Synthesis and characterization of nano-sized nickel catalyst supported on SiO₂–Al₂O₃

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ABSTRACT
SiO₂–Al₂O₃ support material was prepared by sol–gel method, followed by calcination at 500, 1000 and 1500 °C. The supported nickel catalyst containing 5 wt.% was obtained by impregnating a known mass of the calcined support material with nickel sulfate solution followed by drying and reduction with hydrazine hydrate at 80–100 °C. The prepared catalysts were fully characterized by XRD and SEM, EDX and ESR. The hydrogenation of p-nitrophenol into p-aminophenol was performed using hydrazine hydrate as hydrogen donor. The product of the reaction was examined using IR, and NMR. The results showed that the degree of crystallinity of the support affects the catalytic activity of nano-sized Ni catalyst. It was observed that as the degree of crystallinity of the support material increases the catalytic activity increases. On the other hand, intermolecular interaction between nano-nickel clusters disappears completely in samples whose support was calcined at 1500 °C.

1. Introduction
Nickel metal catalyst loaded on SiO₂ or Al₂O₃ catalyst has been used in hydrogenation reactions only as separate oxides [1–8]. However, to our knowledge the catalytic behavior of metallic nickel loaded on mixed SiO₂–Al₂O₃ solid has not been yet investigated.

The present work aimed at shedding more light upon the effect of the degree of the crystallinity of SiO₂–Al₂O₃ support on the catalytic activity of nickel catalyst. The reaction used in this study was the hydrogenation of p-nitrophenol into p-aminophenol. p-Aminophenol is considered to be very important intermediate in the manufacture of many analgesic and antipyretic drugs, such as paracetamol, acetanilide, phentacin, ... etc. [9–15]. It is also used as a developer in photography (under trade names of activol or azol), in addition of its use in chemical dye industries [16].

There are several methods used in the preparation of p-aminophenol from p-nitrophenol such as: (1) metal/acid reduction [17], (2) catalytic hydrogenation [18], (3) electrolytic reduction [19], (4) homogeneous catalytic transfer hydrogenation [20], and (5) heterogeneous catalytic transfer hydrogenation, etc.

Among all previously mentioned methods, direct catalytic hydrogenation of p-nitrophenol to p-aminophenol becomes the most important one. This is because it could be an efficient route for synthesis [15]. Raney nickel [21], nano-sized nickel [22] and several noble metal catalysts, such as Pd/C [15], have been used as catalysts for this reaction. Due to their lowest cost and higher catalytic activity, supported nickel catalysts, are widely used in such reactions [15–21].

Although nickel catalyst is used in hydrogenation reactions [23–29], only few recent researches have been carried out on hydrogenation of p-nitrophenol over nano-sized supported nickel metal catalyst [10,30,31].

The present investigation reports the results of an intensive study on preparation and characterization of nano-sized metallic nickel supported on SiO₂–Al₂O₃ being prepared by sol–gel and calcined at 500–1500 °C. The techniques employed were XRD, SEM, EDX, ESR and hydrogenation of p-nitrophenol.

2. Experimental
2.1. Materials
Tetraethoxysilane (TEOS; Fluka, >98% purity), aluminum nitrate nonahydrate (Al(NO₃)₃·9H₂O), NiSO₄·7H₂O (Merck), Commercial...
Rainy Nickel (Merck), Hydrazine hydrate 80% (Merck), p-nitrophenol (PNP) (Merck) and p-aminophenol (PAP) (as a standard materials), Methanol (spectroscopic grade) (merck).

2.1.1. Preparation of SiO₂–Al₂O₃ mixed oxide support
SiO₂–Al₂O₃ mixed oxide support material was prepared by a sol–gel technique. A 2SiO₂:3Al₂O₃ molar ratio batch of the support was prepared by slow hydrolysis. After gelling and drying the sample was calcined at 500 °C for 2 h in order to remove the residual nitrates and volatiles. The resulted solid is nominated as (SA-500). The sample was then milled using agate mortars and heated at 1000 and 1500 °C for 4 h. The resulted solids are nominated as (SA-1000, and SA-1500) respectively. The surface area of the prepared supports were 50, 20 and 10 m²/g for the supports SA-500, SA-1000, and SA-1500 respectively.

2.1.2. Preparation of nano-sized nickel catalyst
Nickel was loaded on support being calcined at 500, 1000 and 1500 °C; by means of impregnation. The extent of Ni was fixed at 5 wt%. Reduction was done using hydrazine hydrate in an alkaline medium at 80–100 °C in order to obtain the metallic form of nickel.

