One-pot conversion of carbon oxides into formaldehyde and its derivatives in liquid phase reactions

Akshat Tanksale, Ali Mohammad Bahmanpour, Fan Liang Chan, Andrew Hoadley
Catalysis for Green Chemicals Group, Department of Chemical Engineering, Monash University, Clayton, 3800, Australia
*Corresponding author: fax: +61 3 9905 5686, Akshat.Tanksale@monash.edu

Abstract: (Poly)oxymethylene Ethers (OME$_n$, $n \geq 1$) are a class of second generation fuel components that can be blended with diesel in large volume fractions to reduce soot emission and to make transportation fuels more sustainable. OME$_1$ can be produced from methanol and formaldehyde using an acid catalyst, however, there are no reports of direct conversion of carbon oxides into OME$_1$. Our recent discovery of a novel route to produce formaldehyde from CO and CO$_2$ in methanol media enabled us to explore one-pot synthesis of OME$_1$.

Keywords: Formaldehyde, Carbon Dioxide, Carbon Monooxide, Oxymethylene Ether

1. Introduction

Formaldehyde (HCHO) is commodity chemical used for the production of resins, polymers, paints and adhesives. However, increasingly it is being applied in the production of other value added chemicals such as oxygenated fuel additives called as oxymethylene ethers. The production rate of HCHO is in the range of 30 million tons per year globally and the demand of HCHO has grown by 2-3 % per year over the last twenty years [1]. Industrially HCHO is produced via methanol (CH$_3$OH) partial oxidation and/or dehydrogenation but this process suffer from high exergy loss due to high temperature processes and large purification units. Recently, we introduced a novel method of HCHO production through direct CO and CO$_2$ hydrogenation in a catalytic slurry phase reactor [2-4], which can then be further converted into monooxymethylene ether (OME$_1$) in a one pot method.

2. Experimental

In this study, noble metal promoted bi-metallic Ni or Cu based catalysts were used due to the high activity of noble metals in hydrogenation reactions. Different supports were used to vary the acidity of the support to shift the reaction mechanism towards formaldehyde (low acidity) or monooxymethylene ether (high acidity). The catalysts were prepared by wet impregnation method followed by calcination and ex-situ reduction. The reduced catalyst was situated in the slurry reactor which contained 40 ml of solvent. The reactor was pressurised to 100 bar with CO and H$_2$. The HCHO concentration was measured using a FluoroQuik fluorometer version 4.3.A using 360nm/490nm as the excitation/emission wavelengths. OME1 concentration was measured using gas chromatographer (Shimadzu GC2010) using a Stabilwax 30m x 0.25mmID x 0.25µm column and Flame Ionisation Detector.

3. Results and discussion

Figure 1a shows that as the temperature was increased from 353 to 403 K, the yield of HCHO first increased and then decreased beyond 363 K. This is in agreement with thermodynamics which shows that the equilibrium constant of the reaction decreases as the temperature increases [2]. However, the rate of reaction increased with temperature. Therefore at temperature of 353 K higher yield may be obtained at longer residence time. The Arrhenius plot for this reaction at 5 h gives activation energy to be 8.17 kJ.mol$^{-1}$ (Fig 1b).
Increasing the acidity of the catalyst results in consumption of the formaldehyde via acetalization to produce mono-oxymethylene ether OME₁ (scheme 1).

Scheme 1. Reaction Scheme of one-pot conversion of synthesis gas into dimethoxymethane (OME₁) using a combination of metal and solid acid catalyst

4. Conclusions
A new method of formaldehyde and its derivatives production is introduced which utilizes direct CO and CO₂ hydrogenation method in a catalytic slurry phase reactor. Since this method works at low temperatures, bypasses methanol synthesis for formaldehyde production and produced formaldehyde with 100% selectivity, it is expected to be significantly more sustainable than the current industrial methods.

References