

Catalytic Vapour Phase Oxidation of Methanol to Formaldehyde using MnO₂-MoO₃ and V₂O₅ Catalysts

¹Surya P. Sunkavalli, ²Subhasish Roy, ³Suresh. P., ⁴Umesh Devaiah. K., ⁵M. A. L. Antony Raj
^{1,2,3,4,5} Siddaganga Institute of technology, Tumkur, Karnataka, India-572103

Abstract -Formaldehyde is an important chemical used in petroleum, agricultural and textile industries. It is obtained by oxidation of methanol. The present work is undertaken to study the detailed kinetics of this reaction with respect to manganese molybdate and vanadium pentoxide catalysts. The experiments were conducted under three different laboratory operating conditions i.e. different flow rate of reactants, temperature and catalysts. It has been found that manganese molybdate is quite selective to formaldehyde formation compared to V₂O₅ and the experimental data found that as the temperature increases the oxidation will increase and the flow rate of methanol also have the positive affect on conversion of methanol.

Keywords: Methanol, Formaldehyde, oxidation, catalyst, temperature

I. INTRODUCTION

In recent years formaldehyde has become one of the most important industrial chemical. It is used for the protection of agricultural products from decay and for conditioning soil. It is used in special preparation of concrete, plaster and related products in building industries. Formaldehyde destroys fungi, yeast, molds and bacteria. And hence finds the application in fungicides and disinfectants. Formaldehyde is employed in the synthesis of dyes and various special chemicals used in dye industry. Formaldehyde is used in paper industry to improve wet strength, water resistance and shrinkage resistance of paper and paper products. In metal industry formaldehyde is used as an acid inhibitor, reducing agent and electroplating addition agent. In medicine formaldehyde is used in drug synthesis and preparation of anti-perspiration cream and deodorizers. In textile industry it is used for modification of natural and synthetic fibers.

Generally formaldehyde is manufactured by oxidation of methanol with various catalyst namely vanadium pentoxide, ferric oxide, ferric molybdate etc. Oxidation is one of the important unit processes in organic synthesis and also in inorganic field. Oxidations are carried out either in liquid phase or vapor phase, homogeneously or heterogeneously depending upon the characteristics of the system. Vapor phase oxidation is more common and important in these reactions. Air is usually used as source of

oxygen. Air as source of an oxidant in oxidation process has been very economical and also available abundance in nature. Production of nitric acid, sulphuric acid, formaldehyde, benzaldehyde are some examples of principle catalytic oxidation reactions. Formaldehyde was first prepared by Alexander butlerov. In 1859 he published an accurate description of formaldehyde solution, formaldehyde gas with an account of chemical reactions including the formation of hexamethylenetetramine on reaction with ammonia. In 1868 A.W.Hofmann prepared formaldehyde by passing a mixture of methanol vapor and air over a heated platinum spiral. Several methods for the manufacture of formaldehyde have been described in literature. Some of the methods for the manufacturing of formaldehyde are described below.

(1) Reduction of Carbon-dioxide: In this method, formaldehyde is prepared by direct oxidation of CO₂ with H₂. Production of methanol from carbon dioxide and hydrogen under pressure of 117-410 atm. Probably involves formation of formaldehyde as an intermediate and then it is converted to methanol. This process requires very high pressure to obtain useful yields. In addition, extremely active and selective catalyst would be needed to obtain equilibrium at a responsible rate and at the same time to avoid hydrogenation of formaldehyde produced. It is unfavorable for the production of formaldehyde.

(2) Formaldehyde from hydrocarbon gases: Formaldehyde is produced from methanol, propane and hydrocarbon mixture using iron, nickel, aluminum catalyst. Reaction is maintained up to 135 atm. In this method, the hydrocarbon oxidation process involves a controlled reaction of hydrocarbon gas with air or oxygen, followed by abrupt cooling and condensation of products. Formaldehyde is obtained in small amounts along with major products. Hence isolation becomes more expensive.

(3) Oxidation of Methane: Methane is the simplest hydrocarbon gas and would be expected to give formaldehyde uncontaminated with more complex organic compounds, its partial oxidation is extremely difficult. It is not oxidized at an appropriate rate below 600C. Formation of methanol instead of formaldehyde is favored by the use of high pressure with appropriate rate below 600C.

(4) Formaldehyde from methanol in vapor phase: In general, the reaction is carried out by passing a mixture of

methanol and air over the heated stationary catalyst at approximately atmospheric pressure and scrubbing the off gases with water to obtain aqueous formaldehyde. The oxide catalyst process converts methanol to formaldehyde by a simple selective oxidation reaction under proper operating conditions.

