

Short communication

Additives assisted catalytic cyclo-dehydration of diethylene glycol in near-critical water

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Abstract

The additives assisted the cyclo-dehydration of diethylene glycol (DEG) reaction was studied in near-critical water (NCW). Zinc chloride (ZnCl_2) and sodium carbonate (Na_2CO_3) were selected to investigate their effects on the cyclo-dehydration of diol. The influences of reaction temperature, time, pressure, reactant/water ratio (r/w) and the concentration of additives on the product yield of the cyclo-dehydration of DEG were examined. The results showed that the final obtained product was primarily 1,4-dioxane, resulting from the cyclo-dehydration of DEG in NCW. The yield of 1,4-dioxane was only 9.84 wt.% in pure water by reacting at 340 °C for 240 min, but the maximum yield of 1,4-dioxane could reach as high as 50.89 wt.% in the solution of 0.50 wt.% ZnCl_2 at 340 °C for 120 min, and the conversion of DEG was 91.94 wt.%. The complete conversion of DEG was obtained in 1.00 wt.% ZnCl_2 at 340 °C for 120 min, but the yield of 1,4-dioxane was only 10.18 wt.%. In the case of Na_2CO_3 , it did not have significant promotion effect on the cyclo-dehydration of DEG reaction. All these experimental results demonstrated that ZnCl_2 had the positive effects on the dehydration of DEG while Na_2CO_3 depressed the reaction. Based on these results, a possible reaction mechanism and pathway was proposed in NCW.

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Keywords: Diethylene glycol; Cyclo-dehydration; Additives; Near-critical water; Reaction mechanism**1. Introduction**

Water is an ecologically safe substance that it is widely used in industry and everyday life of human beings. Water near its critical points (near-critical water, NCW, $T = 150\text{--}374$ °C, $P = 0.4\text{--}21.83$ MPa) possesses very interesting properties, such as high ion product, low dielectric constant and good solubility of various materials [1–3]. These properties are unique, and can also be tuned easily by changing temperature and pressure, and open the opportunity to use NCW as a reaction medium for many organic reactions [4]. One of these properties, the ion product is up to three orders of magnitude higher than its value at ambient temperature, indicates that water is an acid/base catalyzed precursor to catalyze organic reactions such as dehydration. Dehydration of alcohols is an important type of reaction in biomass transformation. Currently, report are available in the

open literatures main on dehydration of alcohols in near or super critical water ($T_c = 374.1$ °C, $P_c = 21.83$ MPa, $\rho = 0.325$ g/cm³). In those system, most alcohols investigated were aliphatic mono-hydric or polyhydric alcohols [5,6], but hetero-atoms containing polyhydric alcohols were rarely studied.

In this paper, DEG was selected as a model compound to investigate the cyclo-dehydration assisted with additives, because 1,4-dioxane, the cyclo-dehydration product of DEG, is an excellent solvent with high volatility and solubility and is widely used in the manufacture of specialty chemicals, pesticides and bulk drug intermediates [7]. Traditionally, preparation of 1,4-dioxane from the cyclo-dehydration of DEG is carried out employing catalysts such as mineral acids (such as sulphuric acid or phosphorus acid), heteropoly acid, cation exchange resin, or zeolite, etc. [8–11]. However, these catalysts have some disadvantages for cyclo-dehydration of DEG. Mineral acids would either corrode the reaction equipment or bring pollution to the environment; heteropoly acid was too expensive to use; the usage of cation exchange resins would be massive and regenerated; zeolite would be deactivated in the usage of process. For the first time, we used the peculiarity of NCW to synthesize 1,4-dioxane.

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ZnCl₂ and Na₂CO₃ were added in the system to investigate the effects of additives on the cyclo-dehydration of DEG. The influences of reaction temperature, time, pressure, *r/w* ratio and concentration of additives on the yield were considered. Based on the experimental results, a possible reaction mechanism and pathway of dehydration of DEG was proposed.

2. Experiments

2.1. Reaction procedure

All reagents were commercially available from China National Medicines Corporation Ltd. at a purity of ≥ 99 wt.% and were used as received. Pure water was redistilled after deionization. High purity nitrogen was used as the shielding gas.

