

# METHANOL OXIDATION TO FORMALDEHYDE

## A DISSERTATION

*Submitted in partial fulfillment of the  
requirements for the award of the degree*

*of*

**MASTER OF TECHNOLOGY**

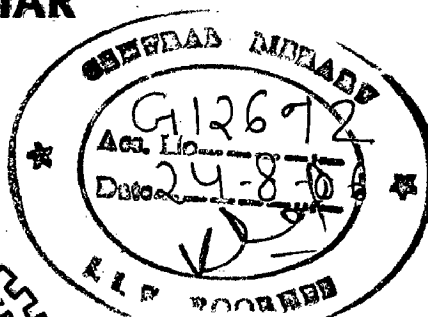
*in*

**CHEMICAL ENGINEERING**

**(With Specialization in Industrial Pollution Abatement)**

By

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**JUNE, 2006**

*Dedicated to  
my parents*

## CANDIDATE'S DECLARATION

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I here by declare that the work, which is being presented in the dissertation work, entitled "**Methanol Oxidation to Formaldehyde**", submitted in partial fulfillment of the requirements for the award of **Master of Technology in Chemical Engineering** with the specialization in **Industrial Pollution Abatement, Indian Institute of Technology Roorkee, Roorkee** is an authentic record of my own work carried out during the period from July 2005 to June 2006 under the guidance of **Dr. Shri Chand**, Professor & Head, Chemical Engineering Department, Indian Institute of Technology Roorkee, Roorkee.

The matter embodied in this project work has not been submitted for the award of any other degree.

Date: 19/06/06

Place: Roorkee

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## CERTIFICATE

This is to certify that the above statement made by the candidate is correct to the best of my knowledge and belief.

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I am feeling great in expressing my profound sense of gratitude first and foremost to the almighty God because all the matter on the earth, undergo upto end by taking power from Him and the power of taking power also comes in the empire of Him.

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(VIVEK KUMAR)

## ABSTRACT

Polymers have great importance in our life. Polymers like urea-formaldehyde, paraformaldehyde, and polyoximethylene are manufactured from formaldehyde. Formaldehyde is produced mainly from catalytic partial oxidation of methanol. In the present work, we prepared catalysts (vanadium based supported on titania and magnesia, and silver supported on iron oxide) by dry mixing method in which their respective nitrates have been mixed and then calcined at 700° C. Characterization of the catalytic materials have been done by XRD, SEM and TGA. The activity of these catalysts for the formaldehyde formation has been found to be appropriate as far as selectivity and conversion concern. From the plot interpretation, 10%V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> calcined for 16 hours at 700° C, proved to be most promising for the desired process.

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# Chapter 1

## INTRODUCTION

In the age of 21<sup>st</sup> century, polymer plays a significant role to give a new shape to our life style and living standard. Polymers like resins in adhesive, PVC and bakelite e.t.c. have become a common commodity in our society. So now the demand of the time is to new inventions and discoveries in this field.

As far as raw material concerned for polymers like urea-formaldehyde, paraformaldehyde, polyoximethylene, formaldehyde is vastly used as a monomer. The common methods used for manufacture of formaldehyde are hydrocarbon process and methanol process. But for industrial and commercial point of view, methanol process is the major one. To keep moving with the fast growing technical world and to get rid of throat cut competition, the task of a process engineer is now clear cut in increasing efficiency and selectivity of the process and for achieving this goal various catalysts such as Ag, Fe, Fe-Mo, V<sub>2</sub>O<sub>5</sub> and some their mixtures e.t.c. are being used. The major problem faced during the commercial manufacture is the preparation method of the catalyst which includes wet-mixing process through dissolution, precipitation and then drying. Thus complete process is not reliable as per time and economic point of consideration. The objective of the present work is to develop a suitable catalytic converter employing catalysts, which are based on metals.

## **1.1 OBJECTIVE OF THE THESIS:**

Thesis objectives have been planned as below:

- (i) Synthesis of  $V_2O_5/TiO_2$ ,  $V_2O_5/MgO$  and  $Ag/Fe_2O_3$  by dry mixing method.
- (ii) Characterization of catalysts using X-ray diffraction (XRD), Thermo Gravimetric Analysis (TGA), and Scanning Electron Micrographs (SEM).
- (iii) Performance studies of the synthesized catalysts for the oxidation of  $CH_3OH$  to produce formaldehyde using a mixture of air and methanol vapor.

## **1.2 ORGANIZATION OF THESIS:**

Thesis consists of three chapters. Chapter 1 includes the introduction of thesis, brief description on catalysis and an overview of different manufacturing methods of formaldehyde with some suggested catalysts and finally objective of the thesis. Chapter 2 gives a brief literature reviewed. Chapter 3 contains details of experimental setup, catalyst preparation and experimental procedure. Chapter 4 consists of results and discussion. Chapter 5 gives concluding remarks and recommendation for future work.

### **1.3 CHEMICALS UNDER CONSIDERATION:**

Our aim is to produce formaldehyde from methanol oxidation. A brief description about methanol and formaldehyde is as follows:

#### **1.3.1 Methanol**

Methanol,  $\text{CH}_3\text{OH}$ , [1] is a colorless neutral liquid at ambient temperatures with a mild odor. It is a highly toxic material whose ingestion or inhalation can cause blindness or death. Methanol has also been called wood alcohol (or wood spirit). True wood alcohol, of which methanol is the principal ingredient, is derived from the destructive distillation of wood and is found in the pyroligneous acid condensate. Wood alcohol has a characteristic pungent odor of its contaminants, mainly acetone, acetic acid and allyl alcohol.

In 1661, Robert Boyle is reported to have discovered methyl alcohol in the form of a 'neutral substance' but its identity was not established until 1834 by Dumas and Peligot. Berthelot first synthesized it in 1857 by saponification of methyl chloride. For almost a century, methanol was commercially available only from pyroligneous acid obtained from wood distillation. Methanol was first synthesized from hydrogen and carbon mono oxide around 1923. This process has gradually superseded the wood distillation method until today. Wood alcohol accounts for only 0.003 % of total methanol produced.

#### ***Manufacture***

Nowadays, the most important method for manufacture of methanol is by a medium pressure process from hydrogen and carbon monoxide containing small amounts of carbon dioxide. It can also be manufactured from hydrogen and carbon dioxide, by direct oxidation of hydrocarbons, and by other processes, such as low-pressure (below 100 atm), two-step hydrogenation of carbon monoxide to methyl formate and of methyl formate to methanol. Methanol can also be obtained as a by-product of Fischer-Tropsch or other syntheses like production of polyethylene terephthalate.

Du Pont accomplished the manufacture of methanol as a by-product of ammonia synthesis in 1927. The ammonia-synthesis gas, which contained 1-2 % carbon monoxide as an impurity, was passed through a methanol converter as a purification step. The catalyst was made of zinc, zinc-chromium, or chromium-copper while the product was removed from the

purified ammonia-synthesis gas by condensation under synthesis pressure. Other processes for methanol manufacture are as follows:

- Saponification of methyl Chloride.
- Low-Pressure Hydrogenation of Carbon Monoxide.
- Methane Oxidation by Sulfur Trioxide.
- Hydrolysis of Methylal.
- Hydration of Dimethyl Ether.

### ***Storage and Shipping***

Methanol is stored in iron or steel tanks, properly supported by reinforced concrete, brick, or steel. Because of the flammability of the product, storage tanks are normally located at some distance from the heart of the industrial plant area, are surrounded by a dike, and protected by a foam-type fire-extinguishing system. In dry air, its flammability limits are 6.7-36 % (volumetric basis). The product is shipped in 1 gal metal containers, 5 or 55 gal metal drums, or tank cars. The latter normally are loaded and unloaded by pump. If a tank car previously was used to ship another material, for example, petroleum, it is advisable to clean it thoroughly, since methanol is readily contaminated by minute amounts of foreign matter. Each shipping container must be properly labeled and handled.

### ***Safety***

Inhalation of methanol vapor should be avoided as 1000 ppm may cause slight symptoms of poisoning when inhaled, and 50,000 ppm will cause profound and perhaps fatal narcosis in 1-2 hr. The maximum allowable methanol-vapor concentration for an 8 hr working period is 200 ppm of air. Blindness may result when methanol is absorbed into the blood stream through the skin or through other means.

All the dangers, however, can be avoided by proper handling. In the case of mishaps, first aid should be given immediately by removing the victim from the contaminated area, removing clothing if contaminated, washing eyes and skin as required, and emptying the stomach if the methanol was ingested.

### **1.3.2 Formaldehyde**

Formaldehyde (methanal (IUPAC)), HCHO, [2] is the unique first member of the series of aliphatic aldehydes. Since pure, monomeric formaldehyde is a gas at ordinary temperatures, it cannot be readily handled in this state. Chemical utility, purity, and low cost, make formaldehyde an outstanding industrial product. It is one of the most important chemicals for the production of urea-phenolic, melamine and acetal resins.

#### ***History of Formaldehyde***

Formaldehyde was first prepared by the Russian chemist A. M. Butlerov in 1859 as the product of an apparently unsuccessful attempt to synthesize methylene glycol by the hydrolysis of methylene diacetate. A.W. von Hofmann synthesized formaldehyde in 1868 by the reaction of methanol and air in the presence of platinum catalyst and established its chemical identity. Commercial production was initiated in Germany in 1888, and manufacture in the U.S. commenced about 1901. However, production was on a limited scale before the commercial development of phenolic resins in 1910. In recent years, increasing quantities of formaldehyde are being manufactured by the oxidation of natural gas and the lower aliphatic hydrocarbons based on the pioneering work of John C. Walker in 1925.

#### ***Uses***

The immense utility of formaldehyde is due to its high reactivity, colorless nature, stability, purity in commercial form, and low cost. It serves as a resinifier, curing agent, synthetic agent, disinfectant, fungicide, and preservative. The major use of formaldehyde and its polymers is in the synthetic resin industry, where it is employed in the production of thermosetting resins, oil-soluble resins, adhesives etc. Formaldehyde finds use as a modifying, resinifying, and synthetic agent in practically every field that involves chemical technology. There are various polymers that are manufactured from formaldehyde such as paraformaldehyde, polyoximethylene, trioxane etc.

#### ***Health and Safety Factors***

Formaldehyde gas irritates the mucous membranes of the eyes, nose, and throat. Its solutions have a hardening or tanning action on the skin and may cause dermatitis in some cases. With



proper precaution, formaldehyde may be handled industrially with little or no difficulty, and the health hazards are not serious. The maximum permissible concentration of formaldehyde in the air as recommended by the American Standards Association is 10 ppm for exposures not exceeding 8 hours daily. Fortunately, in most cases, formaldehyde gas acts as its own warning agent; the least detectable odor is reported as at a concentration of 0.8 ppm by volume. For optimum safety, formaldehyde solutions should be handled in closed equipment. When this cannot be done, ventilating fans and fume hoods should be employed to keep the formaldehyde concentration in the working area within safe limits.

### ***Manufacture***

Formaldehyde is manufactured from partial oxidation of the lower petroleum hydrocarbons or dehydrogenation and oxidation of methanol. The former gives essentially pure formaldehyde containing some methanol and traces of formic acid as a primary, whereas the latter gives mixture of lower aliphatic aldehydes, alcohols, and acids, which on refining yields an extensive group of petrochemicals.

Table 1.1 Properties of Methanol and Formaldehyde

	METHANOL	FORMALDEHYDE
<b>Properties</b>	Clear, colorless, flammable, volatile, very mobile liquid, soluble in water, poisonous when taken internally.	In the pure monomeric form, it is colorless, highly irritating, pungent gas, soluble in water. In both the liquid and gaseous phases, it polymerizes rapidly at normal temperatures and below.
<b>Mol. wt</b>	32.04	30.03 (gas)
<b>m.p</b>	-97.6 <sup>0</sup> C	90.05 <sup>0</sup> C trioxane (CH <sub>2</sub> O) <sub>3</sub> polymer (liquid)* -118 <sup>0</sup> C
<b>b.p</b>	64.6 <sup>0</sup> C	61-62 <sup>0</sup> C* -19 <sup>0</sup> C
<b>Specific gravity</b>	0.792 (at 20 <sup>0</sup> C / 4 <sup>0</sup> C )	114.5-115 <sup>0</sup> C* 0.815 (at -20 <sup>0</sup> C)
<b>Vapor density</b>	1.11 (air = 1)	1.17 (at 65 <sup>0</sup> C/ 20 <sup>0</sup> C)* 1.067
<b>Uses</b>	Formaldehyde, acetic acid, fuel, DMT, methacrylate, methylamines, methyl halides.	Resinifier, curing agent, synthetic agent, disinfectant, fungicide, and preservatives.

\* indicates polymeric form of formaldehyde

Table 1.2 Toxic concentrations of HCHO and CH<sub>3</sub>OH

Chemical	Concentrations which will give rise to severe toxic effects			Concentrations which, if exposure to them continues for more than a short time, may lead to symptoms of illness		Concentrations in general atmosphere of the plant greater than those given below indicate unsatisfactory conditions	
	ppm v/v	mg/m <sup>3</sup> (20 <sup>0</sup> C)	Time of exposure (min)	ppm v/v	mg/m <sup>3</sup> (20 <sup>0</sup> C)	ppm v/v	mg/m <sup>3</sup> (20 <sup>0</sup> C)
HCHO	100	120	1	30	36	10	12
CH <sub>3</sub> OH	2000	2560	60	500	640	200	256

## 1.4 CATALYSIS:

Catalysis [3] is the acceleration of the reaction rate of a chemical reaction by means of a substance, called a catalyst, that is itself unchanged chemically by the overall reaction. The word 'catalyst' has been derived from Greek language and means 'to annul or to untie or to pick up'. Catalysts accelerate the chemical reaction by providing a lower energy pathway between the reactants and the reaction products. This usually involves the formation of one or more intermediates, which cannot be formed without the catalyst. The formation of this intermediate and subsequent reaction generally has a much lower activation energy barrier than is required for the direct reaction of reactants to products as shown in Fig. 1.1. The SI derived unit for measuring catalytic activity is the katal, which is moles per second. The degree of activity of a catalyst can also be described by the turn over number or TON and the catalytic efficiency by the turn over frequency (TOF). The biochemical equivalent is the enzyme unit.

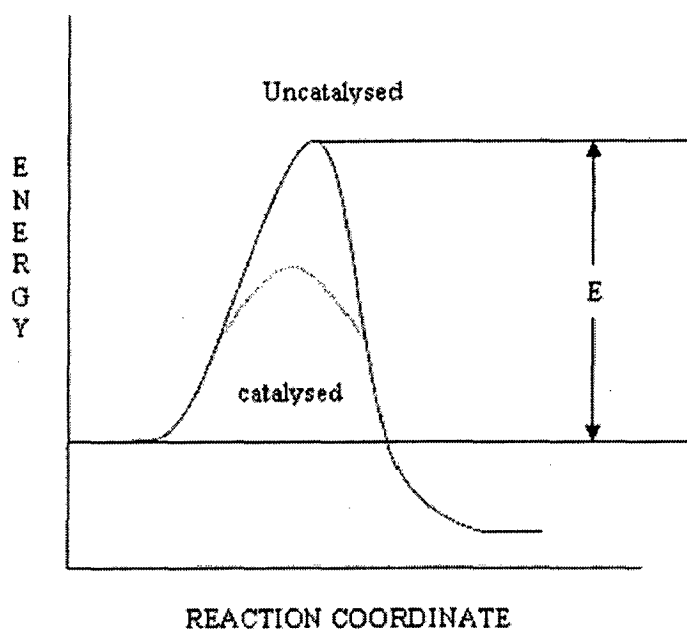


Figure 1.1 Different reaction paths

Two types of catalysis are generally distinguished. In homogeneous catalysis, the reactants and catalyst are in the same phase and in heterogeneous catalysis the catalyst is in a different phase than the reactants and products. A promoter is an accelerator of catalysis, but not a catalyst by itself. A catalyst may be a metal, a compound (e.g., metal oxides, sulfides,

and nitrides), an organometallic complex or an enzyme. Most industrial catalysts are used in the form of porous pellets, each of which contains typically  $10^{18}$  catalytic sites.

#### 1.4.1 Some useful definitions in catalysis

$$\text{TON: turn over number} = \frac{\text{moles of product formed}}{\text{moles of catalyst}}$$

It is a measure of catalyst stability.

$$\text{TOF: turn over frequency} = \frac{\text{Number of moles of product formed}}{\text{moles of catalyst} \cdot \text{time}}$$

It is a measure of catalyst efficiency. In heterogeneous catalysis, the turnover frequency is typically of the order of  $1 \text{ s}^{-1}$ .

$$\text{Selectivity (\%)} = \frac{\text{moles of product produced}}{\text{moles of methanol converted}} \times 100 \times \text{SF}$$

where SF is the stoichiometric factor (moles of methanol/moles of P) as given by reactions. Conversion and selectivity are functions of residence time.

#### 1.4.2 The nature of active sites

Catalysts have some degree of valence un-saturation so that they can form bonds to the intermediates, but these bonds must also be readily ruptured so that intermediates can readily form products. In general, the lower the coordination number, the higher the valence unsaturation attributed to the surface atoms. In his discussion of activation of Pt catalysts, Langmuir concluded:

‘The surface thus becomes a composite, and there is then a relatively small fraction of the surface at which reaction occurs with extreme rapidity while over the larger part of the surface, it takes place at a very slow rate. It was immediately recognized that such a picture gave ready explanation of the fact that trace impurities (in amounts that could react with only a fraction of the surface) could reduce the catalytic activity by orders of magnitude. To explain this we need only assume that the poison reacts selectively with the most active sites.’

### **1.4.3 Selectivity:**

Most heterogeneous catalysts are capable of accelerating a number of chemical reactions, e.g. a typical hydrogenation catalyst may bring about the hydrogenation of a variety of olefins or may convert acetylene into either an olefin or an alkane. The term selectivity is used to describe the actual behavior of the catalyst when alternative reactions are possible.

### **1.4.4 Inhibition or poisoning:**

Poisoning of a reaction may be observed even if no substances other than the reactants and products are present in the catalyst system. The products may compete strongly with the reactants for sites on the surface and thereby reduce the rate of reaction. In other cases, the reactant itself may form strongly absorbed species which inhibit the formation of the less strong absorbed species required for the reaction under study — this is known as self-poisoning and is exemplified by coking up of a cracking catalyst.

### **1.4.5 Selective poisoning:**

It refers to a situation where the presence of a poison causes a catalyst to operate selectively, or more selectively, than it would have without the poison. There are two main systems to be considered - catalysts with uniform sites or catalysts with a variety of active sites.

### **1.4.6 Selection of catalysts and prediction of catalytic properties**

Chemists working in the field of catalysis have realized the need for concentrating considerable efforts towards the development of the scientific principles of catalyst selection [4]. The simplest of them involves the selection of the best (under the given conditions) catalyst among a number of known catalysts for a given reaction as shown in Table 1.3.

Table 1.3 Problems of catalyst selection in order of increasing complexity

A. Selection among known catalysts			B. Search for new catalysts			C. Synthesis of catalysts and construction of catalytic systems with prescribed properties
Best for the given reaction (among known catalysts)	For reactions analogous to known catalytic reactions	For new reactions	For mastered catalytic reactions	For reactions analogous to the mastered	For reactions of new types, having no analogs among mastered reactions	(A problem for the future)

In cases in which the problem is confined to an expansion of the number of known catalysts for relatively simple reactions for which there exists even a single satisfactory catalyst, it would be very useful to use:

- a) Analogies based on the periodic system of the elements and other general laws of chemistry and physics;
- b) Empirical or theoretically predicted laws relating the catalytic properties of solid bodies to their electronic physical properties, the chemical composition, and the structure.

By the above methods it has been possible not only to improve some already known catalysts, but also to discover extensive groups of new catalysts.

## 1.5 FORMALDEHYDE PRODUCTION

Formaldehyde [2] is synthesized from a carbon monoxide-hydrogen mixture produced from coal and water or from natural gas, hydrocarbons may be fundamental raw material in either method of manufacture. Thus basically manufacture of formaldehyde has been categorized as in two processes.

