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LIQUID PHASE HYDROGENATION OF ACETHYDRAZONE TO N´-METHYL ACETHYDRAZIDE OVER Pd/γ-Al_2O_3 CATALYST

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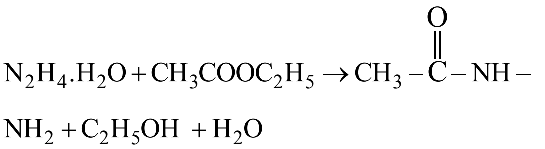
Abstract - Catalytic hydrogenation of acethydrazide (AH) is the main step in the production of N´-methyl acethydrazide (MAH). In this step, AH reacts with formaldehyde to produce acetylhydrazone (AOH). AOH is hydrogenated in the presence of 5% Pd/γ-Al_2O_3 catalyst to MAH. In this paper, the effects of hydrogen pressure, catalyst loading and initial concentration of AOH on the initial rate of hydrogenation were studied in a batch slurry reactor within a temperature range of 303-333K. The hydrogenation rate was first order with respect to hydrogen concentration at lower hydrogen pressures. However, at higher pressures, the rate became independent of both hydrogen and initial AOH concentrations. A single site Langmuir-Hinshelwood type formulation was found to describe adequately the kinetic data. A good correlation was observed between the predicted concentration vs. time profiles and those determined experimentally. The apparent activation energy was calculated from the initial rates as 40.6 kJ/mol.

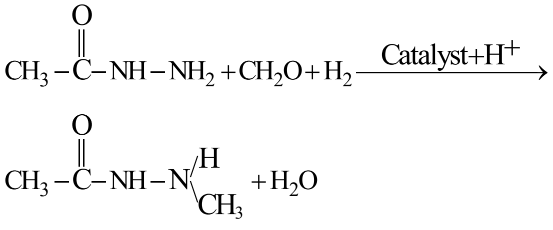
Keywords: Monomethyl hydrazine; Hydrogenation; Pd/γ-Al_2O_3 catalyst; Kinetics.

INTRODUCTION

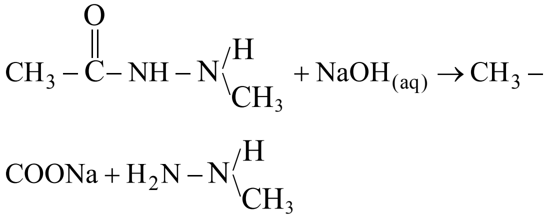
Monomethylhydrazine (MMH) is a storable liquid fuel for use in orbital spacecraft engines. Several methods have been reported for production of this compound. Certain problems facing this process, such as low reaction yields, environmental risk of pollution caused by the reaction byproducts and high cost of production, persuaded scientists to consider alternate methods. One of the safe and economical novel methods is catalytic methylation of acethydrazide (AH) (Schmidt, 2001). This method consists of the three following steps:



$$N_2H_4.H_2O + CH_3COOC_2H_5 \rightarrow CH_3-\overset{\overset{O}{\|}}{C}-NH-NH_2 + C_2H_5OH + H_2O \qquad (1)$$



$$CH_3-\overset{\overset{O}{\|}}{C}-NH-NH_2 + CH_2O + H_2 \xrightarrow{Catalyst+H^+} CH_3-\overset{\overset{O}{\|}}{C}-NH-N\begin{matrix}/H\\ \backslash CH_3\end{matrix} + H_2O \qquad (2)$$



$$CH_3-\overset{\overset{O}{\|}}{C}-NH-N\begin{matrix}/H\\ \backslash CH_3\end{matrix} + NaOH_{(aq)} \rightarrow CH_3-COONa + H_2N-N\begin{matrix}/H\\ \backslash CH_3\end{matrix} \qquad (3)$$

The key step of the process is reaction (2) which is carried out in a three phase slurry reactor under