Reaction was conducted in a closed batch reactor (stainless 316) consisted of a body with a constant volume of 16.5 cm³ and a cap. The upside of the cap outfitted with two pipes was connected with one inlet valve and one outlet valve, respectively. There was a pressure gauge at the same pipe with the outlet valve in the vertical direction; a dip nozzle and an inlet pipe were welded on the underside of the cap as described in the previous literature [12]. New reactor was conditioned with high temperature and pressure water for a few hours to eliminate wall effect before using. Reactant, additive and water were added into the reactor in terms of proportion. The loaded reactor was purged by flowing high purity nitrogen for about 30 min to expel any air in the head space and was sealed with traditional wrenches; the desired pressure was achieved by changing the content of high purity nitrogen. The reactor was put into salt bath which was preheated 60 °C higher than the desired reaction temperature ensuring the reaction system can rapidly reach the desired temperature. About 5 min, the reactor reached the desired temperature and was controlled isothermally by an Omega temperature controller (± 1 °C) with a thermocouple inserted into the dip nozzle in the reactor. The reactor was removed from the molten salts and immersed into ice water bath to terminate the reaction when the desired reaction time had elapsed, and was opened after pressure reduction. The samples were collected and the reactor was rinsed with water for three times to recover the liquid and solid products, including the additives. The final reaction mixture was filtered with a membrane to separate the insoluble residue. Experimental errors were estimated by repeating 3–4 runs at the identical conditions. Experiments were conducted at different batch holding temperatures, times, pressures, *r/w* (wt./wt.) ratios and different concentrations of additives, to determine the influences

of these parameters on the reaction. The experimental conditions examined were: temperature ranges of 250–340 °C, time ranges of 30–240 min, pressure ranging from 8 to 18.4 MPa, *r/w* ratio (wt./wt.) ranging from 1:10 (wt./wt.) to 1:100 (wt./wt.), and different concentrations of additives (0, 0.05, 0.10, 0.50 and 1.00 wt.%). The behavior of the reaction environment under the conditions investigated was almost a complete single phase.

2.2. Analysis

The liquid samples obtained were analyzed quantitatively by Water 1525 HPLC, equipped with Pack Column Zorbax-ODS, (C₁₈) (4.6 mm i.d. $\times$ 250 mm, 5 μ m) column, a mobile phase consisting of acetonitrile/water (*v/v* = 3 : 1), flow rate of 1.0 ml/min, column temperature of ambient temperature, detected wave-length of 200 nm. Products were identified by matching retention times with those of known standards and quantified using calibration curves and qualitatively analyzed by inspecting mass spectra.

3. Results and discussion

Traditionally, the cyclo-dehydration of DEG was carried out by acid catalyst which could offer rich hydronium ions (H⁺) to initiate and promote the reaction. The detected products of selectivity were strongly depending on the concentration of H⁺ in the reaction system [13]. NCW could offer more concentration of H⁺ resulting from its self-dissociation than its concentration at ambient temperature; as a result, NCW had a potential ability to initiate the cyclo-dehydration of DEG. The main reaction mechanism about acid-catalyzed the cyclo-dehydration of DEG in NCW was described as follows (Fig. 1).

3.1. Yield dependence of 1,4-dioxane on different conditions

3.1.1. Yield dependence on time

All the experiments were conducted by holding the following parameters constant: *r/w* ratio (1:10, wt./wt.), reaction temperature (250, 265, 280, 300, 320 and 340 °C) and pressure (15 MPa), while varying the reaction time.

Firstly, the reactivity of DEG in pure water was investigated at 340 °C, pressure 15 MPa and *r/w* ratio 1:10.

