Journal of Scientific Research ISSN 0555-7674
Vol. XXXVIII No. 2, December, 2008

SYNTHESIS AND CHARACTERIZATION OF FORMALDEHYDE BY CATALYTIC OXIDATION OF METHANOL

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Abstract: The catalytic oxidation of methanol to formaldehyde is studied over copper and silver catalysts. The impact of various factors catalytic poisoning, temperature, contact time on the formaldehyde yield have been investigated. An assembly using copper and silver as catalysts has been proposed to prepare formaldehyde in perspective of Pakistan in local industry. All the conditions to optimize the formaldehyde yield were also investigated. The formaldehyde produced was standardized chemically as well as spectroscopically.

Introduction

Formaldehyde was discovered by Wilhelm Von Hofmann with Alexander Butlerov in 1867. It was first synthesized by the Russian chemist Aleksandr Butlerov (1828-1886), but was conclusively identified by August Wilhelm von Hofmann.[1]

Formaldehyde is produced industrially by the catalytic oxidation of methanol. Several catalysts have been used for the preparation of formaldehyde. The most common catalysts are copper metal, silver metal or a mixture of an iron oxide with molybdenum and vanadium. In the more commonly used FORMOX process methanol and oxygen react at 250-400 °C in presence of iron oxide in combination with molybdenum and/ or vanadium to produce formaldehyde according to the following equation.

$$2\ CH_3OH + O_2 \rightarrow 2\ HCHO + 2\ H_2O$$

The silver-based catalyst is usually operated at a higher temperature, about 650°C. Two chemical reactions simultaneously yield formaldehyde: one that shown above and the second dehydrogenation reaction.

$$CH_3OH \rightarrow HCHO + H_2$$

Formaldehyde is readily oxidized by atmospheric oxygen to form formic acid. Formic acid is always found in trace levels in commercial formaldehyde.

Gerhard[2] *and coworkers* manufactured formaldehyde by gas-phase oxidation of methanol vapors with a gas flow containing molecular oxygen in presence of solid bed catalyst containing iron and molybdenum. Vieira and Farinha[3] carried out selective oxidation of methanol to formaldehyde over iron-molybdate catalysts. Isaguliants and Belomestnykh[4] carried out the selective oxidation of methanol to formaldehyde over V-Mg-O catalysts. Vsachev[5] *and coworkers* developed a method for the manufacture of water free formaldehyde by non-oxidative dehydrogenation of methanol. Dai, Weilin[6] *and coworkers* carried out the catalytic oxidative dehydrogenation of methanol to formaldehyde over Ag-SiO_2-Al_2O_3 catalyst prepared by a sol-gel method. Ren, Li-Ping[7] *and coworkers* applied sol-gel method to prepare a novel Ag-SiO_2-Al_2O_3 catalyst which showed high activity in the reaction of direct dehydrogenation of methanol to formaldehyde. They investigated the influence of silver loading, calcinations temperature and reaction temperature on

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the catalytic activity. Wang, Chien-Tsung and Willey, Ronald J.[8] investigated the partial oxidation of methanol over Fe_2O_3 (supported on SiO_2 or MoO_3) aero gels between 225-300˚C.

In present work synthesis of formaldehyde has been carried out using copper and silver metals as catalysts. A schematic assembly set up used for the synthesis of formaldehyde at the laboratory scale is shown in Fig.1. The set up can be magnified at pilot plant level. The set up shown in Fig.1 consists of four main sections. Feeding system, pre-heating zone, reaction column and absorption section. Feeding system involves the use of an air nebulizer to produce methanol/ air mixture in a form of fine mist, which eliminates the need of ordinary feeding system (using air compressor and methanol vaporizer). By using the proposed feeing system the operation becomes more easy to handle and economically favorable.

EXPERIMENTAL WORK

Reagents required

Methanol (commercial); calcium chloride (anhydrous); phenyl hydrazine; potassium ferricyanide; concentrated hydrochloric acid.