From the above description it can be seen that the oxidation of methanol by air is one of the process which is economically feasible. The recent trend in formaldehyde industry is to prepare it by direct oxidation of methanol under controlled conditions, rather than alternative methods explained above. Jiru and Tichy, [1] have studied the oxidation of methanol to formaldehyde at 270C and at atmospheric pressure in an integral reactor with use of chromatographic pulse apparatus. The authors used 17.5% by weight of Fe₂O₃ and 82.5% by weight of MoO₃ catalyst of particle size in the size range of 0.3-0.6 mm. In a later paper the same authors have studied the reaction further with the same catalyst with a circulation differential flow of apparatus. The influence of methanol, oxygen, formaldehyde and water vapor has no effect on the oxidation rate while increasing formaldehyde concentration reduces the rate. Bhattacharya et al 1967 [2], have studied the oxidation of methanol to formaldehyde in the presence of water vapor V₂O₅ catalyst at 246C, 264C and 281C. Effect of particle size, bed-height, partial pressure of water vapor on the rate is negligible while the concentration of methanol and oxygen influence the rate.

Dente et al. 1964 [3], studied the oxidation of methanol to formaldehyde on Fe₂O₃-MoO₃ catalyst in an integral reactor and found that the rate equation based on Mars and van Krevelen, two stage redox model, with orders of reaction m and n. Where m and n are the orders for catalytic oxidation and reoxidation step. The orders m=n=0.5 fitted the experimental data accurately.

It is evident from the literature on methanol oxidation that the numerous catalysts and their relative performance towards formaldehyde formation have been studied by several workers and reported the kinetics of the reaction [4-9]. The catalysts like iron molybdate proved to be excellent for methanol oxidation. The present work makes an attempt to study the vapor phase oxidation of methanol on manganese molybdate and V₂O₅ catalysts chosen based on literature survey. It has been proposed to study the oxidation of methanol to formaldehyde in vapor phase due to its commercial application using manganese molybdate and vanadium pent oxide catalyst. Higher rate of reaction, easier temperature control, retention of catalytic activity for a longer time and very high selectivity are some of the advantages in the pure oxidation process.

II. MATERIALS AND METHODS

The air supply unit consists of a compressor, a series of bubblers and a flow meter. The impurities that are normally present in the air are carbon dioxide, moisture and inert gases. Air drawn from the compressor is passed through a bubbler containing glass wool to remove impurities. It is then sent to the flow meter. An orifice meter connected with

a U-tube manometer is used as a flow meter. The air from the flow meter goes into the bubbler containing methanol. There are three preheaters in which two are same. These two are glass tubes of 75cm long and 1 cm I.D with a B-14 glass joint at both the ends. These preheaters are heated by externally wound kanthal wire with porcelain beads. The terminals are connected to the Dimmerstat and the temperature in the preheater is controlled. These preheaters are insulated using glass wool and asbestos rope. The third one is a tube of 1cm diameter and 80cm long provided with B-14 Glass joint and wound with a kanthal wire, covered with porcelain beads. The terminals are connected to the dimmerstat Mercury thermometers are used to measure the temperature at the indicated points. The air-methanol mixture is heated to required temperature and then sent to the reactor. Reactor is a tube 1.9cm I.D and 50 cm long, it is made up of quartz. The reactor is heated by externally bound kanthal wire with porcelain beads.

Product collection unit consists of two train of bubblers (250ml conical flask provided with two holed rubber corks and connected by glass and rubber tubing) containing distilled water. Here the gas sample condensed in the water and solution is used for analysis. After charging the reactor with the catalyst the dry air was admitted into the apparatus at suitable rates and the preheaters are switched on. First the air flows through the metering unit and then bubbled through methanol. The temperature at the exit of methanol air preheater is maintained between 150-200C depending upon the reaction temperature. Preheat section is at a few degrees less than that in the reaction section of the reactor. Reaction being exothermic, the temperature in the reaction zone is controlled by adjusting the heat input. The reaction is allowed to take place for 30 minutes. After reaching the steady state conditions, product stream is allowed to pass through sampling bubbler train for a known period. After the run, the absorbate solution the sampling train is transferred to a beaker and weighed.

Manganese – molybdate catalyst was prepared by dissolving 20gm manganese-nitrate and 500ml of distilled water, 30gm of ammonium-molybdate was dissolved on 1liter of distilled water in another vessel and cooled to room temperature and 70gm of silica gel was added to ammonium-molybdate solution. Manganese-nitrate solution was added to the ammonium-molybdate solution precipitating manganese-molybdate. The precipitate was filtered, washed and dried in air for about 6hours at 313K. Then it was dried at 673K and cooled gradually to room temperature, crushed and sieved into various size fractions.