### 1) Hydrocarbon processes

These processes involve partial oxidation of a hydrocarbon gas with air or oxygen under pressure, followed by rapid cooling, condensation, and absorption of the products in water to give a crude solution, which must, then be refined to separate formaldehyde from the other reaction products, such as methanol, acetaldehyde, propyl alcohol, propionaldehyde and organic acids.

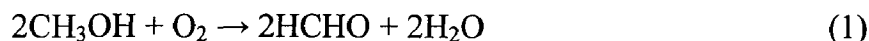
### 2) Methanol processes

These processes involve passing a mixture of methanol vapor and air over a stationary catalyst at approximately atmospheric pressure and absorbing the product gases in water. Formaldehyde is formed by two gas-phase reactions involving the dehydrogenation and oxidation of methanol

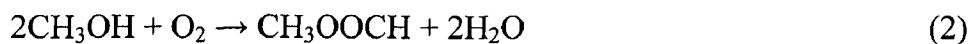


More than 50 % production of formaldehyde is obtained from partial oxidation of methanol globally. Oxidation catalysts are beneficial for such processes but it gives a variety of by-products. The reactions involved are as follows:

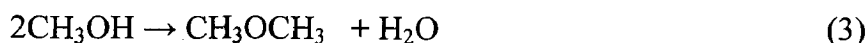
Partial oxidation of methanol to formaldehyde:



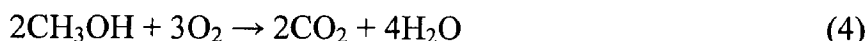
Partial oxidation of methanol to methyl formate:



Dehydration of methanol to dimethyl ether:



Total oxidation of methanol to carbon dioxide:





Therefore, the use of partial oxidation catalyst assumes great significance. The role of metal oxides as partial oxidants has been well documented in literature and the order of the ability of different metal oxides is given as follows:

$V_2O_5 > MoO_3 > WO_3 > U_3O_8 > Sb_2O_4 > Cr_2O_3 > NiO, TiO_2 > SnO_2, Nb_2O_5 > ZnO, MnO_3$   
 $> CuO > Ta_2O_5 > Co_3O_4, ThO_2, ZrO_2 > Fe_2O_3, Bi_2O_3$

In addition, catalysts like Ag, Fe-Mo are widely used for industrial production of formaldehyde from methanol partial oxidation. The route of silver catalyzed process at air-lean conditions, due to its low investment cost, stable production and simple regeneration of Ag plays an important role in formaldehyde production.

## Chapter 2

### LITERATURE SURVEY

This chapter contains a review of the existing research, to the extent available, on the vanadium, silver based mixed and supported oxides and their substituted as catalysts, their characteristics and their performance for the partial oxidation of  $\text{CH}_3\text{OH}$  has been presented as all are basically oriented for producing more  $\text{HCHO}$ .

**Deo and Wachs (1994)** [5] observed the reactivity of the surface vanadium oxide phase as a function of specific oxide support ( $\text{Al}_2\text{O}_3$ ,  $\text{SiC}$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{TiO}_2$ , and  $\text{ZrO}_2$ ) and Vanadium oxide loading for the partial oxidation of methanol. The activity, selectivity, and activation energies of the methanol oxidation reaction for the supported vanadium oxide catalysts are obtained in order to determine the influence of the vanadium oxide loading and the specific oxide support. In addition, temperature programmed reduction experiments were carried out to determine the reducibility of the supported vanadium oxide samples.

All the oxide supports were calcined at 723-773 K and cooled to room temperature in air prior to impregnation with the vanadium oxide precursor. The vanadium oxide over layers was prepared on the oxide support of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{TiO}_2$ , and  $\text{Nb}_2\text{O}_5$  by the incipient wetness impregnation method. The methanol oxidation reaction was carried out in an isothermal fixed-bed differential down flow reactor operating at atmospheric pressure. The reactor was held vertical and made of 6-mm O.D. Pyrex glass. The outlet of the reactor to the gas chromatograph (GC) was heated at 393-403 K in order to avoid condensation of the products.

The methanol partial oxidation activity over the supported vanadium oxide species increases as a function of vanadium oxide loading for sub monolayer and monolayer catalysts. The TOF for  $\text{V}_2\text{O}_5/\text{ZrO}_2$ , and  $\text{V}_2\text{O}_5/\text{TiO}_2$ , catalysts are three orders of magnitude greater than the TOF for the  $\text{V}_2\text{O}_5/\text{SiO}_2$  catalysts. The activation energy for formaldehyde formation on the different supported vanadium oxide catalysts is  $19.3 \pm 2.3$  kcal/mole and is independent of the vanadium oxide loading and oxide support, and corresponds to the C-H bond breaking of the surface methoxy intermediate. The similar activation energies and

different TOFs indicate that the pre-exponential factor of the different supported vanadium oxide catalysts is determined by the specific oxide support.

Thus, the reactivity of the surface vanadium oxide phase is determined by the specific oxide support and is

- (a) Not related to the stability of the surface vanadium oxide phase,
- (b) Not related to the structure of the surface vanadium oxide phase,
- (c) Not related to the terminal V=O bond strength, but is related to the ease of reduction of the supported vanadium oxide catalysts.

**Deo and Wachs (1994)** [6] observed the changes in the structure and reactivity of the surface vanadium oxide phase by Raman spectroscopy and methanol oxidation, respectively after adding different additives ( $\text{WO}_3$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{SiO}_2$ ,  $\text{P}_2\text{O}_5$ , and  $\text{K}_2\text{O}$ ) to 1%  $\text{V}_2\text{O}_5/\text{TiO}_2$  catalyst. Models of the interactions of the various additives with the surface vanadium oxide phase are developed by correlating the structure and reactivity of the surface vanadium oxide phase in the presence and absence of the additives.

Supported vanadium oxide on  $\text{TiO}_2$ , was prepared by the incipient wetness impregnation of vanadium triisopropoxide oxide precursor in a methanol solution. The impregnated catalysts were thoroughly mixed and dried at room temperature for 16 hr in a glove box under a nitrogen environment. Room temperature drying for 16 hr was followed by drying at 100-120°C under flowing nitrogen for 16 hr. Finally the catalysts were dried at 450°C for 2 hr in flowing oxygen or air. The final catalysts were denoted as 1% $\text{V}_2\text{O}_5/\text{TiO}_2$ . Tungsten oxide, niobia, silica, potassium oxide, and phosphorous oxide were added in order to study the effects of additives on the 1%  $\text{V}_2\text{O}_5/\text{TiO}_2$  sample.

Table 2.1 below shows different catalysts with yield of formaldehyde.

Sample	% Yield of FA
0.3% $\text{K}_2\text{O}/1.0\%\text{V}_2\text{O}_5/\text{TiO}_2$	100
1.0% $\text{V}_2\text{O}_5/7.0\%\text{WO}_3/\text{TiO}_2$	99
3.0% $\text{Nb}_2\text{O}_5/1.0\%\text{V}_2\text{O}_5/\text{TiO}_2$	97
1.0% $\text{V}_2\text{O}_5/\text{TiO}_2$	99

The Raman spectra of the dehydrated samples and methanol oxidation behavior of the various additives on the 1% V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> sample reveal that there are essentially two types of interactions between the additives and the surface vanadium oxide phase as follows: Noninteracting additives and interacting additives.

Noninteracting additives (WO<sub>3</sub>, Nb<sub>2</sub>O<sub>5</sub> and SiO<sub>2</sub>) do not significantly affect the structure of the surface vanadium oxide phase, and no change in the methanol oxidation activity or selectivity of the surface vanadium oxide phase is observed. The order of impregnation or preparation method of the noninteracting additive does not affect the structure or methanol oxidation activity of the surface vanadium oxide phase. Interacting additives (P<sub>2</sub>O<sub>5</sub> and K<sub>2</sub>O), however, have a pronounced effect on the structure and reactivity of the surface vanadium oxide phase.

**Pestryakov (1996)** [7] suggested the modification of silver catalysts for oxidation of methanol to formaldehyde. They investigated the reaction of rare and rare-earth metal oxides and electronic, physico-chemical and catalytic properties of silver catalysts in the process of oxidation of methanol to formaldehyde. Oxides of Zr, Rb, Cs, Ce, La and other lanthanides display a strong interaction of metal and support.

10 wt % Ag/support samples were prepared by chemical or thermal reduction of silver from an aqueous solution of AgNO<sub>3</sub>. The modifiers in amounts of 1-10 wt % were coated onto a support (pumice or Al<sub>2</sub>O<sub>3</sub>) of aqueous solutions of nitrates and acetates with the subsequent thermal decomposition of nitrates to oxides at 400°C. Catalytic tests were carried out in a flow catalytic plant at T = 600-700°C. The catalyst samples were pretreated with O<sub>2</sub> at 100-500°C and with H<sub>2</sub> at 100-400°C.

The additions of 1-5 wt% Zr and Ce oxides improve the catalyst performance, oxides of La, Pr, Sm and other lanthanides (except Ce) lower the yield of formaldehyde, but additions of Rb and Cs oxides only slightly affect the process (Fig. 2a). Variations in selectivity of these catalysts have similar differences. All the additions raise formaldehyde yield over the modified support (Fig. 2b) that can not be explained by the intrinsic catalytic properties of the modifiers, as. So we can say that the contribution of modifiers is not principal as it does not explain the decline of selectivity of the catalyst modified by rare earth metal oxides.

**Wachs *et al* (1997)** [8] started that supported vanadium oxide catalysts, containing surface vanadia species on oxide supports, are extensively employed as catalysts for many hydrocarbon oxidation reactions. They discussed the current fundamental information available about the structure and reactivity of surface vanadia species on oxide supports: monolayer surface coverage, stability of the surface vanadia monolayer, oxidation state of the surface vanadia species, molecular structures of the surface vanadia species (as a function of environment and catalyst composition), acidity of the surface vanadia species and reactivity of the surface vanadia species. They compared the molecular structure and reactivity and gave new fundamental insights into the catalytic properties of surface vanadia species during hydrocarbon oxidation reactions: (1) the role of terminal V=O, bridging V-O-V and bridging V-O-support bonds, (2) the number of surface vanadia sites required, (3) the influence of metal oxide additives, (4) the influence of surface acidic and basic sites, (5) the influence of preparation methods and (6) the influence of the specific oxide support phase. The unique physical and chemical characteristics of supported vanadia catalysts, compared to other supported metal oxide catalysts, for hydrocarbon oxidation reactions were also discussed. They concluded that supported vanadia catalysts possessed unique properties among supported metal oxide catalysts. The surface density of the surface vanadia monolayer is typically about twice that of other supported metal oxide catalysts (e.g., oxides of Mo, Cr, Re, etc.). The higher surface density of surface vanadia species increases the number of catalytic active sites and minimizes unwanted side reactions from exposed oxide support sites. The weak acidic character of bulk vanadia relative to other transition metal oxides (e.g., oxides of Mo, Cr, Re, etc.) may also minimize unwanted side reactions.

**Forzatti *et al* (1997)** [9] observed the methanol oxidation over vanadia-based catalysts and reviewed their results on the oxidation of methanol to formaldehyde and methyl formate over V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> systems with regard to the influence of the operating variables, the investigation of the reaction mechanism and the aspects related to the implementation of an industrial process.

*For Methanol oxidation on vanadia-containing mixed oxides and metal vanadates:* The catalytic performances of vanadia for methanol oxidation to formaldehyde can be improved by mixing V<sub>2</sub>O<sub>5</sub> with other transition metal oxides. The V<sub>2</sub>O<sub>5</sub>-MoO<sub>3</sub> system has been the

object of a number of studies. All this is described on different catalysts by Mann and Dosi (1973), Ai (1978) and Malinski et al. (1976) and Monti et al. (1985).

*For Methanol oxidation on other V-containing bulk solids:* Pomonis and Vickerman (1982) investigated this reaction for catalysts constituted by V-containing solid solutions metal oxides. Sorensen and Weber investigated the catalytic activity of  $\text{Na}_{3+n}\text{PV}_n\text{W}_{12-n}\text{O}_{40}$  Keggin-type heteropolysalts, together with those of the Keggin-type compounds  $\text{Na}_5\text{SiVW}_{11}\text{O}_{40}$  and  $\text{Na}_7\text{PV}_{14}\text{O}_{42}$ , all supported on silica.

*For Oxide-supported vanadia catalysts:* Roozenboom et al. (1981) found that, for "monolayer-type" oxide-supported vanadia catalysts, the activity in methanol oxidation follows the trend  $\text{V}_2\text{O}_5\text{-TiO}_2$  (anatase) >  $\text{V}_2\text{O}_5\text{-ZrO}_2$  >  $\text{V}_2\text{O}_5\text{-CeO}_2$  >  $\text{V}_2\text{O}_5\text{-Al}_2\text{O}_3$  > pure  $\text{V}_2\text{O}_5$ , but the selectivity to formaldehyde follows nearly the inverse trend. According to Kuenski et al (1986) that also studied "monolayer-type" oxide-supported vanadia catalysts in the temperature range 500-670 K, vanadia-silica is very active and very selective to formaldehyde (selectivities near 90%). Tatibou (1986) investigated the effect of vanadium oxide loading for  $\text{V}_2\text{O}_5\text{-TiO}_2$  (anatase),  $\text{V}_2\text{O}_5\text{-TiO}_2$  (futile) and  $\text{V}_2\text{O}_5\text{-Al}_2\text{O}_3$ . Srivastava and coworkers (1986) used vanadia-silica doped with alkali metal sulphates as  $\text{K}_2\text{SO}_4\text{-V}_2\text{O}_5/\text{SiO}_2$  and the following kinetic expression was proposed

$$r = k_1 P_M / [1 + k_1 P_M / (2k_2 P_0^{0.5})]$$

They found that varying the V content of the catalysts affects significantly both the conversion of methanol and the distribution of products and further concluded the effect of preparation method and different process variables as feed rate and feed composition on the selectivity of different products and activity of methanol.

**Hutchings et al (1999)** [10] tried to give an approach for the scientific design of new methane partial oxidation catalysts. They studied the activation of methane and oxygen on single metal oxides and the stability of methanol over the same oxides. By studying these interactions the suitability of single oxides for inclusion as components in methane oxidation catalysts can be assessed. Experiments to determine methanol stability were carried out in a conventional liquid feed micro reactor with a fused silica reactor tube. The reaction conditions used a methanol/oxygen/helium feed in the ratio 1/4/12, with a gas hourly space velocity (GHSV) in the region of  $12000 \text{ h}^{-1}$ . Methanol stability was determined in the

temperature range from 100°C to 500°C at atmospheric pressure. Product analysis was performed on-line using a Varian GCMS system. Under normal operation methane and hydrogen (1/1) were passed over the catalyst held in a fused silica reactor tube. Studies were carried out using a gas hourly space velocity of 700 h<sup>-1</sup>. For the oxidation of methane to methanol the design methodology has been used to show that a Ga<sub>2</sub>O<sub>3</sub>/MoO<sub>3</sub> catalyst gives an increased yield of methanol when compared to the homogeneous gas phase oxidation of methane in a quartz chips packed reactor.

**Li et al (1999)** [11] investigated the improvement in reactivity, reproducibility and stability of Fe-Mo catalysts by wet mixing for methanol oxidation. In order to overcome the drawbacks like high manufacturing cost and poor reproducibility, an improved mixing method was developed to prepare Fe/Mo catalysts-wet mixing.

Industrial grade Fe(NO)<sub>3</sub>.9H<sub>2</sub>O and (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>.4H<sub>2</sub>O were used to prepare all the catalysts. Two series of catalysts were prepared, one of them (series I) used conventional dry mixing method in which 5g Fe(NO)<sub>3</sub>.9H<sub>2</sub>O and 5g (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>.4H<sub>2</sub>O were crushed in a mortar and the mixture was ground until a rubbery and transparent green gel was formed. Another series of the catalysts (series II) were prepared by wet mixing in the similar way as used in the conventional mixing except that before grinding, an adequate amount of deionized water was added to the mixture. The thermal treatment of the catalysts was conducted at different temperatures by heating them in an oven at 650°C, 700°C, 750°C, and 800°C in an atmosphere of air. The reactivity measurement was conducted in a fixed-bed tubular reactor. An over-heated gaseous mixture of air and methanol containing 6.5% by volume of methanol passed through the catalyst bed at 280°C, atmospheric pressure.

**Niwa and Igarashi (1999)** [12] studied the role of the solid acidity on the MoO<sub>3</sub> loaded on SnO<sub>2</sub> in the methanol oxidation into formaldehyde. Based on the consideration of variable physico-chemical parameters, e.g., reducibility, bond strength of metal and oxygen, acid-base property, size of metal cation, electro- negativity, etc. of various kinds of metal oxides only tin oxide was utilized as a support. Tin oxide was prepared from a solution of SnCl<sub>2</sub>.2H<sub>2</sub>O which was dissolved into the HCl solution. To the solution, NH<sub>4</sub>OH was added to precipitate the hydroxide, which was then washed to remove the chlorine ion until the pH of the solution

was adjusted to 7.0. The hydroxide gel thus obtained was dried and calcined in air at temperatures from 773 to 1123K for 2 h. Supported catalyst was prepared by an impregnation method. Tin oxide was added to the solution of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ , followed by adjusting the pH to 10 by  $\text{NH}_4\text{OH}$ . Water was evaporated on a hot plate, and then dried at 383 K. It was calcined in a stream of oxygen at 773K for 3 h. The reaction temperature was 498K, and the weight of catalyst was chosen to adjust the conversion of methanol to less than 20%. Products were analyzed by gas chromatography.

Molybdenum oxide readily spread on the tin oxide which was calcined at the temperature from 773 to 1173 K. In order to catalyze the partial oxidation of methanol, two kinds of property, i.e., adsorption of methanol and oxidation activity has to be optimized. The acidity and reducibility were correlated with the activity. They concluded that methanol may be adsorbed on the acid site to form methoxide, and then the methoxide species finally yields formaldehyde.

**Wang and Willey (1999)** [13] proposed the fine particle iron oxide based aerogels for the partial oxidation of methanol. They studied the total oxidation of organics in supercritical  $\text{CO}_2$  at temperatures lower than that used for total oxidation in supercritical water. They found partial oxidation dominated in the studied temperature and residence time ranges.

The aerogels used in this work were based around iron oxide ( $\text{Fe}_2\text{O}_3$ ). The aerogels were compressed to reduce macro volume by about 50%. They were then placed inside a tubular vertical reactor that was heated. Liquid methanol and high pressure oxygen were added to the  $\text{CO}_2$  flow before a static mixer. An oxidative pretreatment was done before each run that consisted of passing an air stream at 475 °C for 2 h across the catalyst bed. By compressing beforehand and using a ½ micron sintered metal filter as a support, the aerogel remained stationary in the reactor bed for the duration of catalytic runs completed.

An evaluation of residence time conducted at 275 °C shows that shorter residence times favored the formation of formaldehyde and longer residence times favored the formation of methyl formate. Pure iron oxide aerogel favorably promotes the formation of dimethyl ether. As iron oxide content increases on silica, methanol conversion decreases with one exception 20%  $\text{Fe}_2\text{O}_3$  - $\text{SiO}_2$  aerogel because it results in  $\text{CO}_2$  totally. Formation of methyl formate is favored when silica is used as the support and iron oxide is well dispersed with its content



below 5%. Another material evaluated was a 20% iron oxide on molybdenum oxide aerogel. This aerogel was extremely selective for the partial oxidation of methanol to formaldehyde. So it can be concluded that the selectivity observed are related to iron oxides ability to be reduced and reoxidized through each cycle of a reaction path.

**Wachs et al (2000)** [14] studied the molecular structure and reactivity of the group V metal oxides. They compared the molecular structure and reactivity properties of the group V metal oxides (especially vanadia and niobia). At first Wachs et al (2000) focused on the solid state structural chemistry, physical and electronic properties, and chemical reactivity of the bulk group V metal oxides in terms of number of active surface sites and their redox/acidic catalytic properties. Secondly they focused on the same properties of the supported group V metal oxides.

