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Original Research Article

Synthesis of Ethane-1,2-diol (Ethylene Glycol) through Formose Reaction in Methanol Solvent

Arash Vojood*

Young Researchers and Elite Club, Ardabil Branch, Islamic Azad University, Ardabil, Iran

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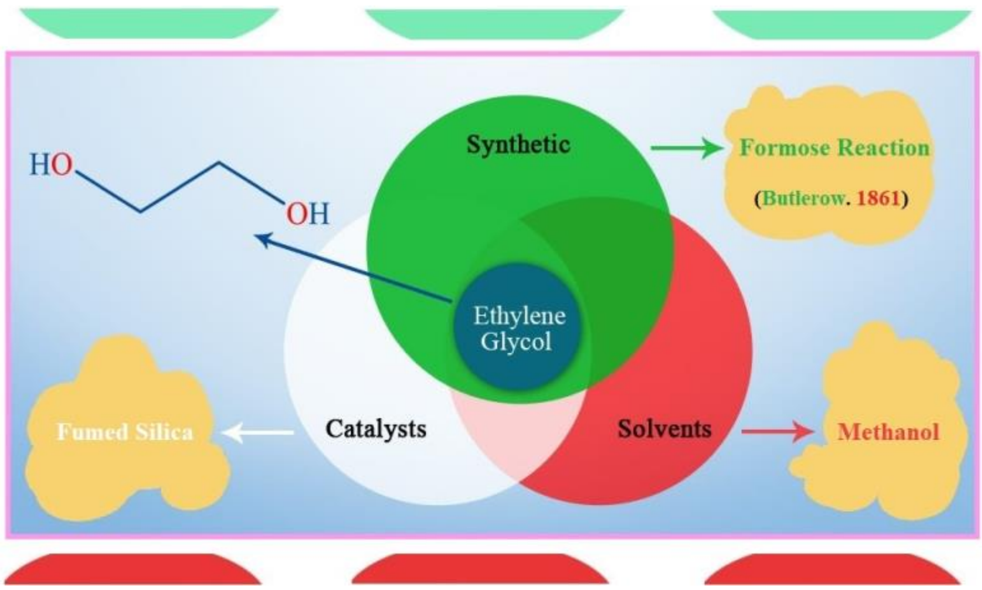
ABSTRACT

The current paper carried out the formose reaction (or the Butlerow reaction) when a fumed (pyrogenic) silica) also known as Aerosil or Cabosil) catalyst is present in methanol, which is one of the simplest forms of alcohol, at pH of 10.6. Ethane-1,2-diol (IUPAC name), also known as ethylene glycol or mono-ethylene glycol, is the reaction's visible product. Furthermore, Aerosil was investigated and identified through various analyses, including Fourier-transform infrared spectroscopy (FTIR), field emission scanning electron microscopy (FESEM), and Energy Dispersive X-ray Spectroscopy (EDS). Generally speaking, the results indicated that formose reaction produces ethylene glycol (simplest diol) with low efficiency in the methanolic medium.

GRAPHICAL ABSTRACT



* Corresponding author: Vojood, Arash
✉ E-mail: voojod.a2012@gmail.com

Introduction

Origin of life on our Mysterious planet, i.e. the Earth where according to the findings, life is flowing on it and nowhere in the universe like it has been discovered yet, is a difficult question and a perplexing conundrum in human knowledge that encompasses multiple scientific domains and it remains an important and challenging topic in scientific research. However, prebiotic chemistry plays a significant part in deciphering this difficult scientific question and specifically, studies and investigates the chemical processes occurring on Earth prior to the life emergence [1-8]. It focuses on understanding how simple organic molecules formed and evolved into more complex molecules, eventually leading to the development of life. By studying the fundamental chemistry that happened in the early Earth environment, scientists can gain valuable insights into the potential mechanisms that could have sparked life's origins [9-16]. Carbohydrates, as essential components of life, serve various functions within living systems, including information storage (DNA and RNA) and structural support, etc (cellulose) [2,17-19]. Given the pivotal roles played by sugars, it is plausible to consider their involvement in the early stages of life's origin. Moreover, investigating how sugars are formed and stabilized is crucial, as it can help us understand the origins of complex biomolecules and the earliest stages of life. The foundation of non-biological chemical reactions that produce sugars is known as the formose reaction. Likewise, the sugars formation during the prebiotic stage is thought to have involved this reaction, which is significant for the study of prebiotic chemistry and the OoL [20-26]. This reaction was first discovered by Russian chemist Alexander Mikhaylovich Butlerow (1828–1886) in 1861 [27-30].

