

Preparation, Characterization, and Hydro-Stability Assessment of Sodium Glyceroxide

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ABSTRACT

The present study described the successful preparation, characterization (XRD and FTIR Spectroscopy), and hydro-stability assessment of sodium glyceroxide (NaOGI), a compound commonly used as a catalyst in the preparation of biodiesel with promising new application in the selective synthesis of monolaurin and monoacylglycerides (MAGs). NaOGI is a crystalline solid that is difficult to handle under “wet” conditions because of its high hygroscopicity and high reactivity with water in air and in solution. The data presented here provides insights into the relevant physicochemical parameters of NaOGI and an analysis of the extent of the working conditions involving NaOGI as a reactant.

Keywords: sodium glyceroxide; sodium 2,3-dihydroxypropan-1-olate; biodiesel; catalyst

INTRODUCTION

Sodium glyceroxide (NaOGI; IUPAC: sodium 2,3-dihydroxypropan-1-olate; other name: sodium α -glyceroxide) is a monosodium salt of glycerol that can be prepared by reacting glycerol with strong bases, such as hydroxide and alkoxides. It is normally prepared *in situ* by reacting glycerol with a concentrated aqueous sodium hydroxide (NaOH) solution, and its most popular application is in the synthesis of biodiesel (Bradley et al., 2016; Fairbourne et al., 1931; Gok et al., 2013; Korchak et al., 2022). The first preparation procedure for NaOGI was reported in the last century (Fairbourne & Toms, 1921) but crystal structure identification only came relatively recently (Schatte et al., 2010). NaOGI adapts a monoclinic assembly where sodium ion (Na^+) is coordinated to five oxygen atoms, resulting in distorted trigonal bipyramidal geometry (Schatte et al., 2010).

A promising new application for NaOGI as a reactant in the selective synthesis of monoacylglycerides (MAGs) has been demonstrated recently (Cayona & Yu, 2023). MAGs are monoesters of glycerol which possess antimicrobial property (Batovska et al., 2009; Bergsson et al., 1998, 1999, 2001, 2002; Conley & Kabara, 1973; Preuss et al., 2005) that are not shared by their corresponding diacylglycerides (DAGs) and triacylglycerides (TAGs). However, the route suffers from poor yield mainly because of NaOGI's high hygroscopicity and high reactivity with water. To better understand the properties of NaOGI, this present study described the preparation, characterization, and hydro-stability assessment of NaOGI in ambient conditions. The data obtained provides insights about the relevant physicochemical parameters of NaOGI and an analysis of the extent of the working conditions involving NaOGI as reactant.

METHODS

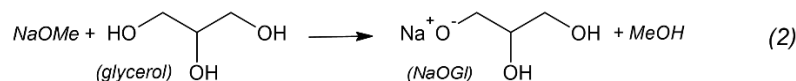
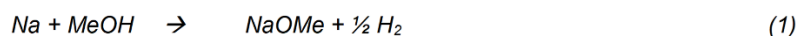
Materials and Equipment. Synthesis quality sodium metal (purity $\geq 99.0\%$, CN: 8.22284.0250, BN: S6999884 731, Merck), methanol (MeOH) (purity = 99.9%, CN: LC1115-G4L, BN: 12030230, RCI Labscan Limited), and glycerol (purity > 99.5%, 2.5L, BN: 0903388, Ajax Finechem Pty Ltd) were obtained from various sources. Compound characterization involved FTIR (Shimadzu FTIR with IR Solution software; KBr pelletized) and XRD (Rigaku Ultima IV) spectroscopy, and pH measurement (Eutech Instruments pH 700).