The curve trend in Fig. 2 shows that, with no additives assisted, the yield is unsatisfactory under the conditions of 340 °C, 15 MPa and *r/w* ratio 1:10 in water. When reaction lasted about 240 min, the yield of 1,4-dioxane was only 9.84 wt.%. It also suggested that the concentration of H⁺ coming from the self-

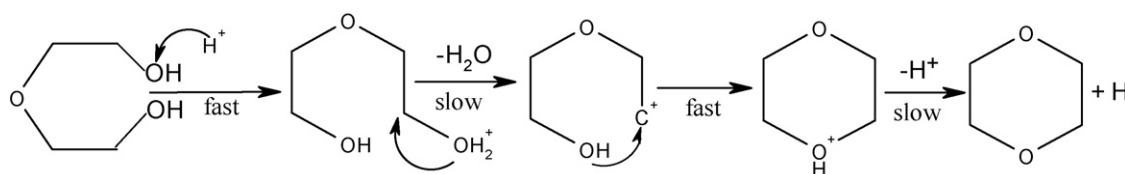


Fig. 1. Main reaction mechanism for the cyclo-dehydration of DEG to 1,4-dioxane.

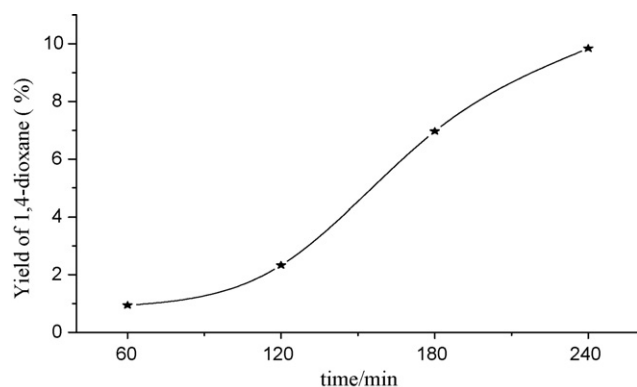


Fig. 2. Yield dependence of 1,4-dioxane on time in NCW at 340 °C, 15 MPa.

dissociation of NCW could not accelerate but merely initiate the cyclo-dehydration of DEG in the reaction system.

The yield did not obviously increase along with the prolonging of the reaction time, and the curve of yield appeared to approach to a horizontal asymptote because of a possible equilibrium between DEG and 1,4-dioxane which could be explained by Le Chatelier's principle. Since the equilibrium existed between them, it's difficult to convert all the DEG to 1,4-dioxane. It supposed that if one of products, such as water, was removed, the equilibrium would shift in the direction favoring the products (1,4-dioxane and water in this experiment). However, the reaction was conducted in a full of water environment, it was a disadvantageous factor for the cyclo-dehydration of DEG according to Le Chatelier's principle [6].

Fig. 3 describes the trends of yield curve dependence of 1,4-dioxane on time in the solution of 0.50 wt.% ZnCl₂ at different temperature. The yield increased with increasing reaction time and temperature, unfortunately, when the reaction time continued to prolong, it decreased gradually. The yield of 1,4-dioxane could reach the maximum at different temperature, near 120 min, and approached as high as 50.89 wt.% at 340 °C, for 120 min. It illustrated that at 340 °C the formation rate of 1,4-dioxane was faster than the rate of its decomposition and was up to the maximum in short reaction time (less than 120 min). From Fig. 3, we concluded that at higher temperature (300–340 °C), the influ-

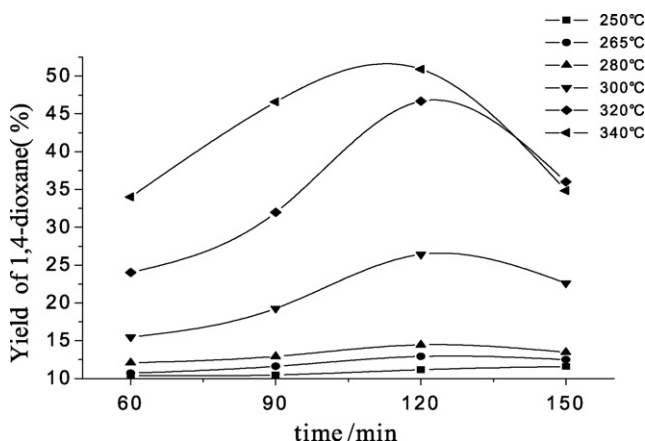


Fig. 3. Yield dependence of 1,4-dioxane in the solution of 0.50 wt.% ZnCl₂ on time at different temperature.

