



Kinetics Studies and Mechanism Evolution of the Cyclization of Ethylene Diamine and Propylene Glycol over Alumina Supported Nanocrystalline Mn-Ferrite

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Abstract- Kinetics of Cyclization of propylene glycol and ethylene diamine to 2-methyl pyrazine has been studied over alumina-supported nanocrystalline MnFe₂O₄ catalyst in a differential flow fixed bed reactor in the temperature range 473 – 573 K. The partial pressures of propylene glycol and ethylene diamine were varied and rates were measured for the formation of 2 Methyl Pyrazine. Product selectivity as well as rate of formation of 2-methyl pyrazine was influenced by partial pressure of reactants. The rate equation $R = k \frac{K_P K_E P_P P_E}{(1 + K_P P_P + K_E P_E)^2}$ deduced, on the basis of adsorption of PG and ED in gas phase represented the data most satisfactorily.

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I. INTRODUCTION

Nanosize materials are known to exhibit certain properties that are different from their bulk counterparts [1] such materials possess higher surface area, band gap, coercivity, acidity / alkalinity and coordination of atoms. The chemical properties also vary because of the changes in the electron density as a function of particle size, resulting thereby in binding modes of the adsorbate molecules that are different than that observed in the case of corresponding bulk materials. Additionally, in case of supported catalysts, the electronic interaction between the nano-dispersed metal crystallites and the support materials are known to influence the chemisorptions properties. Providing support to the nanocrystalline metal oxides avoids their agglomeration in actual reaction conditions and helps achieve highly dispersed and uniform size particles. Anpo *at al.* and Maira *at al.* [2-3] In addition to large surfaces, support helps in the shape selectivity and also provides an inert envelope to protect from the chemical effect of the reaction medium.

2-MP is the pivotal intermediate for obtaining 2-cyanopyrazine, which on hydrolysis yields pyrazinamide, a well-known anti-tubercular drug. Conventionally, chromite catalysts are used for vapour phase synthesis

of 2-MP. There are reports on the use of Palladized Zn-Cr oxide Forni *at al.* [4] ZSM-5 Kulkarni *at al.* [5] Modified copper-chromite Ilnam *at al.* [6] binary catalyst based on oxides of Zn and variable valence metals Balpanov *at al.* [7] Zn-modified zeolites Anand *at al.* [8] Zn-modified ferrite Anand *at al.* [9] and CuO/ZnO/SiO₂ Subramanyam *at al.* [10] as catalysts for synthesis of 2-MP from ED and PG. To the best of our knowledge, there is no report on the kinetics of cyclization of propylene glycol (PG) and ethylene diamine (ED) to produce 2-MP over alumina supported nanocrystalline manganese ferrite. The present problem of kinetic study of synthesis of 2-MP from PG and ED was therefore undertaken with a view (1) to collect data on the kinetics of the vapour phase synthesis of 2MP over alumina support Mn-ferrite (AMF) catalyst (2) to find a suitable rate law, which can explain the data satisfactorily, and (3) to predict a mechanism of the reaction. The catalyst has been characterized using IR, XRD, SEM, besides Surface Area measurement and Acidity measurement with the objective of understanding structure and nature of bonding over the catalyst surface.

In the present investigation of the kinetics of 2 MP synthesis over alumina supported catalyst, we have followed the usual procedure of calculation of partial pressure of reactants and rate of formation of 2-MP and subjected these data to different rate models based on surface reactions. From the derived rate equation, a tentative mechanism of the reaction has been suggested. An endeavour has also been made to support the present mechanism with the help of information to the author from literature.

II. EXPERIMENTAL

a) Catalyst Preparation

For preparation of alumina supported MnFe₂O₄, 16g of sized alumina (6/10 B.S.S. mesh size) was soaked in the dilute solution of manganese and iron salts (3.4 g of MnCl₂.4H₂O and 4.3g of Fe (NO₃)₃.9H₂O in 1 liter of water) for 3-4 hours. 1N NaOH was added to this system to allow precipitation of mixed hydroxides of the metals. The system was allowed to digest at 80°C for 4h. The catalyst was decanted and washed

repeatedly with distilled water till free from chloride and nitrate ions. The material was oven dried and calcined at 500°C for 6h at atmospheric pressure to get alumina supported MnFe_2O_4 (AMF) catalyst.

b) Differential Reactor

In this reactor, only a small amount of catalyst is used so as to keep the conversion level low. This permits direct evaluation of reaction rates. Because of small contact time, the composition remains practically constant throughout the catalyst bed and rates obtained are initial rates. The initial rates obtained under these conditions are extremely helpful in simplifying rate equations. This technique is also helpful in dealing reactions with large heat effects.

