليكا والألومينا وكربونات الكالسيوم والتايتانيا باستخدام الهيدرازين هيدرات كمادة مانحة للهيدروجين. استخدمت كميات مختلفة محملة من النيكل النانو 2.5 و 5 و 10 ٪ . تم توصيف الحفازات المحضرة باستخدام حيود الأشعة السينية والمجهر الإلكتروني الماسح . وجد أن حفاز النيكل على التايتانيا أكثر كفاءة ثم المحمل على كربونات الكالسيوم ثم المحمل على السيليكا ثم المحمل على الألومينا ثم النيكل الغير محمل على شيء . وجد أيضاً أن الكفاءة تتأثر بدرجة البلورة للنيكل . وجد أيضاً أن اختزال كمية معينة من البارانيتروفينول فى خطوة واحدة أسرع من اختزال نفس الكمية فى اكثر من خطوة .