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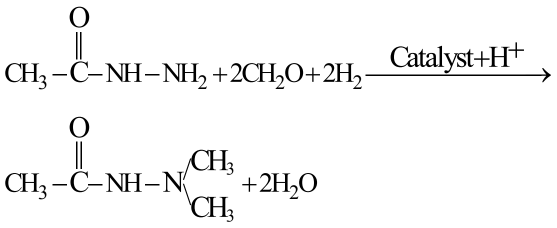
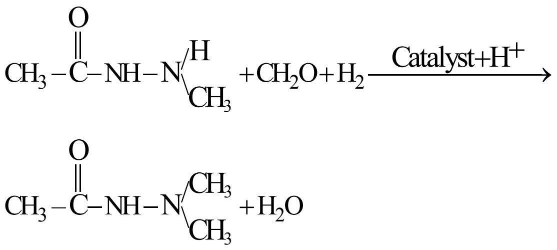
*To whom correspondence should be addressed hydrogen pressure. Platinum, palladium or nickel catalysts have been recommended for the latter step. However, simultaneous production of unwanted N', N'-dimethyl acethydrazide (DMAH) (Malz Jr. et al., 1977; Abdel-Mgid et al., 1996) is the main problem of this process.



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH-NH_2+2CH_2O+2H_2\xrightarrow{Catalyst+H^+} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH-N\begin{matrix}/CH_3\\ \backslash CH_3\end{matrix}+2H_2O \qquad (4)$$

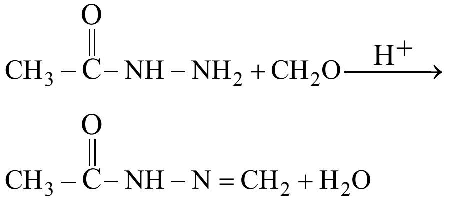
Reaction (4) was studied kinetically on a Pd/C catalyst (Pakdehi et al., 2005). It was observed that the product of reaction (2) is consumed during the formation of DMAH:



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH-N\begin{matrix}/H\\ \backslash CH_3\end{matrix}+CH_2O+H_2\xrightarrow{Catalyst+H^+} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH-N\begin{matrix}/CH_3\\ \backslash CH_3\end{matrix}+H_2O \qquad (5)$$

It is, therefore, necessary to separate completely N´-methyl acethydrazide (MAH) from DMAH. However, this may be avoided by first conducting the reaction between AH and formaldehyde, followed by hydrogenation of the resultant product.

The reaction between AH and formaldehyde was studied in the presence of acetic acid as catalyst. The reaction product is acetylhydrazone (AOH), formed according to the following reaction:



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH-NH_2+CH_2O\xrightarrow{H^+} CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH-N=CH_2+H_2O \qquad (6)$$

This reaction is fast and was observed to be completed within a few minutes (Pakdehi et al., 2005). The kinetics of this reaction has been studied and the operating parameters have been optimized. The reaction rate is first order with respect to both AH and formaldehyde. In the temperature range of 25-55°C and $C_{0,CH_2O}/C_{0,AH}=0.99$, a yield of at least 99% was obtained by removing the water from the reaction medium by molecular sieves. In other words, starting with equimolar concentrations of AH and CH_2O at temperatures of 30°C, 40°C and 50°C, the reaction was complete within 4, 2 and 1 minutes, respectively.

Considering the industrial importance of this reaction system on one hand and the lack of available comprehensive information in the literature on the reaction on the other hand, it is worthwhile to investigate the intrinsic kinetics of catalytic hydrogenation of AOH to MAH. The main objectives of such a study are a detailed analysis of the mass transport effect at different temperatures and setting up a kinetic model suitable for design of the reactor. Carbon may be used as the catalyst support. However, due to some disadvantages of the latter in comparison with alumina, such as low bulk density and poor mechanical strength, it was decided to employ Pd/γ-Al_2O_3 as the catalyst.

Data and information obtained from this investigation may provide the starting basis for further development and optimization of various multiphase reactor performance models utilized in pilot or commercial scale operations.

EXPERIMENTAL

Materials

Acethydrazide was synthesized from the reaction between ethyl acetate and hydrazine hydrate in methanol solvent and purified (Pakdehi et al. 2004). The preferred source of formaldehyde is paraformaldehyde (Malz Jr. et al. 1977). AOH was synthesized according to reaction (6). The solvents used (methanol, ethanol, n-propanol and n-buthanol) were of laboratory reagent grade supplied by Merck Company.

Hydrogen gas (purity of 99.999%) was delivered by Roham Gas Company. A 5wt% Pd/γ-Al_2O_3 catalyst was made by applying incipient wetness impregnation with $PdCl_2$ (Aldrich Chem. Co., 99.999%) as the precursor, dissolved in H_2O at 358K. The catalyst was prepared by impregnation of γ-alumina (Alfa Aesar, BET area of ca 150 m^2/g) with an aqueous solution of $PdCl_2$. The powder was dried at 383K for 24h, pressed, crushed and sieved into 44μm (350 mesh) particles. Prior to the reaction, the catalyst was calcined in air for 5.5h. The calcination temperature was increased from room temperature to 773K in a 30 min ramp (Pakdehi et al. 2005).