The catalyst synthesis procedures are described in publications by Deo and Wachs (supported vanadia catalysts) (1994), Jehng et al. (supported niobia catalysts and surface modified niobia catalysts) (1991, 1992) and Gulians et al. (Nb promoted VPO catalysts) (1999). The spectroscopic characterization instrumentation employed were Raman (1994), IR (1999) and UV-Vis DRS (1999). The surface characteristics of the various catalysts were determined by the N<sub>2</sub> BET method and CH<sub>3</sub>OH chemisorption was performed in either a TGA apparatus or in an IR spectrometer. The number of surface active sites was determined by methanol chemisorption at 100<sup>0</sup>C with 2000 ppm of methanol in He.

**Soarers et al (2001)** [15] studied that deactivation of iron molybdate catalysts during methanol oxidation is usually ascribed to MoO<sub>3</sub> sublimation at catalyst surface. With the main objective of understanding better the deactivation mechanism of iron molybdates in methanol oxidation, they performed the stability tests with stoichiometric (Mo/Fe= 1.5 atomic ratio) and industrial like catalyst (Mo/Fe= 3 atomic ratio). Two iron molybdates were prepared by coprecipitation from aqueous solutions of iron nitrate and ammonium heptamolybdate, one stoichiometric corresponding to Mo/Fe= 1.5 and the other with typical industrial composition Mo/Fe= 3. They concluded that Mo excess improves catalyst stability mainly due to the fact that during reaction Mo seems to migrate from bulk to catalyst surface and then sublimated.

**Wang and Wachs (2004)** [16] discussed the designing of the activity/selectivity of surface acidic, basic and redox active sites in the supported  $K_2O-V_2O_5/Al_2O_3$  catalytic system. They have studied the effects of basic potassium oxide on the nature of the active surface sites of supported  $V_2O_5/Al_2O_3$  and  $Al_2O_3$  catalysts those investigated by using the methanol oxidation. As well as they investigated the surface structures, surface reaction intermediates and the surface reaction mechanisms by Raman and temperature programmed surface reaction (TPSR) spectroscopy studies.

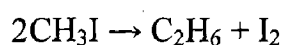
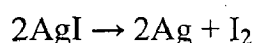
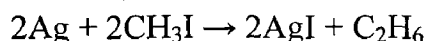
The catalysts were prepared by the incipient wetness impregnation method. The  $Al_2O_3$  was calcined in air at  $500\text{ }^\circ\text{C}$  for about 2 h before being used as support for the catalyst preparations. In order to investigate the effect of preparation sequence on the properties of the catalysts modified by potassium oxide, two  $K_2O-V_2O_5/Al_2O_3$  samples with an inverse  $K_2O$  and  $V_2O_5$  addition sequence were prepared. After impregnation by an aqueous solution of  $KNO_3$ , the samples of the form of  $K_2O$  on  $V_2O_5/Al_2O_3$  were dried at room temperature overnight. The catalysts were subsequently calcined in air at  $600\text{ }^\circ\text{C}$  for 4 h to ensure that  $KNO_3$  completely decomposed. The second inverse form of  $V_2O_5$  on  $K_2O/Al_2O_3$  were prepared by the impregnation of an isopropanol solution of  $VO(OC_3H_7)_3$  under a continuous  $N_2$  flow and the samples were dried overnight in a  $N_2$  flow at room temperature. The samples were subsequently calcined in air at  $600\text{ }^\circ\text{C}$  for 4h. The reaction was performed in an isothermal fixed-bed differential reactor at atmospheric pressure. To maintain differential reaction conditions, the methanol conversion was always maintained below 10% by varying the amount of catalyst sample in the reactor. They got good yield of formaldehyde in case of 20% $V_2O_5$ /11.5%  $K_2O/Al_2O_3$ .

**Qian *et al* (2004)** [17] investigated the effect of  $CH_3I$  addition on formaldehyde selectivity and Ag catalyst activation from the partial oxidation of methanol for a long-time operation. Where the Ag catalyst was treated by 100 ppm  $CH_3I$  added to the feed, the selectivity to the byproducts ( $CO_2$ ,  $H_2$  and  $HCOOH$ ) was also monitored with time in order to gauge the long-time behavior of catalytic activity change resulted from the  $CH_3I$  treatment.

The reaction was carried out in the water ballast mode over an electrolytic silver powder in a tubular fixed-bed reactor at  $823\text{ }^\circ\text{K}$ . Methanol and water were dosed by pumping the appropriate amounts separately with the assistance of  $N_2$  as an inert carrier gas, and the

composition of the feed mixture was kept outside the explosive regime. After a short induction time, the catalyzed conversion of methanol showed a steady performance in a long-time phase with basically constant methanol conversion and formaldehyde selectivity. After 300 days time on-stream, 100 ppm CH<sub>3</sub>I in methanol was introduced into the reaction system by adjusting this composition in the feed for the methanol evaporator.

The color of the effluent in the washing bottle became brownish yellow during the treatment, from the decomposition of CH<sub>3</sub>I at the high temperature as cleared from the following reactions



After the above-mentioned treatment, no more CH<sub>3</sub>I was added in the following experiments, which ran with the I free methanol again.

They concluded that the selectivity of HCHO decreased gradually to about the original 80 % within about two months, whereas conversion of CH<sub>3</sub>OH increased again after stopping the CH<sub>3</sub>I addition.

## Chapter 3

### EXPERIMENTAL SETUP AND PROCEDURE

Having fixed the aims and objectives on the basis of literature review, we embarked upon an extensive research program on catalysts preparation, their characterization and their performance on methanol oxidation to formaldehyde. For reaching to our goal we have decided to prepare Vanadia based supported on Titania and magnesia catalyst and silver based supported on iron oxide catalysts at their different compositions. We have chosen dry mixing method to prepare them rather than using conventional wetness impregnation or co-precipitation

#### 3.1 PREPARATION OF $V_2O_5/TiO_2$ , $MgO$ AND $Ag/Fe_2O_3$ :

According to the availability and as a new way of preparation, dry mixing method is found suitable to be adopted which is described as follows.

##### **Dry mixing method:**

The preparation of the catalysts has a mixing of the stoichiometric amounts of nitrate salts of basic components like vanadium, titanium, magnesium, silver and iron. But we have taken oxides of vanadium and titanium in according to their amounts required. The required amounts of  $AgNO_3$ ,  $Mg(NO_3)_2$  and  $Fe(NO_3)_3$  were taken and grinded into very fine power in a pastel and mortar. After grinding the material was heat treated in an electric furnace.

The calcinations of all the catalyst was done at  $700^\circ C$  upto 6hours. For checking the effect of calcinations time period we have calcined the same compound of  $V_2O_5/TiO_2$  at  $700^\circ C$  for 16hours also. After calcinations the material was allowed to furnace cooling and then the material was grounded in acetone with a pastel and mortar. After the heat treatment the catalyst material was characterized by using XRD, TGA and SEM analysis.

#### 3.2 CATALYST CHARACTERIZATION

##### 3.2.1 X-Ray diffraction (XRD) analysis

The determination of structure of all the catalysts was done by X-ray diffractometer (Philips PW 1140/90) in Institute Instrumentation Center (IIC), IIT Roorkee. The formation of their structure was confirmed by using  $Cu-K_\alpha$  as a source and Ni as a filter. Geniometer speed was

kept at 1°/min and chart speed was 1 cm/min. the range of scanning angle ( $2\theta$ ) was kept at 20-120°. During the analysis the Geniometer was scanned over its angular range and a plot of  $2\theta$  against intensity was obtained. The intensity peaks indicate values of  $2\theta$  where Bragg's law  $n\lambda=2d\sin \theta$  is fulfilled.

### 3.2.2 Scanning Electron Micrograph

To study the surface structure and morphology of the catalysts, scanning electron micrographs were obtained using a Philips SEM-501 microscope at the Institute Instrumentation Centre (IIC), IIT Roorkee. Depending on the clarity of the visible images the magnification and resolution values were selected.

### 3.2.3 Thermo Gravimetric Analysis

Thermo Gravimetric Analysis (TGA), Differential Thermal Analysis (DTA) and Derivative Thermo Gravimetric Analysis (DTGA) were carried out for catalysts, in air by means of Stanton-Reel croft STA 781 thermal analysis system at IIC, IIT Roorkee. Specifications are shown in Table 3.1.

Table 3.1 Specifications for thermal analysis

Sample amount	10 mg
Temperature range	Ambient to 900°C
Heating rate	10° C per minute
Reference material	Alumina
Furnace winding	Rhodium-Platinum
Sample holder	Pt crucible of dia.6 mm and height 4mm

### 3.3 EXPERIMENTAL SET-UP

The activity of the prepared catalysts was tested using an experimental apparatus. The schematic representation of the experimental set-up is shown in Fig. 3.1. The set-up consists of six sections:

1. Mixing of air and methanol vapor
2. Reactor
3. Temperature control
4. Flow measurement
5. Condenser
6. Computer aided analysis and monitoring of the condensed products

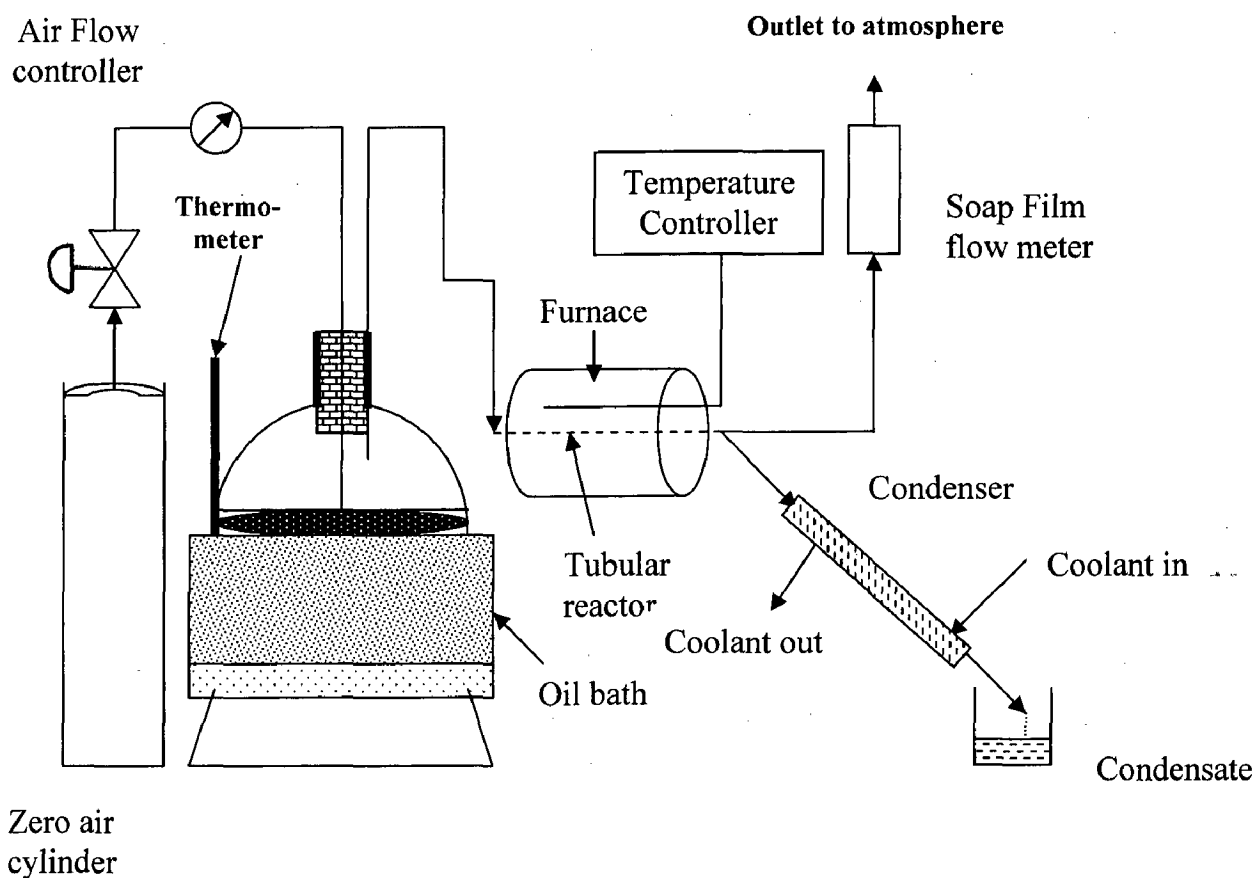


Figure 3.1 Schematic Diagram of the Experimental Setup





Figure 3.2 Experimental Setup in the Laboratory

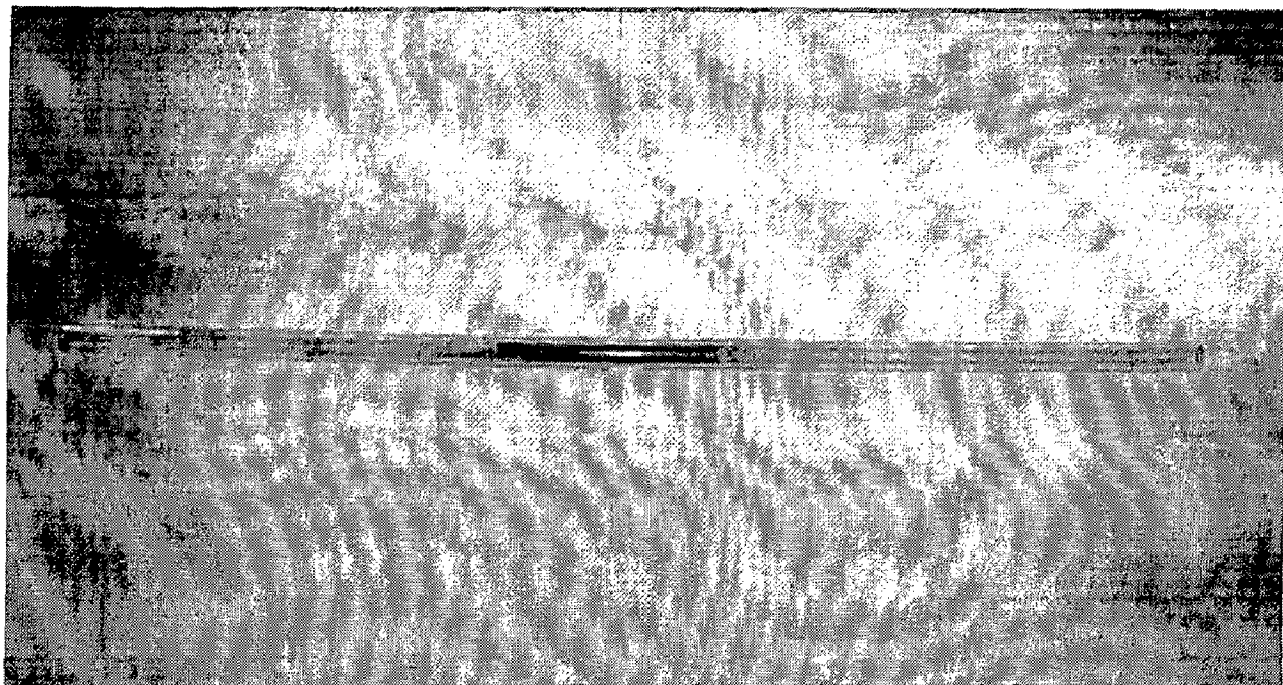


Figure 3.3 Quartz Tube filled with catalyst, used as catalytic reactor



### **3.3.1 Mixing of air and methanol vapor**

The feed to the reactor requires a mixture of methanol vapor and oxygen. For oxygen we used zero air cylinder which contains 21% O<sub>2</sub> by volume and balance N<sub>2</sub>. This air enters a 1000 ml borosil round bottom flask having liquid methanol which is heated on an oil bath at 72-76°C. The required flow rate of the methanol vapor was adjusted by temperature. The flow of the air was controlled by precision valve at a particular pressure with the help of pressure gauge (0-4 kg/cm<sup>2</sup>). Thus a mixture of air and methanol vapor at a specific composition enters the reactor.

### **3.3.2 Reactor**

The reactor used was a quartz glass tube with inner diameter of 4 mm, outer diameter 6 mm and length of 315 mm. The reactor was placed horizontally inside a tubular, electrically heated furnace with a temperature controller. The reactor has three zones; preheating, reaction and the post heating zones. The inlet or preheating zone is 130 mm long and is packed with glass wool. The reaction zone is 40 mm long and is packed with catalyst particles. The post heating zone is 135 mm long and its initial 10 mm portion is packed with glass wool mainly for the purpose of supporting the catalyst. The flow measurement was done with an on-line soap film gas flow meter. Reactor outlet to the condenser was connected by a minimum possible length of tube to minimize the resistance in the flow of the condensate.

### **3.3.3 Analytical system**

The analytical system is interfaced with gas chromatograph having its inbuilt facilities for changing the conditions e.g. injector temperature, carrier gas flow rate e.t.c. and connected with a personal computer, which helps in changing the method of integration and saving data and showing the gas chromatograms of the injected samples. Thus a set of software programs and subroutines permit us to process the analytical data in many different ways. Quantitative analysis of the chromatogram was obtained by electronic integration of the peak areas using the computing integrator attached with the output signals of the GC. Response factors were obtained, by integration of chromatograms for calibration gases.

### 3.4 EXPERIMENTAL PROCEDURE

The process is a continuous catalytic process. Catalytic activity tests were conducted in the reactor assembly equipped with fixed catalyst bed. The catalyst particles were packed in the mid portion of 4 cm length of the reactor. The catalyst was resisted to flow by using glass wool on both sides, which serve as pre- and post- heating zones for the reacting gases and ensure the uniformity of flow of gases in the reactor. 0.2 to 0.4 g of fresh catalyst of particle size 100-200  $\mu\text{m}$  was charged in each run in order to occupy a 4 cm length in the reactor tube. Catalyst volume in all the tests was, thus, kept constant at 0.502  $\text{cm}^3$ . The activity tests were performed at temperatures ranging from 100 - 300°C in 50°C interval. The temperature was maintained to  $\pm 7^\circ\text{C}$  accuracy. Gas Hourly Space Velocity during the tests was kept between 4200 to 4400  $\text{h}^{-1}$  and the ratio  $\text{CH}_3\text{OH}/\text{Air} \sim 2.0$  with a total flow rate of  $\sim 0.6 \text{ cm}^3/\text{sec}$ .

In the starting, the temperature of the reactor was maintained at 100° C for ½ hour then at different temperatures, the samples of amount 3-5 ml have been taken after a 5 min wait at steady state of a particular temperature. Thus upto 300° C all the samplings took  $\sim 2$  hours.

### 3.5 GAS CHROMATOGRAPHIC ANALYSIS

Gas chromatography is essentially a separation technique in which the sample mixture is subjected to a competitive distribution between two phases, one of which is a moving gas stream and the other is a stationary solid or liquid.

In adsorption chromatography the sample constituents are separated by passing them in a stream of carrier gas through a bed (the column) of powdered adsorbent. In partition chromatography, a competitive partition of the sample between the moving carrier and a stationary liquid is used to achieve the separation. The retention time depends on the column temperature, carrier gas flow rate and column length etc. If all these parameters are kept constant the retention time is constant and repeatable.

The separated components emerge from the end of the column in the carrier gas stream and it is necessary to detect and measure them at this point. A variety of detection devices have been developed, all of which generate an electrical signal which is displayed on

a moving chart recorder or a screen. The electrical signal, over a certain range concentration, is proportional to the amount of detected component in the sample i.e.

$$\text{Peak area} \propto \text{Component concentration}$$

Typically, the result of an analysis (called the chromatogram) consists of trace in which each of the sample components is displayed as a peak on a horizontal baseline.

The most satisfactory method of quantitative analysis in gas chromatography is the internal standard technique. This technique involves the addition of a substance not present in the sample which has retention time such that its peak fits into a suitable "gap" in the chromatogram, this substance is used as a reference material and is called the internal standard. The peak areas are measured and the response factor of the detector to each component relative to the internal standard is calculated.