The experimental set-up for kinetic measurement is similar to that described in chapter two. 0.1 g of catalyst was used for kinetic studies.

c) Experimental Procedure

The collection of data for kinetic studies of the vapour phase cyclization of ED and PG were collected at atmospheric pressure in a vertical, down flow, fixed bed reactor. The upper half of the reactor worked as pre-heater and the lower half as the reactor. The fresh catalyst was charged in the center of the reactor. Activation was attained by heating the catalyst in air at 773K for 4h and then cooling to the desired temperatures in a current of nitrogen and finally exposing to feed stream a mixture of ED, PG and water. Besides, functioning as a solvent, steam reduces the dealkylation of 2-MP to pyrazine, avoids charring, and reduces formation of aromatics. The liquid products were collected using a cold-water condenser. A blank run without any catalyst indicated negligible thermal conversion.

d) Identification and analysis of products

Before collecting data on a differential reactor few experiments were performed in a macro-reactor taking 10 g of catalysts and feeding ED, PG and water in the weight ratio of 1:1:2. About 50 ml of the product mixture was collected and was subjected to fractional distillation. The product boiling in the range 130-140°C was collected. A record of FT-IR spectrum of the distillate showed band in the region 2900-3200 cm^{-1} . Band appeared below 3000 cm^{-1} were assigned to C-H stretching modes of CH_3 group while those appeared above 3000 cm^{-1} were assigned to C-H stretching modes of ring hydrogen. There appeared medium to strong bands in the region 1000-1700 cm^{-1} characteristic of C-H / N-H bending modes and ring vibrations. These observations confirmed presence of 2-MP in the product. Further confirmation was made by comparing the FID retention time of 2-MP in the above mentioned distillate with that of standard 2-MP. Quantitative analysis was made on the basis of GLC peak area measurements. A Chemito model 7610 GLC machine

was used for quantitative analysis. The analysis of product composition with differential reactor was made with GLC only.

e) Catalyst Characterization

The XRD records of alumina supported MnFe_2O_4 (AMF), MnFe_2O_4 (MF) were recorded over Rigaku X-ray powder diffractometer using $\text{Cu-K}\alpha$ radiation as source are reproduced. The recordings confirm the crystallinity of the samples and appearance of most of the peaks of support as well as catalyst Cullity *et al.* [11] (Figure 1).

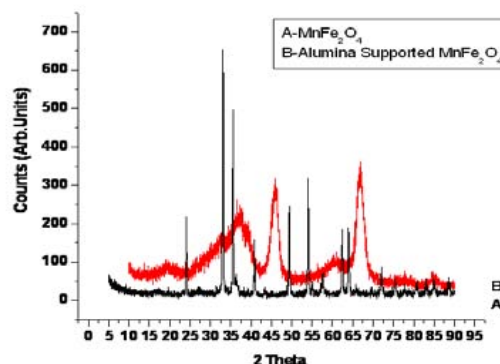


Figure 1 : X Ray Diffractogram of MnFe_2O_4 and Alumina supported MnFe_2O_4

Ammonia desorption experiments were carried out to measure the acidity of the catalyst using ammonia as an adsorbate. Detailed procedure is described elsewhere Cullity *et al.* [12] The BET surface areas were measured by N_2 adsorption at liquid N_2 temperature using BET surface area analyzer (Model SAA-2002, S.P.Consultant, Mumbai) and was found to be 206.6 $\text{m}^2 \text{g}^{-1}$. The FTIR spectrum of the alumina supported manganese ferrite catalyst was recorded on Perkin Elmer series 1600 FTIR spectrometer and are reproduced. Scanning electron microscopy (SEM) pictures were obtained using JEOL JSM-5600 instrument and are reproduced. (Figure 2 and 3).