The product gases contain the oxidation products of methanol besides unreacted methanol. They are absorbed in distilled water where methanol and formaldehyde are absorbed in the water. No formic acid was detected in the produce. The absorption liquor is transferred to the flask and the conical flask used for absorption is washed with the distilled water and the washings are added to the main liquor. The whole mass is weighed and aliquot is used for the determination of formaldehyde and methanol separately.

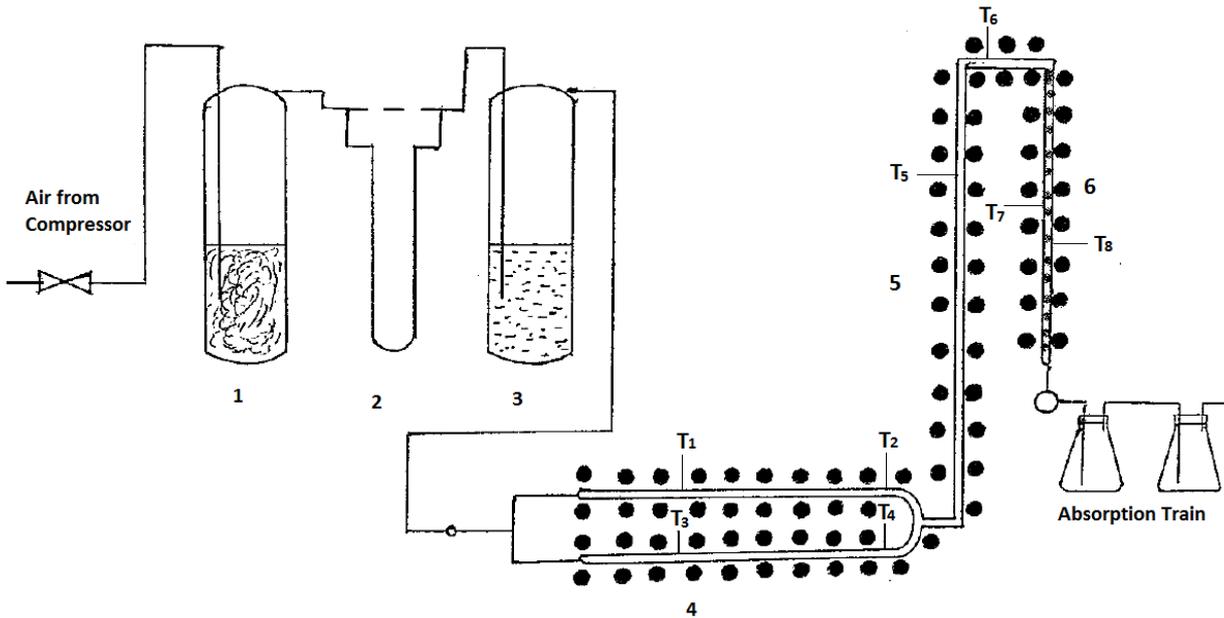


Fig 1.A schematic diagram of the experimental setup where 1) Glass Wool Bubbler 2) Capillary Flow meter 3) Methanol reservoir 4)& 5) Preheaters and 6) Reactor

III. RESULTS AND DISCUSSIONS

First the experiments were conducted with MnO₂-MoO₃ catalyst for all temperatures and all flow rates in a fixed bed reactor described in figure 1. The flow rates of reactant are computed in terms of cc/sec and partial pressure values of methanol and oxygen are calculated and computed in terms of atmospheres. The experimental results ie conversion of methanol for all conditions were tabulated in table 1 with input parameters. The effect of variables like O₂, methanol feed rates and reaction temperature on the conversion of methanol was studied.

A. Effect of temperature

The experiments are conducted at different temperatures from 473K to 573K at constant flow rate of methanol. The figure 2 was plotted by selecting the data (Conversion and Temperature) from table 1 for a constant methanol flow of 7.55×10^{-3} cc/s to study the effect of temperature on methanol conversion. From figure 1 it suggests that initially the conversion did not changed until the temperature reaches 543K and then it increased as temperature increase. We should have done experiments higher than 600K to see the negative effect of temperature on methanol conversion at higher values.