Experimental Procedure

The hydrogenation experiments were carried out in a 300-cm^3 capacity high- pressure hastelloy (C-276) autoclave supplied by Parr Instrument Co., USA. The reactor was fitted with an initial cooling coil and a magnetically driven impeller with a four-blade stirrer capable of operations up to 2000 rpm. The temperature of the liquid in the reactor was maintained at the desired level (with a precision of ± 1K) using a PID controller. In addition, the reactor was equipped with an internal thermocouple and a digital pressure transducer (with a precision ±0.07bar). The relevant safety features like a rupture disk and a high temperature-pressure cut-off were also installed as a part of the reactor set-up.

A methanolic solution of AH was poured into the reactor. Paraformaldehyde was added to the reactor and stirred. After the completion of reaction (6), 5wt% Pd/γ-Al$_2$O$_3$ catalyst was added to the reaction mixture and the reactor was first flushed with nitrogen and then with hydrogen in order to remove any dissolved air or oxygen. In the next step, the reactor was pressurized to the desired level. During the course of reaction, the pressure of H$_2$ in the reactor was maintained constant by supplying hydrogen from the reservoir to compensate the rate of its consumption. The pressure of H$_2$ in the reservoir was monitored continuously, allowing in situ measurement of the instantaneous hydrogen consumption. At the end of the reaction, the reactor was cooled to room temperature and a gas sample was collected for analysis of the final gas phase products. The hydrogenation reaction was carried out isothermally. The autoclave was continuously fed with hydrogen in order to maintain the isobaric reaction conditions.

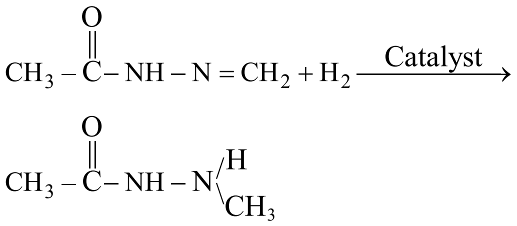
Analytical Procedure

The analysis of the reactant and product (AOH and MAH) was performed using a Perkin Elmer-8420 GC apparatus equipped with a BP-20 capillary column (detector: FID; carrier gas: He with a flow rate of 2cm^3/min; initial temperature: 30°C; final temperature: 250°C; ramp rate: 20°C/min; Injection port and detector temperatures: 300°C).

The MAH standard was prepared by acylation of MMH with acetic anhydride (Condon, 1972).

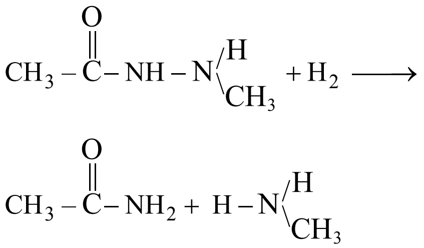
RESULTS AND DISCUSSION

The results of analysis confirmed the occurrence of the following reaction (formation of MAH):



$$CH_3-\overset{\overset{O}{\|}}{C}-NH-N=CH_2+H_2\xrightarrow{\text{Catalyst}} CH_3-\overset{\overset{O}{\|}}{C}-NH-N\langle\begin{smallmatrix}H\\CH_3\end{smallmatrix} \quad (7)$$

In addition, at higher hydrogen partial pressures (in excess of 40 bar) the following hydrogenolysis reaction occurred, forming mono-methyl amine:



$$CH_3-\overset{\overset{O}{\|}}{C}-NH-N\langle\begin{smallmatrix}H\\CH_3\end{smallmatrix}+H_2\longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-NH_2+H-N\langle\begin{smallmatrix}H\\CH_3\end{smallmatrix} \quad (8)$$

No hydrogenation was observed in the absence of the catalyst, indicating that non-catalytic reactions are not involved in this process.

A material balance for the reaction system showed 98% agreement between the experimental and calculated data. Therefore, in all kinetic runs, the reactions were followed by measurement of hydrogen consumption with time. The experimental data were reproducible with a mean absolute deviation of 2%.