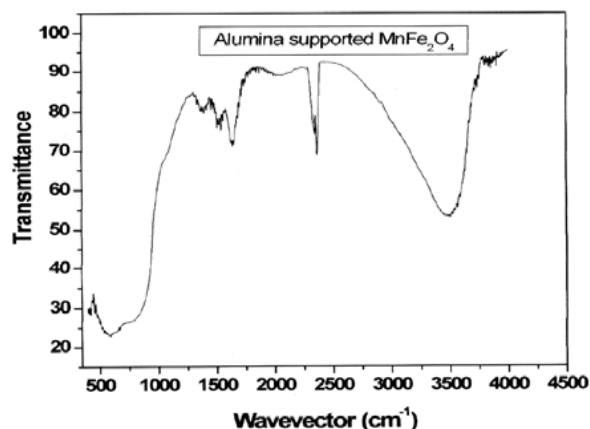


Figure 2 : FTIR Spectrum of Alumina supported MnFe_2O_4

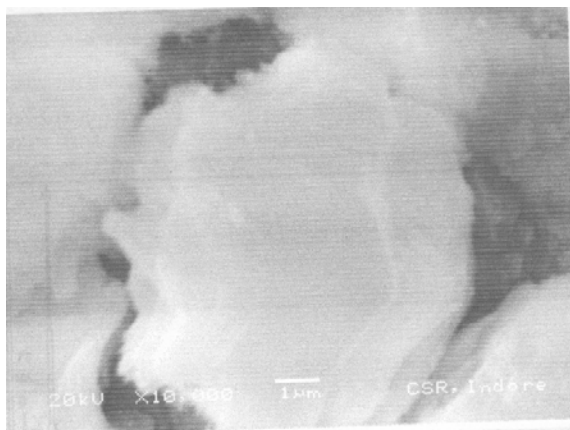


Figure 3 : SEM image of Alumina supported MnFeO₄

III. RESULTS AND DISCUSSION

a) Nomenclature

The reaction rates were calculated from the relation

$$R = F \cdot \frac{X_p}{S}$$

Where F is the flow rate of reactants, X_p is the percent composition of particular product in the reaction mixture as obtained from GLC and S is the surface area of the catalyst.

P_p = partial pressure of propylene glycol

P_E = partial pressure of ethylene diamine

K_p = adsorption equilibrium constant for adsorption of propylene glycol

K_E = adsorption equilibrium constant of ethylene diamine

k = rate constant of the reaction

b) Effect of partial pressure of reactants on rates

All kinetic measurements were performed under low conversion (below 10 % conversion of PG). All measurements were taken after a steady state condition was reached in the catalytic activity. Some standard experiments were performed from time to time to confirm that catalytic activity was constant and did not change with time. No reaction was observed at 350 °C in absence of catalyst even after several hours.

c) Effect of partial pressure of propylene glycol on rates

Effect of partial pressure of propylene glycol on rates was studied by varying the same while keeping the partial pressure of ethylene diamine constant. Total pressure was kept constant by introducing some amount of inert gas in the feed. The data thus obtained are presented at 473 K, 523 K and 573 K [Figure 4, Table 1].

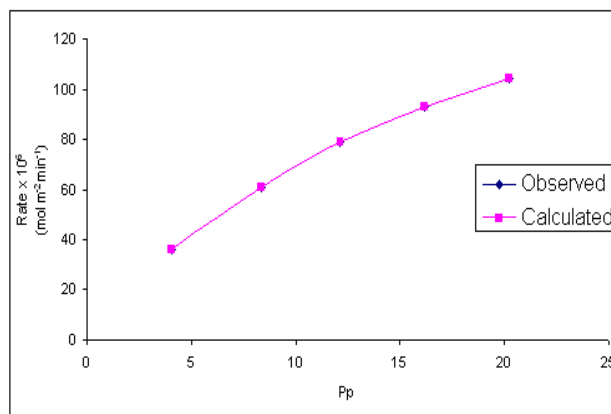


Figure 4 : Effect of Partial Pressure of Propylene Glycol (P_p) on rate of formation of 2 - MP Temp. 573 K

