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Studies on mechanism for homogeneous catalytic hydration of ethylene oxide: Effects of pH window and esterification

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ABSTRACT

Selective hydration of ethylene oxide (EO) was investigated with several inorganic salt systems as homogeneous catalysts. By optimizing reaction conditions, the highest monoethylene glycol (MEG) selectivity of 98% was obtained with >99% EO conversion at a water/EO molar ratio = 10. The effects of pH value and anion addition–esterification on MEG selectivity were systematically studied, and a comprehensive mechanism was proposed based on the results. The conclusion should be useful in developing high performance catalysts for the manufacture of MEG by EO hydration at a low water/EO ratio.

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1. Introduction

Monoethylene glycol (MEG) has been widely used as an intermediate to make various products, such as polyester fiber, antifreeze, lubricant and so on. MEG is commercially produced by thermal hydration of ethylene oxide (EO) with significant amounts of by-products diethylene glycol (DEG) and triethylene glycol (TEG). In pursuit of high selectivity to MEG, a large excess amount of water (about 30 mol water/mol EO) has to be used, which ultimately increases production cost due to high enormous energy consumption occurred during the distillation process to remove water. Therefore, considerable efforts have been made to explore efficient catalysts working at a low water/EO ratio. The catalysts reported in the literature include anion exchange resins [1–4], supported metal oxides and zeolites [5–8], quaternary phosphoniumhalides [9], polymeric organosilane ammonium salts [10] and macrocyclic chelating compounds [11]. However, none of the catalysts has been developed to commercial application. The resins swell and deactivate under reaction conditions. The preparation of other catalysts is too complicated or expensive. On the other hand, some low cost soluble salts were reported as good homogeneous catalysts for EO hydration [12–15]. We chose to study reaction mechanism of EO hydration in the presence of these low cost soluble salts as homogeneous catalysts. The catalysts, inorganic salts and their acid counterparts such as carboxylates, carbonates, phosphates and sulfites were evaluated under both acidic and basic conditions. The effects of pH value and addition–esterification of anion were also studied. Based on our observations, a comprehensive mechanism for EO hydration was proposed, which should be useful in optimizing catalyst composition and reaction conditions, and exploring more efficient catalysts.

2. Experimental

2.1. Materials

All the chemicals used in the present work were purchased and employed without further purification or treatment.

2.2. Catalytic testing

The hydration reaction of EO was carried out in an isothermal batch autoclave reactor with a H_2O/EO molar ratio of 10 under continuous stirring. The reaction temperature was maintained at 120 °C and the pressure was kept as 1.5 MPa by N_2. The amount of catalyst used was normally 0.20 mol/mol EO. After 1 h reaction, the reactor was cooled down and the products were analyzed on a GC920 gas chromatograph equipped with a HP-INNOWAX column and a FID detector. HP6890/5973 GC–MS was used to verify some other by-products. As EO conversion with any catalyst was nearly 100%, MEG selectivity was taken into account as the criterion for comparison of catalyst performance.

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3. Results and discussion

3.1. Reaction results

3.1.1. The effect of pH value

Five soluble salts and their conjugated acids were used as catalysts for the hydration of EO. Fig. 1 shows MEG selectivities of these five catalysts versus pH value. The pH values of the reaction solutions were controlled by adjusting the ratio of the salts and their conjugated acids. To avoid the possible influence of catalyst concentration on the reaction, the total amount of the anions ($A^- = HCOO^-$, CH_3COO^-, CO_3^{2-}, PO_4^{3-} or SO_3^{2-}) in each reaction solution was kept constant at 0.20 mol/mol EO. Although MEG selectivities with these catalysts are quite different, their variations with pH value are similar. The best selectivity with each catalyst was obtained when the pH value is in the ranges of 3.0–6.0 and 7.5–10.0, respectively, which are defined as two pH windows. Similar results were reported previously [16,17]. Although strong acidic or basic catalysts can accelerate reaction rate of the hydration, a low MEG selectivity was obtained. The same group also reported the EO hydration can be catalyzed by soluble amine, bifunctional (EDTA family) and salen compounds, and a catalyst with high MEG selectivity requires a pH value ranging from weakly acidic to weakly basic [17].

