CATALYTIC DEHYDRATION OF METHANOL TO DIMETHYL ETHER OVER MOLECULAR SIEVES 5A

THESIS SUBMITTED BY

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CERTIFICATE

This is to certify that the thesis entitled *CATALYTIC DEHYDRATION OF METHANOL TO DIMETHYL ETHER OVER MOLECULAR SIEVES 5A* , presented by Mr Sudhir Kumar Garg, is worthy of consideration for the award of the degree of *DOCTOR OF PHILOSOPHY* and is a record of the original bonafide research work carried out by him under my guidance and supervision and that the results contained in it have not been submitted in part or in full to any other university or institute for award of any degree.

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ABSTRACT

The present work was undertaken to study the catalytic dehydration of methanol to ethylene using easily available molecular sieves as catalyst. (Molecular sieves of the type ZSM-5, with a stable structure, have a pore diameter of about 6Å, and are not commercially available.) Molecular sieves of the types 3A, 4A, 5A, 10X and 13X are easily available and have pore diameters 3, 3.5, 4, 5, 9 and 10Å respectively. No work has been reported so far on the molecular sieves 10X, and 13X; a small amount of work has been reported with molecular sieves 5A. Types 5A, 10X and 13X were chosen for studies.

Initially, studies with all the three catalysts were carried in a reaction temperature range 300-400°C. At lower temperatures, only dimethyl ether (DME) and water were the reaction products. At relatively higher temperatures, methane as well as C_2 and C_3 hydrocarbons (either saturates or unsaturates or both) were observed in addition to the water.

Among the three catalysts tested, highest conversions were obtained at a particular temperature with the MS

(Molecular Sieves) 5A. The product distribution was comparable with all the three catalysts other experimental conditions being the same. Therefore, it was decided to carry further studies with MS 5A, supplied by Associated Cement Company, India.

It was suspected that formation of methane and other saturated hydrocarbons would be accompanied with carbon formation, and it was observed as well. Because of experimental difficulties in burning off the carbon, it was decided to restrict the studies to a temperature where only dimethyl ether would be formed. The objective was to determine the rate equation and to propose a reaction mechanism.

The experimental set-up consisted of
(i) nitrogen supply, (ii) bubbler containing methanol, (iii) a reactor 1.6 cm in diameter and 27 cm long, and (iv) a gas chromatograph with a flame ionisation detector (FID). Nitrogen gas at a known flow rate was bubbled through methanol, the nitrogen-methanol vapour mixture was passed through the catalyst bed in the reactor, and the reaction products were led on-line to the gas chromatograph. The reactor was heated in a fluidized bed furnace.

During the course of the work the experimental set-up was modified to have two independent supplies of nitrogen gas: (1) the nitrogen gas was bubbled through methanol bubbler and it was termed as primary nitrogen, (2) the secondary nitrogen stream was connected to a point between the bubbler and the reactor. A number of experiments were carried out; parameters were 4 primary nitrogen flow rates, 5 secondary nitrogen flow rates, 3 weights of catalyst (1.64, 3.67, 5.75 g), average particle size 0.042 cm, 6 temperatures (230, 250, 270, 285, 300, 312^{o}C), pressure in the reactor (770 - 875 mm Hg), total molar flow rates of primary nitrogen, secondary nitrogen and methanol (PMS) (0.44 - 2.7 mol/h). Experimental data were collected with almost constant activity of the catalyst.

It was found that at a given temperature and feed concentration of methanol vapour, conversion varied with the ratio W/PMS, irrespective of weight of catalyst (W) and of total flow rate (PMS), indicating that external mass transfer effects were negligible.

In any experiment weight of catalyst, reaction temperature , primary nitrogen flow rate, methanol flow rate, secondary nitrogen flow rate, and pressure in the reactor were known independently. The rate of reaction was defined as:

$$r = -\frac{dC}{dt} = -C_{Ao}\frac{d(1-x)}{d(W/PMS)} \qquad (1)$$

$$r = -\frac{dC}{dt} = -\frac{M}{PMS}\frac{P_t}{RT}\frac{d(1-x)}{d(W/PMS)} \qquad (1a)$$

Experiments with almost equal values of partial pressures of methanol in the reactant stream were grouped together. $C_{Ao}x$ values were plotted against W/PMS for such experiments, and a smooth curve was drawn through those points. A number of such curves were drawn for different partial pressures of methanol in the feed. Slope of such a curve at $x = 0$ would give the initial rate r_o.