The importance of the present study is related to the synthesis of sugar through the formose reaction and its novelty in using methanol solvent and performing the reaction at pH of 10.6. Furthermore, the presence of a heterogeneous catalyst accelerates this reaction in an alkaline medium. In this article, we aim to synthesize ethylene glycol ($C_2H_6O_2$) through the formose reaction using the mineral catalyst Aerosil in a methanolic medium.

Experimental

Chemicals and equipment

The chemicals used are listed in Table 1. The applied instruments were pH meter (WTW, inoLab 720,), analytical balance (Scaltel, SPB55, reading up to a 0.0001 g accuracy), Heater Stirrer (Bibby, HC502), centrifuge (155, Zag Chemie), laboratory oven (Binder, 7200), rotary evaporator (Bibby, RE200), FTIR spectrophotometer (Bruker, TENSOR 27), FESEM device equipped with an EDX analysis device (Tescan, MIRA III), and gas chromatography/mass spectrometry (Agilent, 5975C).

Procedure

In this work, a 250 mL three-necked flask was initially filled with 100 and 11 mL of methanol and aqueous formaldehyde solution (formalin), respectively, and heated to 60 °C, followed by adding 2 M NaOH solution to achieve a pH of 10.6 and ultimately 0.08 g of the Aerosil catalyst to start the reaction, and then, at specific time intervals, 5 mL of the reaction mixture was sampled and subjected to drying in a rotary evaporator, resulting in white solid samples, which were then dissolved in 5 mL of methanol, and subjected to analysis using gas chromatography/mass spectrometry [31].

Table 1. List of required chemicals

Raw material	Molecular formula	Supplier
Aerosil	SiO_2	Sigma-Aldrich
Acetone	C_3H_6O	Merck
Formalin	C_3H_6O	Shimi Delta
Hydrochloric acid	HCl	Merck
Methanol	CH_4O	Merck
Sodium sulfate	Na_2SO_4	Merck
Sodium hydroxide	NaOH	Shimi Delta

Results and discussion

Aerosil characterization

The Aerosil was characterized by FTIR, FESEM, and EDX techniques. one adsorption peak within the 3550 cm^{-1} region highlighted stretching vibrations of the hydroxyl group (O-H) group adsorbed water molecules on Aerosil surface, one peak at 2361 cm^{-1} for CO_2 gas in gas phase, one at 2934 cm^{-1} for stretching C-H, and one at 1633 cm^{-1} possibly associated with the bending vibration in the case of water molecules OH group adsorption on the Aerosil and three peaks at 472, 811 and 1105 cm^{-1}, potentially associated with the stretching and bending Si-O-Si, respectively [2,32-36].

Figure 2 depicts the FESEM images of Aerosil with different magnifications. The presented FESEM images show the amorphous and non-crystalline structure of this material. As seen in FESEM images, Aerosil has many pores between its grains. The EDX image is demonstrated in Figure 3. EDX elemental analysis results show the presence of oxygen and silicon elements. The results in Figure 3 are well compatible with the chemical formula of this material and show that there are no interfering chemicals on the surface of material.

