



Operation condition and Reaction kinetics for hydrogenation of dimethyl-nitrobenzene to dimethyl-aniline by Pd/C catalysts

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Abstract

The liquid-phase catalytic hydrogenation of dimethyl-nitrobenzene (DN) to Dimethyl-aniline (DA) was carried out in ethanol using 5% Pd/C as a catalyst. The effects of hydrogen partial pressure (400–1000 kPa), reaction temperature (343–403⁰K), catalyst loading (5–15 g/lit), speed of stirring range (200-800 rpm) 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. Near first-order dependence on dimethyl-nitrobenzene concentration and hydrogen pressure were observed for the initial rate of dimethyl-nitrobenzene hydrogenation over the 5% Pd/C catalyst. Conventional Arrhenius behavior was exhibited by catalyst, Pd/C showed activation energies of 614 J/mol. A simple power law model was used for analysis of the reaction kinetic data.

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Keywords: Liquid-phase hydrogenation; Pd/C catalysts; dimethyl-nitrobenzene; dimethyl-aniline; 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.

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 used to reduction of dimethyl-nitrobenzene. The average size of Pd/C particles obtained was shown to be 10 μ m. dimethyl-nitrobenzene, ethanol, and distilled 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.

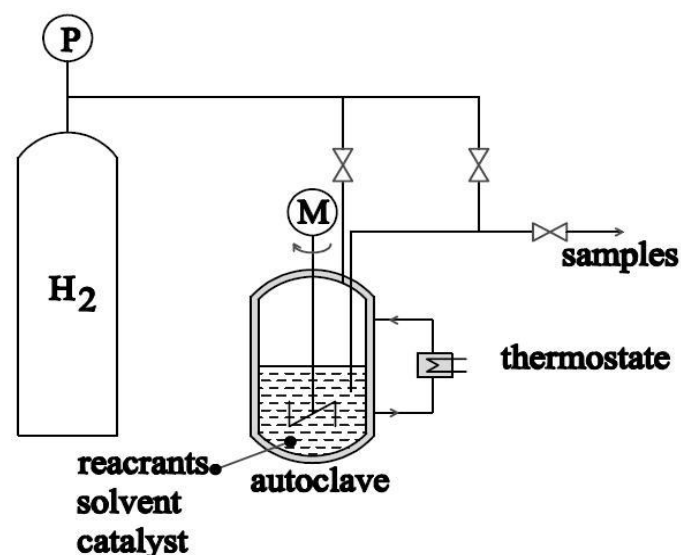


Figure 1: Experimental set-up for the liquid hydrogenation of dimethyl-nitrobenzene

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^oK 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. 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:

- The activity of the catalyst is maintained throughout in all the experiment, that is, that no poisoning or deactivation of the catalyst occurs.
- 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 (Pd/C). 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). 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.

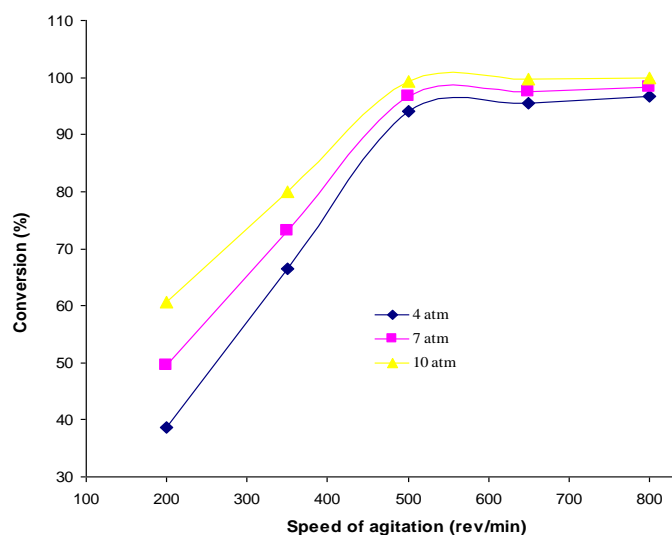


Figure 2: Evolution of the conversion level at different speed of agitation

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^oK under otherwise similar conditions (Fig. 3). The conversion of dimethyl-nitrobenzene increased with increase

in the temperature of the reaction. The Fig. 4 shows the evolution of the conversion with time at different reaction temperatures for a Pd/C 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^oK at a substrate concentration of 2 mol/L in ethanol, pressure of 7 bar and a catalyst loading (1% cat/organic phase) with 3500 cm³ solution. Fig. 4 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^oK more than 97% conversion was obtained at defined conditions.

