International Journal of Research in Engineering and Innovation (IJREI)
journal home page: http://www.ijrei.com
ISSN (Online): 2456-6934

Investigation on operation condition nickel and palladium catalysts in slurry reactors

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Abstract

The liquid-phase catalytic hydrogenation of dimethyl-nitrobenzene (DN) to Dimethyl-aniline (DA) was carried out in ethanol using nickel and 5% Pd/C catalysts. The effects of hydrogen partial pressure (400–1000 kPa), reaction temperature (343–403^0K), catalyst loading and dimethyl-nitrobenzene concentration (0.12–0.75 mol/lit) on the hydrogenation of dimethyl-nitrobenzene and the yield of Dimethyl-aniline have been studied. Dimethyl-aniline was the only reaction product, generated through the hydrogenation of the Nitro group of dimethyl-nitrobenzene. The effects of hydrogen partial pressure, catalyst loading, dimethyl-nitrobenzene concentration and temperature on the reaction conversion have been reported. The results showed that the Pd/C catalyst had a better and faster performance than the Nickel catalyst.

Keywords: Liquid-phase hydrogenation; Pd/C catalysts; Ni catalysts; operation condition

1. Introduction

Aromatic amines, widely used as important intermediates in the synthesis of chemicals such as dyes, antioxidants, photographic, pharmaceutical and agricultural chemicals, can be obtained easily by the reduction of corresponding aromatic nitro compounds using catalytic hydrogenation and a variety of other reduction conditions. Many reductive agents have been recommended for this transformation and the most classic and practical reductants are zinc, tin, or iron in the presence of an acid. However, most of them lack the chemo selectivity over other functional groups and reduction of aromatic nitro compounds often yield a mixture of products. In addition, the reactions are performed in organic solvents or in the presence of acids, which pose waste-handling problems [1-3]. The selective hydrogenation of nitro compounds is commonly used to manufacture amines, which are important intermediates for dyes, urethanes, agro-chemicals and pharmaceuticals. Hydrogenation of nitro aromatics are used to produce aniline derivatives, which can be carried out in gas or liquid phase by using supported metal catalysts and organic solvents such as alcohols, acetone, benzene, ethyl acetate, or aqueous acidic solutions [4]. The use of these solvents has some drawbacks owing to their toxicity, flammability, or environmental hazards. In addition, the solvent may play a crucial role in the stabilization of reactive intermediates and have a decisive influence on chemical reactions. The rate and the selectivity of aromatic nitro-compounds hydrogenation depend upon different factors such as temperature, hydrogen pressure and concentrations of catalyst and a hydrated compound [5-7]. The main purpose of this study was to evaluate the effects of parameters such as hydrogen pressure and temperature on the rate of dimethyl-nitrobenzene hydrogenation over a Pd/C catalyst in ethanol-water two components solvent. Solvents are known to have a significant effect on the rate of catalytic hydrogenations. The effects of solvent are attributed to various factors, which include solubility of hydrogen, thermodynamic interaction of solvent with the reactants and products, agglomeration of catalysts in some solvent and competitive adsorption of solvent [8-10]. The solvent employed was ethanol. Further, the recovery of ethanol in the presence of water (formed during the reaction) will be easy. Hence, ethanol was used as a solvent in this study [11].

In this paper the influence of Operation conditions on the catalytic activity for dimethyl-nitrobenzene hydrogenation in an alcoholic solution is presented. The effect of operating conditions on the reactor performance was studied by comparing the conversion of dimethyl-nitrobenzene, under different reaction conditions.

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2. Experimental

The details of the experimental set-up, experimental procedures and analytical techniques are presented in this section.

2.1 Materials

All the chemicals used were purchased from Pure Chemicals and used without further purification. Dimethyl-nitrobenzene was used. A 5 wt. % Pd/C catalyst and A 40 wt. % Ni catalyst on alumina-silicate support used to reduction of dimethyl-nitrobenzene. The average size of Ni particles obtained was shown to be 50µm. Also, the average size of Pd/C particles obtained was shown to be 10µm. dimethyl-nitrobenzene, ethanol, and distillated water used were of laboratory reagent grade. Hydrogen (cylinder purity 99.98%) was used.

