Chapter 24

CATALYTIC OXIDATION OF METHANOL TO FORMALDEHYDE

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Abstract: Methanol is a clean burning fuel, containing no sulphur or nitrogenous materials. It produces power with very low emissions compared to those of a natural gas-fired, combined-cycle unit. Methanol can also be used as a feedstock for more sophisticated processes in the petrochemical industry. In this study, catalytic oxidation of methanol to formaldehyde was investigated. For this purpose, laboratory type, fixed bed catalytic reactor was used. For this gas-phase reaction iron-molybdate catalysts supported by silica or alumina were used. On silica and alumina supports, different Mo/Fe ratios were investigated for three different residence times (W/FA0) and six different temperatures were tried. The analysis of liquid product was performed by using gas chromatograph. From the results of GC analysis and CO2 analyzer, conversion of methanol to formaldehyde, total conversion and selectivity to formaldehyde were obtained. After the determination of optimum operating conditions for this reaction, kinetic study was performed.

1. INTRODUCTION

A raw material for the methanol synthesis is natural gas. The technology for making methanol from natural gas is already in place and requires only efficiency improvements and scale-up to make methanol an economically viable alternative transportation fuel. Methanol is an inherently safe fuel and can be handled conventionally at the user’s site without the substantial capital investment in special purpose tankers or unloading facilities required by other fuel systems. Methanol is an important industrial material and it is used in the manufacture of formaldehyde.
Formaldehyde, H₂C=O, is the first of the series of aliphatic aldehydes. It was discovered by Butlerov in 1859 and has been manufactured since the beginning of this century. Annual worldwide production capacity now exceeds 12.10⁶ metric ton (calculated as 37 % solution). Because of its relatively low cost, high purity, and variety of chemical reactions, formaldehyde has become one of the world’s most important industrial and research chemicals.

Formaldehyde’s importance is proved by the fact that it is commonly used by industry to manufacture building materials and numerous household products. Because of its water resistance, formaldehyde is used in the manufacture of grocery bags, paper cups and plates, waxed paper, facial tissues, napkins, paper towels, and sanitary napkins. Formaldehyde is also used in cosmetics and fabric softeners besides in agriculture for seed treatment.

2. MATERIALS AND METHODS

Formaldehyde is produced industrially from methanol by three processes. First one is partial oxidation and dehydrogenation with air in the presence of silver crystals, steam and excess methanol at 680-720°C (BASF Process, methanol conversion is about 97-98 %). Second one is dehydrogenation with air in the presence of crystalline silver, or silver gauze, steam and excess methanol at 600-650°C (primary conversion of methanol is 77-87 %). The conversion is completed by distilling the product and recycling the unreacted product. Last process is the oxidation only with excess air in the presence of a modified iron-molybdenum-vanadium oxide catalyst at 250-400°C (methanol conversion is 97-98 %). By-products are carbon monoxide and dimethyl ether, in addition to small amounts of carbon dioxide and formic acid.

In this study, the production of formaldehyde via catalytic oxidation of methanol was investigated by using fixed bed catalytic reactor. The experimental set-up used for the experiments was shown in Figure 1.

The aim of the study is to determination of the optimum conditions by changing catalyst type, support type, residence time and temperature. For this gas-phase reaction iron-molybdate catalysts (Mo/Fe=1.5; 3; 5), on two different supports, silica and alumina, were used. Experiments were performed at three different methanol flowrates. 5 g catalyst amount was kept constant and by changing methanol flowrates, three different residence times (W/Fₐ₀) of 50.63, 33.75 and 20.25 g catalyst.h/mol methanol were tried. For all experiments temperature was changed between the range of