Method. Freshly cut Na metal (about 1.0 g) previously treated to remove the protective oil coating was made to react with an excess of MeOH. Then an excess amount of glycerol that is about twice the stoichiometric ratio with Na (also NaOMe) was added to the mixture, stirred, and heated at 60°C for 30 minutes. The solid NaOGI produced was then filtered and washed multiple times with small volumes of MeOH before drying at 120 \pm 5 °C for 3 hours to remove excess MeOH and glycerol. It was stored in a desiccator before further tests were conducted, which include FTIR and XRD spectroscopy, and pH measurement. Measured quantities of NaOGI powder were exposed to air at 27.0°C room temperature (RT) and 45% relative humidity (RH) and the change in mass of the solid was measured every after 30 minutes until the solid becomes saturated with water. A different set of measured solids were dissolved separately in 25.00mL deionized water and the individual pH values were recorded using a pH meter. All tests were done in triplicate.

RESULTS AND DISCUSSION

Preparation and Characterization of NaOGI. Direct reaction of Na with glycerol akin to hydrogen displacement reaction with active metals did not produce the target product. The highly exothermic nature of reaction caused the glycerol to char very quickly. An indirect method using MeOH (Cayona & Yu, 2023) was utilized to prepare the strong base, NaOMe, which is a stronger base than glyceroxide. The pK_a values of the acidic H's in MeOH and in glycerol (αH) are 15.3 and 14.15, respectively (Serjeant & Dempsey, 1979). In theory, ethanol (BP = 78.4°C), isopropanol (BP = 82.3°C), and other substances with higher pK_a than glycerol can be used; however, MeOH (BP = 64.5°C) was the most suitable for the step because the excess amount in the succeeding step can be easily removed by evaporation as it is the most volatile. In addition, consistent with green chemistry measures, MeOH offers the best atom economy among other options.

The reactions involved are shown as follows:



Glycerol is a transparent, viscous, and hygroscopic liquid. Hygroscopicity is mainly due to the three OHs on glycerol, which have a strong affinity for water. This property is greatly enhanced when it forms a salt with sodium. Freshly prepared NaOgl appeared as gray and “chalky” powder that is very hygroscopic. XRD analysis of the solid reveals sharp peaks (2θ (deg): 10.98, 23.60, 30.36, 35.66) indicative of its crystalline nature (Figure 1). These peaks exactly compare with the data reported in the crystallography database (<https://journals.iucr.org/e/>) by Schatte and co-workers (Schatte et al., 2010). The comparison of peaks was accomplished by exporting the crystallographic information file (CIF) data of NaOgl and the plot was visualized using VESTA software (Momma & Izumi, 2008). The plot is submitted to the journal as supplementary information. This evidence proves the successful preparation of NaOgl. In another preparation procedure (Santos et al., 2024), one of the starting materials (i.e., EtOH) becomes integrated into the crystal structure of NaOgl. For this reason, the XRD plot reported, contrary to the claim, does not represent NaOgl.

The FTIR spectra of NaOgl (solid) and glycerol (liquid) show two different compounds with noticeably different band intensities especially at the O-H stretching region ($3400\text{--}3650\text{cm}^{-1}$) (Figure 2). FTIR characterization for a related glyceroxide, CaOgl also revealed the same O-H stretching band (Esipovich et al., 2018). Furthermore, the absence of a strong stretching band at about 1700cm^{-1} in the spectrum indicated that NaOgl was not converted to an unwanted carbonyl derivative under the prevailing preparation condition.