Table 1 : Effect of partial pressure of propylene glycol on rates

S.No.	Partial pressures of PG	Rate x 10 ⁶ (moles s ⁻¹ m ⁻²)			
		473 K		523 K	
		Observed	Calculated	Observed	Calculated
1	4.05	2.11	2.11	17.70	17.70
2	8.10	3.60	3.60	29.38	29.38
3	12.15	4.72	4.72	37.67	37.67
4	16.21	5.58	5.58	43.86	43.86
5	20.26	6.23	6.23	48.65	48.65

Weight of catalyst : 0.1g, Partial pressure of ethylene diamine :9.11 kPa

None of the plots were linear between rate and partial pressure. All plots are bend towards pressure axis.

d) Effect of partial pressure of ethylene diamine on rates

Effect of variation of partial pressure of ethylene diamine on rates was studied at 473, 523 and 573 K

under constant partial pressure of propylene glycol. The results are presented for the temperatures of 473 and 523. The graphical representation is shown for the temperature of 573 K. In this case also plots were not linear and bend towards pressure axis. (Figure 5 Table 2).

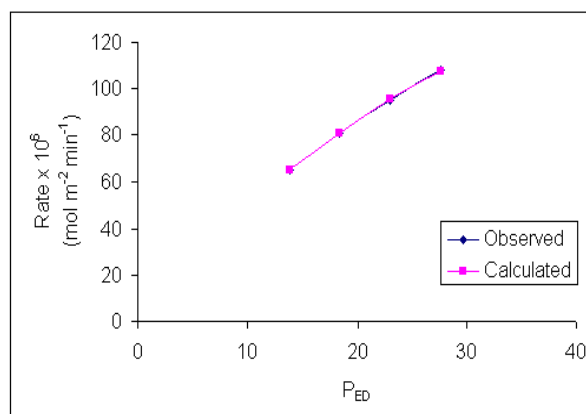


Figure 5 : Effect of Partial Pressure of Ethylene Diamine (P_{ED}) on rate of formation of 2 - MP Temp. 573 K

Table 2 : Effect of partial pressure of ethylene diamine on rates

S.No.	Partial pressures of ED	Rate x 10 ⁶ (moles s ⁻¹ m ⁻²)		523 K	
		Observe	Calculated	Observed	Calculated
1	13.78	4.21	4.21	31.32	31.22
2	18.33	5.01	5.01	38.49	38.49
3	23.00	5.67	5.67	44.75	44.75
4	27.56	6.20	6.00	50.06	50.06

Weight of catalyst: 0.1g, Partial pressure of propylene glycol: 4.05 kPa

e) Effect of temperature on rates

Effect of temperature on rates is studied. Activation energy was calculated from arrhenius plot are shown. The rates increased with temperature. (Figure 6, Table 3).

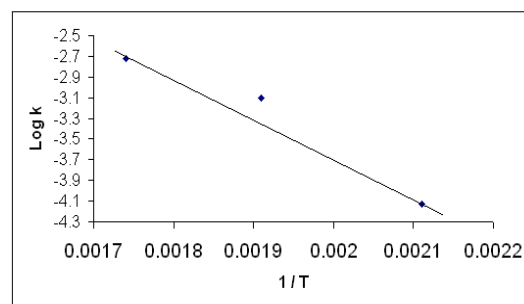


Figure 6 : Log k vs 1/T

Table 3 : Reaction rate constant and adsorption equilibrium constants

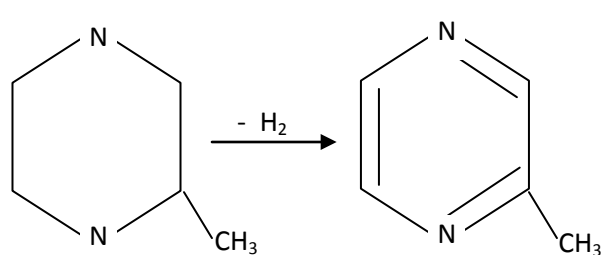
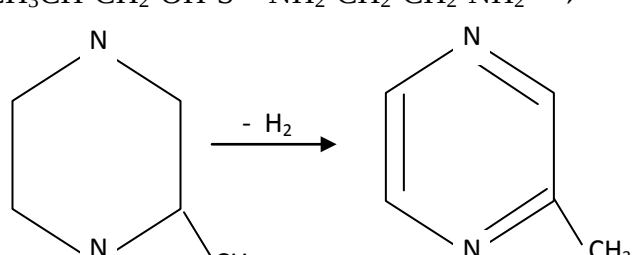
Temperature(K)	1/T	k	Log k	K _A	K _B
473	0.00211	0.000074	- 4.13	38.61	29.51
523	0.00191	0.00077	- 3.10	22.61	11.41
573	0.00174	0.0019	- 2.72	12.49	5.68