2.2 Experimental set-up

The hydrogenation process was carried out in an isothermal 6L stainless steel autoclave, which allows isothermal conditions due to a heating jacket (Fig. 1). The reactor having a diameter of 200 mm (impeller diameter 80 mm) was equipped with an electrically heated jacket, a turbine agitator and a variable-speed magnetic drive ensuring zero leaks. The temperature and the speed of agitation were controlled by means of a controller. The gas inlet, gas release valve, cooling water feed line; pressure gauge and rupture disk were situated on top of the reaction vessel. The liquid sample line and the thermocouple well were immersed in the reaction mixture. The reactor was also provided with a cooling coil. In order to ensure good bubble dispersion, the gas injection is performed through a plunging tube whose exit opening is placed right below the agitation mobile. The hydrogen was supplied at the same rate that it was consumed under isobaric reaction conditions. The samples for the analyses were drawn via a sampling tube. The experiments were carried out using the following procedure; first, DN (99 %) was dissolved in a mixture of 91 %wt of Ethanol (99.9 %) and 9 %wt distilled water. The reactor was filled with 3500 ml solution and the solid catalyst (from 20 to 60 g) was added. Second, the reaction was initiated by removing the air from the reactor by purging with hydrogen and stirring the solution at 200-800 rpm. The temperature was controlled at 343-403 $^{\circ}K$ and the hydrogen partial pressure was kept constant between 4 and 10 bars. The samples were analyzed by gas chromatography and a FID detector [12-14].

3. Experimental procedure

The reactor was first charged with appropriate quantities of the dimethyl-nitrobenzene, the solvent and the catalyst. It was then purged with nitrogen, prior to the start of the experiment to ensure an inert atmosphere in the reactor. Hydrogen from the cylinder was introduced into the reactor and nitrogen was replaced with it. All the lines were closed. The reactor contents were heated to the desired temperature.

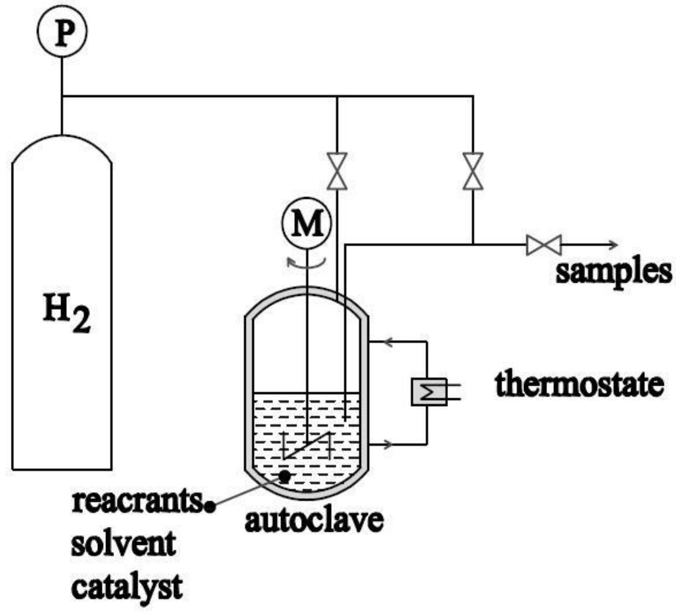


Figure 1: Experimental set-up for the liquid hydrogenation of dimethyl-nitrobenzene

The autoclave was then pressurized with hydrogen to get the desired partial pressure of hydrogen. Agitation was then started at the predetermined speed. The consumption of hydrogen due to reaction as well as due to small sampling led to decrease in the total pressure as indicated on the pressure gauge. So, more hydrogen was charged intermittently from the cylinder through manually operated control valve, thus maintaining a constant partial pressure of hydrogen. Samples were withdrawn periodically after sufficient flushing of the sample line with the reaction mixture [15-17].