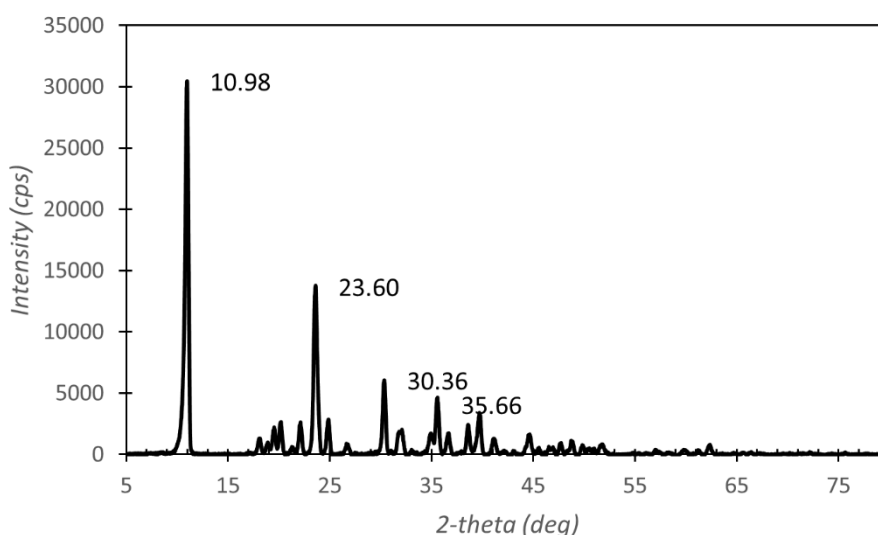


Figure 1. X-ray diffraction spectrum of NaOgl. Instrument parameters: Rigaku Ultima IV, Parallel beam geometry, $2\theta/\theta$ 5.0000 to 80.0000, Sampling width 0.0200, Scan Speed 10.000, Cu target ($k\alpha$ 1.54); diffraction angle is related to Bragg's equation, $n\lambda=2d\sin\theta$; cps, counts per second. The dominant peaks at 10.98, 23.60, 30.36, 35.66° (2θ) and others replicate the peaks in the crystallography database (<https://journals.iucr.org/e/>) by Schatte and co-workers (Schatte et al., 2012) which can be accomplished by exporting the crystallographic information file (CIF) data and plotting them using VESTA software (Momma & Izumi, 2008).

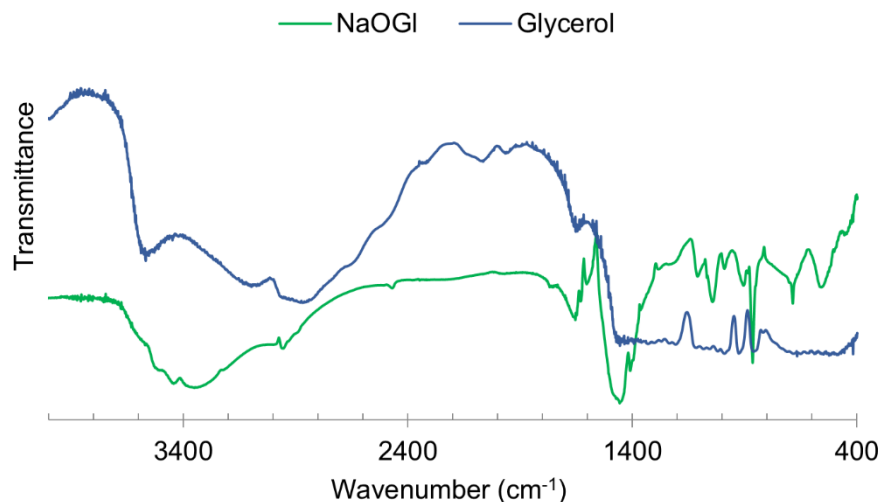


Figure 2. FTIR spectra of NaOGL (solid) and Glycerol (liquid). Shimadzu FTIR with KBr sample matrix and IR Solution software.

Hydro-stability assessment. A measured amount of dry NaOGL samples was allowed to stand in a room at ambient conditions. It revealed that NaOGL can absorb as much as 80% water over its dry mass before saturation after three hours. Interestingly, 50% of this mass is absorbed in the first 30 minutes of exposure to air (Table 1 and Figure 3). In addition to being naturally hygroscopic, NaOGL also reacts rapidly with water, in air and in aqueous solution. NaOGL is an alkoxide, a strong base that is highly reactive to weak acids like water. Aqueous solutions of alkoxides are basic because of the hydrolysis reaction between alkoxides and water-producing free hydroxide ions (OH^-). This characteristic was demonstrated for NaOGL by simple pH measurement (Table 2). Even a small amount (about 100 mg) dissolved in water (25 ml) produces a pH as high as over 12 units. Hygroscopicity and high reactivity with water make handling stoichiometric quantities of NaOGL difficult under “wet” conditions like the one previously attempted (Cayona & Yu, 2023).