2.2. Techniques

2.2.1. Hydrogenation process
Catalytic hydrogenation reaction was done by dissolving p-nitrophenol in an appropriate amount of methanol, followed by addition of hydrazine hydrate as hydrogen source, then heating at 80 °C. The catalyst was added to the heated solution and the time to reach 100% conversion was taken as an express of the catalytic activity. The catalyst:reactant (PNP) was fixed at 1:5 molar ratio. The filtrate was then taken and evaporated at reduced pressure and the residue was recrystallized from hot water to give pure product of PAP in almost 100% yield. The characteristics of the product are listed below:

- IR: (νmax/cm⁻¹): 3423, 3340 (NH₂), 3190 (OH).
- ¹H NMR DMSO-d₆, δ (ppm): 5.98 (s, 1H, OH, D₂O-exchangeable), 6.42 (d, 2H, J = 6.7 Hz, ArHs), 6.99 (d, 2H, J = 6.7 Hz, ArHs), 9.86 (br s, 2H, NH₂,D₂O-exchangeable).

2.2.2. X-ray diffraction (XRD)
X-ray diffractograms of various solids were collected using Bruker D8 advance instrument with Cu Kα₁ target with secondly monochromator 40 kV, 40 mA.

2.2.3. ESR spectroscopy
ESR spectra of different solids were measured using (Bruker Elexysys. 500) operated at X-band frequency. The following parameters are generalized to all samples otherwise mentioned in the text. Microwave frequency: 9.73 GHz, receiver gain: 20, sweep width: 6000 center at 3480, microwave power: 0.00202637.

2.2.4. Infrared spectroscopy
The infrared spectra were recorded in potassium bromide disks Shimadzu FT IR 8101 PC infrared spectrophotometers.

2.2.5. NMR analysis
The NMR spectra were recorded on a Varian Mercury VX-300 NMR spectrometer. ¹H spectra were run at 300 MHz in deuterated dimethyl sulphoxide (DMSO-d₆). Chemical shifts were related to that of the solvent.

2.2.6. SEM and EDX analysis
Images of scanning electron microscope (SEM) different samples and EDX analysis was performed using instrument “JXA-840 A Electron probe Micro Analyzer-Japan”.

2.2.7. Surface area measurements
The surface areas were measured using Quantachrome High Speed Gas Adsorption Nova 2000 instrument at 77 K.

3. Results and discussion
Hydrogenation of p-nitrophenol into p-aminophenol was performed on 5 Ni wt% catalyst, supported on the precalcined supports; SA-500, SA-1000 and SA-1500. The reaction follows the following equation:

\[
\text{OH} \quad \text{Ni} \quad \text{Hydrazine} \quad \text{PNP} \quad \text{Hydrazine} \quad \text{NH}_2 \quad \text{p-aminophenol}
\]

The hydrazine in the previous reaction acts as hydrogen donor. In addition, supported nickel catalyst acts as a bifunctional catalyst. Thus it firstly, decomposes hydrazine into H₂ and N₂. Furthermore, the nickel acts as a catalyst for the hydrogenation of p-nitrophenol using the nascent hydrogen produced from previous step.

During the hydrogenation process, the change in color was observed. Thus, a change from yellow color of PNP into green color (intermediate A) was firstly observed. After that, a discharge of all colors (PAP) was occurred, accompanied with 100% conversion. The mechanism of this reaction is shown in Scheme 1.

The above mechanism enables us to follow the reaction by a self-change in color. This make us to believe in that, the express of the catalytic activity as the time to reach 100% conversion may be the best choice for this reaction.

The supported catalysts were characterized by XRD, SEM, EDX, ESR and measuring the catalytic activity.

![Scheme 1](image-url)
3.1. XRD investigation of different solids

XRD diffractograms were used to follow up the crystalline phases of SiO$_2$–Al$_2$O$_3$ support. Fig. 1 shows the diffractograms of 5 Ni wt% loaded on SA-500, SA-1000 and SA-1500 supports respectively. It is seen from this figure, that, the support material precalcined at 500 and 1000 °C, consists of poorly crystallized aluminas, together with the main diffraction line of metallic nickel. However, the diffractogram of the nickel catalyst loaded on a support precalcined at 1500 °C consists of well crystallized α-Al$_2$O$_3$ (corundum), SiO$_2$ (crystobalite), SiO$_2$–Al$_2$O$_3$ (mullite) and metallic nickel.