Schematic Assembly

A schematic assembly shown in Fig.1 has set up for formaldehyde synthesis consisting an atomizer, preheating zone, reaction column and absorption tower.

EXPERIMENTAL PROCEDURE

1. Synthesis of Formaldehyde

Purified methanol (doubly distilled, using calcium chloride as dehydrating agent) was atomized and mixed with air. The methanol vapors/ air mixture was heated in preheating zone and then entered in reaction column where already heated catalyst converted methanol to formaldehyde. The gaseous formaldehyde was routed towards the absorption tower where it was absorbed in water and formalin was obtained. This process was run continuously until the required concentration of formalin obtained.

2. Characterization of Formaldehyde

The prepared formaldehyde was characterized using spectrophotometric method involving phenylhydrazine and potassium ferricyanide as complecing agents. The formic acid content in prepared formaldehyde was also calculated using standard titration procedure.

Results and Discussion

The concentration of prepared sample was compared with concentration of commercially available formalin and percentage yield was calculated w.r.t commercial formalin.

The concentration of the formaldehyde was determined at different stages during the experimentation process. The concentration of the formalin was dependent on the saturation of the formalin solution. It was observed during the process that when the formalin solution was saturated with the formaldehyde vapors, the formaldehyde vapors began to escape from the surface of the formalin solution.

The heating rate was of prime importance during the synthesis of formaldehyde by the catalytic oxidation of methanol over copper. It was observed that when the catalyst was not heated the poisoning of catalyst occurred which lowered the conversion of methanol vapors into formaldehyde vapor and the synthesis of formaldehyde was hindered.

The purity of the catalyst was also of

great importance. The catalytic oxidation with blackish layer of copper oxide lowered the rate of methanol oxidation.

Using silver as catalyst the problem of catalyst poisoning can be minimized. But it needs sufficient high temperature for conversion. Over heating of catalyst was also observed in case of silver catalyst as the reaction is exothermic itself.

The time for the conversion of liquid methanol to fine mist by atomizer was also noted down. It was observed that 10 mL of methanol always took about 20 minutes to be converted into fine mist.

The concentration of the formalin solution prepared by the catalytic oxidation of methanol using Copper as the catalyst was 36.40% and silver as catalyst was 36.12% of the commercially available formalin.

The capacity of absorption tower was of 600 mL. About sixty six hours were required to complete one batch in case of copper catalyst. While in case silver as catalyst, it took fifty four hours to complete one batch. Which shows silver is more efficient in conversion of methanol to formaldehyde but it needs sufficient high temperature for conversion as compared to copper.

It may be concluded that both copper and silver catalyst are suitable for efficient conversion of methanol to formaldehyde. Methanol should be of maximum purity because water in methanol poisons the catalyst especially copper; in the result the conversion efficiency of catalyst gets minimized. Methanol/ air mixture should be preheated to about 100 °C before entering the reaction column. The catalyst should also be preheated in order to minimize the poisoning problem. Once the reaction starts, the heating rate should also be controlled in order to avoid over heating especially for silver catalyst. Although this process is time gaining but the purity of formalin obtained was appreciable. Only a trace amount of formic acid was found in resulting formalin.

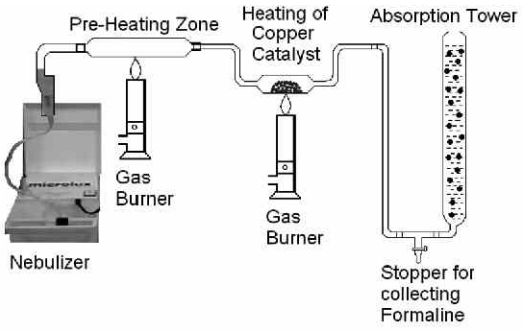

Fig.1. the schematic assembly for methanol Oxidation

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