For the analysis of the reactants and the products, a TRACE GC ULTRA single column gas chromatograph equipped with a stainless steel capillary column HP-1 was used. Flame Ionization Detector (FID) was used in the analysis of the condensed vapors. Nitrogen of grade-I purity was used as the carrier gas with a flow rate of 35 ml/min in the column. For the detection of HCHO and other side products with reactant CH<sub>3</sub>OH in the feed and the product, the test conditions were set as given in Table 3.2. Feeding of the reactor products to the gas chromatograph was done by using a needle type injector.

Table 3.2 GC conditions for product analysis

Type: TRACE GC ULTRA

From: Thermo Electron Corporation

S.NO.	Item	Setting
1.	Detector	FID
2.	Injector temperature	250°C
3.	Detector temperature	280°C
4.	Oven temperature	60-75°C at 5° C/min 75-140°C at 30° C/min
5.	Carrier gas	Nitrogen
6.	Carrier gas flow rate	35 ml/min
7.	Gas chromatographic column	0.25 mm×30 m Capillary type Stainless steel column
8.	Sample injection to GC	2 µl off line

## Chapter 4

### RESULTS AND DISCUSSION

This chapter contains the characterization of synthesized catalysts and their activity for the partial oxidation of methanol. Characterization consists of XRD, TGA and SEM of the catalytic compounds. The activity of the catalyst is highly dependent on various parameters, such as calcination temperature of catalyst, residence time in the reactor, temperature of the reaction, mode of catalyst preparation, ability of medium to give good transportation up to active sites, mode of arrangement of catalyst materials (e.g. pure catalyst, mixed catalyst, supported catalyst, or mixed-supported catalyst).

#### 4.1 CHARACTERIZATION OF SUPPORTED CATALYSTS

##### $V_2O_5/TiO_2$ , $V_2O_5/MgO$ , $Ag/Fe_2O_3$

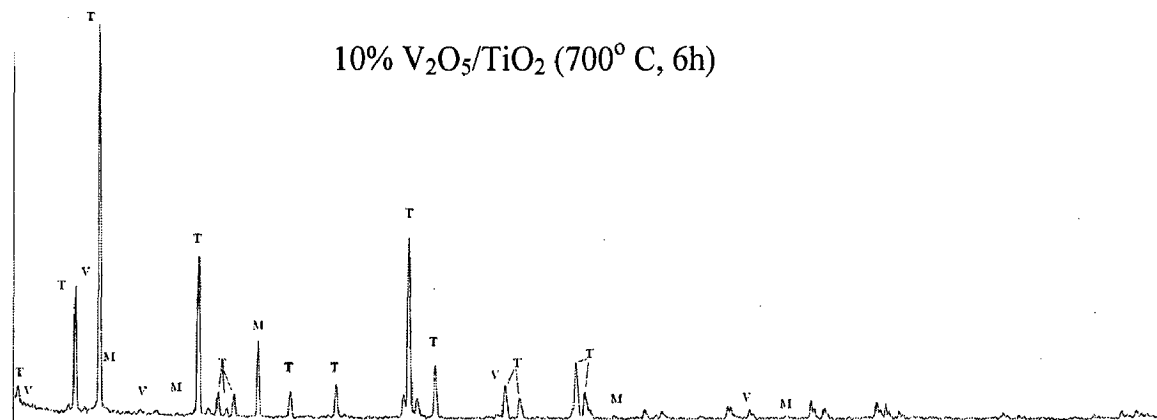
##### 4.1.1 X-Ray Diffraction pattern

The XRD patterns of few catalysts are represented in Fig. 4.1. In Fig. 4.1 (a), the XRD pattern of 10%  $V_2O_5/TiO_2$  calcined at 700°C for 6h shows the prominent peaks of mixed oxide phase at  $2\theta = 28.2, 34.2, 41.2, 72.3$ .  $V_2O_5$  peaks could be identified at  $2\theta = 21.1, 26.2, 31.2$  and  $62.2$  while peaks corresponding to  $TiO_2$  could be observed at  $2\theta = 25.3, 27.6, 36.3, 44.1, 48.1, 55.3, 56.9, 69.1$ .

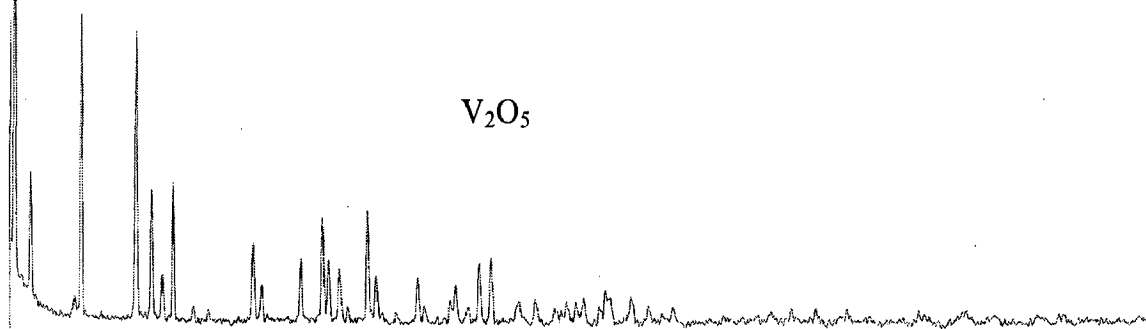
In Fig. 4.1 (b), the XRD pattern of 10%  $V_2O_5/TiO_2$  calcined at 700°C for 16h shows the prominent peaks of mixed oxide phase at  $2\theta = 34.5, 42.1, 52.9, 56.2, 65.0, 72.6, 78.5$ .  $V_2O_5$  peaks could be identified at  $2\theta = 26.2, 31.2, 62.2, 90.9$  while peaks corresponding to  $TiO_2$  could be observed at  $2\theta = 25.3, 27.6, 36.3, 41.5, 44.1, 48.1, 54.5, 69.1, 89.9$ . This pattern shows that there is slightly change to be observed with respect to the same calcined at 700°C for 6h.

In Fig. 4.1 (c), the XRD pattern of  $Ag/Fe_2O_3$  calcined at 700°C for 6h shows the prominent peaks of mixed oxide phase at  $2\theta = 24.4, 33.8, 36.0, 38.3, 41.1, 49.8, 54.5, 62.8$  e.t.c.  $Ag$  peaks could be identified at  $2\theta = 55.8, 74.9$  while peaks corresponding to  $Fe_2O_3$  could be observed at  $2\theta = 47.2, 63.9$ .

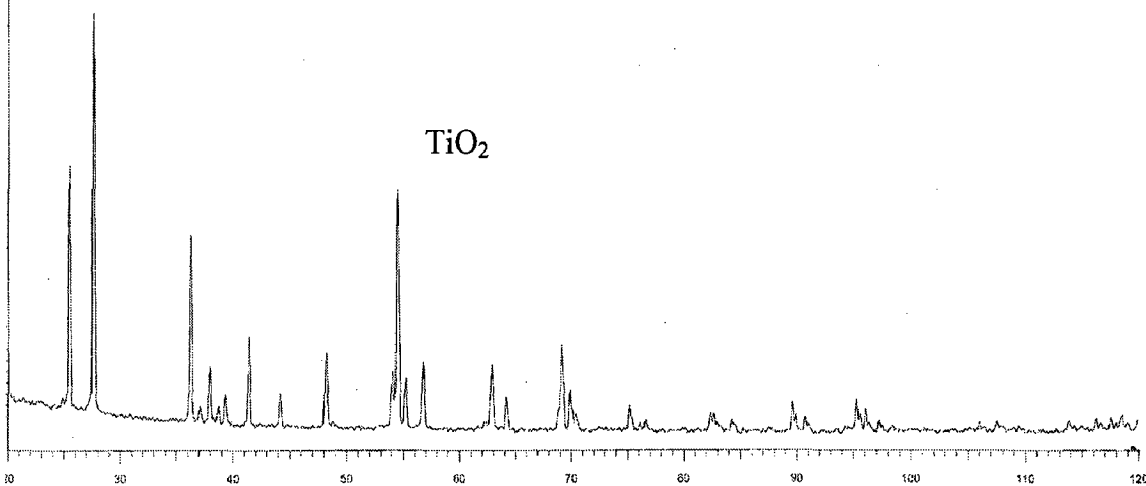
10% V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (700° C, 6h)



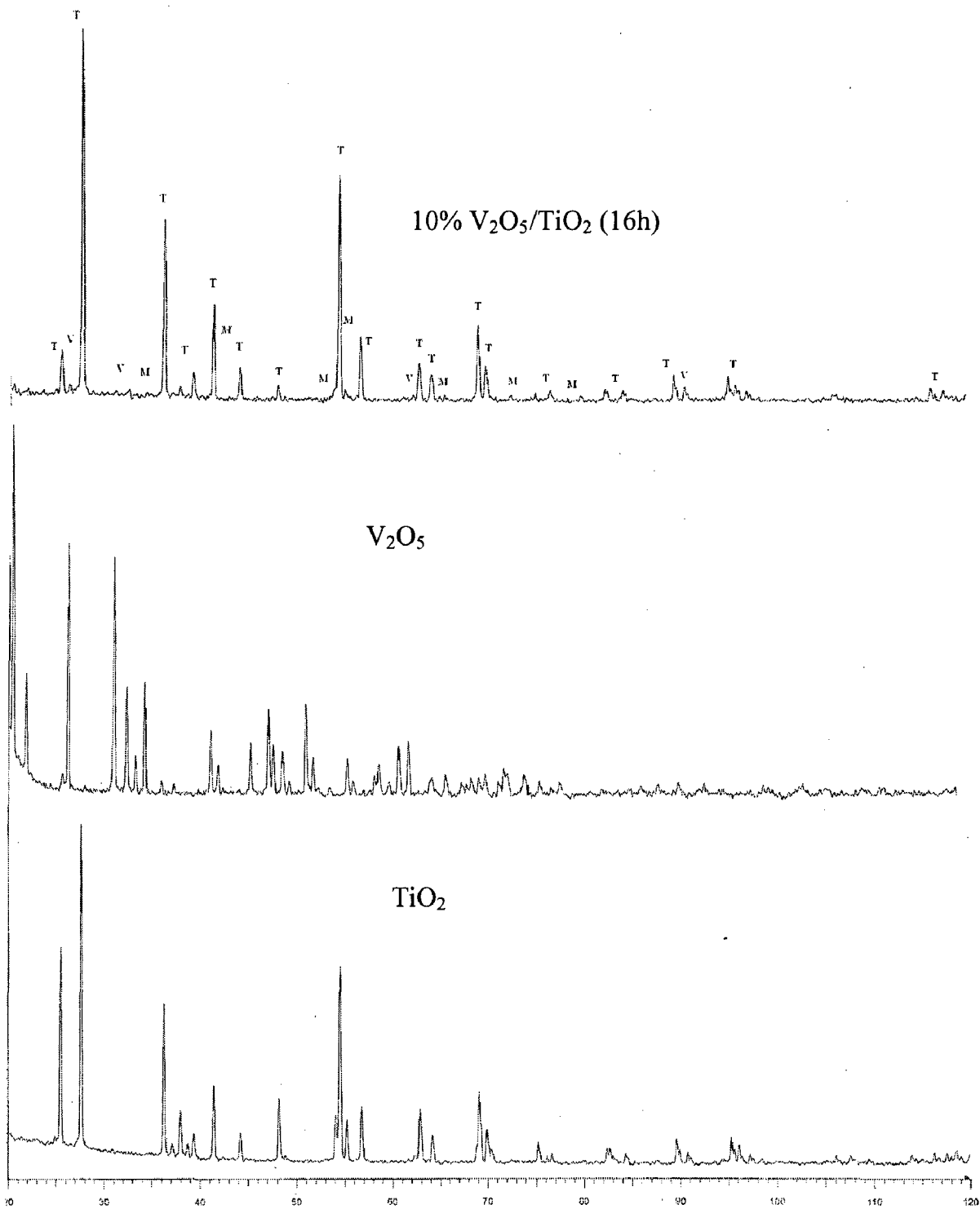
V<sub>2</sub>O<sub>5</sub>



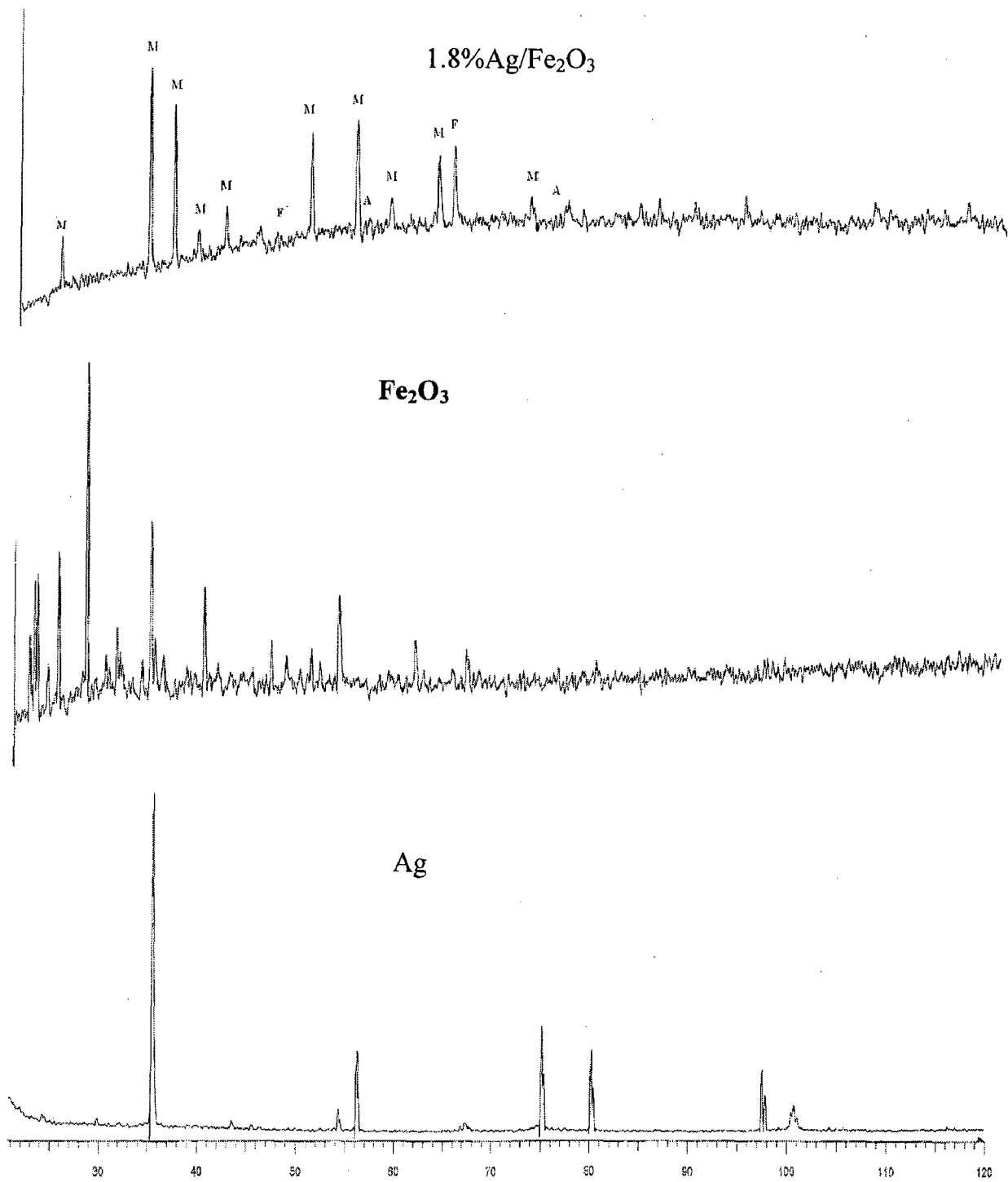
TiO<sub>2</sub>



(i)



(ii)

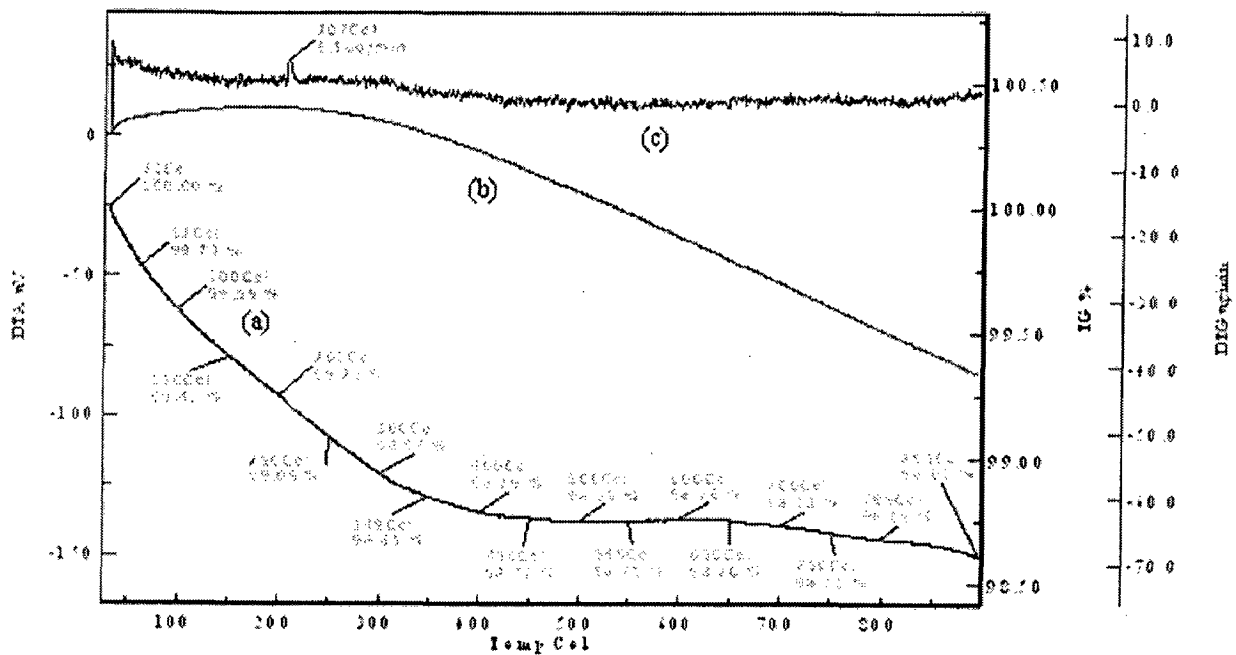


(iii)

Figure 4.1 XRD pattern of  
 (i) 10% V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (700° C, 6h) (M) of V<sub>2</sub>O<sub>5</sub> (V) and TiO<sub>2</sub> (T),  
 (ii) 10% V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (700° C, 16h) (M) of V<sub>2</sub>O<sub>5</sub> (V) and TiO<sub>2</sub> (T)  
 and (iii) 1.8%Ag/Fe<sub>2</sub>O<sub>3</sub>(700° C, 6h) (M) of Ag (A) and Fe<sub>2</sub>O<sub>3</sub> (F)

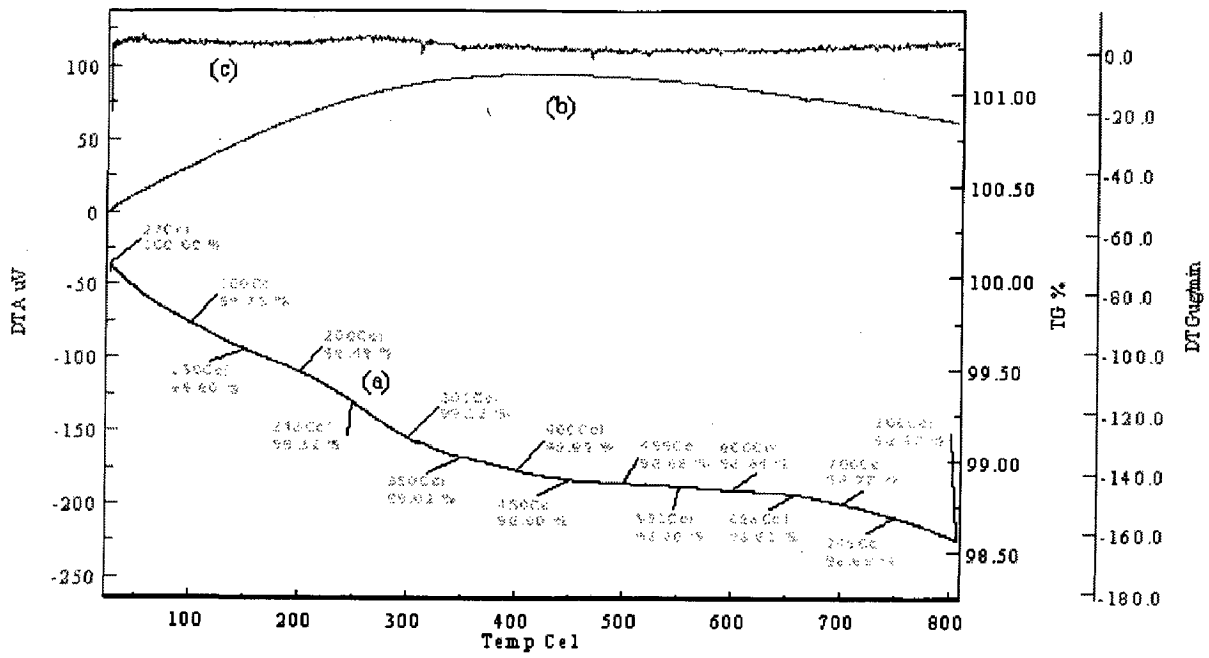
### 4.1.2 Thermo Gravimetric Analysis

This analysis describes how the mass of the compound decreases on increasing the temperature as there can be elimination of some moisture, some volatile oxides or nitrates e.t.c. This is important with respect to the reaction temperature because during the reaction we don't know whether the products coming from the reactor, are reaction products only or they are removal from the catalyst material. Fig. 4.2 shows that there is only maximum 1.3% decrease in the mass of the catalyst upto 300<sup>o</sup> C.