Dehydration of methanol to dimethyl ether may be written as:

$$\underset{2A}{2\ CH_3OH} \xrightarrow{\text{catalyst}} \underset{R}{CH_3O\ CH_3} + \underset{S}{H_2O}$$

Most of the gas-solid catalytic reactions are surface reaction controlled. If the above reaction is also considered as surface reaction controlled, and assuming the reaction between two adsorbed molecules of methyl alcohol to give one molecule of dimethyl ether and one molecule of water, following rate equation may be written

$$r = \frac{k_s\ K_A^2\ (p_A^2 - p_R\ p_S/K)}{(1+K_A\ p_A + K_R\ p_R + K_S\ p_S)^2} \qquad (2)$$

where k_s is reaction rate constant K_A, K_R, K_S are adsorption coefficients for methanol, DME and water respectively, p_A, p_R, p_S are partial pressures of methanol, DME and water respectively, and K is equilibrium constant. k_s and K_A can be evaluated from the initial rate data at different partial pressures of methanol.

$$r_o = \frac{k_s\ K_A^2\ p_{Ao}^2}{(1+K_A\ p_{Ao})^2} \qquad (3)$$

or

$$r_o = \frac{k\ p_{Ao}^2}{(1+K_A\ p_{Ao})^2} \qquad (3A)$$

where $k = k_s\ K_A^2$, p_{Ao} = partial pressure of methanol in feed stream. Data at 285°C were available at different values of parameters like flow rate, feed composition and weight of catalyst. Also from Equation 3A

$$\frac{p_{Ao}}{\sqrt{r_o}} = \frac{1}{\sqrt{k}} + \frac{K_A}{\sqrt{k}}\ p_{Ao} \qquad (3B)$$

k (or k_s) and K_A were evaluated from the plot of $p_{Ao}/\sqrt{r_o}$ vs p_{Ao}.

The values are

$$k_s = 0.284\ .\ 10^{-9}\ (\text{mol/cc})\ (\text{g.s./mol})^{-1} \qquad (4)$$

$$K_A = 27.5\ .\ 10^{-3}\ (\text{mm Hg})^{-1} \qquad (5)$$

Initial rate data at six different temperatures mentioned earlier, and at an average feed partial pressure p_{Ao} of 121 mm Hg of methanol were also available. The experimental data could be correlated by the expressions,

$$k_s = 0.378\ .\ 10^{-3}\ \exp\ (-15{,}640/RT)\ (\text{mol/cc})\ (\text{g.s./mol})^{-1} \qquad (4A)$$

$$K_A = 0.907\ .\ 10^{-9}\ \exp\ (19{,}100/RT)\ (\text{mm Hg})^{-1} \qquad (5A)$$

Equilibrium constant K was calculated from the equilibrium conversion data reported in literature[19]. It could be expressed as

$$RT \ln K = 1900 \qquad (6)$$

Assuming that reaction may be treated as irreversible for small conversions, using experimental rate data and using k_s and K_A values as obtained earlier, K_{RS} ($= K_R + K_S$) values at different temperatures were evaluated.

$$K_{RS} = 26.0 \cdot 10^{-3} \text{ (mm Hg)}^{-1} \qquad (7)$$

Using the k_s, K_A, K_{RS} and K values calculated above, rate data were computed. For different experimental conditions of feed composition, temperature and W/PMS, conversion values were obtained from the smooth plot, and rate computed with the help of Equation 2; Also,

$$C_{Ao} \int_0^x dx = \int_0^{W/PMS} r \cdot d(W/PMS) \qquad (8)$$

Rate r was plotted against W/PMS, and area under the curve would give $C_{Ao}x$; and this x was termed as $x_{predicted}$. $x_{predicted}$ values were plotted against $x_{experimental}$. The values compared well, and there was scatter on both sides of 45^o straight line.

It can be concluded that (i) dehydration of methanol to dimethyl ether and water can be considered as surface reaction controlled; (ii) the reaction is second order with respect to methanol; (iii) adsorption of methanol on the catalyst is very much predominant; (iv) the rate of reaction can be computed for a given set of experimental conditions; (v) a reactor to obtain dimethyl ether from methanol can be designed.

CONTENTS

APPENDICES