4. Results and discussion

Heterogeneous catalytic hydrogenation is a reaction involving gas–liquid–solid-phase operation. Various steps occur in series when a gas–liquid–solid reaction occurs [18]. The minimum speed of agitation used was higher than the minimum speed required for the suspension of the catalyst particles. The following assumption was made while studying the heterogeneous catalytic hydrogenation reactions:

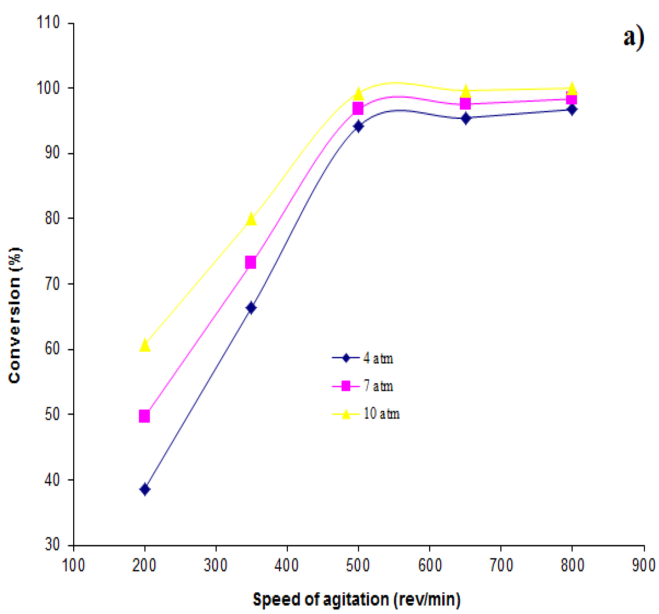
1. The activity of the catalyst is maintained throughout in all the experiment, that is, that no poisoning or deactivation of the catalyst occurs.
2. Desorption of the products offered no resistance [19].

The main objective of the work was to investigate the effect of following various process parameters on conversion of nitro aromatic to aromatic amine.

4.1 Effect of speed of agitation

The catalytic transfer hydrogenation system is a heterogeneous liquid–solid system. The catalyst was in the solid form. At macroscopic level, the reactant, DN, diffuses from bulk of liquid to the catalyst surface and then through micro-pores of the catalyst until it reaches catalytic active centers. The reaction then takes place between adsorbed DN and hydrogen, which in turn reduces NO_2 of DN to NH_2. All the transport processes of substrate to the active center are in series. Thus the reactant substrate has to overcome two diffusional resistances, namely near liquid–solid interface and then intra-particle diffusion in the bulk of the catalyst. The liquid–solid mass transfer resistance depends upon the intensity of turbulence in the liquid phase, which in turn is a function of speed of agitation in the reactor. Therefore, it was thought desirable to study the effect of the speed of agitation on conversion of DN to DA. Fig. 2 shows, with the increase in speed of agitation from 200 to 800 rpm, the extent of conversion increased from 38.58 to 96.74% (at 4 atm pressure), 49.64 to 98.37 % (at 7 atm pressure) and 60.7 to 100 % (at 10 atm pressure) for Pd/C catalyst. Also, Fig. 2 shows, with the increase in speed of agitation from 200 to 800 rpm, the extent of conversion increased from 38.58 to 96.74% (at 4 atm pressure), 49.64 to 98.37 % (at 7 atm pressure) and 60.7 to 100 % (at 10 atm pressure) for Ni catalyst.

It was observed that the speed of agitation has effect on the conversion below 500 rpm and above this there was no effect of speed of agitation under otherwise identical conditions. Therefore, use of agitation speed more than 500 rpm ensured the absence of diffusional resistances and the reaction was confined to kinetically controlled regime. The experiments were performed at 110 °C under reflux condition.



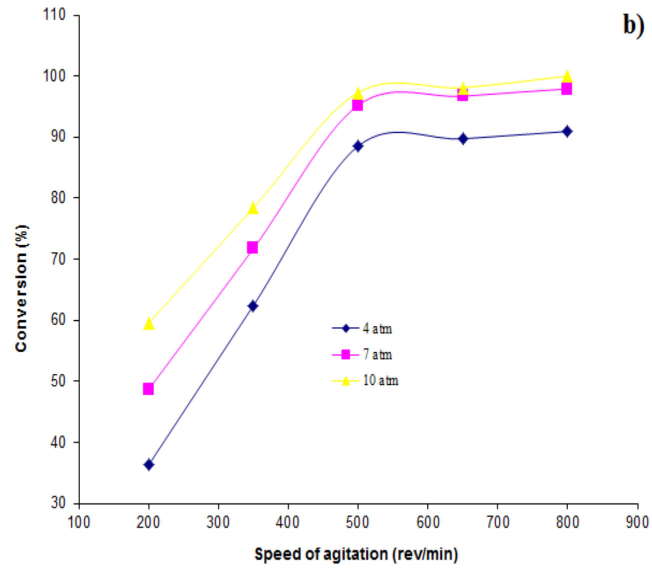


Figure 2: Evolution of the conversion level at different speed of agitation- (a) Pd/C, (b) Ni