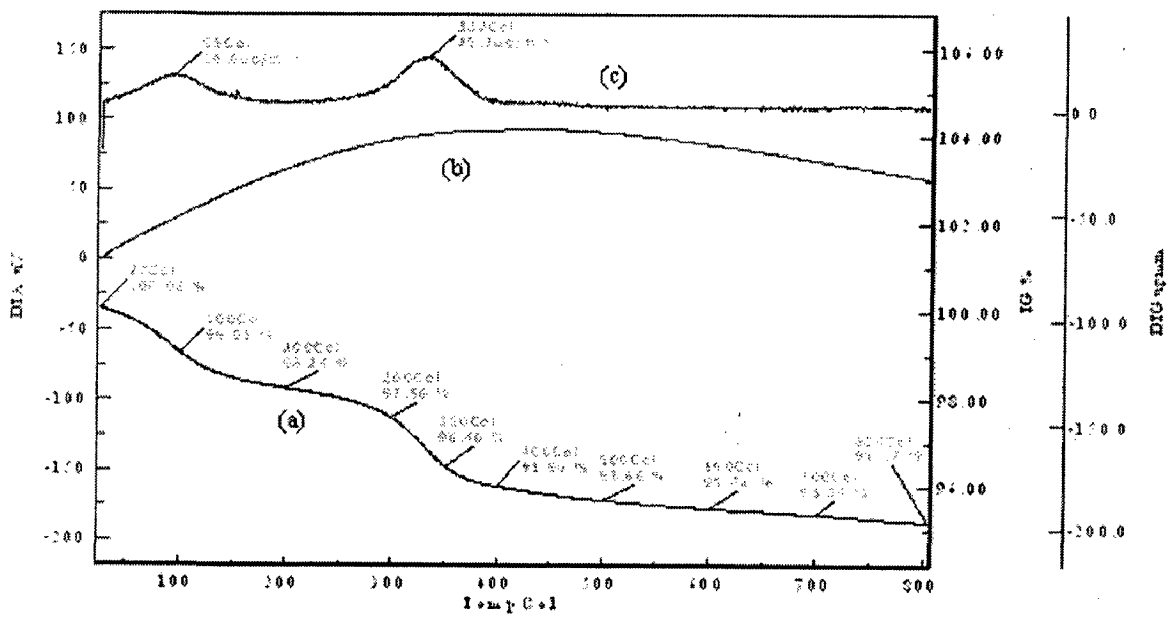


(i)

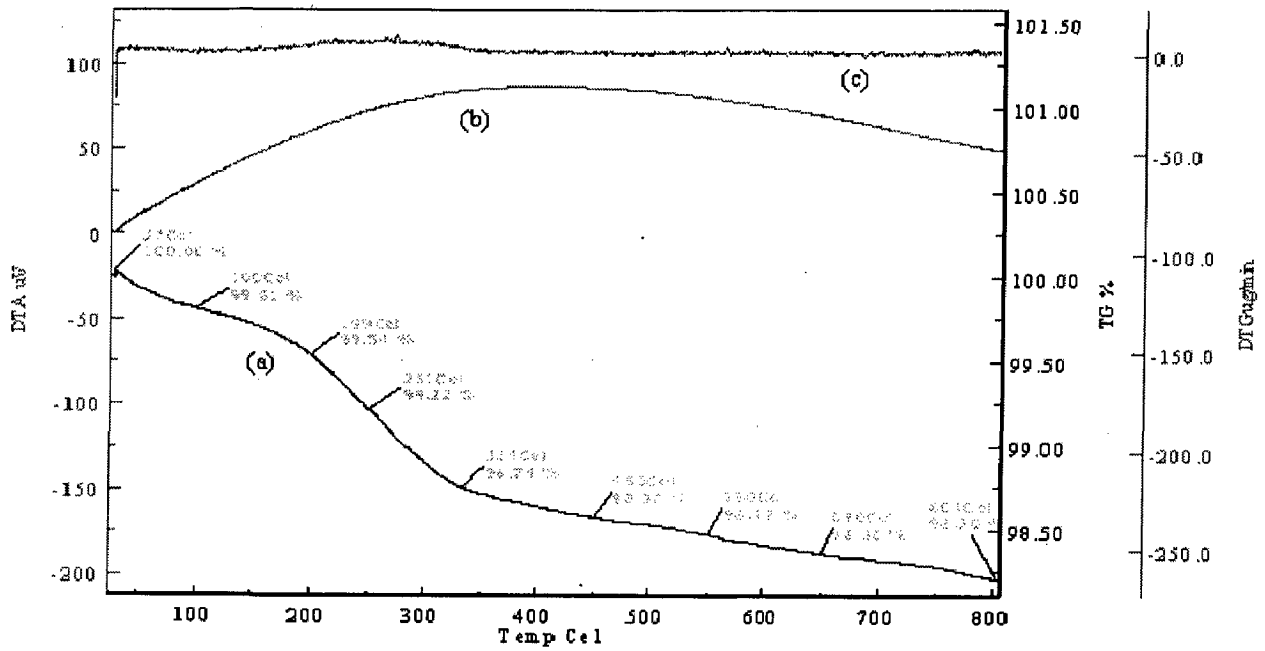




(ii)



(iii)

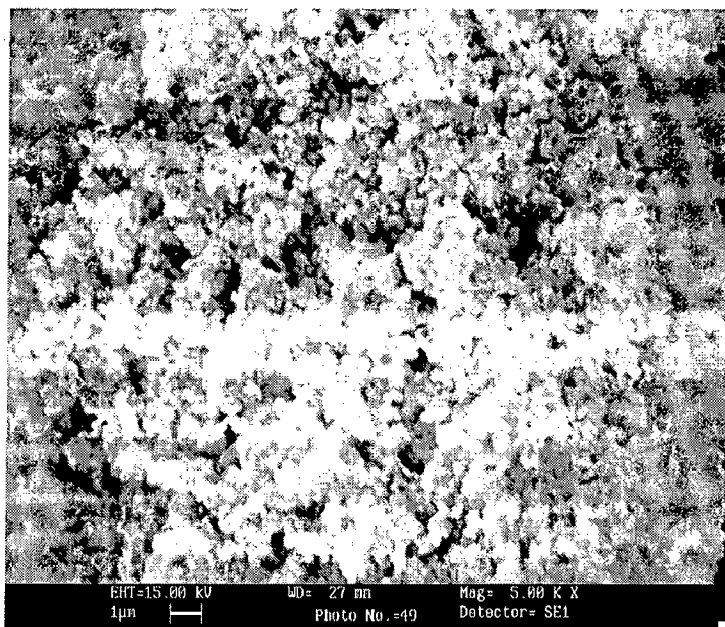


(iv)

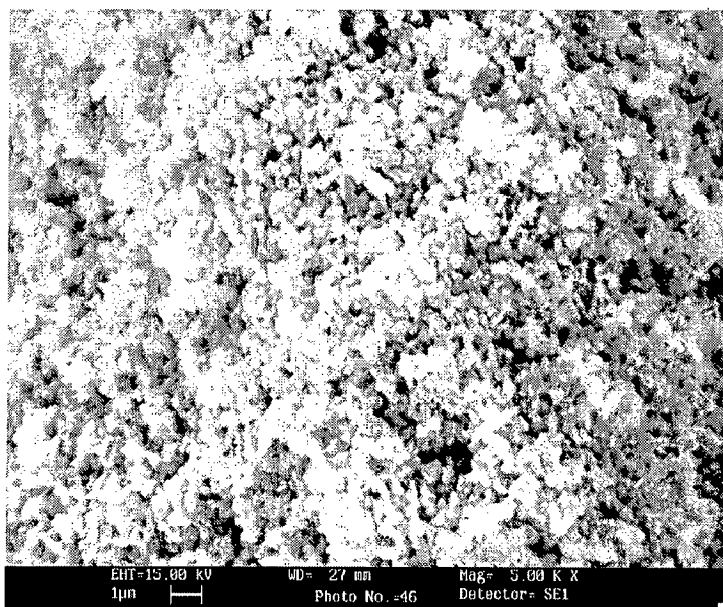
Figure 4.2 TGA (a) of  
 (i) 10%V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (700° C, 6h),  
 (ii) 10%V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (700° C, 16h),  
 (iii) 10%V<sub>2</sub>O<sub>5</sub>/MgO (700° C, 6h),  
 and (iv) 1.8%Ag/Fe<sub>2</sub>O<sub>3</sub> (700° C, 6h)

### 4.1.3 Scanning Electron Micrograph

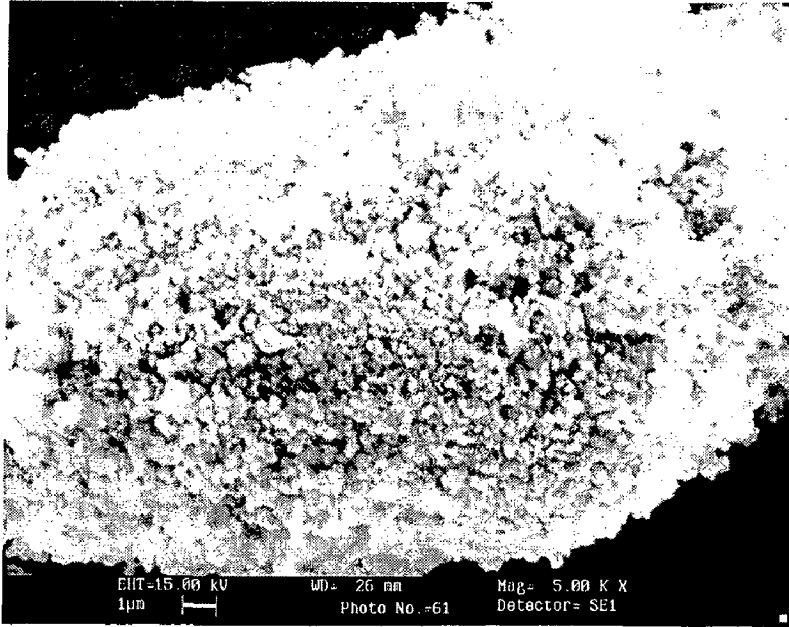
This microscopy shows the micrograms of the solid material. For all the catalysts we can see their micro structures in Fig. 4.3. These structures also show the mixing of the two components at molecular level as well as their equivalent diameter i.e. in between 5-50  $\mu\text{m}$  which will give a good contact area to the reactants for reaction.



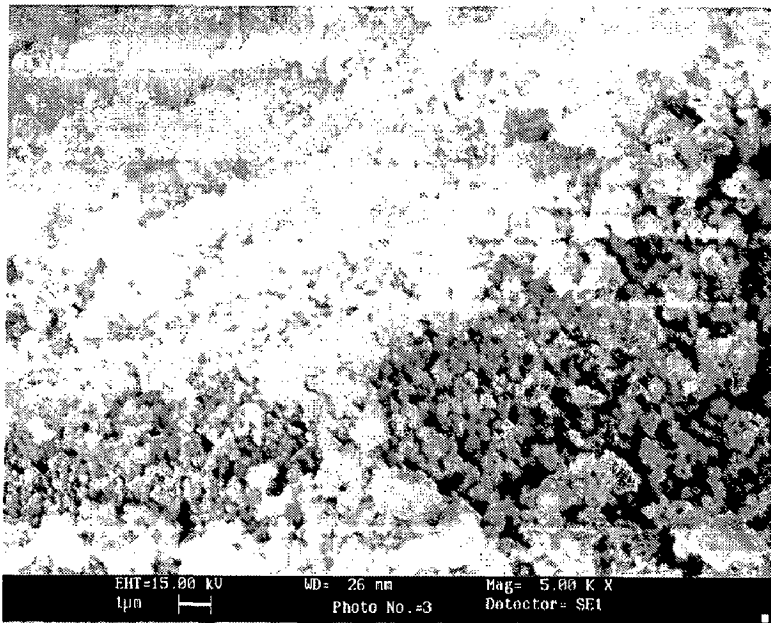
(i)



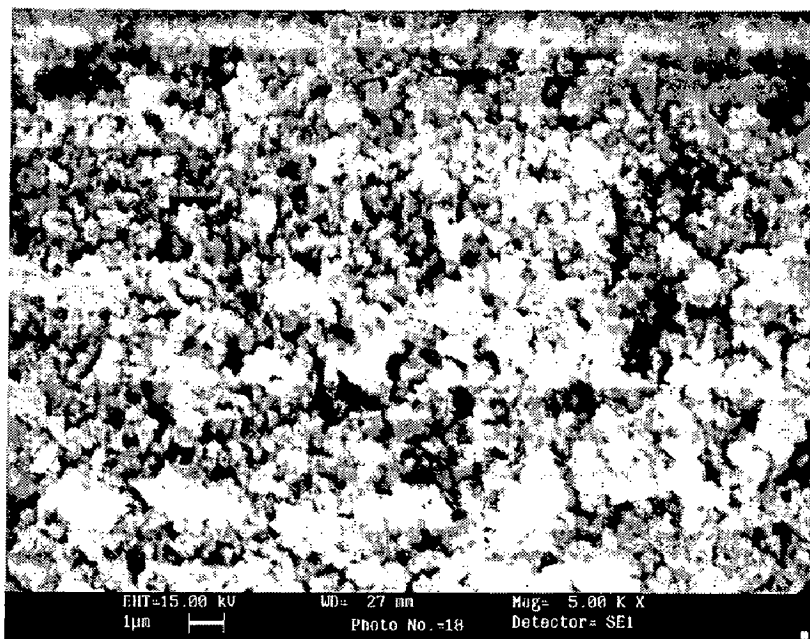
(ii)



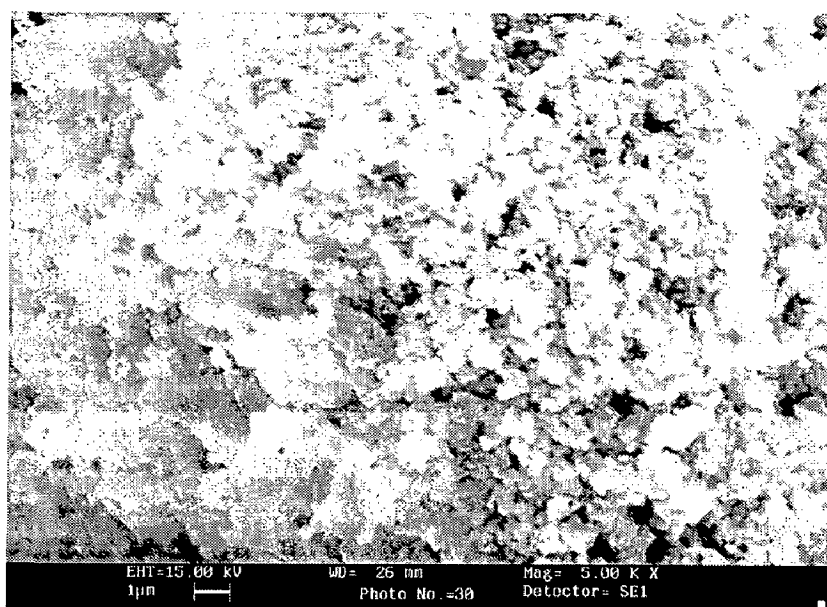
(iii)



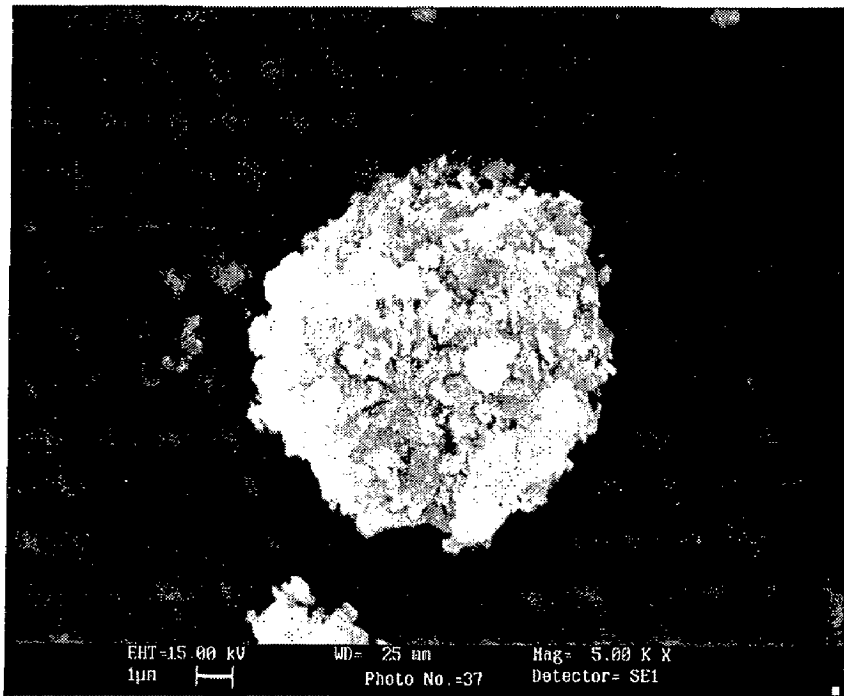
(iv)