Analysis of the initial rate data is useful for understanding the dependence of the reaction rates on the individual parameters and evaluation of the significance of the mass transfer effect. In each kinetic run, the concentrations of AOH and MAH were determined up to approximately 10-15% conversion of AOH. The initial rates of formation of AOH ($r_{o,AOH}$) were calculated from the data obtained at low conversion levels (less than 15% conversion of AOH) under different sets of operating conditions. However, only the results up to 10% conversion were considered for further calculations.

Heat and Mass Transfer Limitations

A critical step in obtaining reliable quantitative kinetic data is to ensure the absence of all transport limitations such as external and internal heat and mass transfer effects and absorption of hydrogen gas in the liquid phase (Singh et al., 2001). The reaction can be considered to occur isothermally (Pakdehi et al., 2005).

In order to determine the significance of gas-liquid mass transfer resistance, the effect of agitation speed on the rate of hydrogenation was studied in the range of 1000-2000 rpm at 323K. The results shown in Fig. 1

indicate that the hydrogenation rate is independent of agitation speed above 1200 rpm (the rate was not controlled by hydrogen mass transfer) at lower catalyst loadings (less than 2.6 g/L). In the case of higher catalyst loadings (10 g/L), however, the rate of reaction was found to be enhanced by an increase in the speed of agitation. These results may indicate that the data obtained at the lower catalyst loadings (2.6 g/L) reflect the kinetic control regime. Further experiments were, therefore, carried out using catalyst loadings within the range of 0.1-2.6 g/L.

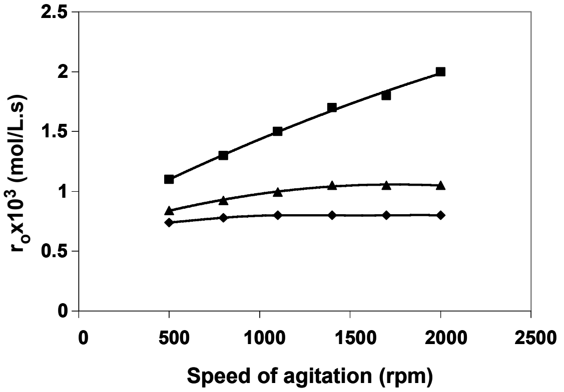


Figure 1: Effect of agitation speed on the initial rate of hydrogenation (methanol as solvent, $C_{o,AOH}$ = 0.1 mol, P_{H2} = 6 bar, T = 323K, ω_c= -■- 8g/L, -▲-2.6g/L, -◆- 0.5g/L)

The effect of catalyst loading on the initial rate of formation of MAH is shown in Fig. 2. The rate of formation was found to increase linearly with the increase in catalyst loading. This linear dependency may indicate the absence of external gas-liquid mass transfer resistance or no bulk diffusion limitations.

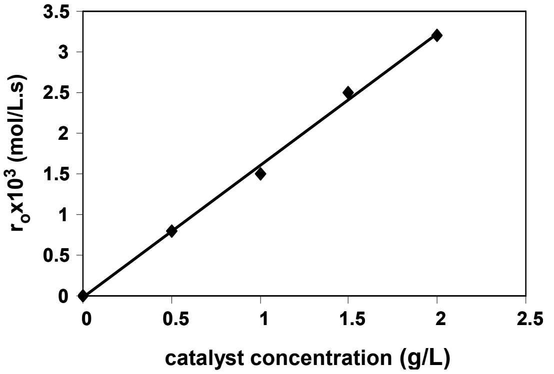


Figure 2: Effect of catalyst loading on initial rate of hydrogenation (methanol as solvent, $C_{o,AOH}$ = 0.1 mol, P_{H2} = 6bar, T = 323K, agitation speed= 1700rpm)

In three-phase reactions, one of the main problems is the limitation imposed by internal and external mass-transfer processes. Therefore, catalyst particles with small diameters are required. The diameters of the catalyst particles should be in the order of several microns and equal to the diameters of conventional suspension catalysts. In this way, the internal mass-transfer limitations could be eliminated.