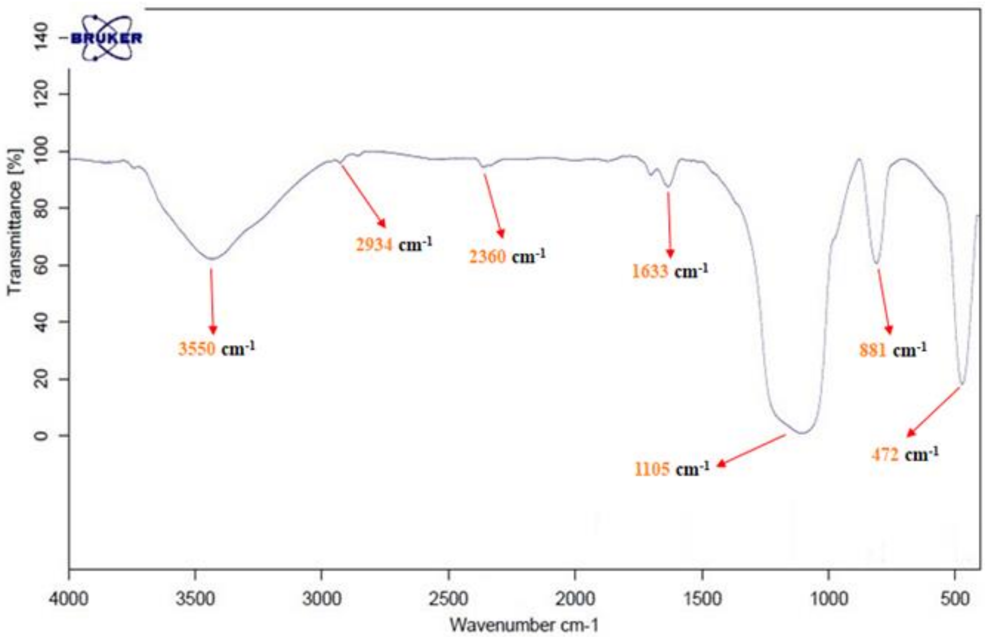


Figure 1. FTIR spectrum of Aerosil.

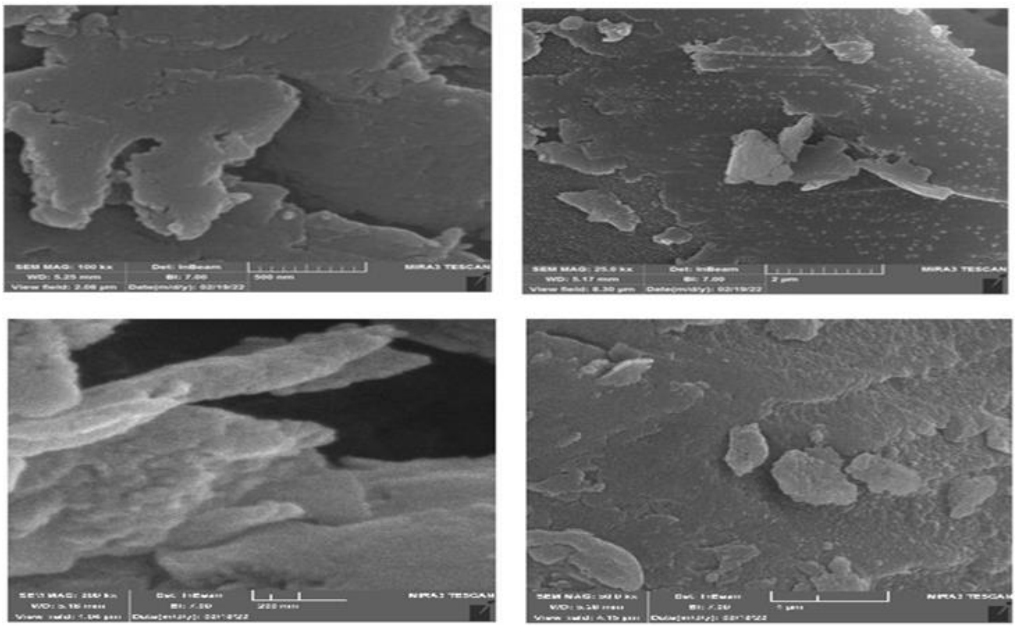


Figure 2. FESEM images of Aerosil.

