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Investigation of three types of catalysts for the hydration of ethylene oxide (EO) to monoethylene glycol (MEG)

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Abstract

Amine compounds, bi-functional compounds (EDTA, ethylene diamine tetra acetic acid type), and Salen compounds were investigated for catalytic hydration of ethylene oxide (EO) to monoethylene glycol (MEG). Many of the catalysts studied are selective for the formation of MEG compared with thermal hydration without any catalyst present. The results of the catalytic hydration with three types of catalysts were rationalized using acid and base catalyzed reaction mechanisms.

Keywords: Ethylene oxide; Ethylene glycol; Catalytic hydration; Amines compounds; Bi-functional compounds; Salen compounds

1. Introduction

Monoethylene glycol (MEG) is an intermediate for production of polyethylene terephthalate (PET) and a major component of antifreeze. Annual world wide consumption of MEG is over 15 million metric tonnes [1]. MEG is produced predominantly by non-catalytic liquid-phase hydration of ethylene oxide (EO). Diethylene glycol (DEG) and triethylene glycol (TEG) are co-products with MEG in this operation and are separated by distillation. Because of its high demand and better price, it is desirable to maximize MEG production. To obtain a high ratio of MEG to higher glycols in the hydration reaction mixture, a large excess of water (20–25 mol water/mol EO) must be used, which necessitates a large steam input for product separations. Companies generally operate under conditions to maximize MEG output; a typical product mixture is approximately 90% MEG, 9% DEG and 1% TEG [2]. Maximization of MEG is the standard practice since MEG is the most important of these glycol derivatives. However, the thermal hydration is run at its economic limit.

The need to increase MEG selectivity and reduce energy cost has spurred the investigation of alternative routes. One potential new process involves reaction of ethylene oxide with carbon dioxide to form ethylene carbonate, which is then hydrolyzed with a small amount of water to carbon dioxide and MEG. This process promises not only a major reduction in steam consumption but also a negligible output of higher glycols. In 2002, Mitsubishi Chemical announced that it developed an MEG process called the MCC Catalytic EG Process, which uses a phosphorus-based halide catalyst to produce ethylene carbonate as an intermediate. The company claims the process is highly selective towards MEG in excess of 99.3% and is superior in terms of capital and operating costs compared with the conventional thermal hydration process [2,3]. Shell, teamed up with Mitsubishi, offers licensing of this new technology now called Only MEG Advance (OMEGA). However, no successful commercial implementations have been reported so far.

Numerous catalysts have been reported for the catalytic hydration of EO to MEG. A large fraction of them covers the use of catalysts immobilized on ion exchange resins [4–11]. The selectivity to MEG is reportedly as high as 98% with higher EO concentration in feed. However, catalyst stability is a major challenge, because the resins swell under reaction conditions [12]. Other catalysts include organic acid-type compounds [13], supported metal oxides [14,15], polymeric organosilane ammonium salts [9], and macrocyclic chelating compounds [16].

The present work aims to explore new types of catalysts for selective catalytic hydration of EO to MEG. Here we report the

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results of three types of catalysts: amines, EDTA type and Salen materials. We rationalize our results using acid and base reaction mechanisms.

2. Experimental

2.1. Catalyst preparation

Three different types of catalysts were studied in the present work: amines, EDTAs, and Salen type compounds. The compounds were obtained from commercially available sources, and used as catalysts with or without further treatment. More details are described as follows.

The amines were obtained from commercial suppliers and used as catalysts in an amount of about 0.20 g, unless specified otherwise: ethylenediamine (EDA, Aldrich 99%), 0.50 g; diethylamine (DEA, Aldrich, 99.5%); hexamethyleneimine (Acros, 99%); Cyclen (1,4,7,10-tetraazacyclododecane, Aldrich 99%); DABCO (1,4-diazabicyclo [2,2,2] octane, Aldrich, 99.5%); 1,5,8,12-tetraazododecane (Strem, 98%); 2-dimethylaminopyridine (2-DMAP, Aldrich, 97%); *N*,*N*′-dimethylaniline (Aldrich, 99.5%), 0.30 g; Pyridine (Aldrich, 99%), 0.074 g; *N*-(1-adamantyl) urea (Acros, 98%), 0.64 g; and 1,10-phenatroline (PHEN, Strem, 99%), 0.35 g. All amines were run under an atmosphere of CO_2.