As the catalyst used in this study was in the form of a fine powder (dp <50 μm), it may be assumed that external diffusion was not effective in the reaction. The Weisz-Prater criterion (Weisz and Prater, 1954) can be used to verify the absence of internal diffusion limitations. According to this criterion, in the absence of pore diffusion resistance, the following condition has to be satisfied:

$$\frac{\tau d_p^2 r_{AOH}}{DC_{AOH}\varepsilon} \langle 1 \qquad (9)$$

where, τ is the tortuosity of the catalyst particles, d_p, is the mean diameter of the particles; r_{AOH}, is the rate of reaction, D, is the diffusion coefficient, C_{AOH}, is the concentration of AOH in the liquid phase and ε is the porosity of the particles. In the present system, the average values for τ and ε were taken to be 4 and 0.68, respectively (Satterfield, 1970). Diffusion coefficient D was estimated to be 6×10^{-8} m^2/min, C_{AOH} and r_o were determined to be 0.5 mol/L and 3×10^{-3} mol/L.s, respectively. The maximum diameter of the particles was 48 μm. Substitution of the above quantities in equation (8) yielded the result 0.8<1.

Effect of Solvent

The effect of solvents on the initial rate was investigated under similar reaction conditions. The solvents used were methanol, ethanol, n-propanol and n-butanol. The results are presented in Table 1. The initial rate of hydrogenation was highest in methanol and lowest for n-butanol. It seems that the hydrogenation rate increased with increase in polarity of the solvent. It has been shown that the rate of reactions yielding products less polar than the reactants, which is the case in the present study, will be promoted by an increase in the polarity of the solvents involved (Frost and Pearson, 1970).

Table 1: Effect of solvent on initial rate of hydrogenation ($Co_{,AOH}$ = 0.1 mol, P_{H2} = 6 bar, T=323K, agitation speed= 1700 rpm, ω_c = 1.5 g/L)

Solvent	Dielectric constant (Lide, 2005)	r_o, (mol/L.s) $\times10^3$
Methanol	32.6	2.5
Ethanol	24.3	2.25
n-Propanol	20.1	1.5
n-Butanol	17.8	0.73

Effect of Hdrogen and AOH

The effect of hydrogen partial pressure on the rate of formation of MAH was investigated in a range of 3-25 bar at various temperatures and the results are presented in Fig. 3. The initial rate increased linearly with hydrogen partial pressure up to 12 bar, beyond which it remained nearly constant at all temperatures.

The effect of AOH concentration was also investigated in the range of 0.1-1.5 mol/L. The rate of hydrogenation was found to be independent of AOH charge under the experimental conditions. The concentration of AOH decreases linearly with time (Fig. 4), indicating a zero order dependence of the reaction rate on AOH concentration. This observation may indicate that, within this range of reactant concentrations, the total catalytic sites on which AOH could be absorbed are occupied by this species.

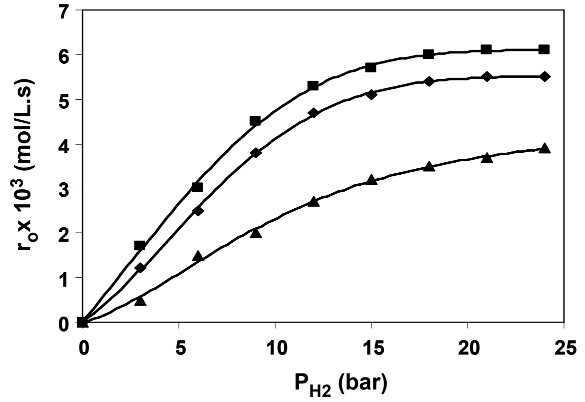


Figure 3: Effect of hydrogen partial pressure on initial reaction rate at different temperatures ($C_{o,AOH}$= 0.5 mol, ω_c= 2.5g/L, agitation speed = 1700rpm, T: -■-333K-, -◆-323K, -▲-308K)

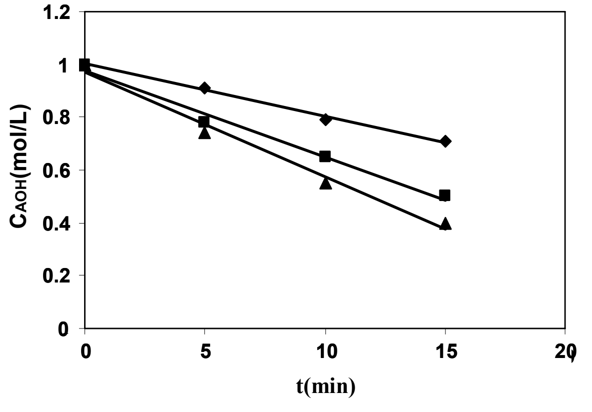


Figure 4: Concentration profile of AOH versus time ($C_{o,AOH}$= 1 mol, P_{H2} = 6bar, ω_c= 2.5g/L, agitation speed = 1700rpm, T: -◆-308K, -■-323K -▲-333K)