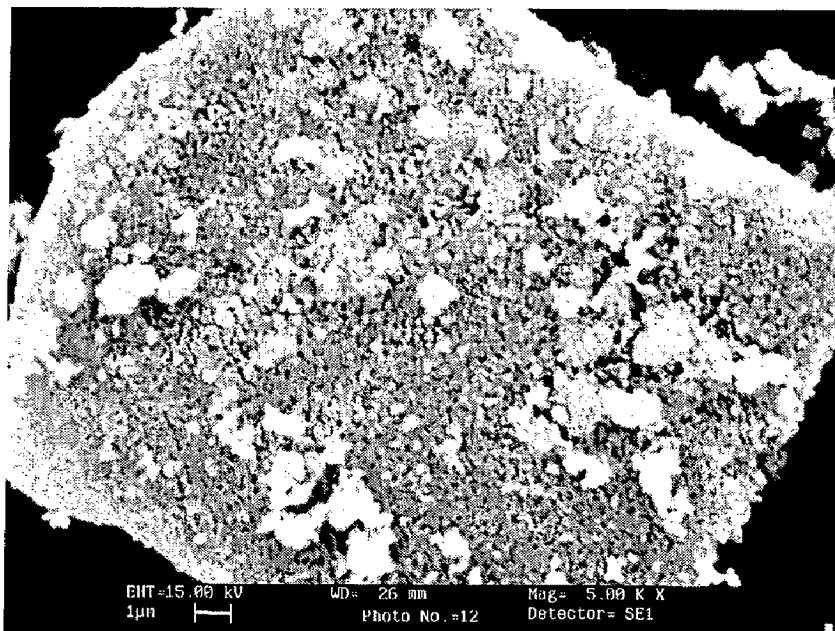
(v)



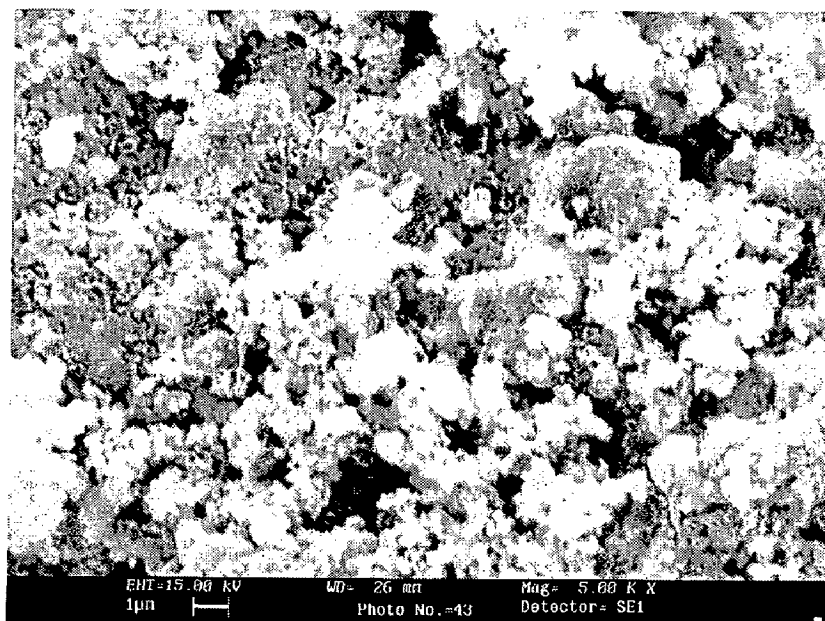
(vi)



(vii)



(viii)



(ix)

Figure 4.3 Scanning Electron Micrograms of  
(i) 1%V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (700° C, 6h), (ii) 3%V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (700° C, 6h),  
(iii) 5%V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (700° C, 6h), (iv) 10%V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (700° C, 6h),  
(v) 1%V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (700° C, 16h), (vi) 5%V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (700° C, 16h),  
(vii) 10%V<sub>2</sub>O<sub>5</sub>/MgO (700° C, 6h), (viii) 0.36%Ag/Fe<sub>2</sub>O<sub>3</sub> (700° C, 6h)  
and (ix) 0.54%Ag/Fe<sub>2</sub>O<sub>3</sub> (700° C, 6h)

## 4.2 ACTIVITY ANALYSIS

This part of the chapter contains activity of different catalysts in terms of the percentage conversion of methanol at different temperatures. With this, the % conversion of methanol to formaldehyde and % selectivity of formaldehyde has also been discussed.

The following tables show the calculated results of the data obtained after conducting the experiments. Table 4.1 shows the compounds name with their given serial no. and their corresponding mass used in the reactor during the catalytic reaction. Table 4.2 represents the % conversion of methanol to formaldehyde and other side products at different reaction temperatures on different catalysts. Table 4.3 represents the selectivity obtained of formaldehyde as a function of reaction temperature on different catalysts.

Table 4.1 Compounds with their given serial numbers and mass in grams used in the reaction

S.No.	Compound	Calcination period (hours) at 700° C	Mass (grams)
1	1%V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub>	6	0.2429
2	3%V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub>	6	0.2262
3	5%V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub>	6	0.2562
4	10%V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub>	6	0.3220
5	1%V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub>	16	0.2342
6	3%V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub>	16	0.2688
7	5%V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub>	16	0.2300
8	10%V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub>	16	0.2665
9	1%V <sub>2</sub> O <sub>5</sub> /MgO	6	0.2464
10	3%V <sub>2</sub> O <sub>5</sub> /MgO	6	0.2520
11	5%V <sub>2</sub> O <sub>5</sub> /MgO	6	0.2593
12	10%V <sub>2</sub> O <sub>5</sub> /MgO	6	0.2532
13	0.18%Ag/Fe <sub>2</sub> O <sub>3</sub>	6	0.2720
14	0.36%Ag/Fe <sub>2</sub> O <sub>3</sub>	6	0.2641
15	0.54%Ag/Fe <sub>2</sub> O <sub>3</sub>	6	0.3520
16	1.8%Ag/Fe <sub>2</sub> O <sub>3</sub>	6	0.3556



Table 4.2 %Conversion of methanol to formaldehyde and other products as a function of reaction temperature on different catalysts with their serial numbers as given in Table 4.1

No	% Conversion of methanol														
	At 100° C			At 150° C			At 200° C			At 250° C			At 300° C		
	HCHO	Other	Total	HCHO	Other	Total	HCHO	Other	Total	HCHO	Other	Total	HCHO	Other	Total
1	0.82	0.75	1.57	1.84	1.23	3.07	15.32	1.15	16.47	30.32	0.92	31.24	40.16	0.35	40.51
2	0	0	0	0.95	0.85	1.80	8.76	0.86	9.62	13.96	0.98	14.94	16.04	0.72	16.76
3	0	0	0	1.43	0.84	2.27	12.92	0.95	13.87	20.29	0.87	21.16	22.32	0.75	23.07
4	0	0	0	1.89	0.93	2.82	15.78	0.84	16.62	48.02	0.78	48.8	54.33	0.98	55.31
5	0.83	0.92	1.75	1.59	0.04	1.63	15.89	0.25	16.14	30.16	0.09	30.25	40.70	0.25	40.98
6	0	0	0	2.05	0.02	2.07	9.27	0.23	9.50	15.05	0.08	15.13	25.80	0.64	26.44
7	0	0	0	6.93	0.04	6.97	10.88	0.10	10.98	16.09	0.04	16.13	30.70	0.06	30.82
8	0	0	0	5.09	0.04	5.13	15.32	0.07	15.39	47.85	0.08	47.93	53.77	0.06	53.83
9	0	0	0	0	0	0	0.56	0.32	0.88	9.54	0.97	10.51	11.33	0.86	12.19
10	0	0	0	0	0	0	0.54	0.52	1.06	7.04	0.99	8.03	8.92	0.89	9.81
11	0	0	0	0	0	0	0.81	0.60	1.41	8.53	1.05	9.58	18.72	1.22	19.94
12	0	0	0	0	0	0	1.23	0.89	2.12	11.02	1.07	12.09	32.33	2.00	34.33
13	0	0	0	1.62	0.89	2.51	3.39	0.97	4.36	5.32	0.99	6.31	2.23	0.98	3.21
14	0	0	0	1.89	1.40	3.29	4.33	1.43	5.76	6.32	1.45	7.77	2.57	1.49	4.06
15	0	0	0	2.09	1.84	3.93	6.52	1.79	8.31	10.43	1.87	12.30	4.22	1.89	6.11
16	0	0	0	2.55	2.04	4.59	8.79	2.05	10.84	14.97	2.10	17.07	3.92	2.14	6.06

Table 4.3 % Selectivity of formaldehyde at different temperatures on different catalysts with their serial numbers as given in Table 4.1.

S No.	% Selectivity of formaldehyde				
	At 100°C	At 150°C	At 200°C	At 250°C	At 300°C
1	52.23	59.93	93.02	97.06	99.14
2	-	52.78	91.06	93.44	95.70
3	-	63.00	93.15	95.89	96.75
4	-	67.02	94.95	98.40	98.23
5	97.65	97.55	98.45	99.70	99.39
6	-	99.03	97.58	99.47	97.58
7	-	99.22	99.09	99.75	99.80
8	-	99.43	99.55	99.83	99.89
9	-	-	63.64	90.77	92.95
10	-	-	50.94	87.67	90.93
11	-	-	57.44	89.04	93.88
12	-	-	58.02	91.15	94.17
13	-	57.45	77.75	84.31	69.07
14	-	53.18	75.60	81.34	63.30
15	-	55.56	78.46	84.80	64.69
16	-	64.54	81.09	87.70	69.47

The results on the basis of the plots obtained with respect to different variables e.g. reaction temperature, % composition of the catalytic material on the supports e.t.c. have been discussed.

#### 4.2.1 Effect of Reaction Temperature

Fig. 4.4 through Fig. 4.7 show the effects of reaction temperature and catalyst composition both, in all the plots for different catalytic materials. Fig. 4.4 shows the variation in total % conversion of methanol as a function of reaction temperature for different compositions of  $V_2O_5/TiO_2$  ( $700^\circ C$ , 6h) catalyst. It is found that there is an increase in conversion of methanol on increasing the temperature for each composition of  $V_2O_5/TiO_2$ . A methanol conversion was 1.57% at  $100^\circ C$  using 1%  $V_2O_5/TiO_2$ , increases on increasing temperature to 40.55% conversion at  $300^\circ C$ . For other compositions of 3, 5 and 10 %  $V_2O_5/TiO_2$  at  $100^\circ C$  there was no conversion but increases on increasing the temperature and at  $300^\circ C$  conversions of 16.76, 23.07 and 55.41% were obtained respectively.

A similar pattern was observed in Fig. 4.5 like Fig. 4.4 for different compositions of  $V_2O_5/TiO_2$  ( $700^\circ C$ , 16h) but for corresponding variables, some higher conversion was observed.

Fig. 4.6 shows the activity of different composition of  $V_2O_5/MgO$ . It is observed that at  $100^\circ C$  and  $150^\circ C$  there was no conversion for all compositions of  $V_2O_5/MgO$  which increased with increase in the temperature for all compositions of  $V_2O_5/MgO$  and reached 12.19, 9.81, 19.94 and 34.33% at  $300^\circ C$ , respectively, for 1, 3, 5 and 10 % composition of  $V_2O_5/MgO$ .

Fig. 4.7 depicts the similar plot for different compositions of  $Ag/Fe_2O_3$ . From this it is observed that at  $100^\circ C$  there was no conversion for all the compositions of  $Ag/Fe_2O_3$  which increased with increase in the temperature for all the compositions of  $Ag/Fe_2O_3$  and reached 6.31, 7.77, 12.3 and 17.07% conversions at  $250^\circ C$  respectively for 0.18, 0.36, 0.54 and 1.80 % composition. On further raising the reaction temperature, the conversion dropped to 3.21, 4.06, 6.11 and 6.06 at  $300^\circ C$ .

Fig. 4.8 through Fig. 4.11 show the effect of temperature on the %selectivity of formaldehyde for different catalysts mentioned above. These curves represent that the selectivity of formaldehyde increases with increasing the reaction temperature and reaches >99% at  $300^\circ C$ .

### 4.2.2 Effect of Catalyst Composition

Fig. 4.12 through Fig. 4.15 show the effect of % composition of the catalyst and their supports on the % selectivity of formaldehyde in the reaction products formed at 150° C, 200° C, 250° C and 300° C. Fig. 4.12 shows that at all four temperatures, the selectivity decreases with respect to the increase in the % composition of V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (700° C, 6h) and further increasing the composition, it increases and reached its maximum values, however corresponding values at 150° C are very low in comparison to other reaction temperatures. Fig. 4.13 shows that at all four temperatures, the % selectivity of formaldehyde decreases with respect to the increase in the % composition of V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (700° C, 16h), except the plot for 150° C reaction temperature that is showing increment in the % selectivity upto 5% V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>, from 3 to 10 %, the % selectivity increases and reached its maximum value at 40.31, 466.32 and 896.17 respectively at 300° C. Fig. 4.14 shows a similar pattern at lower compositions of V<sub>2</sub>O<sub>5</sub>/MgO (700° C, 6h). The % selectivity was very low at all four temperatures and further increase in the composition of V<sub>2</sub>O<sub>5</sub>/MgO (700° C, 6h), increases the % selectivity. Fig. 4.15 shows the same pattern as in Fig. 4.14 because at lower compositions of Ag/Fe<sub>2</sub>O<sub>3</sub>, the % selectivity was very low at all four temperatures and further increase in the composition of Ag/Fe<sub>2</sub>O<sub>3</sub>, increased at a slower rate than the rate in Fig. 4.14.

### 4.2.3 Effect of Different Catalysts

Fig. 4.16 gives an idea about the variation in % selectivity of formaldehyde as a function of reaction temperature for 10%V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (700° C, 6h), 10%V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (700° C, 16h), 10%V<sub>2</sub>O<sub>5</sub>/MgO (700° C, 6h) and 1.8 %Ag/Fe<sub>2</sub>O<sub>3</sub> (700° C, 6h). Here we have chosen the catalysts giving good conversion i.e. found to be at highest composition. In all the cases the selectivity is found to be increasing with respect to the reaction temperature except for 1.8 %Ag/Fe<sub>2</sub>O<sub>3</sub> (700° C, 6h) because here this catalyst gives a decrease in the selectivity after 250° C. In the remaining cases this is in the increasing order as it reached > 99.0 % after 200° C and remain upto 300° C. Here if we compare the effect of the calcinations period as 6h and 16h, we found selectivity reached to maximum in case of 10%V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (700° C, 16h) at faster rate than the same for 10%V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (700° C, 6h).

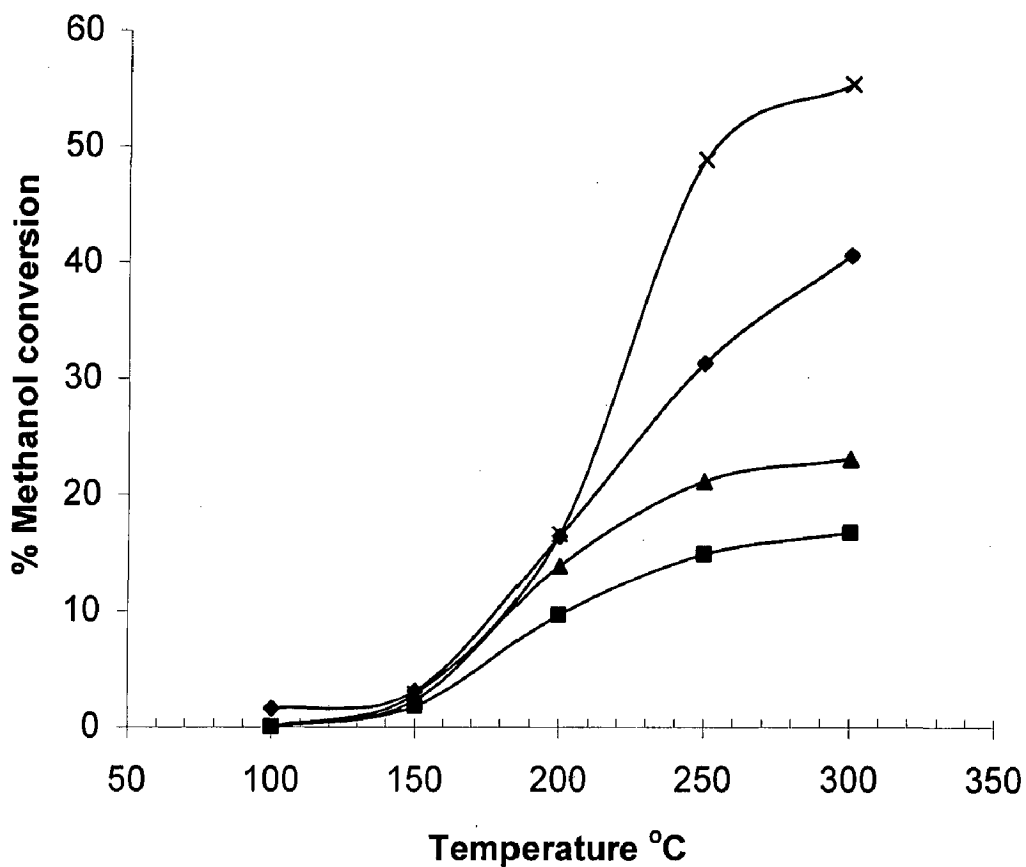
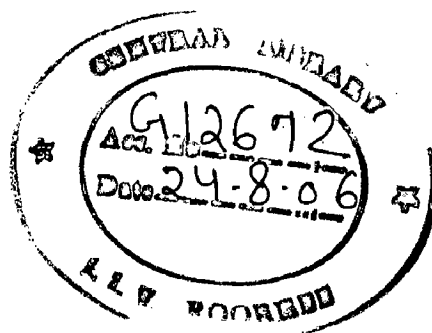


Figure 4.4 Total % conversion of methanol as a function of reaction temperature for different catalysts 1%V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (♦), 3%V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (■), 5%V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (▲), 10%V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (×) calcined for 6h at 700° C, GHSV = 4300 h<sup>-1</sup>, CH<sub>3</sub>OH/Air = 2.0.



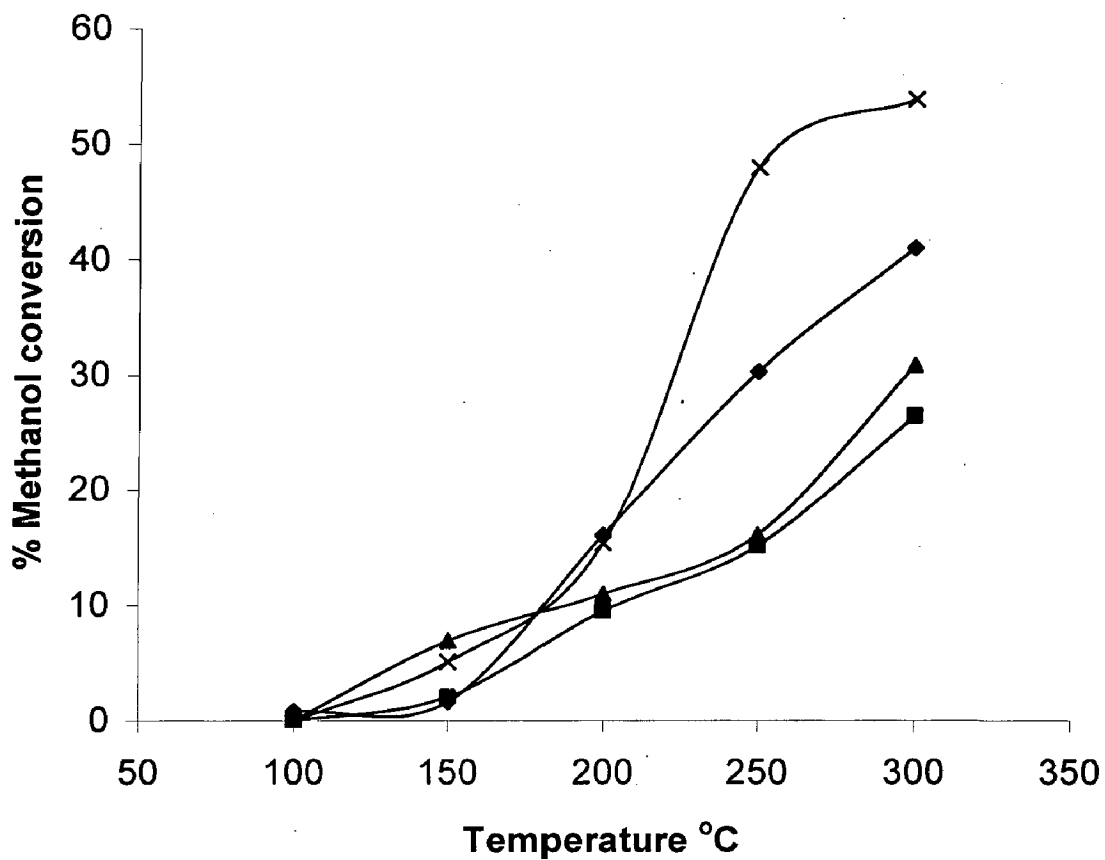


Figure 4.5 Total % conversion of methanol as a function of reaction temperature for 1%V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (♦), 3%V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (■), 5%V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (▲), 10%V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (×) calcined for 16h at 700° C, GHSV = 4300 h<sup>-1</sup>, and CH<sub>3</sub>OH/Air = 2.0.