3.1.2. Effects of anion and concentration

Besides the effect of pH value, it is also observed in Fig. 1 that the catalysts with different acid anions give different selectivities. The formate and carbonate are the best in the acidic and basic pH windows, respectively, whereas the sulfite results in the lowest selectivity in both windows. In order to study the effect of the anions on the hydration, carboxyl acid with different alkyl chain length and β-chlorine substitution were investigated (Table 1). The pH value of the reaction solution was kept at 3.5–3.8 by adding conjugated salts, and the total anion concentrations were 0.20 and 0.10 mol/mol EO in these two cases, respectively. The results show MEG selectivity decreases with increasing alkyl length and increases with increasing chlorine substitution (Table 1). Liu et al. [18] investigated the effect of the alkyl chain length of carboxylic acid on the kinetics of acid-catalyzed esterification in liquid-phase, and found that esterification rate decreased as alkyl chain length increased. It was suggested that the chlorine substitution on β-carbon can decrease the electron density on the carbonyl in chloroacetic acids due to the electron-withdrawing substituent group [19], and consequently increase their esterification capability. The observed high MEG selectivity in the present might be attributed to the esterification effect of carboxyl groups.

Table 1
Effects of alkyl length and β-chlorine substitution for carboxyl acid systems on MEG selectivity.

Catalyst type	Catalyst amount (mol/mol EO)	pH	MEG selectivity (%)
$HCOONa–HCOOH$	0.2	3.7	97
$CH_3COONa–CH_3COOH$	0.2	3.8	93
$C_2H_5COONa–C_2H_5COOH$	0.2	3.8	91
$CH_3COONa–CH_3COOH$	0.1	3.8	89
$CHCl_2COONa–CHCl_2COOH$	0.1	3.5	91
$CCl_3COONa–CCl_3COOH$	0.1	3.5	94

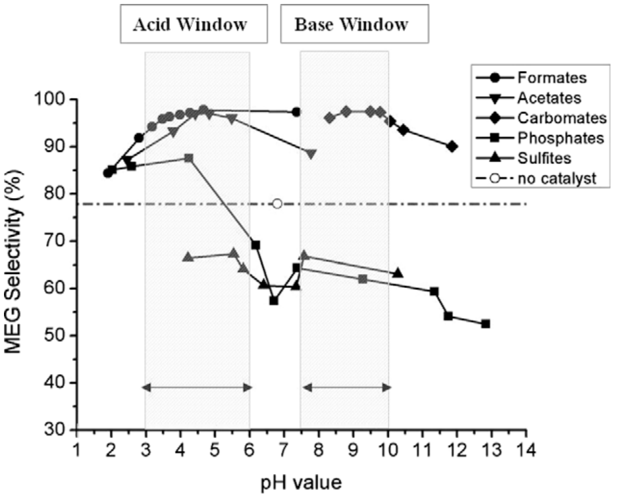

Fig. 1. MEG selectivities of different catalysts versus pH value.

The esterification effect of acid anions on MEG selectivity is shown in Fig. 2. The pH value was controlled by fixing CH_3COONa/CH_3COOH (pH = 3.7) and $Na_2CO_3/NaHCO_3$ (pH = 9.8) ratios. The two anions have the same effect. The selectivity rapidly increases with the amount of catalyst used till its concentration reaches 0.15 mol/mol EO after which no significant increase is observed. The highest MEG selectivity in both systems is over 97%. Again, almost complete EO conversion was achieved.

The acetates with Na^+, K^+ and Ca^{2+} were examined for the hydration under identical conditions to investigate the effect of cations. It was found that the MEG selectivity varied very little in the presence of the acetate catalysts solutions with different cations, indicating that the influence of the cations on this reaction can be ignored.

3.1.3. Effects of reaction temperature and water/EO ratio

Fig. 3 shows the effects of reaction temperature and water/EO ratio on EO conversion and MEG selectivity using sodium formate as catalyst. MEG selectivity slightly increases with reaction temperature up to 120 °C, but decreases rapidly at higher temperatures. The highest MEG selectivity is about 97% at 100–120 °C. Water/EO ratio strongly influences MEG selectivity. At a water/EO ratio of 10, the MEG selectivity is ca. 97%, further increasing of water/EO ratio has negligible influence on the MEG selectivity. In any case, EO conversion was high.

For comparison, the additive results of thermal hydration on the condition of different reaction temperature and water/EO ratio are shown in Fig. 3. It is found that the EO conversion in thermal hydration is much lower than the formate catalyzed system up to a reaction temperature of 120 °C for its lower reaction rate at low temperature, and almost no difference is found between blank

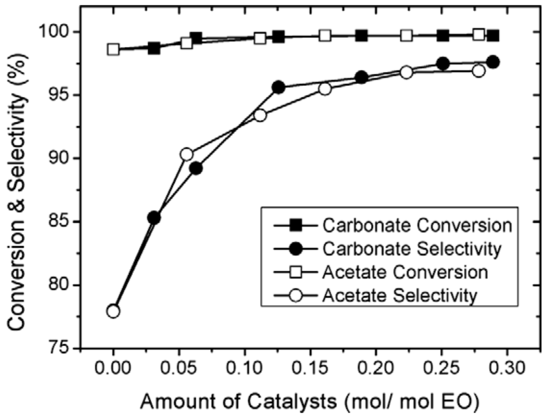

Fig. 2. Effect of catalyst concentration on MEG selectivity and EO conversion for carbonate and acetate systems.