The Rate Model and the Suggested Mechanism

A single site Langmuir-Hinshelwood mechanism was proposed for the reaction (7) as follows:

$$AOH + \xleftrightarrow{K_1} AOH^* \tag{12}$$

$$H_2 + * \xleftrightarrow{K_2} H_2^* \tag{13}$$

$$AOH^* + H_2^* \xrightarrow{k_3} MAH^* \tag{14}$$

$$MAH^* \xleftrightarrow{K_4} MAH + * \tag{15}$$

where * is an active site.

In such a mechanism, it was assumed that hydrogen adsorbs on the catalyst sites in molecular form and that equation (14) is the rate-determining step and irreversible.

The basic property of AOH and the acidic nature of the γ-Al_2O_3 support lead to a strong adsorption of AOH molecules. A further assumption was also made that adsorption of AOH and desorption of MAH are both rapid enough so that the quasi-equilibrium hypothesis may be applied. The initial rate of hydrogenation is, therefore, given by:

$$-r_{o,H_2} = \frac{kK_{H_2}C_{H_2}}{1+K_{H_2}C_{H_2}} \tag{16}$$

In which k and K_{H2} are the reaction rate constant for hydrogenation and the adsorption equilibrium constant, respectively.

It seems, therefore, that hydrogen can occupy any free active site on the Pd surface. In other words, hydrogen must compete with AOH for adsorption at the catalyst's active sites. However, it has been observed that adsorption of AOH on the catalyst's surface is stronger than that of hydrogen (Rylander, 1967).

Regarding the effects of AOH concentration, catalyst loading and hydrogen partial pressure on the reaction rate discussed above, a single site Langmuir-Hinshelwood formulation was proposed for this process:

$$-r_o = \frac{k_1.\omega_c.C_{H_2}}{1+K_A C_{H_2}} \tag{10}$$

where $-r_o$ is the initial reaction rate (mol/L.s); ω_c is the catalyst loading (g/L) and C_{H2} is the concentration of dissolved hydrogen in the solution.

To determine the kinetic parameters k_1 and K_A, equation (10) was rearranged as follows,

$$\frac{-1}{r_O}=\frac{1}{k_1.\omega_c.C_{H_2}}+\frac{K_A}{k_1.\omega_c} \tag{11}$$

A plot of $-1/r_o$ versus $1/C_{H2}$ yields a straight line with the slope of $1/ k_1.\omega_c$. Knowing the k_1 value, the value for K_A may be calculated from the intercept of such a graph (Fig. 5). The C_{H2} values (i.e., dissolved hydrogen concentration in methanol) were calculated at the given pressures from the solubility data available in the literature (Radhakrishnan et al., 1983). The values of k_1 and K_A determined at different temperatures are given in Table 2.

From the kinetic parameters, obtained by the method described above, the apparent activation energy was calculated from the Arrhenius plot (Fig. 6) to be 40.6 kJ/mol. The heat of adsorption was also determined from a plot of $\ln K_A$ against 1/T as 45.9 kJ/mol (Fig. 7).

A comparison between the experimental and predicted rate data is given in Fig. 8. The degree of agreement is above 96%.

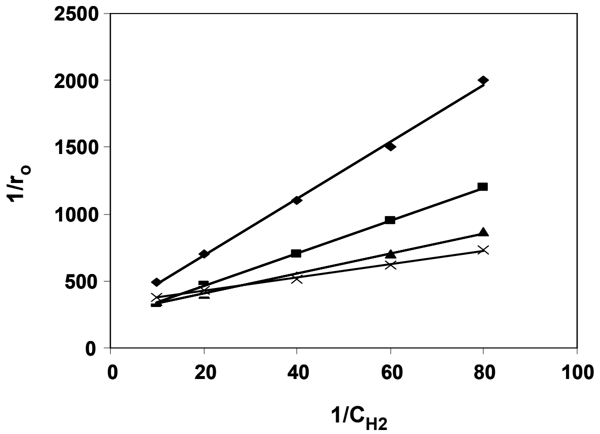


Figure 5: Plot of $-1/r_o$ versus $1/C_{H2}$ at different temperatures ($C_{o,AOH}$= 0.5 mol, catalyst concentration= 1 g/L, ω_c= 2.5g/L, agitation speed = 1700rpm, T: -♦-303K-, -■-313K, -▲-323K, -×-333K)