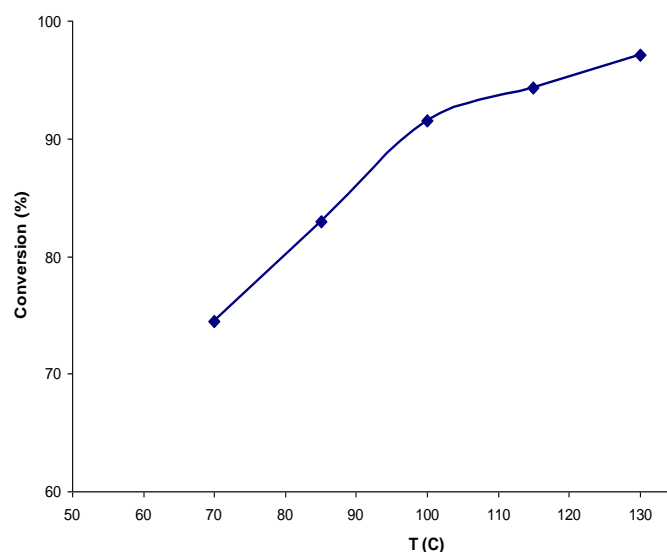


Figure 3: Evolution of the conversion level at different temperature

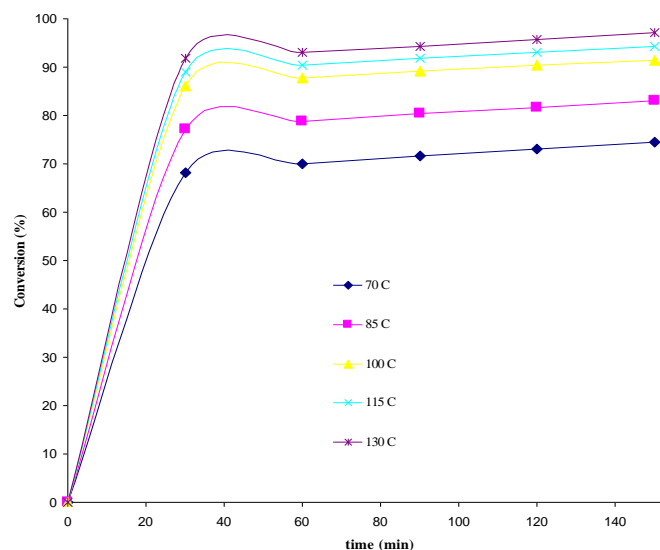


Figure 4: Evolution of the conversion level with time at different temperature

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. 5 shows, for the Pd/C catalyst, the evolution of the conversion level with time at constant hydrogen pressure (10 bars), temperature (363⁰K) and weight of catalyst (40 g). Percent conversion was measured using dimethyl-nitrobenzene in the range 1-3 mol in 3500 cm³ ethanol.

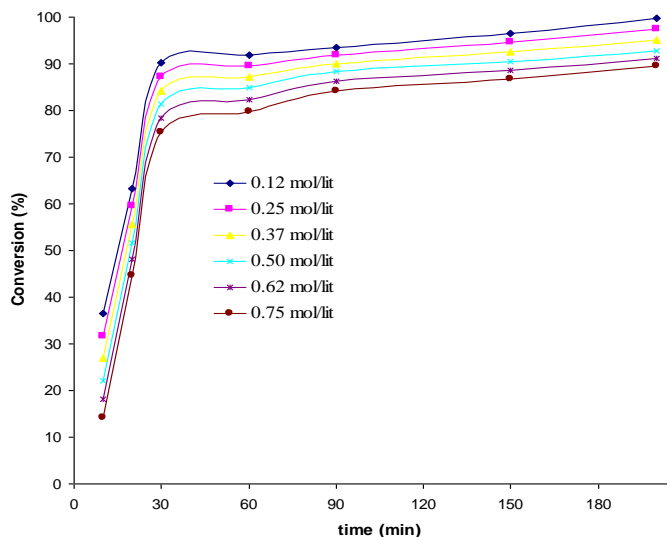


Figure 5: Evolution of the conversion level with time at different dimethyl-nitrobenzene concentration