4.2 Effect of temperature

Catalytic transfer hydrogenation is highly temperature dependent. The reaction did not proceed at room temperature and at lower temperature partially hydrogenated product was obtained, thus the effect of temperature was studied from 343 to 403^0K under otherwise similar conditions.The conversion of dimethyl-nitrobenzene increased with increase in the temperature of the reaction. The Fig. 3 shows the evolution of the conversion with time at different reaction temperatures for Pd/C catalyst and Ni catalyst. An important enhancement in the catalytic activity as reaction temperature increases can be noted. However, no changes in the selectivity were detected and only dimethyl-aniline was the product obtained. To study the effect of temperature on conversion of dimethyl-nitrobenzene, experiments were carried out in the temperature range of 343-403^0 at a substrate concentration of 2 mol/L in ethanol, pressure of 7 bar and a catalyst loading (1% cat/organic phase) with 3500 cm^3 solution. Fig. 3 shows that with increase in temperature, the conversion increase at all the temperature levels. These results were obtained after 150 min of reaction time. At temperature of 403^0K more than 97% (for Pd/c catalyst) and 95% (forNi catalyst) conversion were obtained at defined conditions.

4.3 Effect of the dimethyl-nitrobenzene concentration

The effect of dimethyl-nitrobenzene concentration on the hydrogenation rate was examined by using three different dimethyl-nitrobenzene concentrations (0.12, 0.25, 0.37, 0.50, 0.62 and 0.75 mol/lit) in ethanol. Fig. 4 shows, for the Pd/C catalyst, the evolution of the conversion level with time at constant hydrogen pressure (10 bars), temperature (363^0 K and weight of catalyst (40 g for Pd/C and 50 g for Ni). Percent conversion was measured using dimethyl-nitrobenzene in the range 1-3 mol in 3500 cm^3 ethanol.