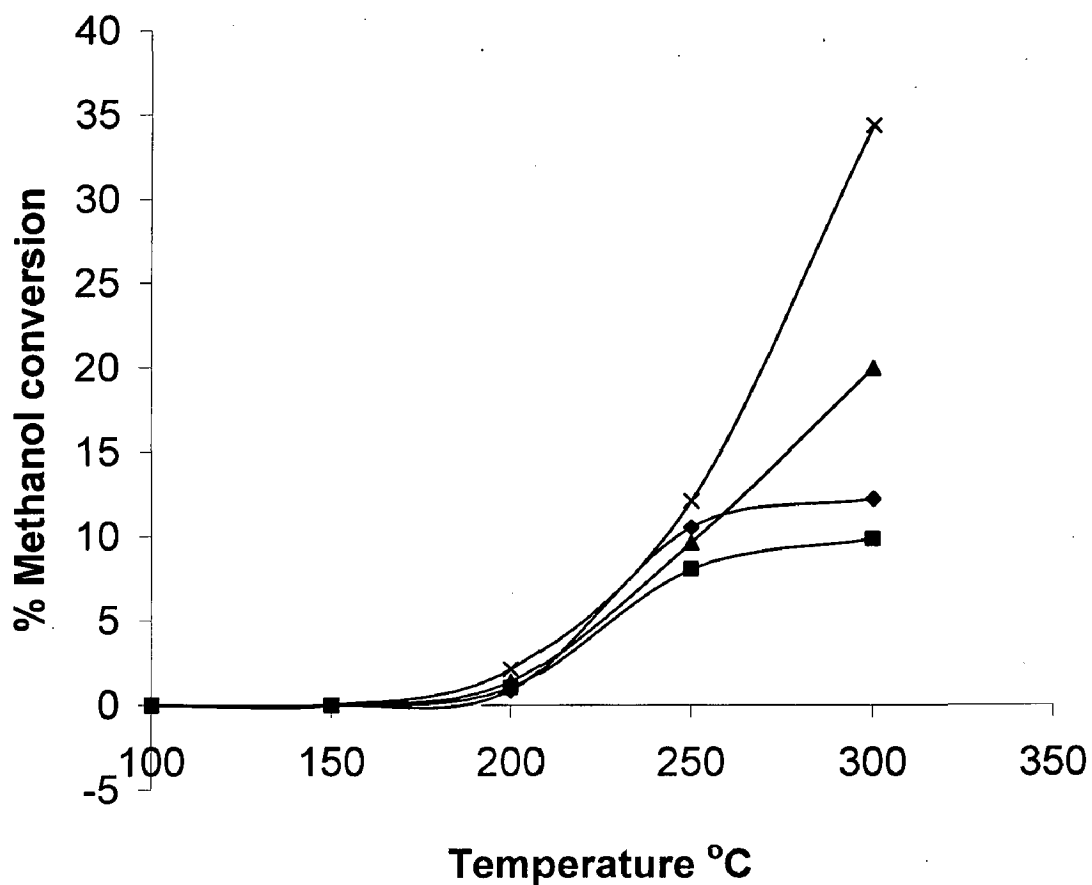


Figure 4.6 Total % Conversion of methanol as a function of reaction temperature for 1%V<sub>2</sub>O<sub>5</sub>/MgO (◆), 3%V<sub>2</sub>O<sub>5</sub>/MgO (■), 5%V<sub>2</sub>O<sub>5</sub>/MgO (▲), 10%V<sub>2</sub>O<sub>5</sub>/MgO (×) calcined for 6h at 700° C, GHSV = 4300 h<sup>-1</sup>, CH<sub>3</sub>OH/Air = 2.0.

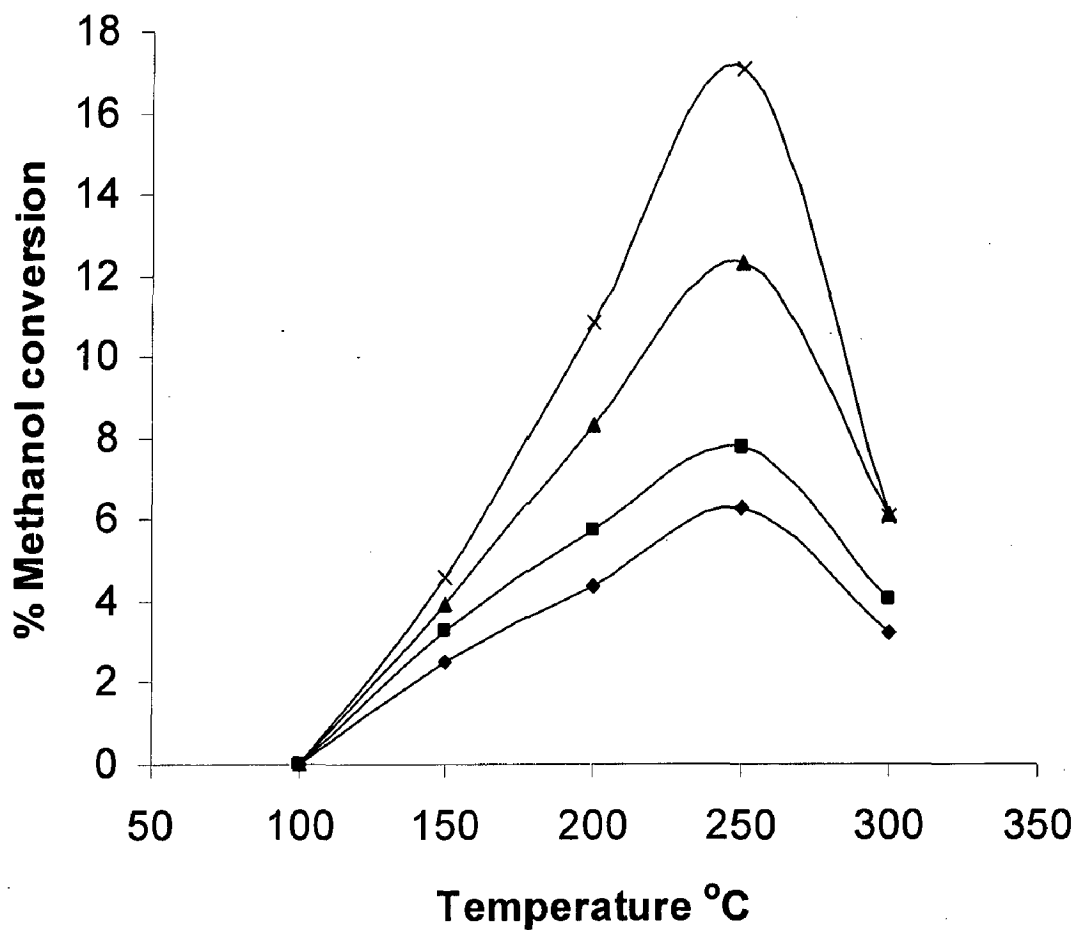


Figure 4.7 Total % conversion of methanol as a function of reaction temperature for 0.18%Ag/Fe<sub>2</sub>O<sub>3</sub> (◆), 0.36%Ag/Fe<sub>2</sub>O<sub>3</sub> (■), 0.54%Ag/Fe<sub>2</sub>O<sub>3</sub> (▲), 1.8%Ag/Fe<sub>2</sub>O<sub>3</sub> calcined for 6h at 700° C, GHSV = 4300 h<sup>-1</sup>, CH<sub>3</sub>OH/Air = 2.0.



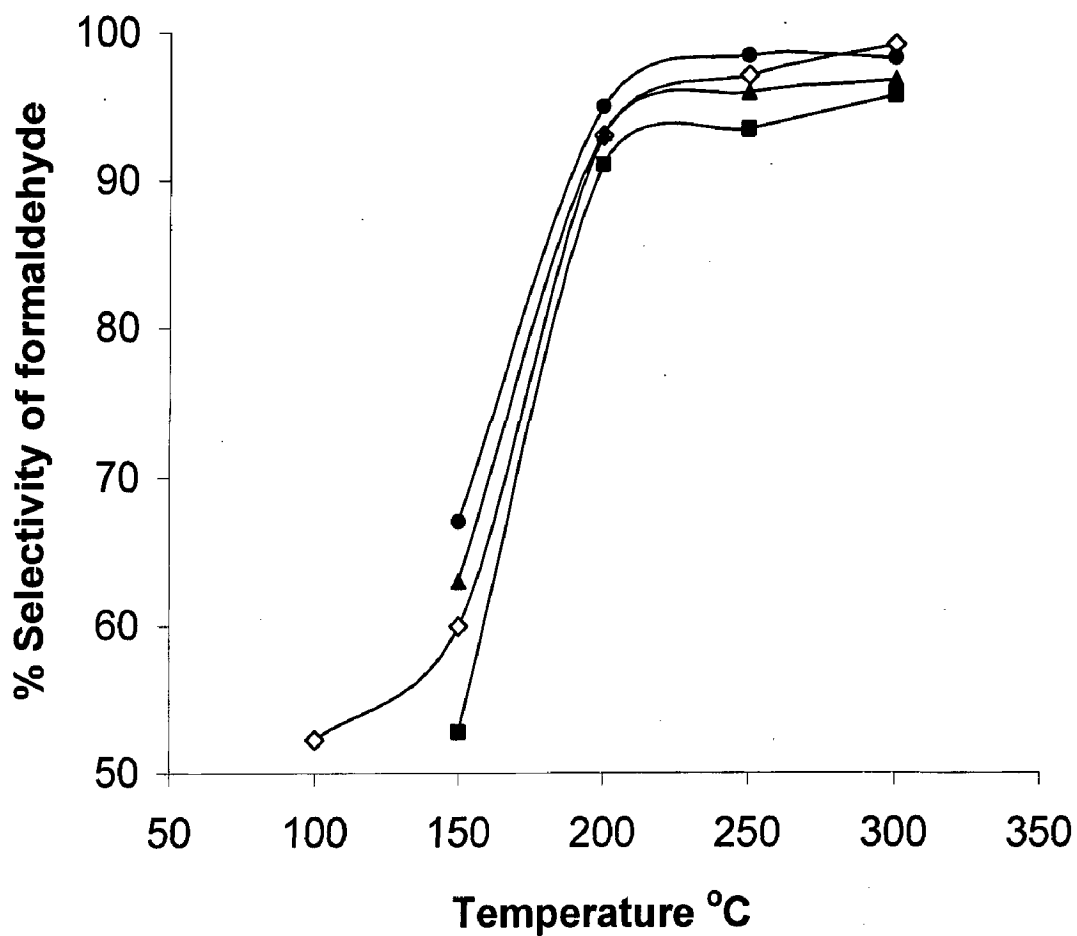


Figure 4.8 % Selectivity of formaldehyde as a function of reaction temperature for different catalysts 1%V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (♦), 3%V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (■), 5%V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (▲), 10%V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (×) calcined for 6h at 700° C, GHSV = 4300 h<sup>-1</sup>, CH<sub>3</sub>OH/Air = 2.0.

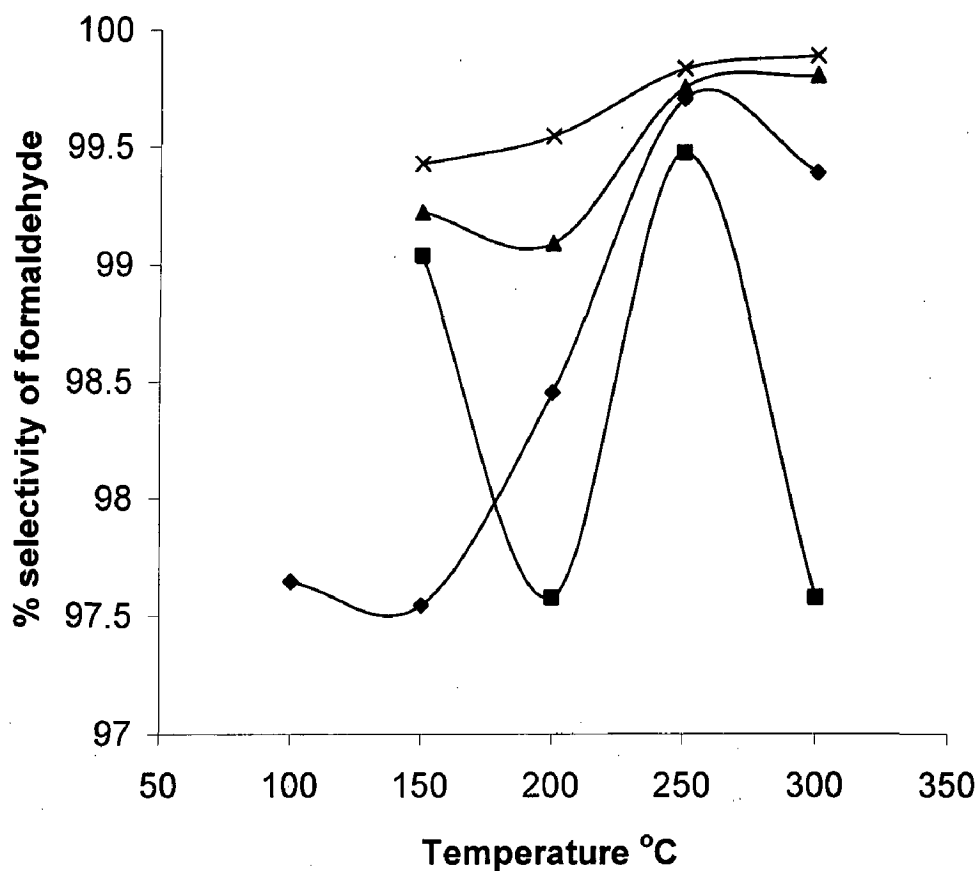


Figure 4.9 % Selectivity of formaldehyde as a function of reaction temperature for 1%V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (♦), 3%V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (■), 5%V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (▲), 10%V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (×) calcined for 16h at 700° C, GHSV = 4300 h<sup>-1</sup>, CH<sub>3</sub>OH/Air = 2.0.

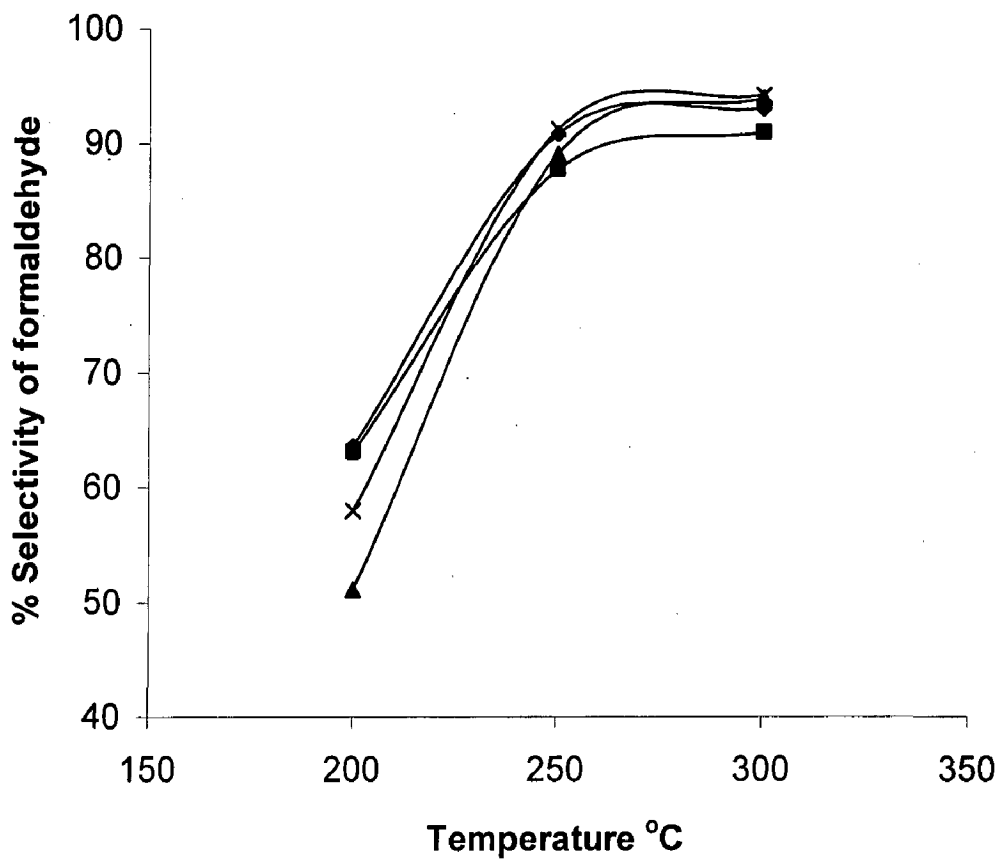


Figure 4.10 % Selectivity of formaldehyde as a function of reaction temperature for 1%V<sub>2</sub>O<sub>5</sub>/MgO (♦), 3%V<sub>2</sub>O<sub>5</sub>/MgO (■), 5%V<sub>2</sub>O<sub>5</sub>/MgO (▲), 10%V<sub>2</sub>O<sub>5</sub>/MgO (×) calcined for 6h at 700° C, GHSV = 4300 h<sup>-1</sup>, CH<sub>3</sub>OH/Air = 2.0.

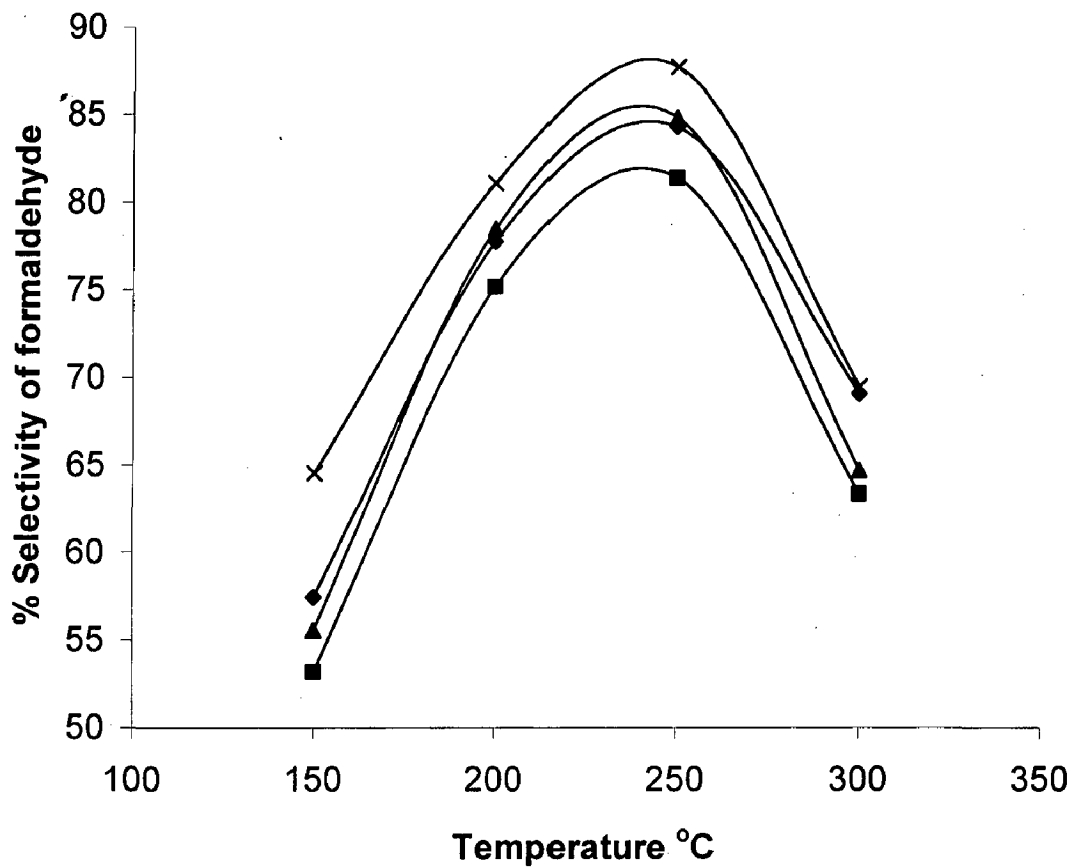


Figure 4.11 % Selectivity of formaldehyde as a function of reaction temperature for 0.18%Ag/Fe<sub>2</sub>O<sub>3</sub> (♦), 0.36%Ag/Fe<sub>2</sub>O<sub>3</sub> (■), 0.54%Ag/Fe<sub>2</sub>O<sub>3</sub> (▲), 1.8%Ag/Fe<sub>2</sub>O<sub>3</sub> (×) calcined for 6h at 700° C, GHSV = 4300 h<sup>-1</sup>, CH<sub>3</sub>OH/Air = 2.0.