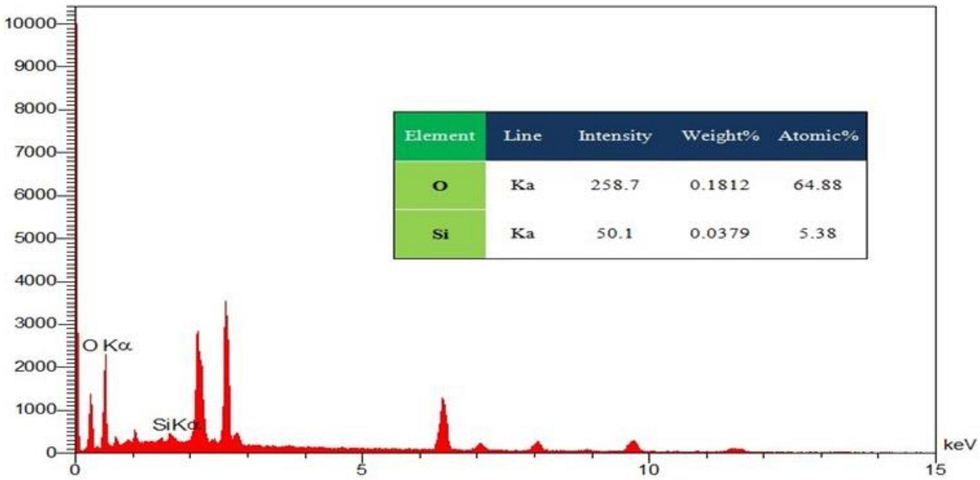


Figure 3. EDX pattern of Aerosil.

Formose reaction in methanol solvent

Figure 4 illustrates the gas chromatography /mass spectrometry results of the formose reaction conducted at pH of 10.6 in a methanolic medium with a heterogeneous Aerosil catalyst. The ethylene glycol concentration within the mixture gradually increased throughout the reaction, reaching a 0.5 mmol/dl maximum after 90 min.

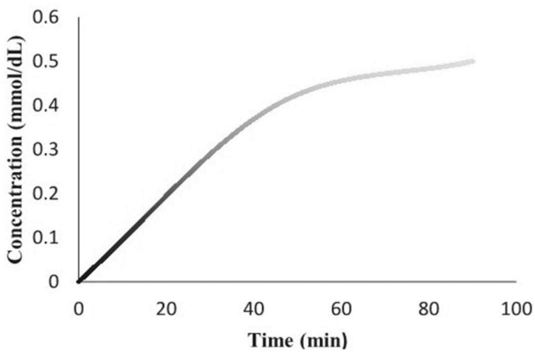


Figure 4. Various ethylene glycol concentrations obtained in the methanol solvent throughout time using formose reaction under pH = 10.6.

Conclusion

Prebiotic chemistry (beginning before life started or resulting in life on Earth, and probably on other planets) contributes significantly to studying life's origin and emergence on Earth and other planets. On the other hand, the formose reaction plays a critical role in prebiotic chemistry and the OoL, facilitating non-biological chemical reactions for sugar production. This study conducted the formose reaction in a methanolic medium with a fumed silica catalyst, consequently producing ethylene glycol. Nevertheless, ethylene glycol synthesis showed relatively low efficiency in this medium.

In addition, 2,3-dihydroxypropanal (IUPAC name), with the chemical formula $C_3H_6O_3$, was not observed during the formose reaction when methanol solvent was used at pH 10.6.

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Disclosure statement

The author declares that there is no conflict of interest in this study.

Orcid

Arash Vojood : 0000-0003-3503-2523

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