Catalytic hydrogenation of p-nitroaniline and 2-methoxy-5-nitroaniline

Sunil P Bawane & Sudhirprakash B Sawant*
University Institute of Chemical Technology, University of Mumbai, Matunga, Mumbai 400 019, India
Received 27 August 2002; revised received 31 March 2003; accepted 28 April 2003

Catalytic hydrogenation of p-nitroaniline (PNA) to p-phenylenediamine (PPD) was carried out in methanol using 5% Pd/C as a catalyst at hydrogen pressures in the range of 200-1000 kPa, reaction temperatures 313-333 K, catalyst loadings 200-500 mg dm$^{-3}$ and PNA concentrations 0.3-1.02 mol dm$^{-3}$. Catalytic hydrogenation of 2-methoxy-5-nitroaniline (MNA) to 4-methoxy-1,3-benzenediamine (MBD) was carried out in dimethylformamide as a solvent using 5% Pd/C as catalyst at hydrogen pressures 1000-2000 kPa, reaction temperatures 413-433 K, catalyst loadings 200-600 mg dm$^{-3}$ and MNA concentrations 0.22-1.7 mol dm$^{-3}$. Speed of agitation beyond 17 rps had no effect on the progress of the reaction. The study shows that PNA and MNA can be selectively hydrogenated to PPD and MBD, respectively and the initial rate of hydrogenations showed first order dependence on the reactant concentration, hydrogen partial pressure, and the catalyst loading for both the reactions. The activation energies for the catalytic hydrogenation of PNA and MNA were found to be 37.26 and 93.73 kJ mol$^{-1}$, respectively.

The hydrogenation of nitro aromatic compound to the corresponding anilines is an example, where, a process change is necessary for prevention of environmental pollution. Reduction using iron-acid, sulphides or polysulphides is known to generate substantial waste. Therefore, catalytic hydrogenation is the method of choice for the large-scale manufacture of many aromatic and aliphatic amines from the corresponding nitro compounds. The objective of the present work was to study the catalytic hydrogenation of p-nitroaniline (PNA) to p-phenylenediamine (PPD) and 2-methoxy-5-nitroaniline (MNA) to 4-methoxy-1,3-benzenediamine (MBD) using 5% palladium on carbon catalyst under a wide range of operating conditions. PPD is useful in the photographic and dye industries and widely used as antioxidant and antiozonants for elastomers, plastics and petroleum products. MBD is used as an intermediate in the dyes industry. Various methods have been described in the literature for the synthesis of PPD$^{10}$ and MBD$^{11}$. However, very limited kinetic information concerning the hydrogenation reaction of PNA to PPD has been published. Practically no literature is available regarding the catalytic hydrogenation of MNA to MBD. The synthesis of MBD by catalytic hydrogenation of 2,4-dinitroanisole using Pd/C as a catalyst has been reported$^{11}$.

Experimental Procedure

Materials

PNA and MNA were obtained from Arati Industries Ltd, Mumbai, India. Methanol and dimethylformamide used were of laboratory reagent grade and obtained from s. d. fine chemicals Ltd., Mumbai, India. Hydrogen (purity, 99.98%) was obtained from India Oxygen Limited, Mumbai, India and used as such. Commercially prepared 5% Pd/C was obtained from Parekh Platinum Ltd, Mumbai, India.

Method

Experiments were carried out in an autoclave (diameter = 65 mm, 100 mL capacity). The reactor had provisions for automatic temperature control, variable agitation speed, a safety rupture disk and the sampling of the liquid phase. Methanol and dimethylformamide were used as a solvent for the catalytic reduction of PNA and MNA, respectively. The appropriate quantities of the reactant, the solvent and the catalyst were added to the clean and dry autoclave. Before heating the autoclave to the required temperature, it was repeatedly purged first with nitrogen and then with hydrogen at room temperature without stirring. Once the required temperature was reached, it was pressurized with hydrogen to get the desired partial pressure of hydrogen and stirring was started. As the reaction
Proceeded, the hydrogen consumed was made up, so as to maintain a constant pressure. Samples (2-3 mL) were withdrawn through the sample outlet at regular time intervals and analyzed on a GC using a SS column, which was 2 m long and packed with 5% SE-30 on chromosorb WHP material. The conditions of analysis for both the reaction mixtures were: FID temperature: 573 K; injection temperature: 573 K; column temperature: 443 K; carrier gas, \( \text{N}_2 \): \( 1.9 \times 10^{-5} \text{ m}^3 \text{ min}^{-1} \).