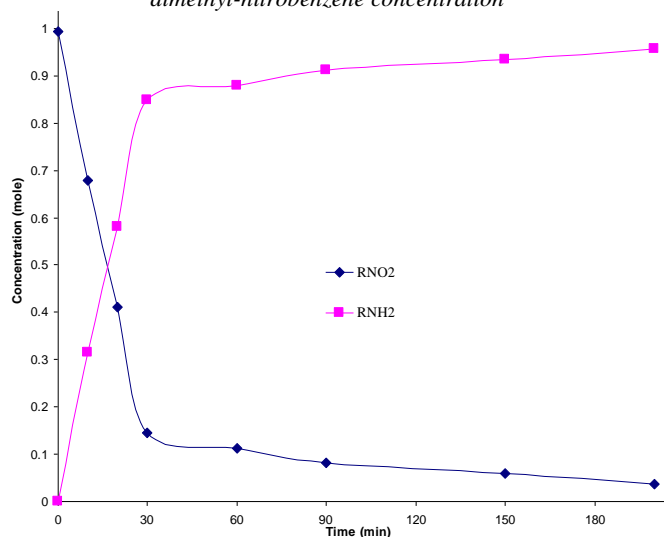


Figure 6: Dimethyl-nitrobenzene and dimethyl-aniline concentrations in solution verses time of reaction

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. Fig. 5 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.

The effect of time on concentration of dimethyl-nitrobenzene and dimethyl-aniline is shown in Fig. 6. 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.

4.4 Effect of hydrogen partial pressure

To study the effect of pressure on conversion of dimethyl-nitrobenzene, experiments were carried out in the pressure range of 4–10 bars at a dimethyl-nitrobenzene concentration of 0.25 mol/L in ethanol, temperature of 363⁰K. The catalyst loading was kept constant by varying the residence time. Fig.7 shows a plot of the conversion vs. hydrogen pressures. Fig.7 indicates that the conversion increases with increase in pressure in the range of pressures studied