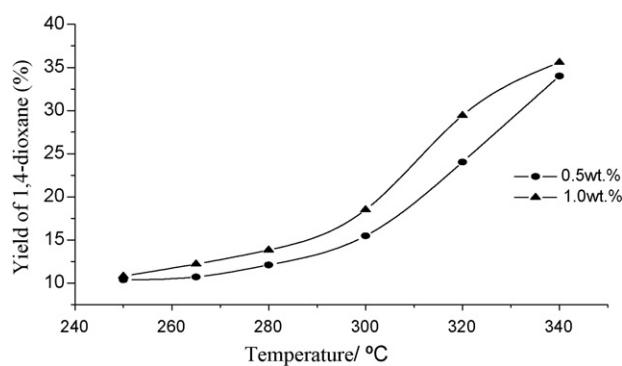


Fig. 4. Yield dependence of 1,4-dioxane on temperature at 60 min with different concentration of additives.

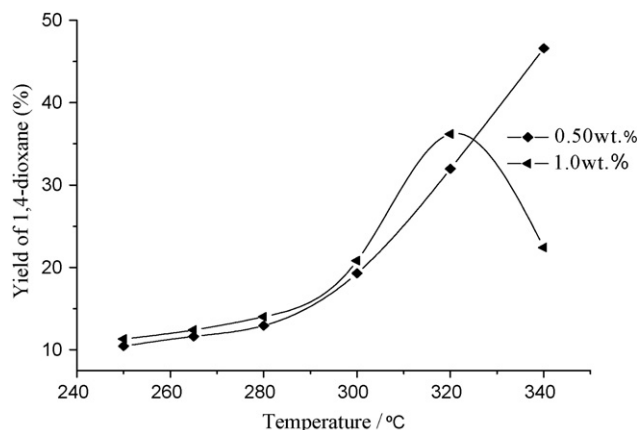


Fig. 5. Yield dependence of 1,4-dioxane on temperature at 90 min with different concentration of additives.

ences of reaction time on the yield were prominent while at lower temperature (250–280 °C) the influences were not as distinct as those at higher temperature.

3.1.2. Yield dependence on temperature at different concentration of additives

Figs. 4–6 present the yield dependence of 1,4-dioxane on temperature at 60 min, 90 min, 120 min with different concentrations of additive and the same *r/w* (1:10) ratio.

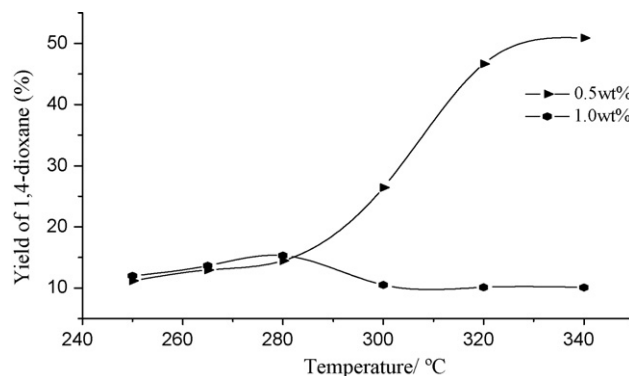


Fig. 6. Yield dependence of 1,4-dioxane on temperature at 120 min with different concentration of additives.

At reaction time of 60 min, the curve trend in Fig. 4 pointed out that higher yield of 1,4-dioxane was achieved in the solution of 1.00 wt.% ZnCl_2 than that of in 0.50 wt.% ZnCl_2 . The same variation of yield was found in the solution of 0.50 wt.% ZnCl_2 and 1.00 wt.% ZnCl_2 as the reaction time elapsing, the increasing speed of yield in 0.50 wt.% ZnCl_2 was much slower than that of in 1.00 wt.% ZnCl_2 under 300 °C, contrary trend of yield was found beyond 300 °C.

At reaction time of 90 min, the yield of 1,4-dioxane reached the highest (36.18 wt.%) at 320 °C in the solution of 1.00 wt.% ZnCl_2 , and decreased when the temperature continued increasing. In case of the solution of 0.50 wt.% ZnCl_2 , the yield of 1,4-dioxane was always enlarging within the investigated temperature.