IV. TREATMENT OF RATE DATA

The activation energy was found to be 34.32 k cal. mol⁻¹. In the present study of the vapour phase kinetics of cyclization of propylene glycol and ethylene diamine to 2-methylpyrazine over alumina supported manganese ferrite catalyst, we collected data under conditions that conversion was below 10 %. Rate data collected under this condition can be termed as initial rates. Besides we used only 0.1 g of catalyst so as to minimise mass transfer and diffusional effects. Since mass transfer from gas phase to the catalyst surface

and diffusion through the catalyst bed were not rate controlling, the possibility of surface adsorption of reactants and surface reactions as rate controlling steps were left. We tested two most popular models applied for such cases namely Langmuir-Hinshelwood model and Reidel model. The former assumes reaction between adsorbed PG and adsorbed ED, while the latter assumes reaction between an adsorbed reactant and another one remaining in gas phase. The rate laws derived on the basis of these two models are presented. (Table 4).

Table 4 : Models Tested for Cyclization of Propylene Glycol and Ethylenediamine

Model No.	Langmuir-Hinshelwood model	Resulting rate equation
1.	$\begin{array}{c} \text{OH} \\ \\ \text{CH}_3\text{CH}-\text{CH}_2-\text{OH} \end{array} + \text{S} \rightarrow \begin{array}{c} \text{OH} \\ \\ \text{CH}_3-\text{CH}-\text{CH}_2\text{OH}-\text{S} \\ \text{NH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2 + \text{S} \rightarrow \text{NH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2-\text{S} \\ \begin{array}{c} \text{OH} \\ \\ \text{CH}_3\text{CH}-\text{CH}_2-\text{OH}-\text{S} + \text{NH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2-\text{S} \end{array} \rightarrow$ 	$R = k K_p K_E P_p P_E / (1 + K_p P_p + K_E P_E)^2$
2.	$\begin{array}{c} \text{OH} \\ \\ \text{CH}_3\text{CH}-\text{CH}_2\text{OH} \end{array} + \text{S} \rightarrow \begin{array}{c} \text{OH} \\ \\ \text{CH}_3-\text{CH}-\text{CH}_2\text{OH}-\text{S} \\ \text{CH}_3\text{CH}-\text{CH}_2-\text{OH}-\text{S} + \text{NH}_2-\text{CH}_2-\text{CH}_2-\text{NH}_2 \rightarrow$ 	$R = k K_p P_p P_E / 1 + K_E (P_E)$

S = Surface, P_p = Partial pressure of Propylene Glycol, P_E = Partial pressure of Ethylene diamine, K = Equilibrium Constant, k = Rate Constant

As the rate constants are physical quantities their values can not be negative. An inspection of Table 4 reveals that positive constants are found only for Reidel model assuming one reactant adsorbed on the surface and another one remaining in gas phase. A plot of observed rates along with calculated rates obtained from reidel model are shown. (Figure 7).

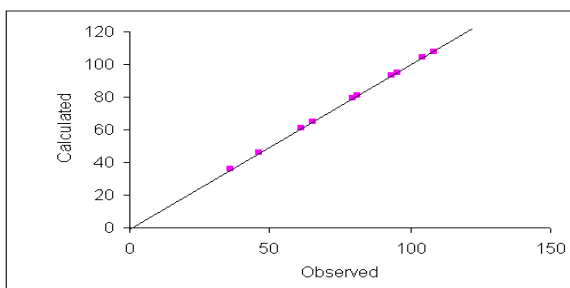


Figure 7 : Calculated Rates v/s Observed Rates

Reasonable agreement between observed rates and calculated rates confirm the validity of Reidel model. Further confirmation of the model was obtained by plotting observed rates vs calculated rates. The plot is found to be a straight line with an inclination of 45 degree passing through origin. This again confirms the validity of the model. A plot of observed rates vs. residuals is shown. The plot does not show any heteroscedic pattern (Figure 8).