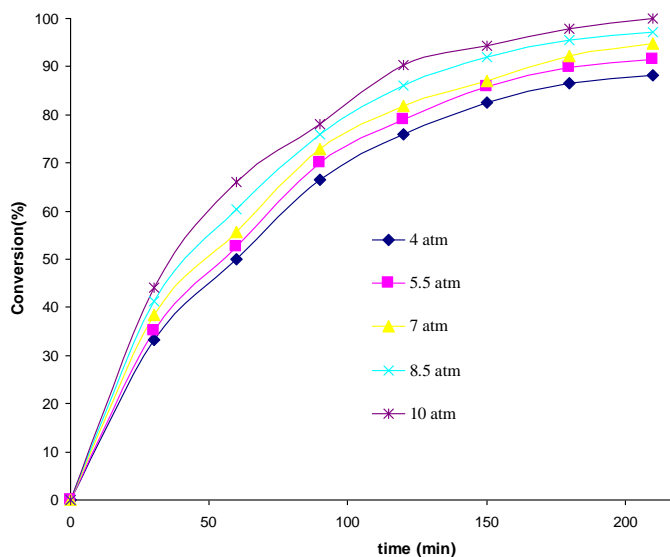


Figure 7: Evolution of the conversion level with time at different pressure

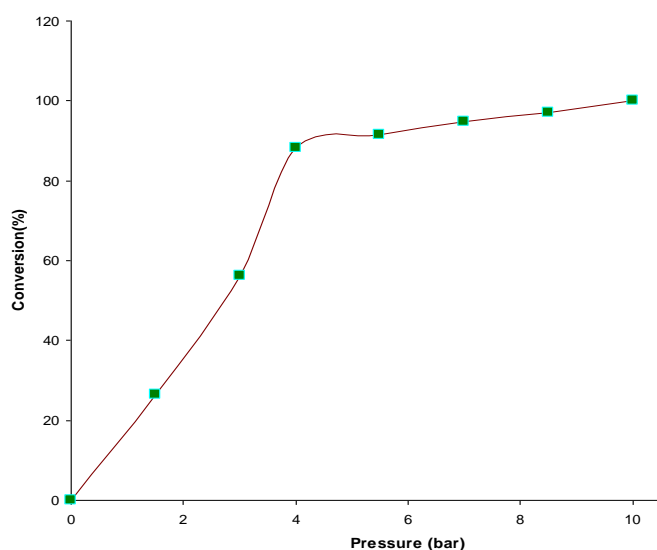


Figure 8: Evolution of the conversion level at different pressure

This increase in conversion of dimethyl-nitrobenzene is attributed to the increase in the concentration of dissolved hydrogen with increase in pressure, thereby resulting in a higher reaction rate. However, pressure has effect on the conversion at constant loading catalyst because the increase in the reaction rate at higher pressure is countered by the decrease in the catalyst loading. It can be seen that the activity increases as hydrogen pressure increases. Fig. 8 show, when hydrogen pressure increases to 4 atm the rate of dimethyl-nitrobenzene hydrogenation rate increases linearly, then this linearity is destroyed and when the pressure reaches 10 atm the rate of dimethyl-nitrobenzene hydrogenation ceases to be dependent upon hydrogen pressure.

4.5 Effect of catalyst concentration

The effect of catalyst (Pd/C) concentration on conversion of dimethyl-nitrobenzene was studied in the concentration range of 0.00268–0.00805 mol/lit of organic phase, while keeping the other experimental conditions constant as shown in Fig. 9.

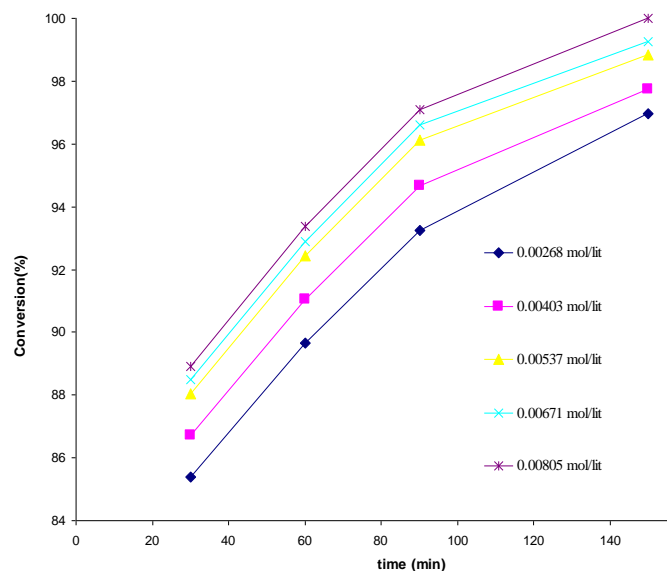


Figure 9: Evolution of the conversion level with time at different weight of catalyst

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.

5. Analysis of initial rate data

The effect of speed of agitation on the rate of reaction of dimethyl-nitrobenzene was studied in the range 200–800 rpm in the presence of a Pd/C catalyst, as shown in Fig. 10. As it is evident from the figure, the variation of reaction rate with speed of agitation is so small that the reactions may be considered as kinetically controlled for all the dimethyl-nitrobenzene. All other experiments were performed at 500 rpm in order to avoid the effects of mass-transfer resistance on the reaction kinetics.

The effect of catalyst loading on the initial rates was studied in the range of catalyst concentrations 5.7–17.1 gr/lit, at 363^oK and 1000 kPa hydrogen partial pressure. These results are shown in Fig.11. The initial rates increased linearly with the catalyst loading in the range studied. The effects of various reaction parameters such as hydrogen partial pressure and feed DN concentration on the initial rate were studied at 343-403^oK and are described below.

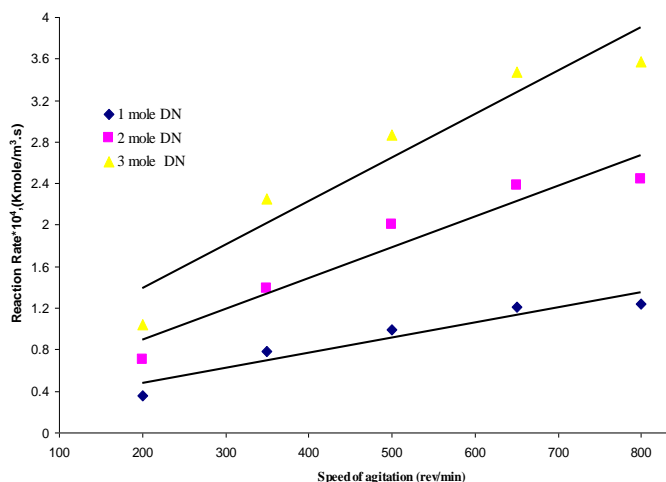


Figure 10: Effect of speed of agitation on initial rates of reaction (363^oK, H₂ pressure 1000 kPa)