At reaction time of 120 min, showing in Fig. 6, there was the same curve tendency as in Fig. 5. At lower temperature (<300 °C), the yield of 1,4-dioxane arrived at the highest (15.30 wt.%) at 280 °C in the solution of 1.00 wt.% ZnCl_2 . When the temperature exceeded 300 °C, worse yield was obtained and kept almost constantly; the yield was only about 10.18 wt.% at 300 °C. In the solution of 0.50 wt.% ZnCl_2 , the yield always increased under 320 °C and reached the maximum at 320 °C, a flat tendency of yield was followed when temperature was in the range of between 320 and 340 °C.

Based on above mentioned results, we found that high concentration of ZnCl_2 or too long reaction time was disadvantageous for the formation of 1,4-dioxane, but favorable for the conversion of DEG. Almost complete conversion of DEG was achieved in the solution of 1.00 wt.% ZnCl_2 at 340 °C, 120 min. In higher concentration solution of ZnCl_2 under the condition of elevated temperature or long reaction time, 1,4-dioxane was unstable and would convert to 2-methyl-1, 3-dioxane because of its isomerization [14].

For comparison, we conducted the dehydration of DEG in the solution of 0.50 wt.% Na_2CO_3 at 340 °C, at which temperature the maximum yield of 1,4-dioxane was obtained in ZnCl_2 solution, to study the influence of base salt on the reaction. In the case of Na_2CO_3 , no product was observed even at the reaction time of 180 min, the yield of 1,4-dioxane was zero, and the conversion of DEG was extremely low at the same time. It indicated that Na_2CO_3 could not promote the formation of 1,4-dioxane and suppressed the cyclo-dehydration of DEG, while low concentration of H^+ coming from the hydrolysis of ZnCl_2 was able to enhance this type of reaction, which was consistent with the reported literature [15].

According to the comparison, we conclude that the mechanism of cyclo-dehydration of DEG in NCW is similar to that of traditional conditions dehydration of diol. Weak acidity environment resulting from the hydrolysis of ZnCl_2 can promote the cyclo-dehydration of DEG, not for the basicity environment resulting from the hydrolysis of Na_2CO_3 .

3.1.3. Yield dependence on r/w (wt./wt.) ratio

Fig. 7 depicts the yield dependence of 1,4-dioxane on different r/w ratios at four different temperatures. The investigated r/w ratios were ranging from 1:10 to 1:100 with keeping ZnCl_2 /reactant (ZnCl_2 /DEG, a/r) ratio 1:20 (wt./wt.), at 60 min

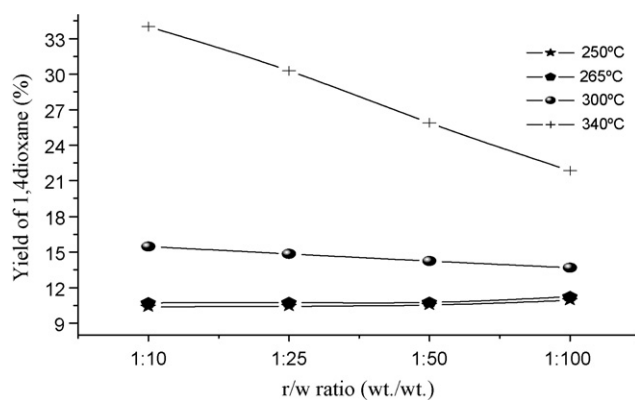


Fig. 7. Yield dependence of 1,4-dioxane on r/w ratio at 60 min with different temperature.

and 15 MPa. The trends of curve in the figure showed the yield of 1,4-dioxane increased slightly at lower temperature (250 and 265 °C) with increasing the content of water in solution; On the contrary, with temperature increasing gradually (300 and 340 °C) the yield of 1,4-dioxane decreased in the same variation content of water. While the yield of 1,4-dioxane at higher temperature was still higher than that at lower temperature. At lower temperature, it is possible that cyclo-dehydration of DEG was easily affected by ion product effect of water. That is because when temperature was around 250 °C, the ion product of water could approach the maximum and provide the maximum concentration of H^+ at its Sat'd vapor pressure, while the ion product of water decreased with temperature increasing when it exceeded 265 °C [16]. At higher temperature, between 300 and 340 °C, the temperature effect was dominant and exceeding the ion product effect of water (which was also called as effect of H^+ concentration). The yield of 1,4-dioxane reached the highest with r/w ratio of 1:10 when temperature arrived at 340 °C. From Fig. 7, we found the ionization of ZnCl_2 was enlarged with the scale-up of r/w , leading to the acceleration of the reaction, but the content of water increasing was disadvantageous for the cyclo-dehydration according to Le Chatelier's principle. According to the aforementioned conclusions, it could be considered that the factor which was dominant at the examined conditions would direct the trend of yield curve.