Results and Discussion

The stoichiometric reactions involved in the catalytic hydrogenation of PNA and MNA are:

\[
\begin{align*}
\text{(1)} & \\
\text{PNA} & + 3\text{H}_2 \rightarrow \text{PPD} + 2\text{H}_2\text{O} \\
\text{(2)} & \\
\text{MNA} & + 3\text{H}_2 \rightarrow \text{MBD} + 2\text{H}_2\text{O}
\end{align*}
\]

Initial experiments on catalytic hydrogenation of PNA and MNA were carried out to establish the material balance of reactants consumed and products formed and the balance to the extent of minimum 98% as per the stoichiometry given by reaction 1 and 2 was established for the organic reactants and products. For kinetic experiments, progress of the reaction was monitored by analyzing the reaction mixture and calculating the moles of the reactants consumed as a function of time in each run. Based on the moles of reactants consumed, the initial rates were calculated graphically using third order polynomial equation.

Effect of speed of agitation

The effect of impeller speed on the conversion of PNA and MNA in the range 10-24 rps is shown in Figs 1 and 2, respectively. The conversion was found to increase when the speed increases from 10 to 17 rps. This indicates that gas to liquid and/or liquid to solid mass transfer resistance is significant between 10-17 rps. The impeller speed was not observed to have any effect on the conversion after 17 rps,
indicating absence of external mass-transfer limitation, beyond the speed of agitation of 17 rps.

**Effect of catalyst loading**

The catalyst loading was varied between 200 to 500 mg dm\(^{-3}\) for the catalytic hydrogenation of PNA and 200 to 600 mg dm\(^{-3}\) for the catalytic hydrogenation of MNA. The initial rate of reaction was found to increase linearly with the catalyst loading.

**Effect of hydrogen partial pressure**

The effect of hydrogen partial pressure was studied in the range of 200-1000 kPa for the catalytic reduction of PNA and in the range of 1000-2000 kPa for the catalytic hydrogenation of MNA. The rate was found to increase linearly with the hydrogen partial pressure. The result indicates first order dependence of the initial rate of reaction on the hydrogen partial pressure.

**Effect of reactant concentration**

The reactant concentration was varied from 0.3 to 1.02 mol dm\(^{-3}\) for the catalytic hydrogenation of PNA and from 0.22 to 1.7 mol dm\(^{-3}\) for the catalytic hydrogenation of MNA. The initial rate was found to increase with increasing the reactant concentration and showed a first order dependence on the reactant concentration.

**Effect of temperature**

The reactions were studied at different temperatures in the range of 313-323 K for the catalytic hydrogenation of PNA and in the range of 413-433 K for the catalytic hydrogenation of MNA. It was found that the initial rate of catalytic hydrogenation increases with increasing the temperature.

The optimum reaction conditions to get maximum hydrogenation of PNA and MNA are listed in Table 1. All the experiments were carried out to eliminate the external mass-transfer resistances by operating at high impeller speed (24 rps). It was found that temperature has strong effect on the initial rate of the reaction and initial rate of reaction varies linearly with the hydrogen partial pressure as well as with the reactant concentration. Intraparticle diffusion was eliminated by using very fine catalyst particles\(^{12}\).

Hence, on the basis of above observations it can be assumed that surface reaction is the rate-controlling step.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>PNA hydrogenation</th>
<th>MNA hydrogenation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate concentration (mol dm(^{-3}))</td>
<td>0.6</td>
<td>0.22</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>333</td>
<td>433</td>
</tr>
<tr>
<td>Hydrogen partial pressure (kPa)</td>
<td>1000</td>
<td>2000</td>
</tr>
<tr>
<td>Catalyst loading (mg dm(^{-3}))</td>
<td>360</td>
<td>600</td>
</tr>
<tr>
<td>Time for complete conversion (s)</td>
<td>2400</td>
<td>5800</td>
</tr>
<tr>
<td>Speed (rps)</td>
<td>24</td>
<td>24</td>
</tr>
</tbody>
</table>

The rate equation for the catalytic hydrogenation of PNA when the surface reaction between the adsorbed species controls the progress of the reaction can be written as,

\[
\begin{align*}
\frac{\dot{c}}{C_{H_2}C_{PNA}} &= K_1 a_p C_{H_2}^* C_{PNA}^* C_{H_2} C_{PNA} \\
\frac{\dot{c}}{C_{H_2}C_{PNA}} &= K_2 a_p K_1 C_{H_2} C_{PNA} \\
\frac{\dot{c}}{C_{H_2}C_{PNA}} &= K_2 a_p K_1 K_1 \\
\end{align*}
\]