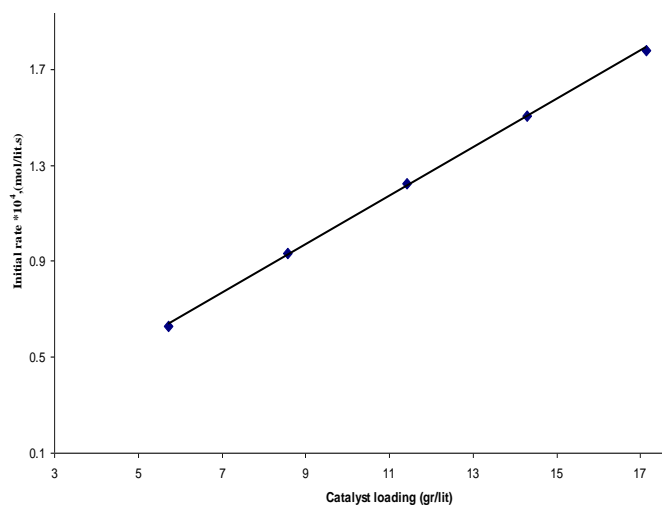


Figure 11: Effect of catalyst loading on initial rates of reaction (363^oK, H₂ pressure 1000 kPa)

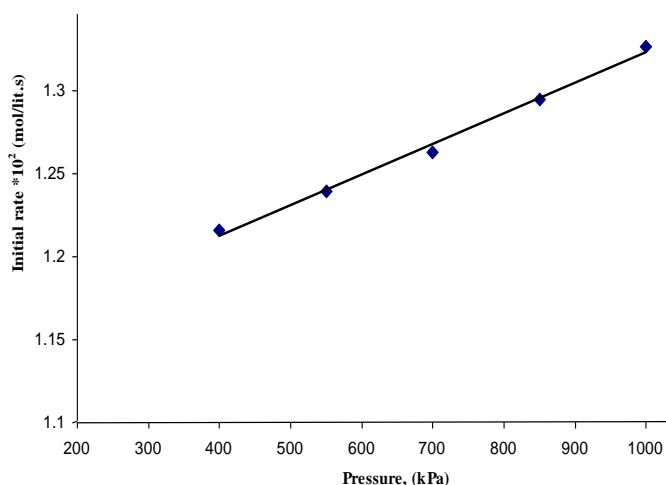


Figure 12: Effect of hydrogen partial pressure on initial rates (initial DN concentration 0.5 kmolm⁻³, Catalyst loading 10 kgm⁻³, 363^oK)

The effect of hydrogen partial pressure on initial rates was studied in the range of hydrogen partial pressures 400–1000 kPa at an initial DN concentration of 0.5 kmolm⁻³. The initial rate was found to increase linearly with the hydrogen partial pressure. The results are shown in Fig. 12. These results are shown that reaction order, being a first-order dependence on hydrogen pressure for the Pd/C catalyst. On the other hand, a first-order dependence on hydrogen for Pd/C catalyst was found.

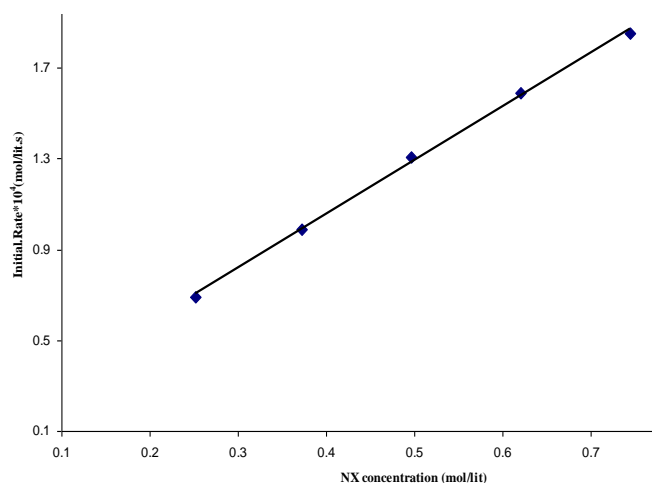


Figure 13: Effect of initial DN concentration on initial rates (H₂ pressure 700 kPa, catalyst loading 10 kgm⁻³, 363^oK)

