PRODUCTION OF FORMALDEHYDE BY CATALYTIC CONVERSION OF METHANOL

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ABSTRACT

Production of formaldehyde by catalytic conversion of methanol was carried out using the commercial and prepared Fe2O3/ MoO3 catalysts in a continuous laboratory tubular bed reactor. The catalyst was prepared by using kneading, precipitation and coprecipitation methods. The reaction temperature varied from 200 to 350 oC. The pressure and fed methanol-oxygen mixture were kept constant at 10atm. and 5.5% respectively. The results show that the catalyst prepared by coprecipitation method exhibits a good catalytic activity in comparison with the commercial catalyst. Also the reaction temperature at 300 oC gives higher percentage of formaldehyde products.

INTRODUCTION

Formaldehyde is an important chemical of widespread industrial uses; among these are the productions of urea, melamine, and phenolic resins in addition to ethylene glycol. Huge amount of CH_2O was used in fertilizer and paint industries. In medicine it is used as preserver agent (1).

Formaldehyde was produced via two methods, from methanol and hydrocarbons. In the first the methanol - air mixture was passed over a catalyst surface at suitable conditions and the products were absorbed in water where formaldehyde formed in two steps. In the first step methanol undergoes dehydrogenation reaction while in the second it undergoes an oxidation one as given below (2-4).

$CH_3OH \leftrightarrow CH_2O+H_2$ $\Delta H= +84$ KJ/mole

$H_2+ 1/2\ O_2 \rightarrow H_2O$ $\Delta H= -243$ KJ/mole

$CH_3OH+ 1/2\ O_2\rightarrow CH_2O+H_2O$ $\Delta H= -159$ KJ/mole

$CH_2O + 1/2\ O_2 \leftrightarrow CO +H_2O$ $\Delta H= -215$ KJ/mole

Where the hydrogen combustion reaction was thought to provide the exothermic heat required for the process. The second method involves the partial oxidation of hydrocarbon gases under pressure, the reaction products depends upon the type of aliphatic hydrocarbon used. Methane (5) oxidized at 600°C to CH_2O which decomposes at about 400°C. High molecular hydrocarbon requires lower temperatures; the most important process involves the oxidation of propane and butane at 400 °C and 20-30 atm with air.

Several types of supported catalysts were tested for the conversion of methanol to formaldehyde, as the chemical composition is the major factor for determining the catalytic properties. However the catalytic characteristics may vary over a wide range depending on the methods and conditions of catalyst preparation, owing to the changes in the nature of interaction of catalyst compositions, dispersion, pore structure, crystal chemical changes (6). It should be stressed that catalyst structure depends also on other parameter such as metal loading, surface area of the carrier and drying and calcinations temperatures (7).

Silver supported catalyst (3, 8) was used in a process operated at 450-650 °C for the oxidation of methanol /air mixture. Later copper (9, 10) was introduced as a metal active component in the catalyst, and the development continues until tin oxide /molybdenum oxide was examined as a catalyst candidate for the process, as it decrease the reaction temperature to about 180 °C if compared to TiO_2/MoO_3 catalyst system in which methanol underwent the oxidation at a temperature higher than 350 °C.The other used catalyst (Joachim Sauer(11) and Monti et al(12)) was V_2O_5/K_2SO_4 in the oxidation of methanol at 275-475 °C to give 15% selectivity at 10-20% V_2O_5.

Soares et al. [13] used the Fe/Mo catalyst and showed by physicochemical characterization that the excess Mo bring an increase in the surface area and also improve catalyst stability mainly due to the fact that during reaction Mo seems to migrate from bulk to catalyst surface and then sublimated. On the other hand Soares et al. [14] also proved that the $Fe_2(MoO_4)_3$ is the active phase of the Fe/Mo catalyst.