The EDTA type compounds (ethylene diamine tetra acetic acid) were purchased as ACS grade or better: iminodiacetic acid disodium salt (Fluka >95%); PIPES (Aldrich >95%), dipotassium salt (Fluka >99%); diammonium EDTA (Fluka >99%); disodium nitrilotriacetic acid (Strem, >99%); poly-D,L-aspartic acid (Aldrich, MW = 3000, 40% aqueous); 3-pipiridano-1,2-propanediol (Alfa, >99%); D,L-picolinic acid (Acros, >99%). The chelating resins were obtained from the manufacturers in the commercial grade and converted to the desired acid form or salt form per the manufacturers recommendations (typically, treating with dilute inorganic acid or sodium hydroxide): Dianon CR-11 from Mitsubishi Chemicals, Lewatit TP-208 from Bayer Chemicals, and IRC-748 from Rohm & Haas. All of these resins have an imino-diacetate functionality. The EDTA salts were all purchased except for the monosodium EDTA, which was prepared in situ from EDTA and disodium EDTA.

The Salen compounds were purchased as ACS grade or better from Aldrich and used without any treatment: *N*,*N*′-bis(salicylidene)ethylenediamine, *N*,*N*′-bis(salicylidene)-1,3-propanediamine, *N*,*N*′-bis(salicylidene)-1,4-butanediamine, *N*,*N*′-bis(salicylidene)-1,6-hexane-diamine, *N*,*N*′-bis(salicylidene)-1,2-phenylenediamine, (*R*,*R*)-(−)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine or (*S*,*S*)-(+)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine.
Jacobsen's catalyst was obtained from Aldrich and activated as described in the literature with air and acetic acid [17]. Bisacetylacetone-ethylenediamine and *N*-salicylidene-aniline were prepared from the aldehyde or ketone and amine by using a method similar to the literature described for *N*,*N*′-bis(salicylidene)ethylenediamine [18,19].

2.2. Catalyst testing

All experiments were performed in a batch mode in a Multiclave™. The Multiclave™ has 10 reactor tubes with glass liners inside; nine were used for reaction and one for temperature monitoring. The catalysts of EDTA and Salen types in an amount of 1 mmol, unless specified otherwise, were weighed out before the reaction in the glass liners and then dissolved in or diluted with 5 mL deionized water. One liner did not contain any catalyst and was filled with 5 mL deionized water for thermal hydration as a control experiment. Alternatively, the catalysts were added to the liners without any deionized water. The former is referred as diluted conditions in this work, while the latter undiluted conditions. The weights of the liners and the catalyst were recorded and the liners were placed in the Multiclave™ reactor tubes; 10 mL of water/EO feed as described below was added at 100 °C into the individual tubes of the Multiclave™ using a stream selector valve, a pump and a timer. The first reactor had a thermocouple inserted in place of the feed line to estimate the internal temperature of the other reactors and this reactor liner was filled with 10 mL of water.

Ethylene oxide (99.5%) was purchased from Specialty Gas Company and used as received. Deionized water with Diglyme added as an internal standard (∼2%, w/w) was used for dilution of the ethylene oxide (water/EO ratio is 4:1 by weight) under nitrogen pressure. The mixture of EO and water was then shaken or stirred by magnetic agitation to assure a uniform mixture that was used as stock solution to load the Multiclave™ reactor.

After pressure checking the reactor with N_2, the nitrogen pressure was reduced to about 200 kPa. Carbon dioxide could then be introduced into the system as this point, if desired. The catalyst was then agitated by Teflon™ coated magnetic stir bars and the internal temperature was raised to about 100 °C. A pump for the EO/water mixture was run at 5 mL/min and a 12-port valve was used to advance the flow of the EO/water to each of the nine reactor cells for exactly two minutes as controlled by an external programmable timer. In this manner, about 10 mL of the EO/water mixture was delivered to the nine available reactor cells; the 10th cell was used for temperature monitoring. The system was then pressurized to about 1.7 MPa using either nitrogen or carbon dioxide. The reactor cells with catalysts and reactants were maintained at 100 °C for 10 h to assure complete conversion of EO before being cooled to room temperature. Jacobsen's catalysts were run at room temperature for 72 h.