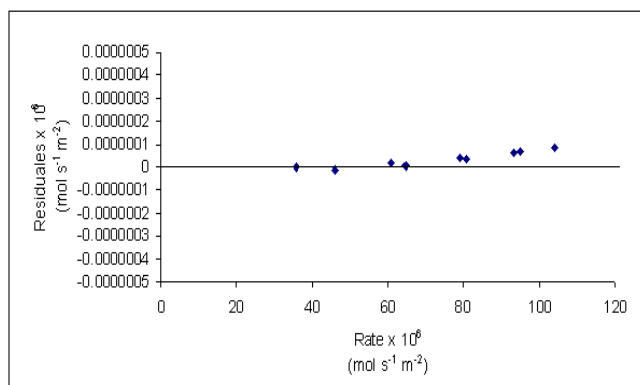


Figure 8 : Residuals v/s Calculated Rates

V. MECHANISM OF THE PROCESS

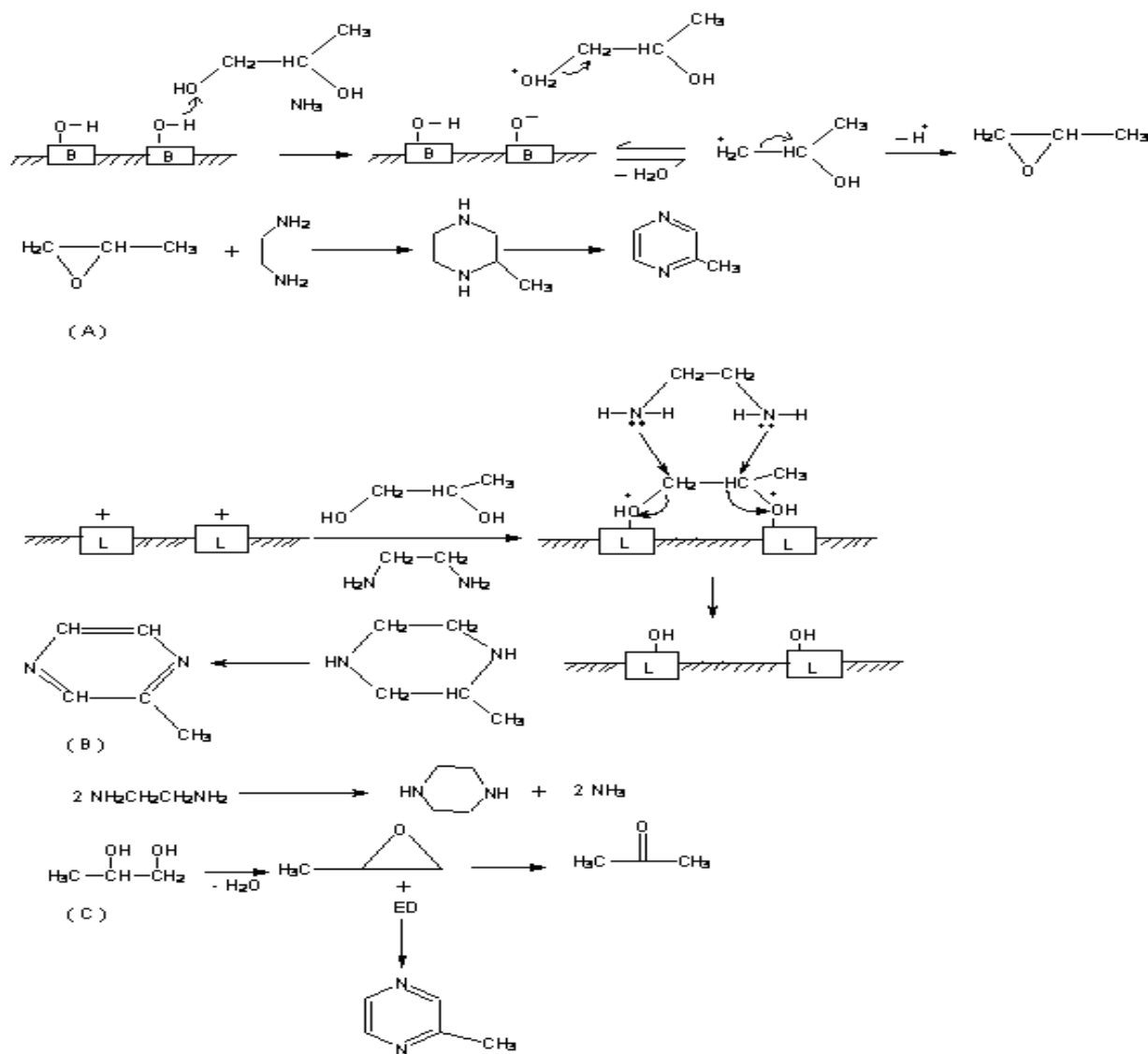
2-methyl pyrazine was found to be major product in the present study. Acetone was also detected in traces. When 2-methylpiperazine alone was passed over the catalyst in the reactor, 2-MP was found to be the only product. When PG alone was fed over the catalyst we obtained acetone as the major product. Passing hydrogen peroxide in the feed stream has no effect, indicating that free radical mechanism was not operative. Based on these observations, analysis of products and on the fact that kinetics follows a Reidel type of mechanism, an attempt is made here to predict a mechanism for the reaction.