3.1.4. Yield dependence on pressure

Influence of pressure on the yield was investigated with pressure range of 8–18.4 MPa at the same temperature (300 °C), reaction time (120 min) and equivalent amount of ZnCl_2 (0.50 wt.%), as shown in Fig. 8. Pressure effect was not as prominent as the effects of other parameters on the yield. The ion product of water increased with increasing pressure, which made the concentration of H^+ increased and the dehydration of DEG became easily.

3.2. Conversion dependence of DEG on temperature

Fig. 9 describes the conversion dependence of DEG on temperature in three different r/w ratios solution, at reaction time of 60 min, 15 MPa and a/r ratio of 1:20. In the r/w ratio of 1:10

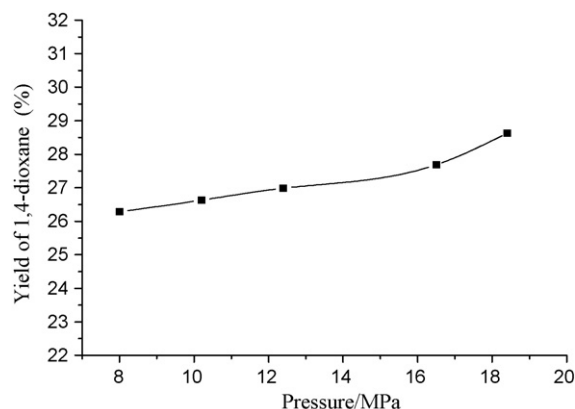


Fig. 8. Yield dependence of 1,4-dioxane on pressure at 120 min and 300 °C.

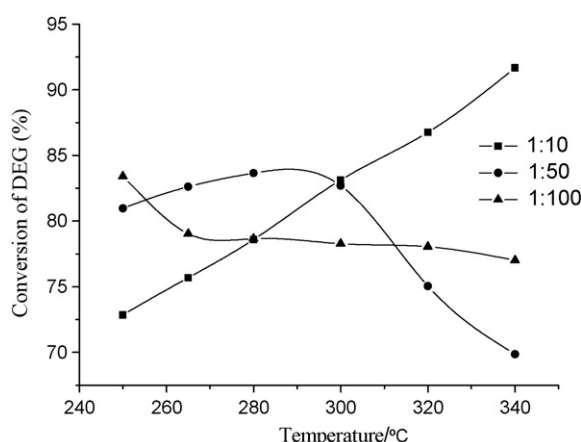


Fig. 9. Conversion dependence of DEG on temperature under the condition of various r/w ratios, 60 min, a/r ratio of 1:20.

solution, there was a large scale of increasing in conversion of DEG with temperature ranging from 250 to 340 °C. A similar trend of the conversion variation investigated at lower temperature was observed in the r/w ratio of 1:50 solution, while the trend of conversion began to decrease as temperature beyond 300 °C. In the r/w ratio of 1:100 solution, with increasing reac-

tion temperature, there was opposite conversion trend of DEG contrary to the trend in the r/w ratio of 1:10 solution. We kept the content of water constant in the reactor by changing the amount of DEG in water to realize the r/w ratios of variation. The concentration of ZnCl_2 gradually decreased with the enlargement of r/w ratios, which caused the concentration of H^+ became very low in larger r/w ratio solution. From aforementioned experimental result, it is known that high concentration of ZnCl_2 was favorable for the conversion of DEG in the range of investigated temperature. Therefore, high concentration of ZnCl_2 would get high conversion of DEG at the same reaction time.