Products were analyzed by a Varian 3900 GC using an FID detector. Selectivities to MEG, DEG, and TEG are calculated using the number of moles of EO used to form the glycols divided by total moles of EO converted. The selectivity of the catalytic hydration was compared to that of the thermal hydration under identical conditions. Because EO conversion is essentially 100% (by GC) under the conditions employed in the present work, the catalysts are compared in terms of the selectivites to MEG. The criterion used to identify a selective catalyst is that its selectivity is higher than that of the thermal hydration by at least two percentage points under identical reaction conditions.

3. Results

3.1. Amines

The use of tertiary and pyridine amines in the presence of CO_2 for the catalytic hydration of EO to MEG has been reported [20]. The authors used mono functional amines. We found that the selectivity to MEG increased with an increasing number of amine functionalities, and then expanded our catalyst screening to secondary and primary amines. These compounds were not expected to be selective for the formation of MEG on the basis that amines with an active hydrogen usually form polyols with the amine group as the end-cap. U.S. Patents 4,243,759 [21] and 4,521,548 [22] disclose preparation of polyether polyols by reacting toluenediamine with ethylene oxide and propylene oxide in the presence of aqueous potassium hydroxide. The reaction of isopropylamine and water with ethylene oxide in the presence of concentrated hydrochloric acid yields β-isopropylaminoethanol [23].

When we first tested ethylenediamine, the resulting solution after the reaction was clear and light yellow. The sample was analyzed by G.C. to give a selectivity of 92% relative to the thermal hydration control sample of 88%. Following ethylenediamine, various other amines as catalysts were tested in the Multiclave™ under identical conditions. The catalysts studied include primary amines such as ethylenediamine, secondary amines such as diethylamine (DEA) and *N*-(1-adamantyl)urea, tertiary amines such as dimethylaniline, cyclic amines such as 1,4,7,10-tetraaza cyclododecane (Cyclen), and 1,4-diaza bicyclo[2,2,2]octane (DABCO), and aryl amines such as pyridine. The results of the catalytic hydration over these catalysts as well as the thermal hydration as a control experiment are summarized in Table 1.

The objective of evaluating the amines was to find possible correlation between catalyst performance in terms of MEG selectivity and the structure or properties of the amine used as a catalyst. We found the catalyst performance is related to the pK_a value of the amine. As presented in Table 1, the amines with pK_a values between 8 and 11, except diethylamine, are selective catalysts for the formation of MEG. As a comparison, we tested four amines with pK_a values of about 5 or below. The results show none of them is a selective catalyst. The selectivities to MEG with these four catalysts are similar to that of the thermal hydration under identical conditions. The results suggest that the amines with moderate basicity are selective for the formation of MEG.

Table 1
Selectivity to MEG using amines as catalysts

Catalyst	pK_a	Selectivity (%)
Ethylenediamine (EDA)	10	92
Diethylamine (DEA)	11	90
Hexamethyleneimine	10	93
1,4,7,10-Tetraaza cyclododecane (Cyclen)	11–13[a]	92
1,4-Diaza bicyclo [2,2,2]octane (DABCO)	9	96
1,5,8,12-Tetraazadodecane	11	93
2-Dimethyl aminopyridine (2-DMAP)	9	92
Dimethylaniline	5	88
Pyridine	5	87
N-(1-Adamantyl)urea	0.2	90
1,10-Phenathroline (PHEN)	4	90
Thermal hydration	–	88

All the hydration experiments were carried out under the diluted conditions.
[a] Estimated value.

3.2. Bifunctional EDTA type compounds

It is known that rate of EO hydration can be enhanced by either acid or base. Our assumption was that amphoteric compounds that have both acidic and basic functional groups (or acid and base moieties) might work for the catalytic hydration too. The concurrent use of an acid and its conjugate base for the catalytic hydration of EO to MEG is known. [24]. Partially amine-neutrilized sulfonic acid resins have also been used for this purpose [25]. We speculated that the presence of the acid and the conjugate base in the same molecule as well as the tertiary amine function would improve the catalyst performance. Readily available examples of the compounds that meet these criteria are of the EDTA family. They encompass compounds where multiple carboxylic acid functions are tethered to a tertiary amine.