Ivanov et al [15] stated that the x-ray diffraction and chemical studies of the prepared Fe-Mo-W catalysts revealed the formation of two types of solid solutions with composition $Fe_2(Mo_xW_{1-x}O_4)_3$ and $(Mo_xW_{1-x})O_3$. The solid solutions formed are characterized by high activity for methanol oxidation, in addition to being operated at lower temperature.

In the present work the Production of formaldehyde by catalytic conversion of methanol was carried out using the commercial and prepared Fe_2O_3/MoO_3 catalysts in a continuous laboratory tubular bed reactor.

EXPERMANTAL WORK

Raw Materials

The materials used in the preparation of the catalysts were analytical grade of high purity.

1. Ammonium molybdate (NH4)6 Mo7O24-4H2O of molecular weight 1235.86 kg.kmole-1 of density of 2.498 kg.L-1, light yellow color, with>99% purity on dissociation it can produce 81-83% MoO3.
2. Ferric nitrate nanohydrate Fe(NO3)3-9H2O with a purity of not less than 99.5% and a yellow color crystals , upon dissociation yields 20% Fe2O3
3. Methanol of 99.9% purity.
4. polyvinyl alcohol of high purity (PVA).
5. Sodium hypoiodate and iodine of high purity (99%).

Catalyst Preparation

Several methods were used to prepare the Fe_2O_3/MoO_3catalyst.The most important three were applied as follows:

Kneading Method (first catalyst)

In this method the catalyst was prepared by dissolution of the ferric nitrate in a minimum amount of distilled water, and then this slurry is added gradually to the ammonium molybdate with continuous stirring to obtain a homogeneous paste. The molybdate was used as powder. Then the paste was dried in an oven at 110 oC for two hours then calcined at 400-500oC in the presence of current of air for 4hr.

Precipitation and Concentration Method (second catalyst)

To Produce the catalyst by this method, ammonium molybdate and ferric nitrate were precipitated at a pH of about 2, then the precipitate was decanted overnight and then concentrated at room temperature .Finally drying and calcining at 110 °C for two hours and at 400-500 °C for 4hr respectively was carried out.

Coprecipitation Method (third catalyst)

Here in coprecipitation step of catalyst preparation were carried out mention before at pH = 2, then the precipitate was filtered off and washed several times with distilled water until the pH of the filtrate reaches 7. Finally the catalyst dried and calcined as described before. The reaction can be represented as follow:

$$2Fe(NO_3)_3+(NH_4)6Mo_7O_{24}\rightarrow Fe_2Mo_7O_{24}+6NH_4NO_3$$

Catalyst Formulation

Since the catalyst operates in a fixed bed reactor, the prepared catalyst must be formulated to the desired shape. The calcined catalyst was crushed to small pieces then converted to powder using a ball mill. The 100 mesh fraction was mixed with 3% PVA dissolved in distilled water thoroughly. The produced catalyst paste is then dried, crushed, sieved as above and a tablet press under a pressure of 2 tam was used to produce tablets of 7mm diameter and 4mm height. Finally it was calcined at 500 °C in order to dissociate the PVA.

Composition of the Catalysts

Analysis of iron and molybdenum of the prepared catalysts were carried out by using atomic absorption spectrophotometer (PYE UNICAM Spa).

X-Ray Diffraction:

The x-ray diffraction of the prepared catalyst was carried out by using Philips x-ray diffractmeter with CuKα(Wave Length 1.542A)$^{(16)}$, 40kVand 20mA.Radiation range of angles scanned was to 70 on 2θ.

Peaks identification were made on the basis of d spacing of typical compounds given in the ASTM powder diffraction files $^{(17)}$. The keys used to identify the peaks in the x-ray diffraction, are obtained and applied in this work.

Surface Area, Pore Volume, Density and Hardness

Surface area of the prepared catalysts are measured by using BET method $^{(18)}$, the apparatus used was carloEraba sorptomic series 1800. pore volume and density are determined experimentally using liquid impregnation method as described by satter F.and Charles N. $^{(19)}$. While hardness test is measured by using special equipment (ERWEKA. TBH28) $^{(20)}$.