Fig. 2 depicts the XRD diffractograms of 5 Ni wt%-catalyst loaded on SA-500, SA-1000, and SA-1500, before and after several successive uses in hydrogenation of p-nitrophenol. From this figure, it can be observed that, a crystalline Ni metal phase is detected in all freshly prepared catalysts (showed by dashed line). The relative intensity of metallic nickel phase decreases progressively as the number of uses increases. This finding may indicate that, the crystalline nickel metal phase looses its degree of crystallinity via partial transformation into an amorphous phase during the hydrogenation reaction. In case of SA-1500 sample, a decrease in the degree of crystallinity of both crystalline nickel and other crystalline phases (crystobalite, corundum, and mullite) was observed after successive uses of catalyst several times.

3.2. SEM and EDX results

Fig. 3 represents the images of 5 Ni wt% fresh catalyst loaded on SA-500 and after 5 times of use in catalytic hydrogenation of PNP at 80 °C. From this figure, it can be observed that, only some crystallites of alumina phases existed in the SEM images, as being evidenced by EDX analysis (Table 1) and XRD (Fig. 1).
Moreover, after 5 times of use, aggregation of the catalyst was observed, which is much clear at lower magnification. The EDX analysis (Table 1) for this sample was taken for two different positions. The first position showed only the presence Al and O atoms, indicating the presence of Al₂O₃, while the second position showed the presence of Si, Al, and O, which is indicative for the presence of precursors of aluminosilicates.

In addition, the Si and Al surface concentration, in the second position of the fresh catalyst, are much close to the calculated bulk values [Si exp, 9 atom%; Si cal, 9, Al exp, 33 atom%; Al cal, 28 atom%]. On the other hand, the Ni surface concentration is much bigger than that of calculated bulk value by 82% [Ni exp, 10 atom%, Ni cal, 2 atom%]. The previous remarks indicate that the impregnation method increases the surface atom % of Ni. This finding is expected for solid samples prepared by wet impregnation method.

Fig. 4 shows the images of 5 Ni wt% fresh catalyst loaded on SA-1000 and after 5 times of use in hydrogenation of PNP. From this figure, it can be observed that, some crystallites are beginning to be formed. Moreover, the aggregation of the catalyst after 5 times of successive use was also observed, and this is accompanied by the disappearance of the crystalline shapes. Moreover, EDX analysis of this sample (Table 1) showed that, there is an effective migration of Ni from the surface to the bulk by successive use (4 → 1 atomic%). This process is accompanied also by a migration of some Si from bulk to the surface, while, Al and O remained almost unchanged. It can be also observed that, the surface atom concentration of Si, Al, O and Ni atoms are much closer to the calculated bulk values after 5 times of successive use, which may affect the specific catalytic activity of this catalyst as will be seen in the section of catalytic activity.

Fig. 5 represents the images of 5 Ni wt% fresh catalyst loaded on SA-1500 and after 5 times of use, compared with bare support sample. From this graph one can observe the clear formation of highly crystalline forms of the support. The aggregation of the catalyst particles after several times of use is also observed here. The EDX analysis showed that the Ni migrates completely from the surface to the bulk (5 → ~0.0 atomic%), while a high migration of Si from bulk to the surface is observed (5 → 31 atomic%). The Al atoms migrate also, but this time from surface to bulk (39 → 19 atomic%). These findings may be explained by, assuming the collapse of the crystalline forms of the support which was confirmed formerly by XRD.

From the previous observations the following remarks may be drawn:

(i) For the fresh catalyst sample, the surface concentration of nickel loaded on SA-1500, and SA-1000, reaches 5 and 4
atomic% respectively. These values are closer to the calculated values of loaded Ni (2 atom%), comparing with the high value of surface Ni concentration (10 atom%) loaded on SA-500. This means that the Ni atoms are not equally distributed between surface and bulk, and are much higher concentrated on the surface. This may be explained assuming that the interaction between Ni atoms and the amorphous support is higher than that of crystalline one. In other words, as the

Fig. 4. SEM images of 5 Ni wt% loaded on SA-1000: (a) freshly prepared and (b) after 5 times of successive using in hydrogenation reaction.

Fig. 5. SEM images of bare support SA-1500: (a) freshly prepared 5% Ni wt%-SA-1500 and (b) after 5 times of successive using in hydrogenation reaction.
degree of crystallinity of the support increases the interaction between Ni and the support decreases which was formerly observed from XRD and SEM results.

(ii) It can be generally observed that, as the calcination of the support increases, the distribution of surface Si and Al deviated from the calculated bulk values. As a consequence of successive use of the catalyst, a migration of both Si and Al, and even O occurs. The migrating atoms concentrations were found to be much closer to the calculated bulk values. This leads us to conclude that, as the catalyst is being used, the crystallinity of the support is being affected, i.e. the support transforms into amorphous phase.