All the experiments with the bifunctional compounds as catalysts were conducted under 1.7 MPa of N_2 as described in the experimental section. The results with the EDTA type of catalysts are shown in Table 2. A good correlation between catalyst performance, i.e., MEG selectivity, and pH value of the compound in water solution was established. The results suggest that the bifunctional catalysts, EDTA and its sodium derivatives are good catalysts when the solution is from acidic to mild basic. When the solution with a bifunctional catalyst compound is strongly basic, the catalyst is not selective at all. In fact it enhances further reactions to form DEG and higher glycols. Due to the higher EO concentrations present at the undiluted conditions, the MEG selectivity of the control (or thermal hydration) is lower as compared to using the diluted conditions (Table 1).

Another type of bifunctional catalysts is chelating resins. The results with this type of catalysts are shown in Table 3. It can be seen that the acid form of the chelating resins have higher MEG selectivity than the salt form. With a mixture of the salt and acid forms of the chelating resins one would expect to have selectivity between the selectivity for the salt form alone and the selectivity for the acid form alone. However, the results show as long as the molar ratio of the salt form over the acid

Table 2
Selectivity to MEG using EDTA and its sodium derivatives as catalysts

Catalyst	pH value	Selectivity (%)
None (or control)		83
EDTA	2	86
NaEDTA	4	89
Na_2EDTA	7	86
Na_3EDTA	10	55
Na_4EDTA	11	55

All the hydration experiments were carried out under the undiluted conditions.

Table 3
Selectivity to MEG using chelating resins

Catalyst	pH value	Selectivity (%)
None (or control)		83
CR11: Na_2^+	12	68
CR11: Na_2^+:H_2^+ = 2:1 (molar)	8	80
CR11: Na_2^+:H_2^+ = 1:1 (molar)	7	86
CR11: Na_2^+:H_2^+ = 1:2 (molar)	7	89
CR11: H_2^+	5	87
TP208: Na_2^+	11	73
TP208: Na_2^+:H_2^+ = 2:1 (molar)	6	83
TP208: Na_2^+:H_2^+ = 1:1 (molar)	7	86
TP208: Na_2^+:H_2^+ = 1:2 (molar)	6	88
TP208: H_2^+	4	87

All the hydration experiments were carried out under the undiluted conditions.

form is 1 or less, the selectivity has no significant change comparing to that of the pure acid form. When the molar ratio is 2, the selectivity is much lower, but still much higher than that of the salt form. These results suggest that a catalyst of the chelating resin type that is too basic (pH $\geq$ 10) is not selective for the formation of MEG. When the acid and salt forms of the chelating resins are mixed, they form a buffer solution with pH values between 6 and 8 as shown in Table 3.

3.3. Salen

The use of Salen type compounds for the hydration of epoxides is also known. Salen compounds are named after the original ligand which was prepared from salicyl aldehyde and ethylene diamine. Countless compounds based on this structural motive have been reported with different properties [26]. Jacobsen and co-workers have shown that a Co(III) Salen compound can kinetically resolve the R and S components of racemic propylene oxide by hydrating one of the two enatiomers to the corresponding chiral glycol [27–29]. The reaction is performed by oxidizing a Co(II) Salen compound with air to the Co(III) compound in the presence of acetic acid. The oxidized compound is then used for the resolution of the racemic mixture. An acid is always present in the reaction [17]. Jacobsen's catalysts refers to metal Salen compounds with (1*R*,2*R*)-(−)-[1,2-cyclohexanediamino-*N*,*N*′-bis(3,5-di-*t*-butylsalicylidene)] and its optical isomers as ligand.

Although the hydration of EO to MEG has no chiral concerns or interests, the high diol yields of this resolution (>95%) reaction at a very high epoxide concentration that this reaction is run at, water is the limiting reagent, led us to believe that this class of compounds can also be used for highly selective EO hydration. We tested Jacobsen's catalyst at room temperature for the hydration of EO to MEG in 72 h of reaction time. We found that even a small amount of this catalyst (0.7 wt%) was sufficient to obtain high MEG selectivity (97%). The control experiment under identical conditions gave very little EO conversion (by GC). To prove that the catalyst was actually responsible for the high conversion and selectivity, we tested acetic acid, the ligand, the Co(II) salt, and a combination of the ligand and acetic acid.