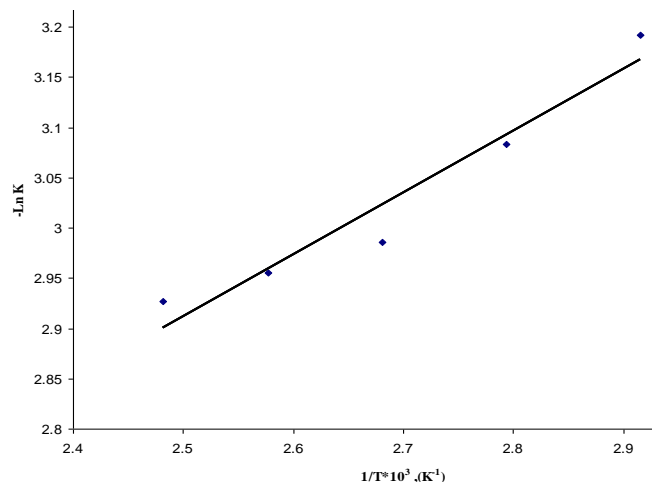


Figure 14: Arrhenius plot for 5% Pd/C catalyst

Experiments were conducted at varying feed DN concentrations in the range 0.12–0.75 mol/lit, at 1000 kPa hydrogen partial pressure. The dependence of the initial rates on feed DN concentration is presented in Fig. 13.

The effects of hydrogen catalyst loading and partial pressure on the initial rate of reactions are shown in Figs. 11 and 12. The rate was found to increase linearly with the catalyst loading and with the hydrogen partial pressure for the reaction. The results indicate first order dependence of the initial rate of

reaction on the hydrogen partial pressure for the reaction. Fig. 13 shows that the initial rate of dimethyl-nitrobenzene hydrogenation increases linearly with increasing the dimethyl-nitrobenzene concentration indicating the first order dependence of initial rate on dimethyl-nitrobenzene concentration. This order was confirmed by applying initial rate at different temperatures. These are found to be first order with respect to hydrogen for the reaction, first order with respect to dimethyl-nitrobenzene concentration for dimethyl-aniline formation. It was found that reaction temperature had a strong effect on the initial rate of the reactions. The initial rates were found to increase with increasing the reaction temperature for the reaction. The effect of temperature on the rate of reaction of dimethyl-nitrobenzene with aqueous ethanol was studied in the range of 343–403^oK in the presence of a catalyst, Pd/C. The reaction rate increases with temperature for the dimethyl-nitrobenzene. The initial rates were calculated at different temperatures and an Arrhenius plot of ln (initial rate) against 1/TK⁻¹ was made (Fig. 14). The apparent activation energies for this kinetically controlled reaction were calculated from the slopes of the straight lines as 614 J/mol. The high values of apparent activation energy confirm that the reaction systems are kinetically controlled.

5.1 Power law model

The reaction kinetics was modeled by fitting a power law model to the experimental data. The rate of reaction was represented as $r = k [A]^m [B]^n$, where $[A] = (H_A P_A)$. A and B denote hydrogen and DN, respectively, and H_A is the solubility parameter. The solubility of hydrogen in ethanol at the given partial pressure was used. The values of m and n were found using regression analysis.

The resulting rate expression was

$$r = 15.79 \exp\left(-\frac{73.85}{T}\right) [A]^{0.25} [B]^{0.96},$$

Where T is in Kelvin. The activation energy obtained from this expression was 614 J mol⁻¹. This indirectly confirms the absence of diffusional (mass transfer) resistances. The power law model is always useful for identifying controlling regime (mass transfer or kinetics) while designing a commercial reactor. Heterogeneous models based on reaction mechanisms were proposed for a further in-depth study on the observed reaction kinetics.

6. 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^oK using a hydrogen partial pressure range of 4–10 bars, with a 5% Pd/C 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. The reaction kinetic data were modeled using the power law rate expression. The order of the reaction with respect to dimethyl-nitrobenzene was 0.25 and that of hydrogen was 0.96.

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