(iii) After successive use of the catalyst several times, the concentration of the surface nickel atoms decreases. This decrease is inversely proportional to the calcination temperature, reaching to minimum at 1500°C (nearly no nickel observed at EDX analysis). It was suggested that, as the degree of crystallinity of the support increases, the collapse of the crystals during the successive use of the catalyst increases. This leads to a migration of the nickel species inside the bulk.

Fig. 6. Surface Ni atom% of catalyst after 5 times using against calcination temperature.

Fig. 7. ESR spectra of different samples of 5% Ni loaded on SA-500, SA-1000 and SA-1500°C as freshly prepared catalysts and after successive times of using. The dimensions given in the figures are driven from Eq. (1).
Thus, the Ni mobility is directly proportional to the degree of the crystallinity of the support as can be drawn from Fig. 6.

4. ESR investigation of different catalyst samples

ESR technique is usually used to characterize the paramagnetic centers in the sample where a free electron exists. Although this technique can characterize effectively paramagnetic species of metal particle, it has a special interest when these particles diminished to a nano-scale, such as in our case, where nano-sized metal particles are existed.

Moreover, Kawabata [32] demonstrated his famous relation hypothesizing that the broadening of ESR signal of nano-metal particles are suffering from quantum size effect and can be correlated to the size of the nano-metal particle.

Accordingly, direct relationship between the line width \(\Delta H_{pp}\) (or peak to peak width) of the signal of nano-particle in ESR spectra and its particle size are given in the following relation:

\[
d = a \cdot \Delta H_{pp}^{0.5}
\]

where \(d\) is the particle size in nm, \(\Delta H_{pp}\) is the line width of ESR signal in mT and \(a\) is the proportionality constant.

The proportionality constant “\(a\)” for our case nickel metal was found to be 1.2 [8]. This relation enables us to estimate correctly the average particle size of nickel even it is not existed in crystalline form. Thus, Fig. 7 represents the ESR spectra of samples under investigation under different calcination temperatures and after successive times of use. From these spectra one can observe that the characteristic signal of nickel metal appeared at \(g = 2.2\) and existed in all samples [8]. Moreover, additional overlapping low magnetic field signals appeared in different samples. These lower magnetic field signals were assumed to be attributed to the existence of strain between nano-nickel particles [33,34].

We assume that the disappearance of this strain means that nano-sized nickel particles are well separated among each others. In other words, the interaction between the metal and the support is minimum. According to this assumption, one can observe easily from the ESR spectra of the samples (Fig. 7) that, the freshly prepared nickel catalyst supported on SA-1500 exhibits no strain and this means that the interaction between metal and the support is minimum. XRD Diffractograms of the catalysts (Fig. 2) show also that it has the larger degree of crystallinity.

It is clearly shown from Fig. 7 that the particle size decreases progressively by increasing the number of use. A decrease of 30% after using the catalyst supported on SA-1500 was observed. Furthermore, the Ni phase turned into almost an amorphous phase which agreed well with the XRD investigation.

Moreover, using the calculation of particle size using Kawabata equation (labeled on each samples in Fig. 7), it can be observed that, as the number of successive times of use of catalyst in hydrogenation reaction increases, the particle size of nickel decreases. In other words, the amorphization of nickel is increasing which previously concluded from XRD diffractograms.

In contrast to the previous observation, the particle size of Ni in the catalyst sample whose support was SA-500 seems to be increasing after successive use. This indicates that the mode of deactivation of this catalyst sample may suffer also from some kind of sintering.

In order to eliminate the possibility of leaching of Ni metal from the support during the hydrogenation reaction, elemental analysis for nickel in supernatant was done after each experiment. The results showed that the amount of Ni leached in all samples was very small and can be neglected.

5. Catalytic activity

The catalytic activity of catalyst samples under investigation was carried out by hydrogenation of PNP into PAP. This reaction was carried out using hydrazine hydrate as hydrogen donor at 80 °C. As being mentioned before, it seems that the express of the catalytic activity as a time to reach 100% conversion being the best express. This is because the 100% conversion is accompanied by an indicative change in color (green → colorless) which acts as a self indicator for ending the reaction.

The catalytic activity of the bare supports calcined at 500, 1000 and 1500 °C (SA-500, SA-1000, and SA-1500) were examined and showed no catalytic activity. Further 5 wt% Ni was loaded on the precalcined supports and reduced using Hydrazine hydrate at 80–100 °C.

The loaded Ni-support catalysts were then examined in prementioned hydrogenation reaction.

Fig. 8 shows the time in seconds for 100% conversion as a function of calcination temperature of the support material.

