

Hydrogenation Process Analysis in a Slurry Reactor

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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 (343–403 °K), 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.

Keywords— *Liquid-phase hydrogenation; Pd/C catalysts; dimethyl-nitrobenzene; dimethyl-aniline; operation condition*

I. INTRODUCTION

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 [1-4]. 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.

II. EXPERIMENTAL

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

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 10µm. dimethyl-nitrobenzene, ethanol, and distilled water used were of laboratory reagent grade. Hydrogen (cylinder purity 99.98%) was used.

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 °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].

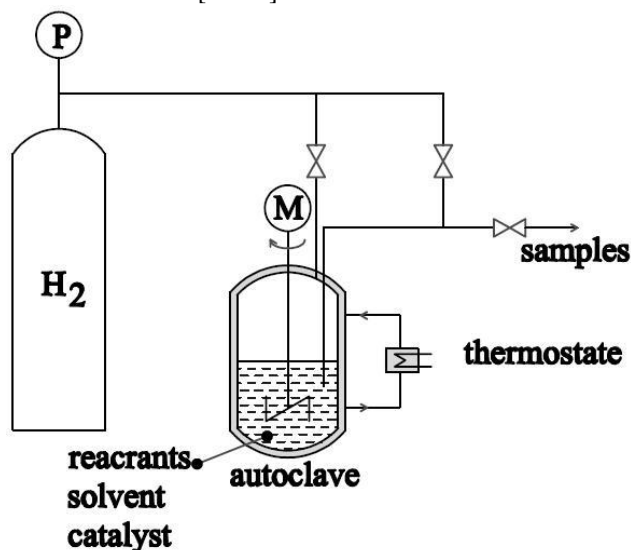


Figure 1: Experimental set-up for the liquid hydrogenation of dimethyl-nitrobenzene

III. 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].

IV. 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.

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 NO₂ of DN to NH₂. 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.

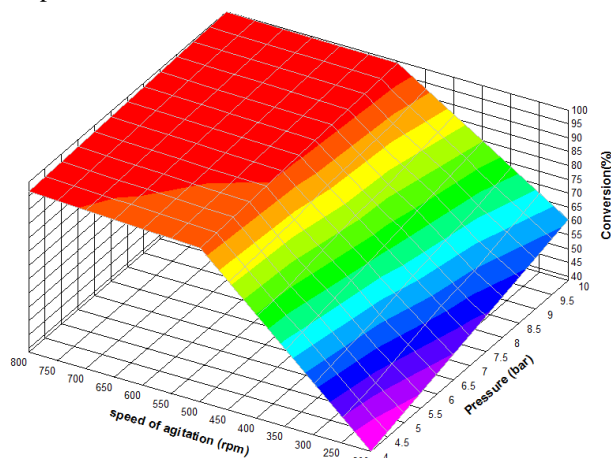


Figure 2: Evolution of the conversion level at different speed of agitation

Effect of temperature

Catalytic transfer hydrogenation is highly temperature dependant. 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 °K 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 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 °K 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. 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 °K more than 97% conversion was obtained at defined conditions.

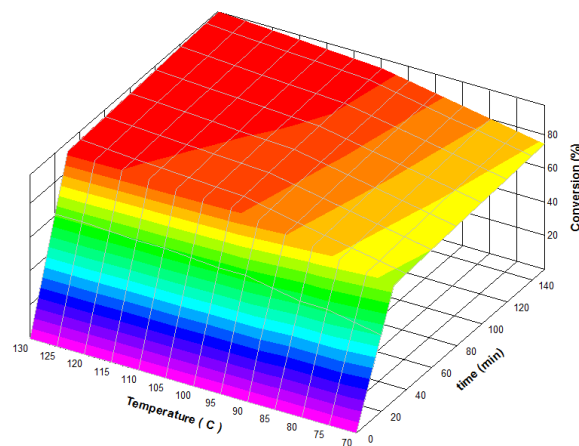


Figure 3: Evolution of the conversion level with time at different temperature

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.

The effect of time on concentration of dimethyl-nitrobenzene and dimethyl-aniline is shown in Fig. 4. 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.