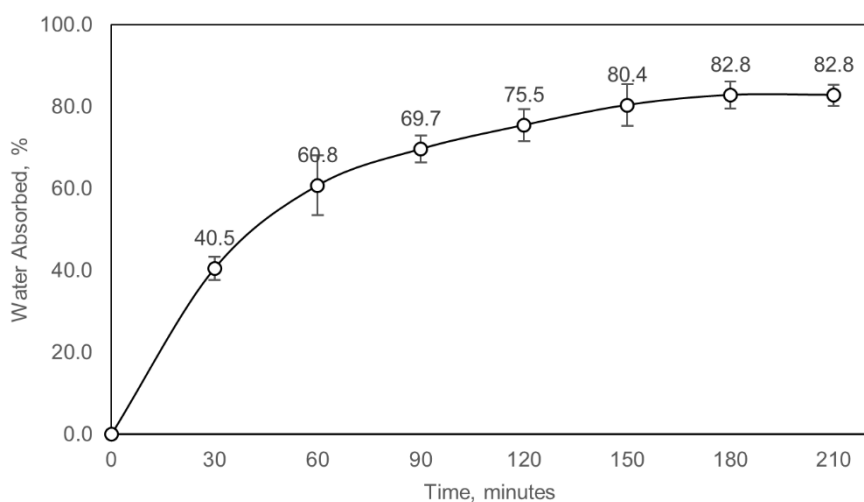


Figure 3. Water absorption profile of NaOGL. Experiment was done at ambient laboratory condition ($T = 27^\circ\text{C}$; $\text{RH} = 45\%$); mean of three trials per data point; $\% \text{Water absorbed} = \frac{m_t - m_0}{M_0} \times 100\%$; m_t , mass of sample (in g) at time, t (in minutes); m_0 , mass of dried sample.

Table 1. Raw data for the absorbed water of NaOgl sample at different time intervals.

Time interval, min	Sample mass, g			Water absorbed, %				Standard deviation
	Trial 1	Trial 2	Trial 3	Trial 1	Trial 2	Trial 3	Average	
0	0.109	0.110	0.107	0.0	0.0	0.0	0.0	0.00
30	0.155	0.151	0.152	42.2	37.3	42.1	40.5	2.80
60	0.182	0.168	0.174	67.0	52.7	62.6	60.8	7.30
90	0.185	0.183	0.185	69.7	66.4	72.9	69.7	3.27
120	0.194	0.188	0.190	78.0	70.9	77.6	75.5	3.97
150	0.200	0.192	0.196	83.5	74.5	83.2	80.4	5.08
180	0.201	0.197	0.198	84.4	79.1	85.0	82.8	3.27
210	0.200	0.198	0.198	83.5	80.0	85.0	82.8	2.58

Note: Measured at RT = 27°C and RH = 45%.

Table 2. pH of NaOgl solution at 27.0°C.

Trial No	Dry Mass, g	Volume, mL	Concentration, mol/L	Actual pH at 27.0°C	Average
1	0.109	25.00	0.0382	12.27	12.29
2	0.110	25.00	0.0386	12.32	
3	0.107	25.00	0.0375	12.28	

Instrument parameters: Eutech Instruments pH 700 pH/mV/°C/°F; calibration buffers pH 4, 7 and 10; slope of the line, 98.7 %.

CONCLUSIONS

NaOgl, a compound commonly used as a catalyst in the preparation of biodiesel with promising new application in the selective synthesis of MAGs, was successfully synthesized using the method described previously (Cayona & Yu, 2023). The XRD result of the synthesized material corroborated with the data available in the crystallographic database while FTIR spectroscopy revealed its characteristic features. Hydro-stability assessment revealed that NaOgl is a highly hygroscopic solid that can absorb 50% of the total amount of water until saturation within 30 minutes. In addition, NaOgl is also deactivated by water in the air and in the solution. As previously reported, hygroscopicity and high reactivity towards water are the main sources of inefficiency in the synthesis of MAGs under ambient conditions. To be able to utilize NaOgl effectively in the synthesis of MAGs and other related applications, the reaction must be carried out under an inert (e.g., dry air, inert gases) environment.

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