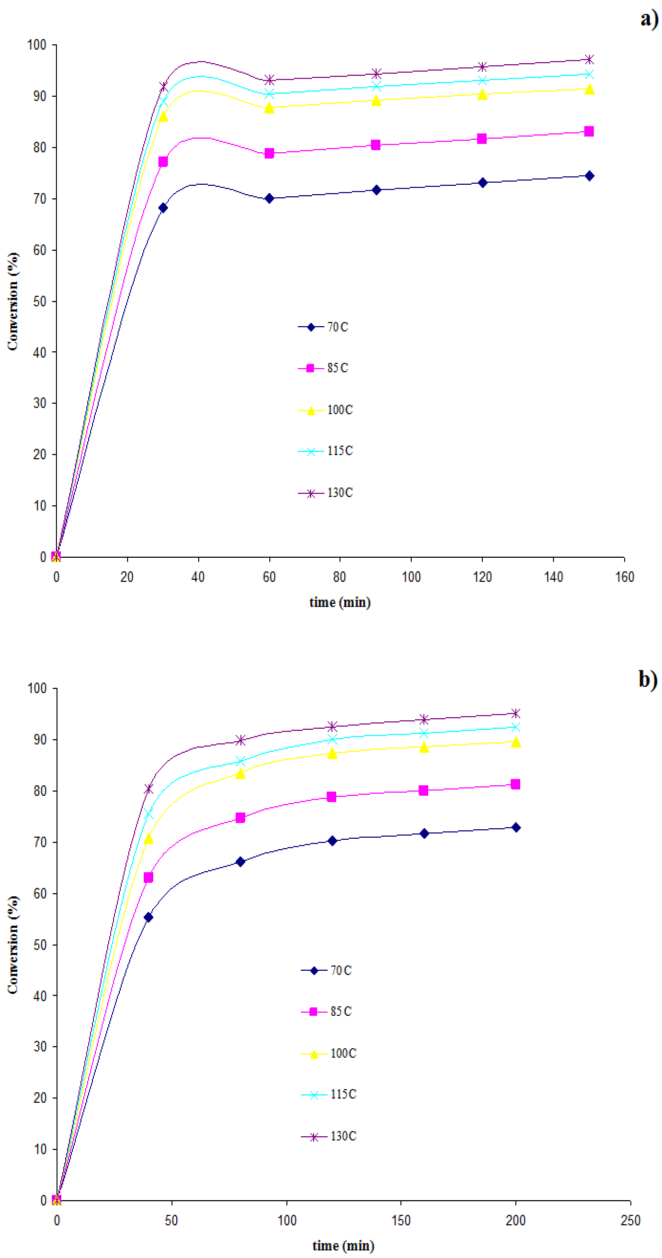


Figure 3: Evolution of the conversion level with time at different temperature- (a) Pd/C, (b) Ni

After reaction time of 210 min, it was observed that with an increase in substrate concentration (dimethyl-nitrobenzene) percent conversion increased almost linearly up to 2.7 mol of dimethyl-aniline then surprisingly started decreasing. An increase in the activity as decreasing the dimethyl-nitrobenzene concentration can be observed. However, if the conversion of the reaction (expressed as the percentage of dimethyl-nitrobenzene hydrogenated in the mixture) is studied as a function of the reaction time, significant changes are observed. At short reaction times, dimethyl-aniline was produced, but at longer reaction times rate of conversion is lower up to reaching a constant value. The higher proportion of dimethyl-nitrobenzene found at lower conversion levels is attributed to the fact that the lower dimethyl-nitrobenzene concentration ratio to catalyst loading is easier to hydrogenate compared to the higher dimethyl-nitrobenzene concentration.

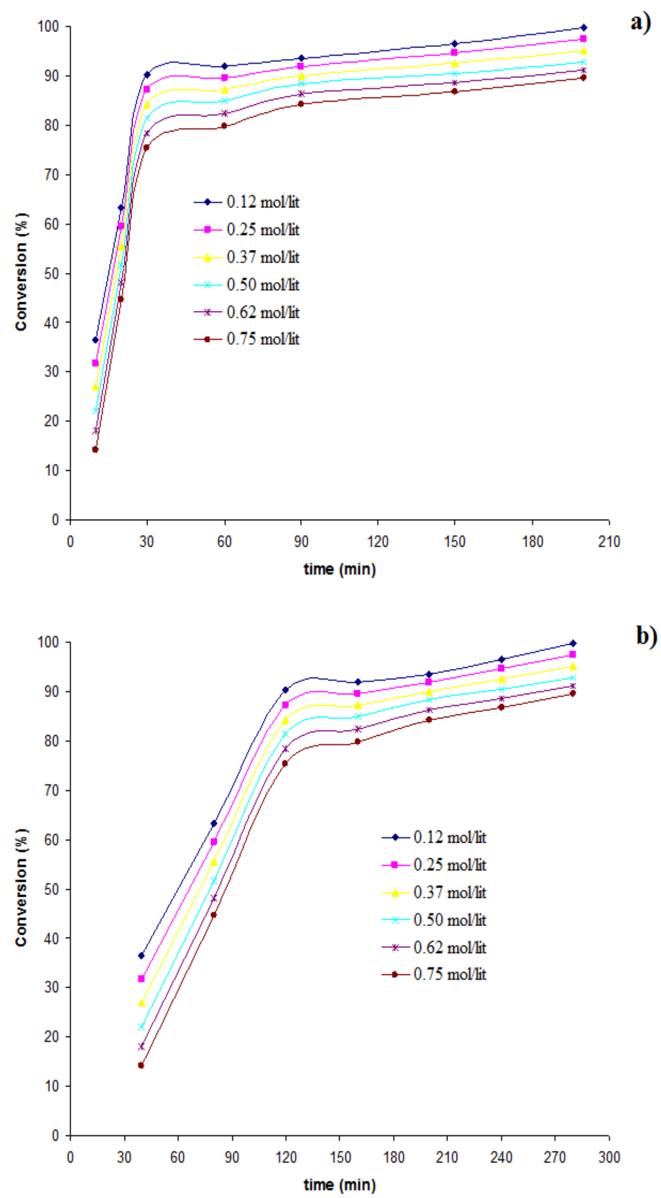


Figure 4: Evolution of the conversion level with time at different dimethyl-nitrobenzene concentration- a) Pd/C, (b) Ni