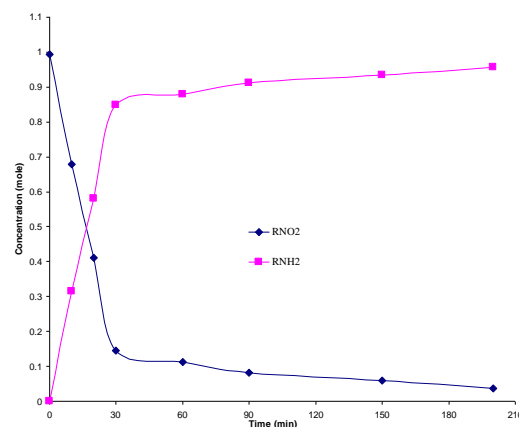


Figure 4: Dimethyl-nitrobenzene and dimethyl-aniline concentrations in solution verses time of reaction

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 363 °K. The catalyst loading was kept constant by varying the residence time. Fig. 5 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.

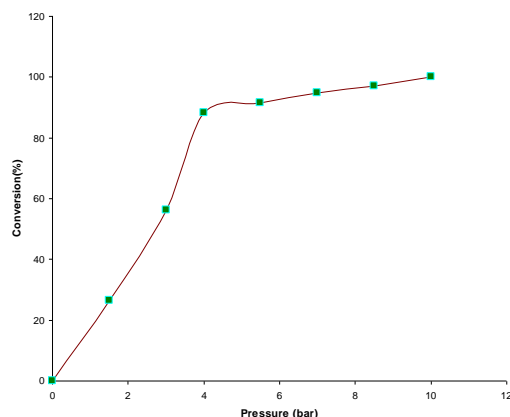


Figure 5: Evolution of the conversion level at different pressure

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. 6. 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.

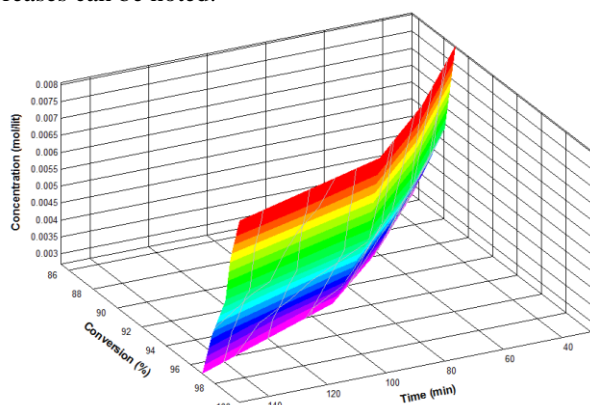


Figure 6: Evolution of the conversion level with time at different weight of catalyst

V. 5. ANALYSIS OF INITIAL RATE DATA

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. 7.

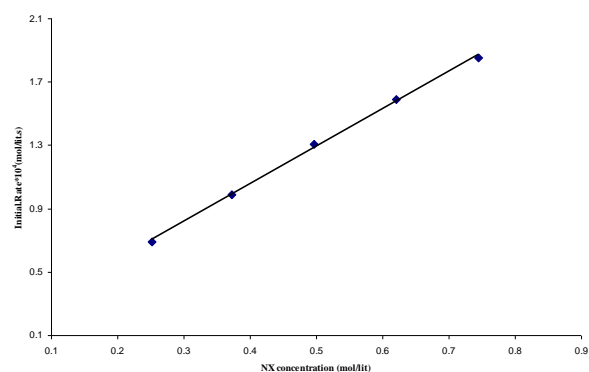


Figure 7: Effect of initial DN concentration on initial rates (H_2 pressure 700 kPa, catalyst loading 10 kg m^{-3} , 363°K)

Fig. 7 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 $343\text{--}403^\circ \text{K}$ 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 $\ln(\text{initial rate})$ against $1/T \text{ (K}^{-1}\text{)}$ was made (Fig. 8). 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.

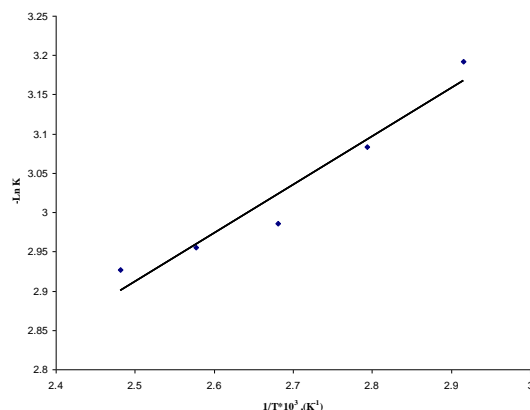


Figure 8: Arrhenius plot for 5% Pd/C catalyst

VI. 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.

VII. 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°K 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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