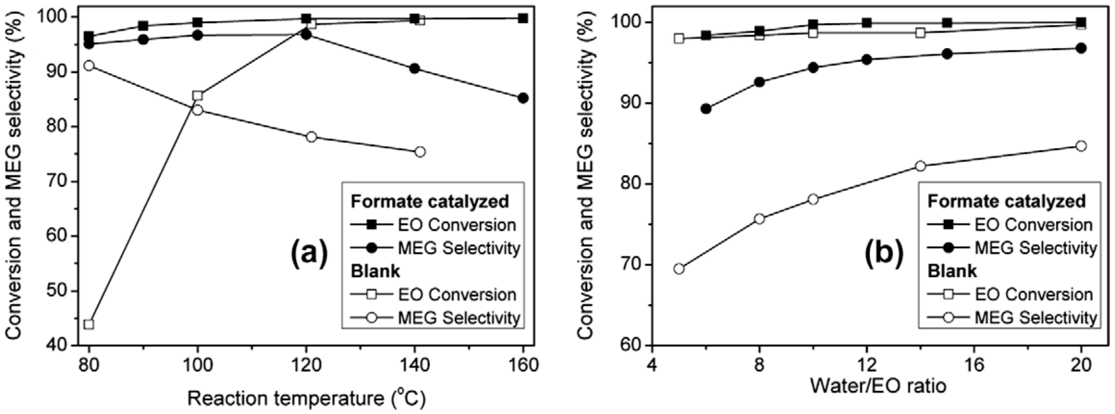

Fig. 3. Effects of (a) reaction temperature and (b) water/EO ratio on EO conversion and MEG selectivity in formate catalyzed and thermal hydration (blank test).

and catalyzed reactions with the changing of water/EO ratios. However, MEG selectivity in thermal hydration is much lower than the catalyzed system. Even at a water/EO of 20, the MEG selectivity of blank system is still lower than formate catalyzed system at a water/EO of 5.

3.2. Mechanism of EO hydration in acidic and basic solutions

As shown in Section 3.1, the pH value plays a key role on MEG selectivity, and esterification effect of acid anions further enhances the selectivity. Similarly, Shvets et al. [12,20–22] studied the kinetics of EO hydration using homogeneous salts as catalysts and suggested a possible process of ester formation. van Hal et al. [16] proposed a reaction mechanism to explain a good correlation between catalyst performance and its acidity/basicity. However, it seems difficult to explain why MEG selectivity increases with the increasing of the catalyst concentration since pH value of the reaction solution was kept constant. On the basis of the facts found in this paper and those reported previously, a more comprehensive mechanism was proposed, as shown in Fig. 4.

For acid-catalyzed reaction (Fig. 4a), a protonated EO (EOH^+) is formed as an initial active intermediate. In thermal hydration without any catalyst, H_2O can attack a carbon atom in the EOH^+ through S_N2 mechanism, producing one MEG with releasing of a proton (Route 1). At the same time, the EOH^+ can also be attacked by an unprotonated EO to form undesirable by-products of oligomers through Route 3. Therefore a large amount of excess water is necessary to ensure the high MEG selectivity by promoting Route 1 [23]. In the presence of an acid catalyst, the anion A^- can also attack the carbon atom in the EOH^+ to form an ester intermediate leading to MEG with releasing of a proton (Route 2). These three routes proceed in parallel and are competitive, and the MEG selectivity is ultimately determined by their relative rates which depend on pH value and esterification capability of the anions.

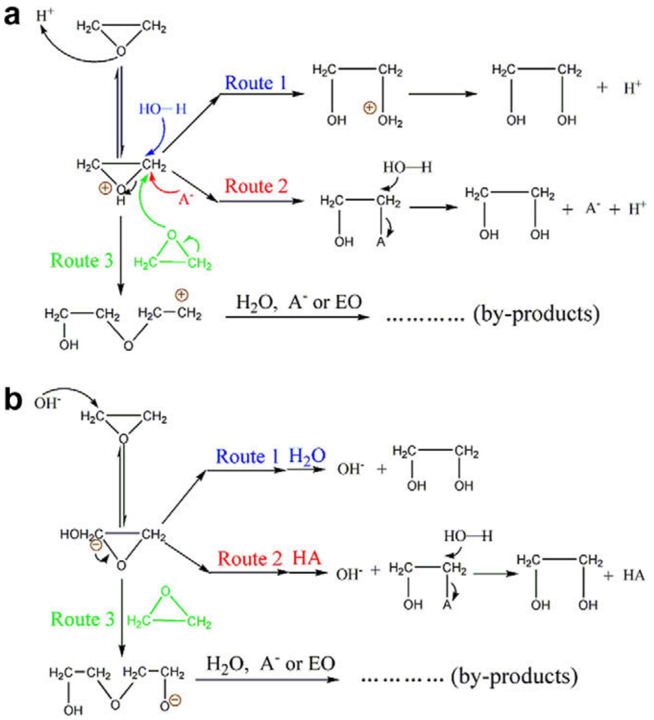

Fig. 4. Schematic diagrams of reaction mechanisms in (a) acidic and (b) basic systems.