It is clearly shown from Fig. 8 that the increase in the precalcination temperature of the support material within 500–1500 °C led to a progressive increase in the catalytic activity. This being evidenced from the progressive significant decrease in the time for attaining 100% conversion. This increase in the precalcination temperature from 500 to 1500 °C decrease the time of 100% conversion from 107 to about 70 s.

XRD investigation of the catalyst samples shows clearly that the increase in calcination temperature of the \(\text{SiO}_2–\text{Al}_2\text{O}_3\) support material within 500–1500 °C much increase the degree of crystallinity of the phases present in the support. So, the increase in crystallinity of the support material showed a parallel progressive increase in catalytic activity.

In order to make a comparison between the catalytic activity of the system investigated with the commercial catalyst (Raney Nickel), the hydrogenation reaction was carried out for this commercial sample under the same conditions and ratios used in other samples. The time needed to obtain 100% conversion attained 260 s instead of 69 s of the catalyst investigated whose support was SA-1500. In other words the prepared catalyst showed a catalytic activity about 4-fold than that of Raney nickel catalyst.

In order to shed some light on the durability of the prepared catalyst, the reaction was done several successive times (5 times) and the effect of this parameter is readily illustrated in Fig. 9.

It is clearly shown from this figure that the catalytic activity suffer slight decrease in its catalytic activity during the 3 successive...
uses. However, the 4th use of the catalyst whose support is SA-500 lost most of its catalytic activity showing no measurable catalytic activity in the 5th use. While the catalysts whose support are SA-1000 and SA-1500 lost some of their activity after 5th use. The decrease was, however, more pronounced in case of catalyst sample whose support is SA-1500. This finding suggested that the catalyst whose support calcined at 1000 °C is recommended for such reaction for its obvious durability.

Returning to EDX results which showed the surface nickel in the sample whose support is SA-500 decreases from fresh to 5th used catalyst as (10 — 4 atomic%) (Table 1). Thus it can be concluded that not all surface Ni atoms are catalytically active. In case of catalysts based on SA-1000 and SA-1500 supports, the durability is being higher than that of those based on SA-500 support. Thus, although the sharp decrease was observed in the surface Ni atoms during the reaction in case of both catalysts based on SA-1000 and SA-1500 supports (Table 1), the catalytic activity is being not affected mainly. This leads us to conclude that in these samples both surface and bulk nickel participate in the reaction while in SA-500 sample only a part of surface nickel is activated. In other words, as the degree of the crystallinity of the support increases number of active nickel species increases and hence catalytic activity and durability increase. This may be because of that in case of crystalline samples diffusion of the reactants into the bulk is much easier than that of the amorphous ones.

It seems that the change in surface concentration of Ni atoms as a function of calcination temperature of the support material may have a decisive role in changing the catalytic activity. This has been done by following the change in the catalytic activity, expressed as time to reach 100% conversion, as a function of the difference between the surface Ni of the 5th used catalyst subtracted from the calculated bulk concentration of Ni. The results obtained are given in Fig. 10.

From this figure, it can be shown that the sample whose support is SA-1000, has the lowest difference to the calculated bulk values after 5 times of use. This may explain the highest durability of this sample.

This led us to assume that as the atomic percent of Ni approaches the calculated bulk values, the catalytic activity reaches maximum.

The %atomic Ni after 5 times of using the nickel catalyst subtracted from calculated bulk atomic% of Ni loaded on SA-500, SA-1000 and AS-1500 supports, the durability is

6. Conclusions

The following conclusions can be drawn from this research:

1. Nickel loaded on SiO$_2$-Al$_2$O$_3$ support being very effective catalyst in hydrogenation of p-nitrophenol to p-aminophenol. That it was attained 100% conversion in only 69 s instead of 260 s for commercial Raney nickel. In addition the possibility of reuse it more than one time with great efficiency give it another advantage to commercial Rainey nickel which cannot be used more than one time.

2. The crystallinity of the support plays a very important role in the catalytic activity of the nickel catalyst. The increase in the precalcination temperature of the support material within 500–1500 °C increases the degree of crystallinity of the support and also increases the catalytic activity of the catalyst.

3. The catalyst investigated showed high durability. The optimum durability was attained at catalyst sample whose support is precalcined at 1000 °C (SA-1000).

4. The mechanism of hydrogenation reaction is supposed according to the change in color during the reaction. Change in color in the reaction make a self-indication of 100% conversion which save the time and effort for following up the reaction.

5. In comparison of our previous work with 5 wt% nickel catalyst supported on single oxides of SiO$_2$ and Al$_2$O$_3$ [35], the nickel catalysts supported on mixed oxides were proven to be higher in both catalytic activity and durability than those catalysts supported on single oxides.

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