Catalyst Performance:

The activity of the prepared catalysts is carried out in a continuous pilot plant as in Fig (1). Fig (2) shows a front view section of the tubular reactor. The represented schematically reactor is made of stainless steel (316-heat resistance) of 800mm length and 19 mm inside diameter. For uniform feed distribution two penetrated disk is used. The reactor was packed with 110 ml of catalyst that inserted between two layers of inert material (glass balls). The heaters are in the form of four separately heat-controlled block shells.

The operating conditions of the reaction were, temperature varied from 200 to 350 °C, flow rate at 15.858 cm^3/s, pressure and fed methanol-oxygen mixture at 10 tam and (5.5%) respectively.

The reactor was purged with N2 gas, and then the temperature was raised. After attending steady state conditions, the reaction was started; the methanol was pumped upward in to the reactor after being mixed with oxygen. Products passed through a series of three traps filled with cooled water (5 °C) in order to ensure the absorption of the formaldehyde, unreacted methanol and any side products.

The chemical analysis of products was performed periodically. The formaldehyde was analyzed by reacting with sodium hypoiodate which is back titrated with iodine of known concentration. The amount of unconverted methanol was determined by using gas chromatography technique with povapak type T column at 147 °C $^{(12)}$. The side products were calculated by difference.

RESULTS AND DISCUSSION

The results of the chemical composition of the commercial and the prepared catalysts are shown in Table (1). It is obvious that the chemical composition of the third catalyst prepared by coprecipitation method was found to be 19.73% and 80.20% for Fe_2O_3 and MoO_3 respectively which is very close to the commercial catalyst with composition of 20% and 80% respectively. This was incorporated with the color and other physical properties as shown in Table (2).

The activity of the prepared catalysts (Fe_2O_3/MoO_3) was studied in comparison with the commercial one by studying the production of formaldehyde form methanol. The results of the weight percent of formaldehyde, the weight percent of unreacted methanol and the weight percent of other products at different reaction temperatures, using the commercial and the prepared catalysts are shown in Table (3). Fig (3) shows the weight percent of formaldehyde against reaction temperature for the commercial and the three prepared catalysts, whereas Fig (4) show the weight percent of unreacted methanol versus the reaction temperature for the commercial and the prepared catalysts. From Table (3) and Figs (3 and 4), it was noticed that the catalyst prepared by coprecipitation method reflects a reasonable and better activity in compassion with the commercial catalyst.

The identification of the catalyst components was confirmed by the X-ray diffraction spectra of the prepared catalysts by copricipitation and commercial catalyst which demonstrate the similarities chemical composition with the different mentioned catalysts in literatures. As shown in fig(5) the catalyst composed of mixed oxide Fe_2O_3 and MoO_3 as a complex $Fe_2Mo_7O_{24}$ which stochiometrically equivalent to two ferric oxide molecules and seven molybdenum oxide molecules, although some literatures indicated that the first is $Fe_2(MoO_4)_3$ (dspacing =3.88X,3.475,4.084) and the other is $4MoO_3$ (dspacing =3.92X,3.605,3.393) as shown in Fig(5).

Fig (3) show that the production of formaldehyde increase with increasing the reaction temperature and reaches to a maximum at temperature of 300°C and then decreases for all the catalysts tested as a results of the decomposition which leads to increase the other products as shown in Table (3)

CONCLUSIONS

From the comparison of the commercial and the prepared catalysts behavior, it is clear that the coprecipitation is the best method for Fe_2O_3/MoO_3 catalyst Preparation, as it reflects better properties and activity after being operated in the conversion of methanol to formaldehyde in a continuous trickle bed reactor under different temperatures. Also it was found that the optimum temperature was 300 °C.

Table (1) the chemical composition analysis of commercial and prepared catalysts.