Kulkarni et al [5] have proposed a mechanism for synthesis of 2-MP from PG and ED over ZSM -5 catalyst. According to these authors, PG is adsorbed over the catalyst, gets protonated, loses a molecule of water and is converted into carbonium ion. The carbonium ion loses a proton and produces propylene oxide. Propylene oxide can react with ED to produce 2-methyl piperazine, which is dehydrogenated to produce 2-methyl pyrazine. Although, this sounds well, it does not support the Reidel type of mechanism in which PG is adsorbed on the surface and reacts with ED present in Gas phase.

VI. REACTION MECHANISM

The present catalyst contains both Lewis as well as Brönsted sites. While Lewis sites come from MnFe_2O_4 , Brönsted sites come from hydroxyl group of alumina. It seems Lewis as well as Brönsted sites activate reaction of PG and ED. In case of Brönsted sites PG is adsorbed first, gets protonated, loses a molecule of water and produces a carbonium ion. The carbonium ion loses a proton and produces propylene oxide. Propylene oxide can react with ED to produce 2-methyl piperazine, which is dehydrogenated to produce 2-methyl pyrazine. In order to confirm this we passed 2-methylpiperazine alone over the catalyst in the reactor, and obtained 2-MP as the only product. Propylene oxide can also rearrange to produce acetone. In fact, when

PG alone was fed over the catalyst we obtained acetone as the major product. This mechanism is consistent with the mechanism proposed by Kulkarni et.al [5] for synthesis of 2-MP from PG and ED over ZSM-5 catalyst. The mechanism over Brönsted sites is shown. Over Lewis acidic sites above type of mechanism is rather unlikely, because of (1) absence of, Brönsted sites (2) high possibility of ED over PG for adsorption over Lewis Sites (ED is stronger base than PG). However, because of much higher concentration of PG & H_2O over ED, it is possible that they displace few adsorbed ED molecules and produce Brönsted sites. Once such Brönsted sites are produced, the mechanism will follow the usual route of PG protonation, dehydration, formation of propylene oxide and reaction with ED to produce 2-methyl piperazine followed by its dehydrogenation to give 2-methyl pyrazine. This mechanism is consistent with the mechanism proposed by Forni and Paolo in their studies on TPD-TPR-MS Mechanistic study of the synthesis of 2-methylpyrazine over palladized Zn-Cr Oxide. The mechanism over Lewis sites is shown. When ED alone was fed over the catalyst ammonia and pyrazine were obtained. The mechanism of by products formation is shown. (Scheme 1 (a), (b) and (c)).



Scheme 1 : Reaction mechanism of vapour phase catalytic synthesis of 2-MP over alumina Supported manganese ferrite catalysts (a) bronsted sites (b) Lewis sites (c) formation of by products

VII. ACKNOWLEDGEMENTS

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