There was no 1,4-dioxane detected and no conversion of DEG when Na_2CO_3 instead of ZnCl_2 with the same concentration. Obviously, ZnCl_2 did catalyze the cyclo-dehydration of DEG and the acidity was a predominant factor for the reaction, while the basicity environment, which was coming from the hydrolysis of Na_2CO_3 , exerted an opposite effect on the reaction so that DEG hardly reacted in NCW.

4. Reaction mechanisms

According to the detected product and reaction principles of cyclo-dehydration of DEG [17], a probable reaction mechanism of the dehydration of DEG was proposed and presented in Fig. 10. NCW could provide rich source of hydronium ions (H^+) because of its self-dissociation and this self-dissociation would be intensified by the introduction of ZnCl_2 , which offered high concentration of H^+ by the hydrolysis of ZnCl_2 .

First of all, one of the hydroxyl radicals ($-\text{OH}$) in the DEG is attacked by H^+ to form the transition state I (step 1), which transforms to state II immediately with elimination of a water molecular (step 2). There are two possible routes to undergo for state II (step 3a; step 3b). 1,4-Dioxane (V) is formed following step 3a (which also shown in Fig. 1), and 2-methyl-1,3-dioxane (X) is formed adopting step 6b or step 6a. A possible side reaction is the polymerization of DEG and XI is the production.

Step 3a and step 3b are competing reactions, but the transfer of the end carbon cation (C^+) to the neighbor carbon of methylene (step 3b) is more difficult than that of the end car-

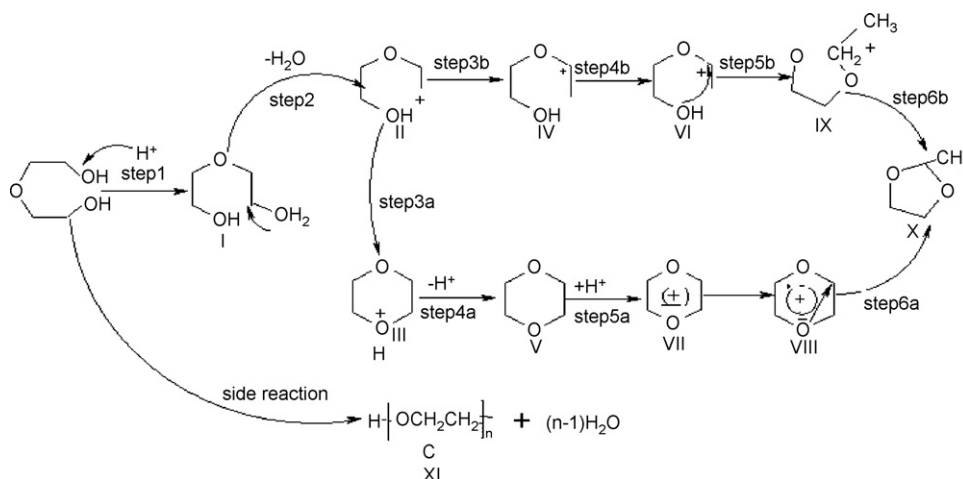


Fig. 10. Global reaction scheme for dehydration of DEG in NCW.

bon cation (C^+) combining with oxygen atom of $-OH$ on the other end of DEG (step 3a). So, step 3a is preferred as the major pathway of the reaction [18]. With the accumulation of 1,4-dioxane (V), the reaction rate of step 5a is quicker than that of step 4a, which leads to the formation rate of 1,4-dioxane (V) become slower than its isomerization rate and forms 2-methyl-1,3-dioxane (X). It makes the yield of 1,4-dioxane decreased. The trend of curve shown in Fig. 3 verifies this possible reaction pathway.

5. Conclusions

The work presented herein discloses a cleaner and more environmentally benign approach for synthesizing 1,4-dioxane from cyclo-dehydration of DEG with additives in NCW compared with conventional methods. The effects of reaction conditions such as reaction temperature, time, r/w ratios, pressure and concentration of additives on the yield of 1,4-dioxane were investigated. The yield of 1,4-dioxane was low (9.84 wt.%) at 340 °C, 240 min without additives in NCW. The maximum yield of 1,4-dioxane was observed (50.89 wt.%) by using $ZnCl_2$ as additive at 340 °C, 240 min, while the yield of 1,4-dioxane was zero by using Na_2CO_3 as additive under the same reaction condition. According to the product and reaction principles, the probable mechanism of the dehydration reaction of DEG was proposed. The simple experimental procedure, fast reaction, easy product detection could be expected to contribute to the development of clean and environmentally benign strategy for the cyclo-dehydration of DEG.