Wt% / composition	Commercial catalyst	Prepared by Kneading first Catalyst	 Precipitations second catalyst	 Coprecipitation Third catalyst
Fe	14	17.23	15.60	13.80
Mo	53	50.20	51.70	53.40
Fe2O3	20	24.60	22.30	19.73
MoO3	80	75.4	77.70	80.20

Table (2) the physical properties of the commercial and prepared catalysts.

Catalyst	Color	Shape	Hardness (dyne)	Solid Density gm/cm3	Bulk Density gm/cm3	Pore Volume cm3/gm	Surface Area m2/gm
Commercial	Yellow	0.45*0.4cm	2.3*105	0.50	1.10	0.35	290
First Cat. Prepared by kneading	Yellow Green	0.9*0.9cm	1.7*105	0.53	1.05	0.28	283
Second Cat. prepared by precipitation	Yellow Green	0.9*0.9cm	1.63*105	0.50	1.05	0.30	282
Third Cat. prepared by Coprecipitation	Yellow	0.9*0.9cm	2.1*105	0.52	1.05	0.40	287

Table (3) the percent of products for commercial and prepared catalysts

Temp.(C^o)	Commercial Catalyst			First Catalyst(prepared by kneading)		
	% of HCHO products	% of CH3OH unreacted	% of other products	% of HCHO products	% of CH3OH unreacted	% of other products
200	25.20	60.26	14.54	15.16	61.20	23.64
225	33.31	53.13	13.56	18.21	58.12	23.67
250	40.13	47.18	12.69	26.17	55.31	18.52
275	43.02	4.09	12.89	35.11	47.28	17.61
300	49.16	40.28	10.56	38.26	44.13	17.61
325	42.31	38.19	19.50	34.11	39.14	26.75
350	38.18	36.21	25.61	31.17	40.09	28.74
Temp.(Co)	Second Catalyst (prepared by precipitation)			Third Catalyst (prepared by copreciptation)		
	% of HCHO products	% of CH3OH unreacted	% of other products	% of HCHO products	% of CH3OH unreacted	% of other products
200	18.11	63.21	18.68	24.14	58.06	17.80
225	24.10	60.36	15.54	33.21	52.13	14.66
250	2.20	54.12	3.68	41.22	45.21	13.57
275	38.11	49.29	12.60	42.16	44.30	13.54
300	42.21	45.18	12.61	48.21	40.26	11.53
325	37.16	38.35	24.63	40.11	38.18	21.71
350	34.17	37.13	28.70	35.15	38.21	26.64