The results reported in this paper may well be explained in this mechanism. For acidic systems, when its pH value is low, the strong acidity may accelerate the rate of the EOH^+ formation. However, Route 2 would be suppressed because the anion species predominantly exist in the form of unionized form in the solution at a low pH value, thus resulting in the relatively low MEG selectivity. On the other hand, if the acidity is too weak, the rate of EOH^+ formation would be low because of the low concentration of H_3O^+, consequently a large amount of unprotonated EO will favor the oligomerization through Route 3. When the A^- anions with high esterification capability exist in the reaction system, such as formate and acetate, the route via the ester intermediate (Route 2) will occur in addition to the traditional hydration by water (Route 1), enhancing overall MEG selectivity. Such a promotion effect could be optimized by careful selection of the type (Table 1) or concentration (Fig. 2) of acid anions.

The mechanism of EO hydration in basic systems (Fig. 4b) is rather similar to that in acidic solutions. The EO molecule is first activated by hydroxyl anion in the solution to form an intermediate that will further react via three competitive routes in parallel. When a catalyst is added, Route 2 via ester intermediate will greatly enhance the formation of MEG. A catalyst concentration up to 0.15 mol/mol EO will benefit for the esterification and thereby enhance the MEG selectivity.

It is also noted that MEG selectivity in some solutions, such as sulfite, is even lower than that of thermal process without any catalyst (Fig. 1). To understand the reason for the low MEG selectivity, pH values of all the catalyst solutions were measured before and after the reaction. It is found that the pH values of the solutions

Table 2
Difference of pH value before and after reaction corresponding to the MEG selectivity for different systems.

Carboxylate systems		Phosphate system		Carbonate system		Sulfite system	
Selectivity (%)	pH rising	Selectivity (%)	pH rising	Selectivity (%)	pH rising	Selectivity (%)	pH rising
84	0.8	83	0.1	96	0.2	63	3.2
92	0.2	85	0.3	97	0.3	67	5.9
94	0.2	85	0.1	97	0.3	61	6.7
96	0.2	86	−0.1	95	0.3	67	4.8
96	0.2	88	1.0	90	0.5	–	–
97	0.2	69	2.2	–	–	–	–
97	0.1	57	4.3	–	–	–	–
98	0.1	64	4.6	–	–	–	–
96	0.1	62	3.6	–	–	–	–
96	0.5	59	2.0	–	–	–	–
97	0.3	54	1.6	–	–	–	–

with low MEG selectivity dramatically increased after the reaction, while those with high MEG selectivity only had minor change throughout the whole reaction process (Table 2). As can be seen, the pH value increase after the reaction is 2.0 or more for the sulfite system with low MEG selectivity (<70%), while that for the systems with high selectivities (>90%), such as carboxylate and carbonate, is typically $\leqq 0.5$. The same correlation between pH value increase and MEG selectivity was also observed with the phosphate system covering a wider range of pH value. It is interesting to note the sudden transition of pH value as the selectivity decreases from >85% to <70%. GC–MS results confirmed the formation of glycol oligomers in solutions encountered pH rising, such as DEG, TEG and tetraethylene glycol. These by-products containing more ester linkages can strongly adsorb water and capture H_3O^+, leading to the pH of reaction solution alkalization. Once the alkalization happens, the solution might jump out the pH window to produce more by-products. And the by-products will further alkalize the solution through capture H_3O^+, causing the reaction system to enter a vicious circle and further lower MEG selectivity.

4. Conclusions

Several inorganic salt systems were investigated as homogeneous catalysts for EO hydration. The comprehensive mechanisms with both acidic and basic catalysts were proposed based on the experimental observations. Two pH windows having pH values of 3.0–6.0 and 7.5–10.0 for optimizing the MEG selectivity were discovered. Moreover, the esterification effect of the acid anion is also proved to enhance the MEG selectivity. Formate, acetate and carbonate are found to be the best catalysts because of their adjustable pH range and suitable esterification capability. By optimizing the reaction conditions, the highest MEG selectivity of 98% was obtained with >99% EO conversion under the water/EO molar ratio of 10. The results revealed in this paper should be useful in exploring and designing efficient catalysts for EO hydration at a low water/EO ratio.

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