Taking the initial values,

\[
\begin{align*}
\frac{\dot{c}_{i}}{C_{H_2}C_{PNA}} &= K_1 a_p K_2 K_1 \\
\frac{\dot{c}_{i}}{C_{H_2}C_{PNA}} &= k_i \\
\end{align*}
\]

where,

\[
k_i = K_1 a_p K_2 K_1
\]

Solubility of hydrogen in methanol and dimethylformamide was estimated by a correlation for hydrogen solubility given by Shaw\(^{17}\).

The Arrhenius plot of In \(k_i\) versus \(1/T\) gave a straight line as shown in Fig. 3, and an activation
energy of 37.26 kJ mol\(^{-1}\) for catalytic hydrogenation of PNA.

Similarly, the rate equation for the catalytic hydrogenation of MNA, when the surface reaction between the adsorbed species controls the progress of the reaction, can be written as,

\[
\frac{r_2}{C_{\text{H}_2} C_{\text{MNA}}} = K_2 a_2 K'_2 C_{\text{H}_2} C_{\text{MNA}} \quad \ldots (11)
\]

Taking the initial values,

\[
\frac{r_2}{C_{\text{H}_2} C_{\text{MNA}0}} = K_2 a_2 K'_2 \quad \ldots (12)
\]

\[
\frac{r_2}{C_{\text{H}_2} C_{\text{MNA}0}} = k_2 \quad \ldots (13)
\]

where,

\[k_2 = K_2 a_2 K'_2\]

The Arrhenius plot of \(\ln k_2\) versus \(1/T\) gave a straight line (Fig. 4), and value of activation energy as 93.73 kJ mol\(^{-1}\) for catalytic hydrogenation of MNA. These high values of activation energies indicate that the reactions are kinetically controlled.

**Conclusion**

\(p\)-nitroaniline and 2-methoxy-5-nitroaniline can be selectively hydrogenated to \(p\)-phenylenediamine and 4-methoxy 1,3, benzenediamine, respectively using 5% Pd/C as a catalyst. The initial rate of hydrogenation had first order dependence with respect to the reactant concentration, hydrogen partial pressure, and the catalyst loading for both the reactions. The activation energies for the catalytic hydrogenation of \(p\)-nitroaniline and 2-methoxy-5-nitroaniline were found to be 37.26 and 93.73 kJ mol\(^{-1}\), respectively.

**Nomenclature**

- \(C_{\text{PNA}0}\) = initial concentration of PNA, mol dm\(^{-3}\)
- \(C_{\text{PNA}}\) = liquid phase concentration of PNA, mol dm\(^{-3}\)
- \(C_{\text{PNA}a}\) = adsorbed concentration of PNA, mol dm\(^{-3}\)
- \(C_{\text{MNA}0}\) = initial concentration of MNA, mol dm\(^{-3}\)
- \(C_{\text{MNA}}\) = liquid phase concentration of MNA, mol dm\(^{-3}\)
- \(C_{\text{MNA}a}\) = adsorbed concentration of MNA, mol dm\(^{-3}\)
- \(C_{\text{H}_2}\) = concentration of hydrogen in liquid phase, mol dm\(^{-3}\)
- \(C'_{\text{H}_2}\) = adsorbed concentration of hydrogen, mol dm\(^{-3}\)
- \(C_{\text{H}_20}\) = initial concentration of hydrogen in liquid phase, mol dm\(^{-3}\)
- \(r_1\) = rate of the catalytic hydrogenation of PNA, mol dm\(^{-3}\) s\(^{-1}\)
\[ r_o = \text{initial rate of catalytic hydrogenation of PNA, mol dm}^{-3} s^{-1} \]
\[ r_i = \text{rate of the catalytic hydrogenation of MNA, mol dm}^{-3} s^{-1} \]
\[ r_{50} = \text{initial rate of catalytic hydrogenation of MNA, mol dm}^{-3} s^{-1} \]
\[ K_1 = \text{rate constant for catalytic hydrogenation of PNA} \]
\[ K_2 = \text{rate constant for catalytic hydrogenation of MNA} \]
\[ K_1 K', K''_2 = \text{equilibrium constants} \]
\[ a_p = \text{specific surface area of the catalyst, m}^2 \text{ m}^{-3} \]

**References**