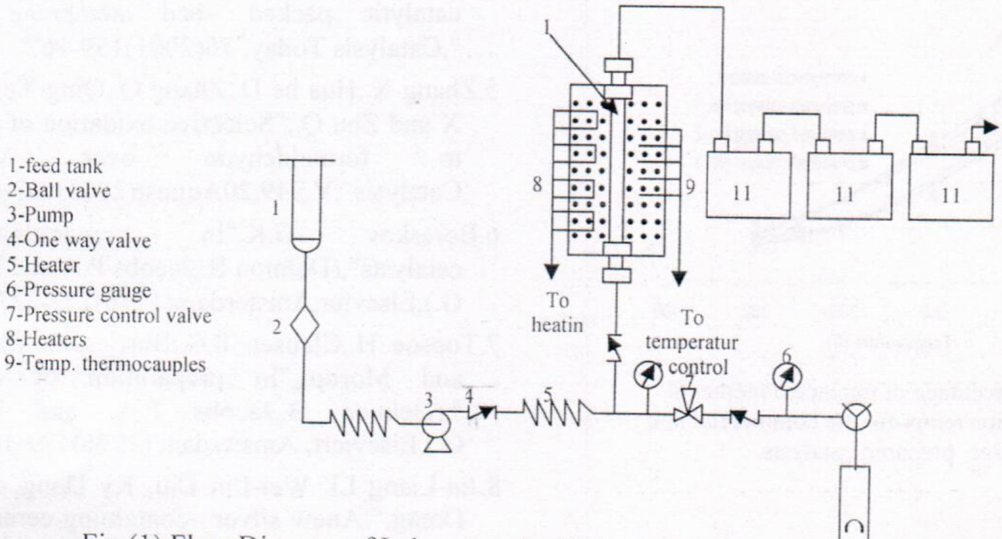

Fig.(1) Flow Diagram of Laboratory Oxidation of methanol Unit

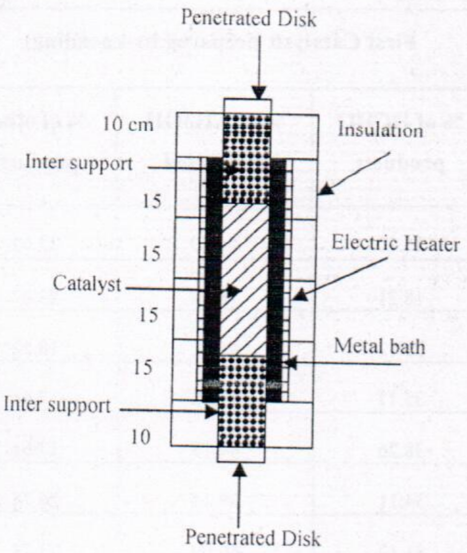

Fig (2) Front view section of the tubular reactor.

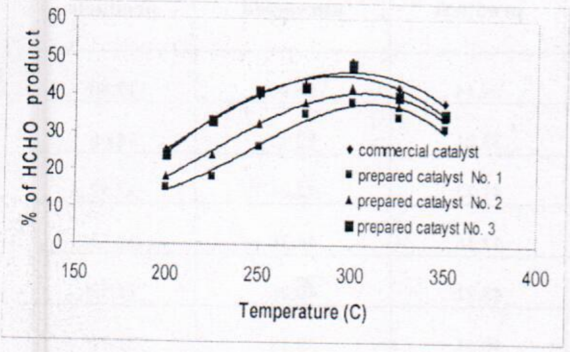

Fig (3) percentage of formaldehyde product versus reaction temp. for the commercial and three prepared catalysts .

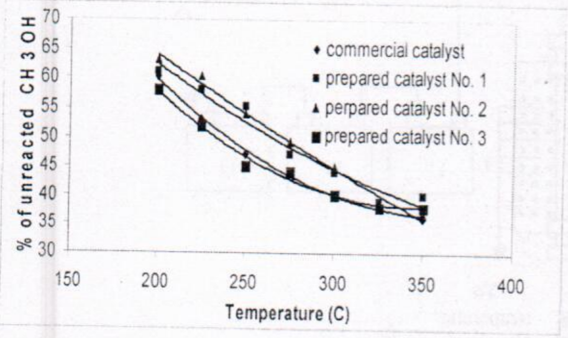

Fig (4) percentage of unreacted methanol versus reaction temp. for the commercial and three prepared catalysts.

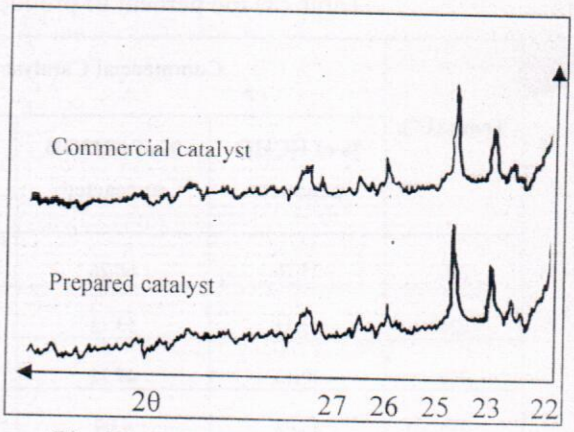

Fig. (5): X-ray of Commercial & Prepared Fe2O3 / MoO3 Catalysts.

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