TABLE 1 Experimental data from oxidation of methanol using MnO₂-MoO₃ catalyst

Sl no	T	Fm x103	Fair	Wme	X
1	473	4.6	9.3	0.107	0.033
2		5.82	11.8	0.179	0.043
3		6.586	13.35	0.216	0.0459
4		7.55	15.35	0.255	0.0467
5	543	5.2	10.53	0.144	0.039
6		5.86	11.89	0.188	0.045
7		6.75	13.7	0.232	0.048
8		7.55	15.35	0.27	0.0502
9	573	4.88	9.92	0.245	0.07
10		5.86	11.89	0.314	0.075
11		6.75	13.7	0.386	0.08
12		7.55	15.35	0.475	0.088

TABLE 2 Experimental data from oxidation of methanol using V2O5 as catalyst at 573 K

Sl no	T	Fm x103	Fair	Wme	X
1	573	4.88	9.92	0.194	0.0557
2		5.86	11.89	0.245	0.058
3		7.55	15.35	0.345	0.064

Where T - Temperature (K), Fm - Methanol flow rate (cc/s), Fair - Air flow rate (cc/s), Wme - Weight of methanol converted (gms) and X - Fractional conversion

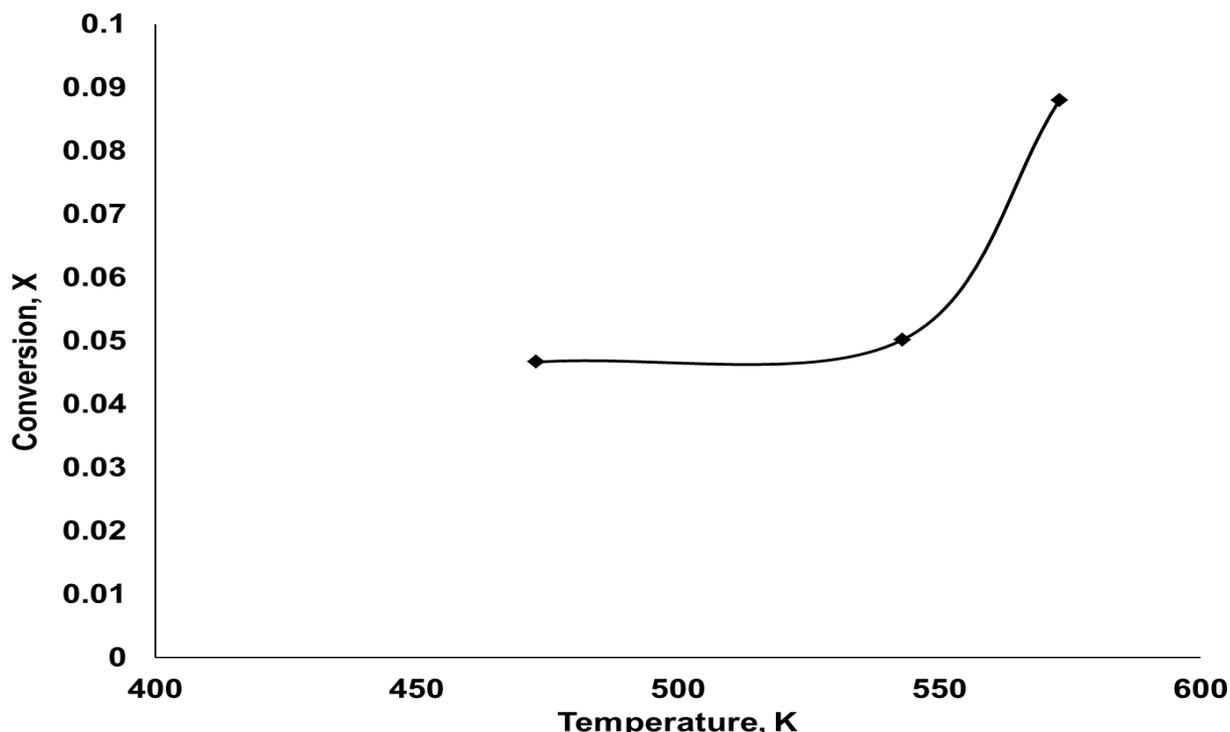


Fig 2. Conversion of methanol with respect to temperature by using MnO₂-MoO₃ as catalyst for a constant methanol flow of 7.55 10⁻³ cc/s

B. Effect of flow rate of methanol

The experiments were continued at a optimum temperature of 543K as per previous section, for different flow rate of methanol using both catalysts. The results obtained for V₂O₅ catalyst are shown in table 2. From figure 3a and 3b, it is clear that as flow rate of methanol increases the conversion of methanol is higher. The comparison between figure 3a and 3b shows that the oxidation of methanol is favorable with MnO₂-MoO₃ catalyst compared to V₂O₅ as we see higher conversion at same temperature, flow rates of reactants and other parameters.