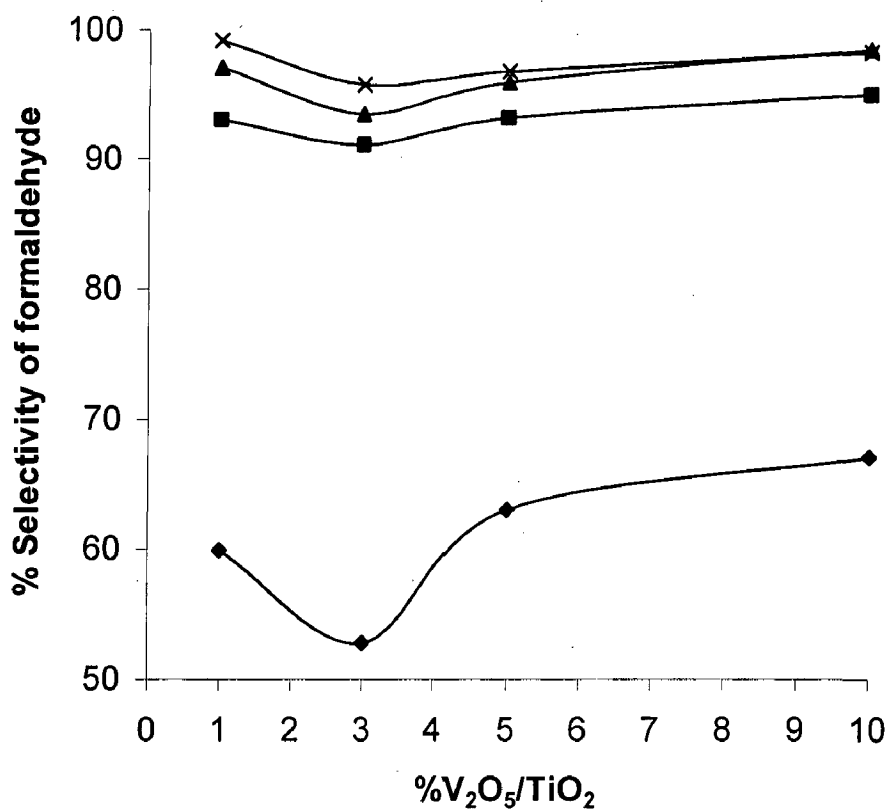


Figure 4.12 % Selectivity of formaldehyde as a function of %V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (calcined for 6h at 700° C), at 150°C (◆), 200°C (■), 250°C (▲) and 300° C (×) (GHSV = 4300 h<sup>-1</sup>, CH<sub>3</sub>OH/Air = 2.0).

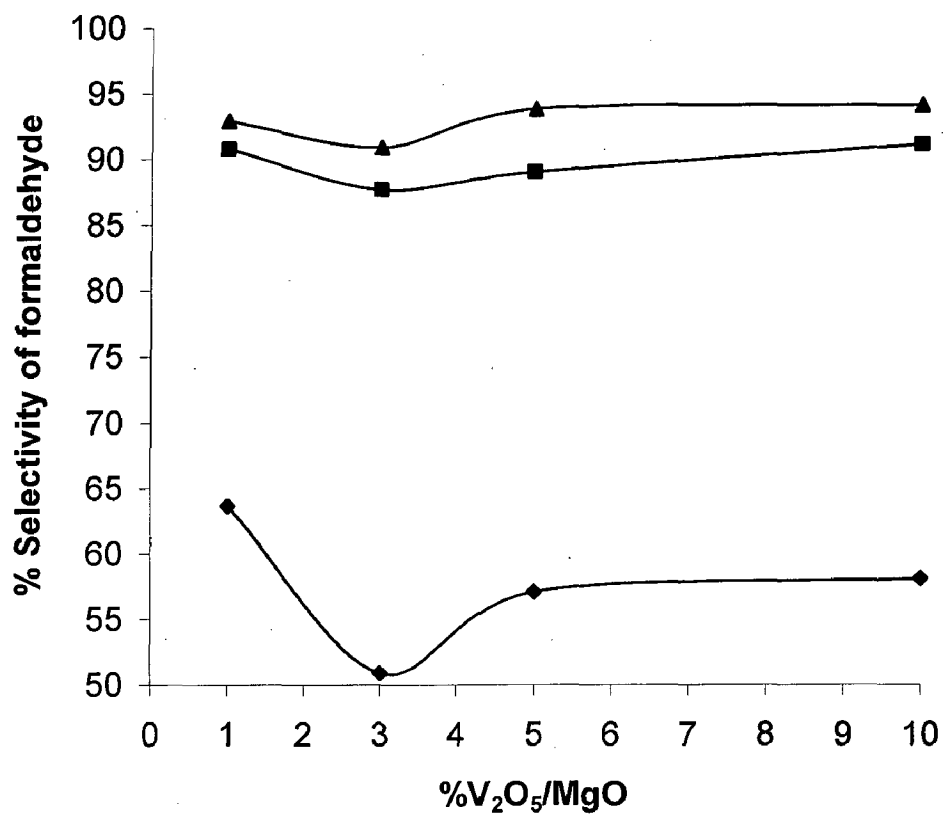


Figure 4.14 % Selectivity of formaldehyde as a function of %V<sub>2</sub>O<sub>5</sub>/MgO (calcined for 6h at 700° C) at 200°C (♦), 250°C (■) and 300°C (▲), GHSV = 4300 h<sup>-1</sup>, CH<sub>3</sub>OH/Air = 2.0.

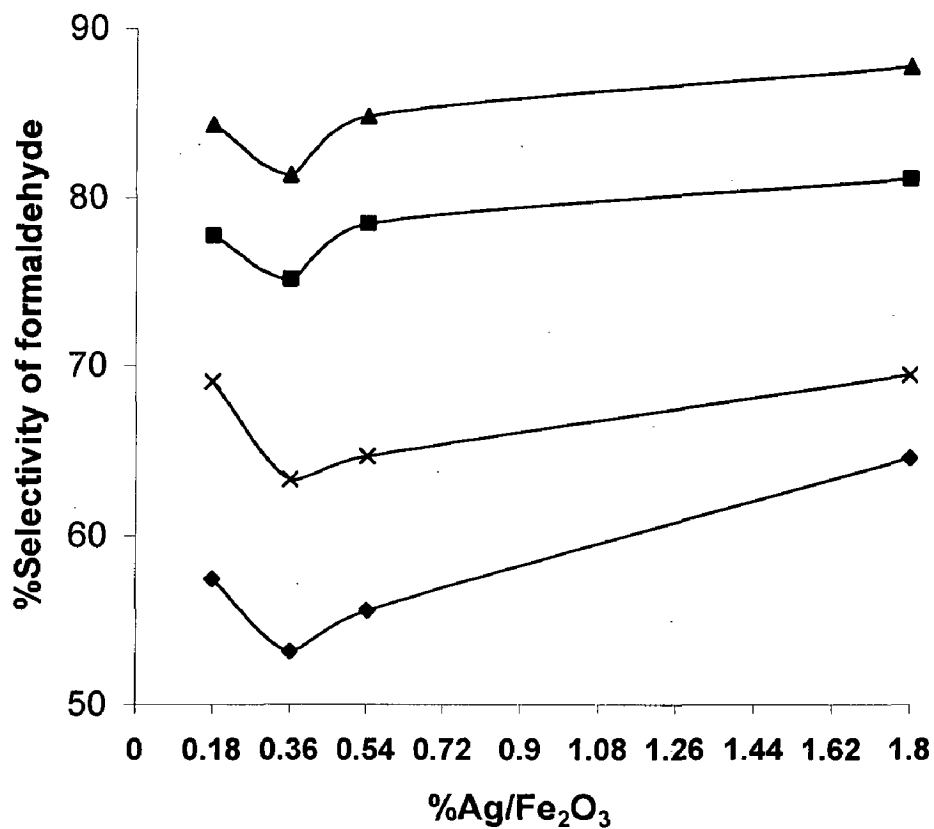


Figure 4.15 % Selectivity of formaldehyde as a function of %Ag/Fe<sub>2</sub>O<sub>3</sub> (calcined for 6h at 700° C) at 150° C (♦), 200° C (■), 250° C (▲) and 300° C (×), GHSV = 4300 h<sup>-1</sup>, CH<sub>3</sub>OH/Air = 2.0.

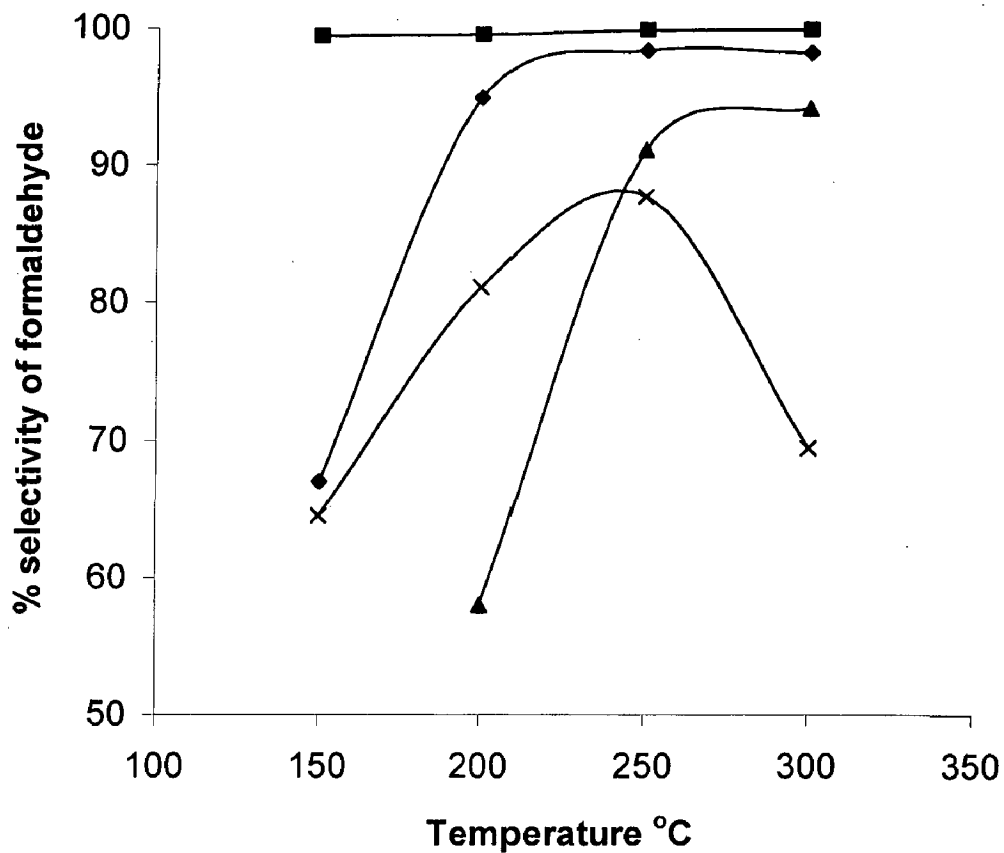


Figure 4.16 % Selectivity of formaldehyde as a function of reaction temperature for 10%V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (700° C, 6h) (◆), 10%V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (700° C, 16h) (■), 10%V<sub>2</sub>O<sub>5</sub>/MgO (700° C, 6h) (▲), 1.8 %Ag/Fe<sub>2</sub>O<sub>3</sub> (700° C, 6h) (×), GHSV = 4300 h<sup>-1</sup>, CH<sub>3</sub>OH/Air = 2.0.



## DISCUSSION:

Fig. 4.4 through 4.6, Fig. 4.8 and Fig. 4.10 show higher conversion of methanol at higher reaction temperatures, with high selectivity to formaldehyde for different compositions of the catalysts. The reason for this may be attributed to the endothermic nature of the reaction. On increasing the percentage composition of the  $V_2O_5/TiO_2$  from 1 to 10 there was a substantial increase in the conversion. This was due to the dehydrated surface vanadia species on other oxide supports possessing identical molecular structures as probed by Raman, IR, and solid state V NMR. Their molecular structural studies suggested that the dehydrated surface vanadia species on these oxide supports are primarily present as isolated and polymerized  $VO_4$  units as shown in Fig. 4.17. Low loading of the  $V_2O_5$  suggests isolated whereas high loading suggests polymerized surface vanadia species. The molecular structures of these surface vanadia species are tentatively thought to consist of a terminal  $V=O$  bond and three bridging  $V-O$ -support bonds for the isolated species, and for the polymerized species, it has a terminal  $V=O$  bond with one bridging  $V-O$ -support and two bridging  $V-O-V$  bonds. Thus in case of polymerized surface vanadia species, there is a more availability of active sites for the reaction. Fig. 4.9 shows a sequential change in the pattern of the plots with the variation in the reaction temperature for all compositions of the catalysts. Here at lower temperature, high selectivity decreased and again there was an increment and further a sequential decrement in the % selectivity was observed. For understanding this, few causes have been given but due to complex nature of catalytic reactions and specific nature of catalyst, it has not been clearly explained, however it has happened [9, 15]. Further in case of  $Ag/Fe_2O_3$  (Fig. 4.7 and Fig. 4.13) the catalytic surface was found to be poisoned giving a decrease in the conversion above  $250^\circ C$ . Further from Fig. 4.12 to Fig. 4.15, we can understand that at lower and higher composition of  $V_2O_5$  (1% and 10%) good % selectivity of formaldehyde was obtained at different reaction temperatures. In case of  $V_2O_5/MgO$  we found very low conversion of methanol, because unlike the  $TiO_2$  supported vanadia catalysts, the magnesia supported vanadia catalyst system cannot form a completely close packed surface vanadia monolayer because of the acid-base reaction between acidic vanadia and basic magnesia. The strong interaction between vanadia and magnesia might have resulted in the formation of a mixed metal oxide compound rather than a stable surface vanadia overlayer on the magnesia support [18]. Fig. 4.16 gave a comparison of % selectivity at different catalysts of high

composition for different reaction temperatures. Plot corresponding to 1.8%Ag/Fe<sub>2</sub>O<sub>3</sub> shows an increment and then decrement in the % selectivity of formaldehyde on increasing the reaction temperature due to catalyst deactivation. Plot of 10%V<sub>2</sub>O<sub>5</sub>/MgO shows a lower selectivity in comparison to V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalysts due to decrement of the active sites resulting from acid-base reaction of V<sub>2</sub>O<sub>5</sub> and MgO. For the case of V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (700° C, 16h), the selectivity is very high in comparison to V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (700° C, 6h) at starting temperatures also. This can be understood from the proposed structure of vanadium oxide species on TiO<sub>2</sub> supports under dehydrated conditions. In case of V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (700° C, 16h), there might be a more possibility of formation of more polymerized form of VO<sub>4</sub> units due to longer calcination at the same temperature in comparison to V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> (700° C, 6h), that gave a better selectivity of formaldehyde.

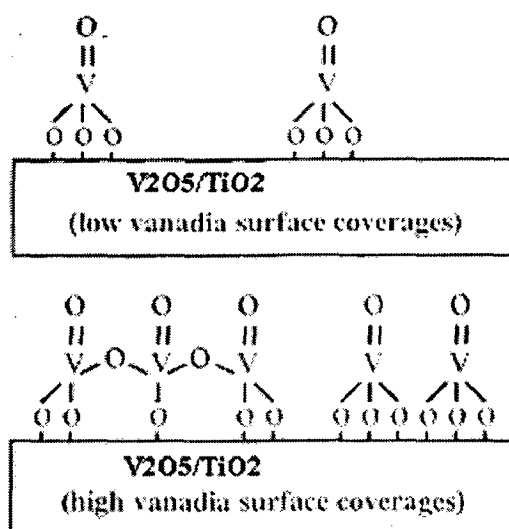


Figure 4.17 Proposed structure of vanadium oxide species on TiO<sub>2</sub> supports under dehydrated conditions.

## Chapter 5

### CONCLUSION AND RECOMMENDATION FOR FUTURE

#### CONCLUSIONS:

The following conclusions may be drawn on the basis of the present study on the partial oxidation of methanol over supported catalysts:

1. Among the  $V_2O_5/TiO_2$  (700° C, 6h),  $V_2O_5/TiO_2$  (700° C, 16h),  $V_2O_5/MgO$  (700° C, 6h) and  $Ag/Fe_2O_3$  (700° C, 6h) catalysts prepared by dry-mixing method, 10% $V_2O_5/TiO_2$  (700° C, 16h) has shown best catalytic activity.
2. The  $V_2O_5/TiO_2$  (700° C, 16h) catalysts performed better than  $V_2O_5/TiO_2$  (700° C, 6h) catalysts.
3. Near 250° C reaction temperature, most of the catalysts gave a high % selectivity of formaldehyde.
4. In case of  $Ag/Fe_2O_3$ , the selectivity of formaldehyde is least among all the catalysts at different reaction temperatures due to catalyst poisoning.
5. In general the order of activity is found as follows:  $V_2O_5/TiO_2$  (700° C, 16h) >  $V_2O_5/TiO_2$  (700° C, 6h) >  $V_2O_5/MgO$  (700° C, 6h) >  $Ag/Fe_2O_3$  (700° C, 6h).
6. The effect of the support has been observed in case of  $V_2O_5$  supported on  $MgO$ , where due to acid -base reaction of  $V_2O_5$  and  $MgO$ , the activity has decreased in comparison to  $V_2O_5$  supported on  $TiO_2$ .

## RECOMMENDATIONS:

On the basis of present study the following recommendations can be made for future investigations.

1. To study the effect of the
  - (i) variation in the feed composition,
  - (ii) space velocity making as higher as  $GHSV > 40000 h^{-1}$
  - (iii) and variation in the calcination temperature.
2. To determine the kinetic mechanism for methanol partial oxidation to formaldehyde.
3. The catalytic activity analysis can be done by replacing the air from zero air cylinder with the pure oxygen, which can give better oxidation of methanol.
4. The catalytic activity analysis can be done by using more %composition of Ag on  $Fe_2O_3$  and by using mixed supported catalysts like  $V_2O_5$ - Ag / $TiO_2$ .
5. The study of the effect of  $H_2O$  vapor on the catalysts performance for the methanol partial oxidation can be done.
6. The study of the stability of the catalysts under more severe environment: longer on reaction-operation at higher temperatures ( $\sim 500^\circ C$ ) and subjecting the catalyst to rigorous thermal ageing at higher temperature ( $> 700^\circ C$ ).
7. The nanoscale catalytic materials can be prepared by using nanoparticle preparation techniques like sol-gel, wet impregnation. The nanocatalysts have higher surface area than the catalysts prepared by ordinary methods like co-precipitation and dry-mixing methods.

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