Acknowledgement

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Appendix A. Nomenclature

a/r	additive/reactant ratio
P	pressure (MPa)
r/w	reactant/water ratio

References

- [1] K. Tanaka, Solvent-free organic synthesis, Chem. Rev. 100 (2000) 1025–10740.
- [2] P.T. Anastas, T.C. Williamson, Green Chemistry: Theory and Practice [M], Oxford Science Publications, London, 1998.
- [3] A. Kruse, E. Dinjus, Hot compressed water as reaction medium and reactant: 2. Degradation reactions, J. Supercrit. Fluids 41 (2007) 361–379.
- [4] P.E. Savage, Organic chemical reactions in supercritical water, Chem. Rev. 99 (1999) 603–621.
- [5] R. Thomas, V. Herbert, The dehydration of 1,4-butanediol to tetrahydrofuran in supercritical water, Chem. Eng. Technol. 24 (2001) 340–343.
- [6] V.I. Anikeev, A. Ermakova, D. Manion, et al., Reaction kinetics of 2-propanol dehydration in supercritical water, Kinet. Catal. 2 (43) (2002) 189–194.
- [7] Y.-M. Park, H. Pyo, S.-J. Park, et al., Development of the analytical method for 1,4-dioxane in water by liquid–liquid extraction, Anal. Chim. Acta 548 (2005) 109–115.
- [8] K. Dilip, S.W. Mahajan, A.K. Mandol, et al., Cyclodehydration of non-aromatic diols on Al [III]-montmorillonite clay: reactivity and mechanism, J. Chem. Soc., Perkin Trans. (1988) 1749–1751.
- [9] K. Yoshie, K. Masahiro, Shape selectivity of sepiolite for catalytic cyclodehydration of diethylene glycol to dioxane, Chem. Express. 5 (8) (1990) 545–548.
- [10] J.-F. Liu, Y. Liu, P.-G. Yi, Synthesis of diethylene glycol ethyl ether with diethylene glycol and ethanol by the catalysis of heteropoly acid, Appl. Catal. A 227 (2) (2004) 167–171.
- [11] A. Wali, S.M. Pillai, S. Unnikrishnan, et al., HZSM-5 catalyzed cyclodehydration of diethylene glycol and its derivatives, J. Mol. Catal. A: Chem. 109 (2) (1996) 149–155.
- [12] P.-G. Duan, X. Wang, L.-Y. Dai, Noncatalytic hydrolysis of idna in near-critical water—a green process for the manufacture of IDA, Chem. Eng. Technol. 30 (2007) 265–269.
- [13] S.E. Hunter, C.E. Ehrenberger, P.E. Savage, Kinetics and mechanism of tetrahydrofuran synthesis via 1,4-butanediol dehydration in high-temperature water, J. Org. Chem. 71 (2006) 6229–6239.
- [14] G.R. Wang, X.S. Wang, Y.C. Yuan, et al., Study on preparing dioxane with the ZSM-5 zeolite catalyst, Special. Petrochem. (China) 3 (1991) 32–36.
- [15] Z.-Y. Dai, B.-P. Hatano, H.-Y. Tagaya, Catalytic dehydration of propylene glycol with salts in near-critical water, J. Appl. Catal. A: Gen. 258 (2004) 189–193.
- [16] W.L. Marshall, E.U. Franck, Ion product of water substance, 0–1000 °C, 1–10,000 bars new international formulation and its background, J. Phys. Chem. Rev. Data 10 (1981) 295–304.
- [17] J.-F. Liu, G.-P. Yi, Y.-S. Qi, Cyclization of diethylene glycol on heteropoly acid, J. Mol. Catal. (China) 13 (6) (1999) 419–425.
- [18] S.R. Yang, S. Lin, A study on kinetics of liquid phase dehydration reaction of diethylene glycol forming 1,4-dioxane, J. Petrochem. Technol. 20 (9) (1991) 625–629.