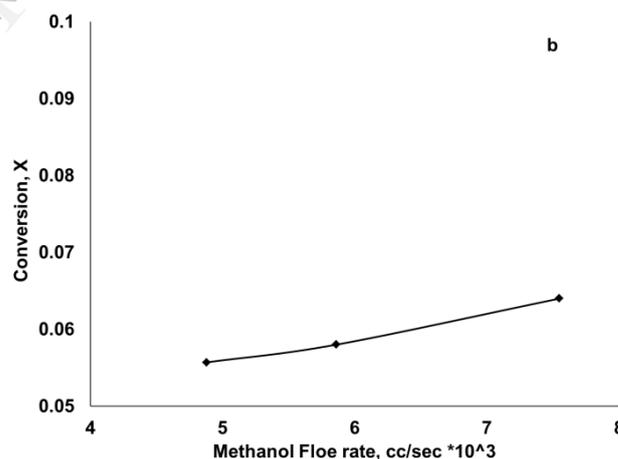
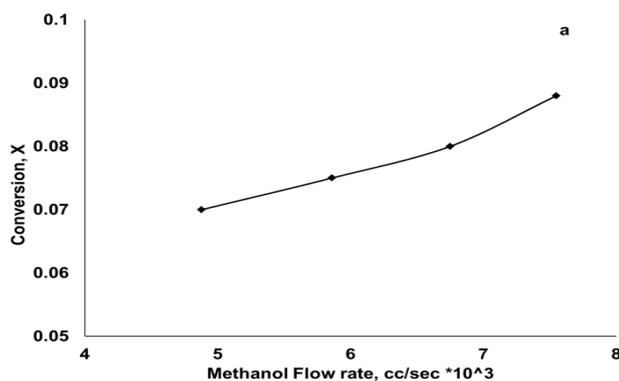


Fig 3. Effect of methanol flow rate (cc/s) on conversion of methanol where a) MnO₂-MoO₃ as catalyst and b) V₂O₅ as catalyst



IV. CONCLUSION

The conclusions drawn from the present study over the number of variables experimented may be summarized as follows.

Not much increase in conversion until the temperature reaches 543K. Then the reaction rate is found to increase with temperature. Conversion of methanol also increases with increase in flow rates of methanol and oxygen. The oxidation of methanol to formaldehyde is more favorable

with manganese molybdate catalyst compared to vanadium pentoxide catalyst.

ACKNOWLEDGMENT

We would like to thank Siddaganga Institute of Technology for their financial sponsorship and The Department of Chemical Engineering for their technical support during the project.

REFERENCES

- [1] Jiru, P., B. Wichterlova, and J. Tichy. in Third International Congress on Catalysis. 1965. Amsterdam.
- [2] Bhattacharyya, S.K., K. Janakiram, and N.D. Ganguly, Kinetics of the vapor-phase oxidation of methyl alcohol on vanadium pentoxide catalyst. *J Catal*, 1967. 8(2): p. 128 -136.
- [3] Dente, M., R. Poppi, and J. Pasquon, Kinetics of the oxidation of methanol to formaldehyde with Catalyst based on Fe and Mo *Chim Ind*, 1964. 46(11): p. 1326.
- [4] Waters, T., R.A.J. O'Hair, and A.G. Wedd, Catalytic Gas Phase Oxidation of Methanol to Formaldehyde. *J. AM. CHEM. SOC.*, 2003. 125: p. 3384-3396.
- [5] Behera, G.C. and K. Parida, Selective gas phase oxidation of methanol to formaldehyde over aluminum promoted vanadium phosphate. *Chemical Engineering Journal*, 2012. 180: p. 270– 276.
- [6] Häggblad, R., et al., Oxidation of methanol to formaldehyde over a series of Fe_{1-x}Al_x-V-oxide catalysts. *Journal of Catalysis*, 2008. 258: p. 345–355.
- [7] Andreasen, A., et al., Simplified kinetic models of methanol oxidation on silver. *Applied Catalysis A: General*, 2005. 289: p. 267–273.
- [8] Kim, T.H., et al., Selective oxidation of methanol to formaldehyde using modified iron-molybdate catalysts. *Catalysis Letters*, 2004. 98: p. 161- 165.
- [9] Yao, S., et al., A kinetic study of methanol oxidation over SiO₂. *Applied Catalysis A: General*, 2000. 198: p. 43–50.

IJERT