Fig. 4 shows that decrease in dimethyl-nitrobenzene concentration increases the conversion. The conversion is lower at higher dimethyl-nitrobenzene concentration indicating that the rate of dimethyl-aniline formation has a dependency on the dimethyl-nitrobenzene concentration. Dimethyl-nitrobenzene concentration was varied from 1.0 to 0.05 mol for the catalytic hydrogenation of dimethyl-nitrobenzene. We observed that the rate of dimethyl-aniline formation at high concentrations of dimethyl-nitrobenzene is low because of substrate inhibition effect present at such high concentrations. Another reason could be that at such high concentrations, external mass transfer resistance may become significant because of the low solubility of hydrogen at high concentrations of the reactant. Therefore low concentrations (0.25-0.5 mol/l) of dimethyl-nitrobenzene were used for the kinetics studies.

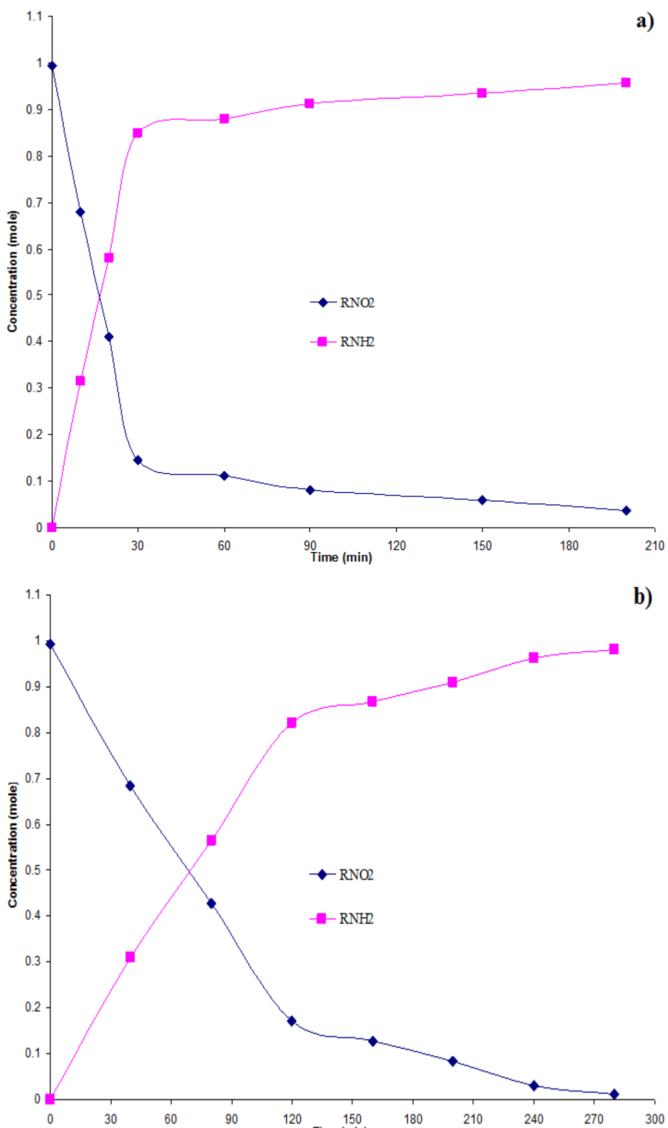


Figure 5: Dimethyl-nitrobenzene and dimethyl-aniline concentrations in solution verses time of reaction- (a) Pd/C (b) Ni

The effect of time on concentration of dimethyl-nitrobenzene and dimethyl-aniline is shown in Fig. 5. The dimethyl-aniline concentration increases with decrease in dimethyl-nitrobenzene concentration with time. The rate was also reported as proportional to the concentration of dimethyl-nitrobenzene for its reduction with hydrogen. As can be seen, the reaction rate in palladium catalyst is higher than nickel catalyst. Also, the time to achieve high conversion rates for palladium catalyst is shorter.