Table 2: Values for the kinetic parameters at different temperatures

Temperature (K)	k_1 (L/g.s)	K_A (L/mol)
303	0.047	12.478
313	0.08171	20.3
323	0.1334	34.329
333	0.20172	65.719

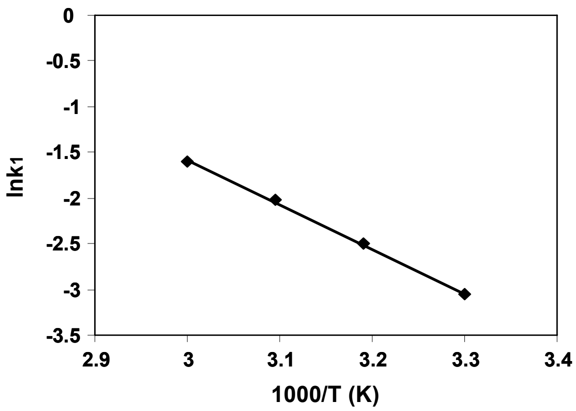


Figure 6: Arrhenius plot for apparent activation energy

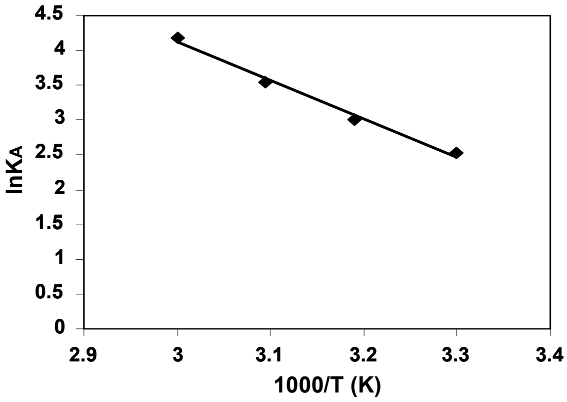


Figure 7: Arrhenius plot for heat of adsorption

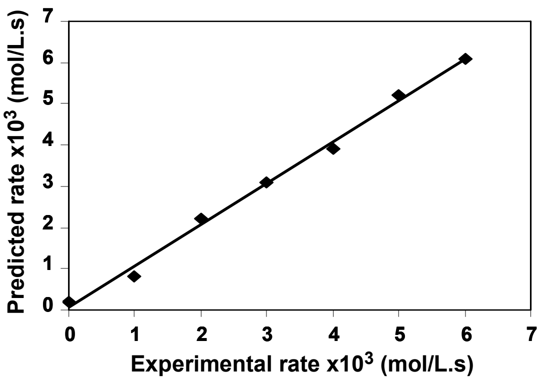


Figure 8: Experimental versus predicted rates

CONCLUSIONS

The kinetics of catalytic hydrogenation of AOH to MAH with 5% Pd/γ-Al_2O_3 was investigated. The reaction rate was zero order with respect to AOH and first order with respect to hydrogen at lower pressure of the latter, approaching zero order at pressures above 15 bar. On the basis of data obtained in the kinetic regime, a single site Langmuir-Hinshelwood type rate equation was proposed. The apparent activation energy was calculated to be 40.6 kJ/mol. The heat of adsorption was also determined to be 45.9 kJ/mol.

NOMENCLATURE

AH	Acethydrazide	
AOH	Acetylhydrazone	
DMAH	N', N'-dimethyl acethydrazide	
MAH	N′-methyl acethydrazide	
AOH*	concentration of catalyst sites occupied by AOH	mol/L
MAH*	concentration of catalyst sites occupied by MAH	mol/L
$C_{o,}$	initial concentration of i-th component	mol/L
C_i	concentration of i-th component	mol/L
D	diffusion coefficient	m^2/min
d_p	mean diameter of the particles	µm
k	reaction rate constant for hydrogenation	L/g.s
K_{H2}	adsorption equilibrium constant	L/mol
r_o	initial rate of hydrogenation	mol/L.s
T	tortuosity of the catalyst particles	(-)
ε	porosity of the particles	(-)
*	catalyst active site	(-)
ω_c	catalyst concentration	g/L

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