Table 4
Selectivity to MEG on Salen ligands in the absence or presence of CO_2

Catalyst	MEG selectivity with N_2 (%)	MEG selectivity with CO_2 (%)
Thermal hydration	83	88
N,*N*′-Bis(salicylidene)ethylenediamine	52	93
N,*N*′-Bis(salicylidene)-1,3-propanediamine	62	93
N,*N*′-Bis(salicylidene)-1,4-butanediamine	48	92
N,*N*′-Bis(salicylidene)-1,6-hexanediamine	66	91
N,*N*′-Bis(salicylidene)-1,2-phenylenediamine	82	89
Bisacetylacetone-ethylenediamine	79	91
N-Salicylidene-aniline	79	90

All the hydration experiments were carried out under the undiluted conditions.

Table 5
Selectivity to MEG using Salen ligands in the presence of acetic acid

Catalyst	Acetic acid	Selectivity (%)
None	None	88
None	0.01–1 M	89
N,*N*′-Bis(salicylidene)ethylenediamine	None	66
N,*N*′-Bis(salicylidene)ethylenediamine	1 mmol	74
N,*N*′-Bis(salicylidene)ethylenediamine	2 mmol	93
N,*N*′-Bis(salicylidene)ethylenediamine	3 mmol	94
N,*N*′-Bis(salicylidene)ethylenediamine	4 mmol	95
N,*N*′-Bis(salicylidene)ethylenediamine	5 mmol	95
N,*N*′-Bis(salicylidene)-1,3-propanediamine	2 mmol	90
N,*N*′-Bis(salicylidene)-1,3-propanediamine	4 mmol	93

All the hydration experiments were carried out under the diluted conditions.

Our experiments using Salen compounds as catalysts for the EO hydration were conducted under nitrogen as well as CO_2 blanket. We used the CO_2 since that was shown to be beneficial for some amine compounds reported in this paper. Table 4 shows the results of the hydration using Salen compounds as catalysts. As can be seen, none of the catalysts for the catalytic hydration is as good as thermal hydration under identical reaction conditions in the presence of nitrogen as an inert blend. On the other hand, the results with any catalyst are better than that of thermal hydration in the presence of CO_2. These results suggest that the Salen compounds may be too basic for the selective hydration of EO to MEG. The presence of CO_2 may modify the basicities of the compounds such that are suitable as selective catalysts for MEG formation.

The results of the catalytic hydration using Salen ligands in the presence of acetic acid are shown in Table 5. With the two Salen ligands tested, we observed a similar trend. The presence of acetic acid greatly enhances selectivity to MEG, and the selectivity increases with acetic acid concentration within the range evaluated. The results once again demonstrate the effect of modification of the basicities of the Salen ligands.

4. Discussion

It is generally accepted that mineral acid catalyzed homogeneous EO hydration proceeds as follows: EO first