4.4 Effect of catalyst concentration

The effect of catalyst (Pd/C and Ni) concentration on conversion of dimethyl-nitrobenzene was studied in the concentration range of 0.00268–0.00805 mol/lit (Pd/C) and 0.00403–0.00939 mol/lit (Ni) of organic phase, while keeping the other experimental conditions constant as shown in Fig. 6.

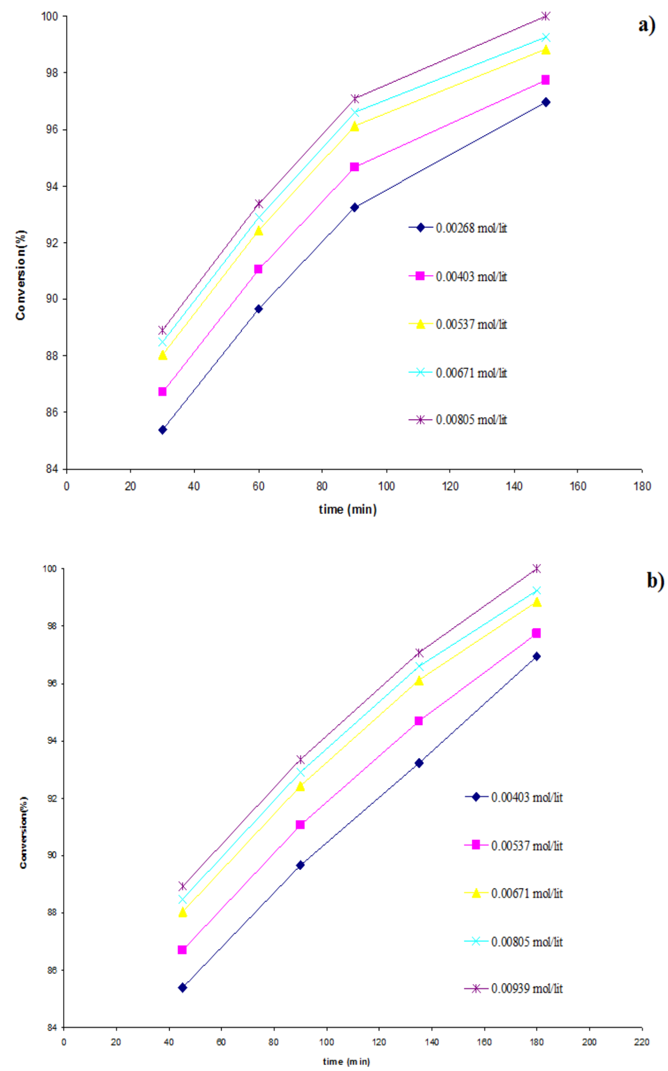


Figure 6: Evolution of the conversion level with time at different weight of catalyst- (a) Pd/C, (b) Ni

The conversion increased with increase in [catalyst], which is due to the proportional increase in the number of active sites. From the results obtained we can say that as the concentration of catalyst increases, the conversion of dimethyl-nitrobenzene to dimethyl-aniline with 100% selectivity. An increase in the activity as the catalyst weight increases can be noted. As can be seen, the palladium catalyst consumption is less in the same conversion rates.

5. Conclusions

The kinetics of liquid-phase catalytic hydrogenation of dimethyl-nitrobenzene to dimethyl-aniline was studied in a stirred three-phase slurry reactor between 343 and 403^0 using a hydrogen partial pressure range of 4–10 bars, with 5% Pd/C catalyst and with a 40% Ni catalyst. Ethanol was used as the reaction medium. The effects of various parameters on the reactions of DN were studied to determine the dependencies of the reaction rates on the concentrations of various species present in the reaction system. The following sections report the effects of different parameters on the rates of dimethyl-nitrobenzene reduction by aqueous ethanol in the presence of a catalyst (Pd/C or Ni). The results of the comparison of the two catalysts showed that palladium has a faster and better performance than nickel.

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