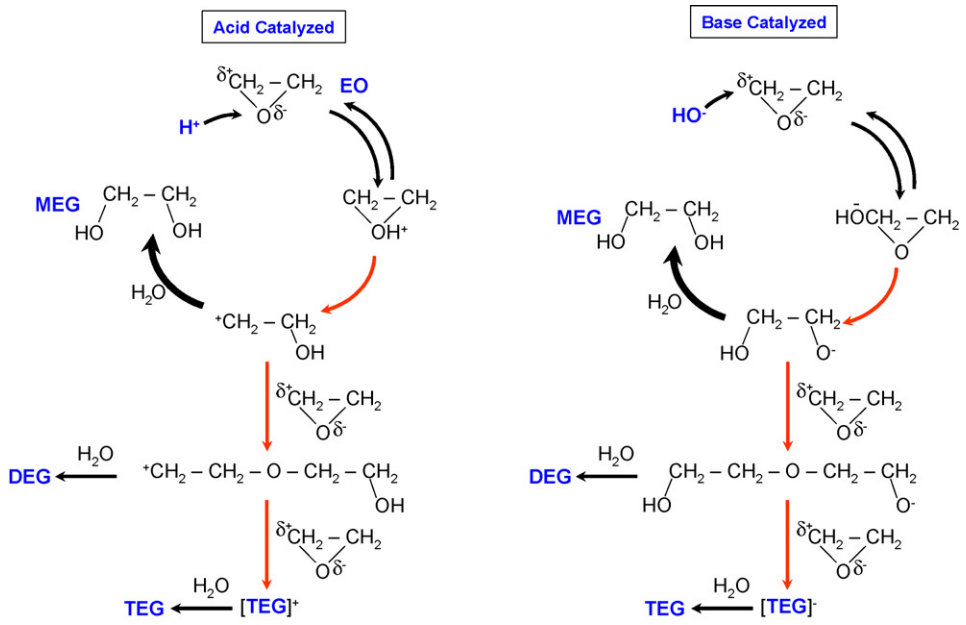

Fig. 1. Schematic diagram of reaction mechanisms of acid and base catalyzed hydration of ethylene oxide to ethylene glycols.

reacts with a proton to form a protonated EO, the protonated EO further reacts with nucleophilic H_2O to form a protonated glycol, and the protonated glycol transfers a proton to a molecule of H_2O to form the glycol and hydronium ion [30]. For solid acid catalysts, Li et al. [15] proposed a similar reaction mechanism. Here we propose reaction mechanisms for acid and base catalyzed hydrations of EO to MEG to explain the results obtained with three types of the catalysts investigated. These two mechanisms have the same sequences leading to the desired product, MEG, as well as the undesired products, higher glycols. Because of the difference in acidity and basicity of the catalysts used, the major intermediate species are different. We found our results are consistent with either the acid or base catalyzed reactions mechanisms depending on the acidity or basicity of the catalyst used. The mechanisms may be better explained in reaction schemes as depicted in Fig. 1. For acid catalyzed reaction, a proton first attacks the nucleophilic oxygen of an EO molecule to form an intermediate species, $CH_2(OH^+)CH_2$, which subsequently changes to a more stable one, $^+CH_2(OH)CH_2$. The second intermediate species reacts with an H_2O molecule to form a monoethylene glycol and at the same time releases a proton that maintains the constant acidity of the reaction solution. The second intermediate species can also react with another EO to form diethylene glycol. Triethylene and higher glycols may be formed with the same mechanism. For base catalyzed reaction, there are also two intermediate species formed, and the sequences of formation of MEG, DEG, and TEG are the same. The base catalyzed hydration of EO may be described as a classic S_N2 mechanism [31]. The nucleophilllic base attacks an EO molecule forming a negatively charged glycol anion, which subsequently picks up a proton. The glycol anion can also react with another EO to form diethylene glycol and higher glycols with the same mechanism. The pH value of the solution will determine the amount of glycol anion in the solution and hence the overall selectivity to MEG.

It is known that strong acid [13] and strong base [32] can increase the rate of EO hydration. However, the catalytic hydration in the presence of strong acid and strong base as catalysts are not selective for the formation of MEG compared to the thermal hydration without any catalyst present. Our results with catalysts having strong acidity or basicity are consistent with the literature information. We postulate that the effective catalysts we found balance the rate increase with minimizing the undesired reaction which would occur at too acidic or basic conditions. This postulation correlates well with the pK_a and pH values we found with the amines and bi-functional compounds, respectively. As far as the catalytic hydration by the Salen ligands is concerned, we speculate the reaction is probably governed by the same mechanism as found for the amine catalysts since the presence of CO_2 or acetic acid improved catalyst performance by modifying the basicities of the catalysts.

5. Conclusions

Three catalyst systems were investigated for the catalytic hydration of ethylene oxide (EO) to monoethylene glycol (MEG): amine compounds, bi-functional compounds, and Salen compounds. A good correlation between catalyst performance and its acidity/basicity was established. While both strong acidic and basic catalysts accelerate reaction rate of EO conversion, they are not selective toward MEG formation. A selective catalyst causes a pH value ranging from weakly acidic to weakly basic.

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